Otolith Microchemistry: the Geochemical Link Between Environment and Biomineralization in Fish

by

Lisa Anne Friedrich

A Thesis submitted to the Faculty of Graduate Studies of
The University of Manitoba
in partial fulfilment of the requirements of the degree of

Doctor of Philosophy

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THE UNIVERSITY OF MANITOBA

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Abstract

Assessing environmental change relies on monitoring physical, chemical, and biological parameters over extended periods of time. However, detecting change is difficult in areas where base-line data is sparse or non-existent. Biominerals, which may archive chemical information, are becoming important tools for monitoring environmental change. In particular, otoliths have been referred to as continuous recorders of exposure to the environment. Otoliths are calcified structures in the inner ear of teleost fish that are composed of alternating layers of calcium carbonate (typically aragonite), separated by thin bands of protein. They are metabolically inert, unlikely to be resorbed, and grow throughout the life of the fish, and their annular structure produces a time scale that may be added to the record. However, previous studies indicate that only selected trace elements in otoliths are influenced by water composition, a relationship that is complicated by fish physiology and habitat of the fish.

This study examines if the geochemistry of a habitat has an affect on otolith microchemistry, specifically, if otoliths retain a chemical signature that may be related to the geology of the watershed. Otoliths were taken from four geologically distinct areas in Manitoba that have been influenced by mining activity. In each case, a suite of elements indicative of the surrounding geology was chosen for LA-ICP-MS analyses across the annuli. Otoliths from fish captured near and downstream from a rare element pegmatite mine contain signatures of Li, Cs, and elevated Rb, whereas those from lakes distant to or upstream from the pegmatite do not have such concentrations of those elements. Otoliths taken from lakes adjacent to Cu, Pb, and Zn mining contain coincident peaks of the three metals that are interpreted to indicate when the fish came into contact with the tailings.

Constant levels of Ni detected in otoliths from lakes near Ni mining operations suggest that the fish are exposed to consistent levels of the metal. Fish stocked in a closed open-pit Ni-Cu mine contain constant levels of these base metals throughout their life history. These cases indicate the affect habitat has otolith microchemistry and highlight the possibility of using otolith microchemistry to develop base-line chemical signatures for environmental assessments.

Acknowledgements

I would like to thank my advisor Dr. Norman Halden for his support and guidance over the past 5 years. For access to samples, data, and properties, thanks to Karen Mathers (TetrES Consultants Inc.); Dave Tyson (Wardrop Engineering); the staff of Tanco Mine; Doug Leroux and Ken Kansas (Manitoba Conservation). For assistance with sample preparation and analysis, thanks to John Babaluk and Rick Wastle (Department of Fisheries and Oceans); Panseok Yang, Sergio Mejia, Gregg Morden, and Neil Ball (Department of Geological Sciences). Thanks to my many field assistants: Marty, Neil, Cam, Chris, Ben, Aaron, Jared, and Marie. Funding for this project was provided by the Natural Science and Engineering Council of Canada and a Discovery Grant.

Special thanks to my family and friends for their unwavering support, which has helped me more than they can imagine. I dedicate this work to my parents who have been my biggest cheerleaders from the very beginning. Thank you.

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Chapter 1 Introduction

In the early 1990s, several studies downstream of pulp and paper mills in Canada noted changes in the physiological, biological, and reproductive responses of wild fish (Walker *et al.*, 2002). As a result of these and other assessment studies, a series of amendments to the Pulp and Paper Effluent Regulations (PPER) was developed to improve the quality of effluents from Canadian pulp and paper mills (Munkittrick *et al.*, 2002). Similarly, development of Environmental Effects Monitoring (EEM) program for the metal mining industry began in 1993 with a program that evaluated the effectiveness of federal effluent regulations under the *Fisheries Act* (Dumaresq *et al.*, 2002). The objective of these EEM programs is to assess the adequacy of effluent regulations by monitoring effects on fish, fish habitat, or the utilization of the fisheries resource (Munkittrick, 1992).

To assess the impact of environmental contamination, monitoring programmes and studies rely on measurements of the physical and chemical environments, as well as the biota (de Pontual and Geffen, 2002). However, monitoring and assessment require long-term studies as well as baseline data in order to detect environmental contamination. As well, toxicological studies are often hampered by concerns of fish residency in affected areas (Palace *et al.*, 2007). Recent exposure to contaminants has been identified through the use of muscle or visceral tissues (Lemly, 1993, 1997), however metabolism can redistribute or eliminate contaminants, and these tissues do not provide any temporal trend data (Palace *et al.*, 2007). Chemical analysis of biominerals may offer significant improvements in detecting current, recent, and historical levels of contamination at both the individual and population levels (de Pontual and Geffen, 2002). Being chemically inert, fish otoliths in particular have the potential to contain life-long chemical records that, when coupled with the annular structure, can provide a year-by-year account of changes in trace element levels in the environment. This thesis is a study of otolith microchemistry, its relationship with the geochemistry of an environment, and its potential for use in EEM studies to monitor environmental changes in lakes that are adjacent to mining effluents.

1.1 Biominerals

Biomineralization is the process by which organisms form intracellular or extracellular skeletal structures comprising crystalline or amorphous inorganic substances (Lincoln *et al.*, 1998). The term biomineral refers to a mineral produced by an organism that is generally a composite material composed of both mineral and organic components (De Yoreo and Vekilov, 2003). The shape, size, crystallinity, isotopic and trace element characteristics of biominerals are quite unlike their inorganically formed counterparts as a result of being formed under controlled conditions (Weiner and Dove, 2003). For nucleation and growth to occur, biomineral formation requires a localized zone that maintains a sufficient supersaturation of the mineral constituents. In most biological systems, the site of mineral deposition (extra-, inter-, or intracellular) is isolated from the environment by a physical barrier that must limit diffusion into or out of the system. Organisms use a variety of anatomical arrangements to facilitate ion movement by one of two means: active pumping associated with organelles near the site of mineralization or passive diffusion gradients (Weiner and Dove, 2003).

Calcareous biominerals have surprisingly different properties when compared with the chemically precipitated equivalent (Baronnet *et al.*, 2008). Hatchett (1799) first recognized the layered organization of mollusc shells and the presence of organic lamellae. Using thin sections, Bowerbank (1844) and Carpenter (1845) discovered that these calcareous layers were not simple aggregates of Ca-carbonate particles, but were built by geometrically well-defined units. Since these pioneering studies, calcium carbonate biomineral structures of brachiopods, corals, and molluscs have been frequently analyzed owing to their abundance, diversity, and unique material properties in a variety of scientific fields (Perez-Huerta *et al.*, 2008). Brachiopods have a long geologic history and are widely abundant making them ideal for evolutionary studies and in investigating marine paleoenvironments (Schmahl *et al.*, 2008). Biominerals are also widely recognized in material science and nanotechnology as prototypes for advanced materials (Schmahl *et al.*, 2008). In particular, considerable efforts in research of biomaterials, composite materials, nanostructures, and biomimetic processes have focused on the investigation of structural and mechanical properties of mollusc shells (e.g., Barthelat and Espinosa, 2007; Gao, 2006). Specifically, aragonite nacre (nanoscale aragonite platelets in an organic matrix) is intensively studied because of its excellent mechanical properties and the possibility of mimicking its structure at the nanoscale (Perez-Huerta *et al.*, 2008).

Mineral-producing organisms exert acute control on all aspects of biomineral production (Perez-Huerta *et al.*, 2008). Despite this, biologically produced minerals often contain signatures that reflect the external environment in which the animal lived embedded within their compositions (Weiner and Dove, 2003). However, the controlling biological processes can sometimes either completely eliminate the signals or shift them, a phenomenon known as the vital effect (Urey *et al.*, 1951). The most common approach used to resolve this issue has been identifying taxa that faithfully record environmental parameters, and avoiding those known to be affected (Weiner and Dove, 2003). Through this method, researchers have successfully used biominerals to extract environmental signals for past seawater temperatures, salinities, productivities, extent of seawater saturation (ibid). Following from these studies, the extraction of environmental signals from biominerals has expanded into the development of environmental monitoring studies. Otoliths have several properties that make them ideal for these types of studies, namely their annular structure and their potential to retain a complete chemical history spanning the life of the fish. These and other features of otoliths are described in the sections below.

1.2 Otoliths

All jawed vertebrates have an inner ear that functions in both hearing, as an auditory system that detects sound waves, and balance, through the vestibular system, which detects linear and angular accelerations (Wright *et al.*, 2002). The inner ear of fish consists of paired canals, sacs, and endolymph fluid-filled ducts that occur on either side of the head, embedded in the cranium (ibid). Teleost, or bony, fish have three semi-circular canals that open into a series of interconnected chambers, or otic sacs, that contain a sensory tissue (macula), which detects linear accelerations and sound (Figure 1.1). Each of these sacs contains a calcareous structure (otolith) that acts as a mechanoreceptor stimulating the "hair cells" of the macula. Each otolith is fixed over the macula by an otolithic membrane. The sacs are the sacculus, utriculus, and lagena, which contain the sagitta, lapillus, and asteriscus otoliths, respectively (Figure 1.2). Within an individual fish, the otoliths of the three otic sacs differ in size and shape. The sagitta tend

Figure 1.1: Position of the otoliths within the inner ear of teleost fish. a) Dorsal view of the vestibular apparatus in a typical teleost species. The top of the cranium is cut away (frontal section). b) Otoliths within the labyrinth system of typical teleost fish. *Ast: asteriscus; Lag: lagena (vestibule); Lap: lapillus; Sac: sacculus (vestibule); Sag: sagitta; Utr: utriculus (vestibule)* (Secor *et al.*, 1992). Reproduced with the permission of The Department of Fisheries and Oceans Canada (figure originally printed in *Canada Special Publication of Fisheries and Aquatic Sciences*, Vol. 117, p.32).

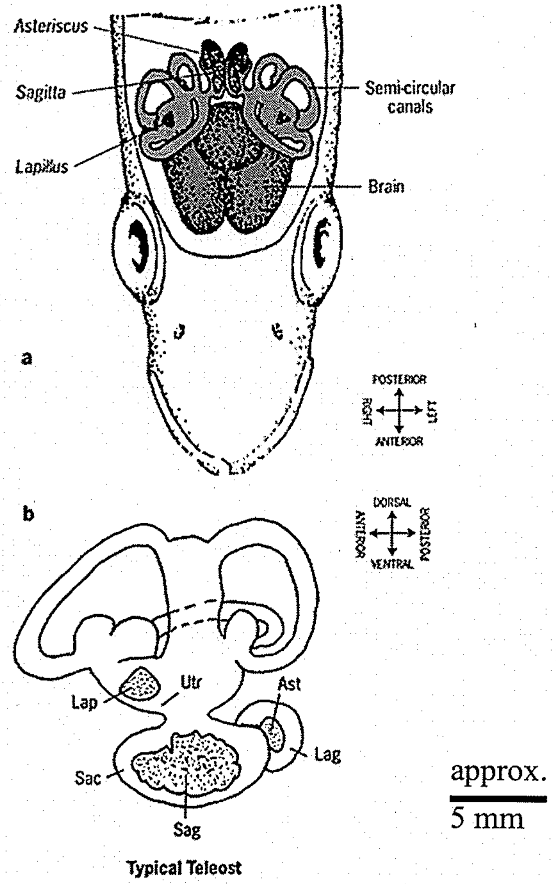
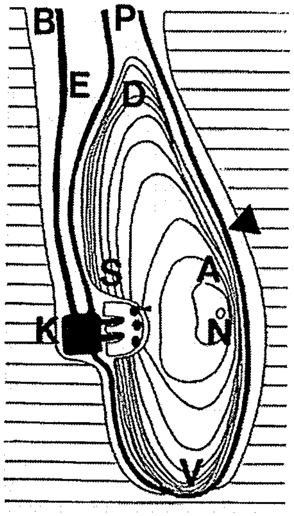


Figure 1.2: A schematic cross-section of a sagittal otolith indicating main features. Scale approximately 1 cm = 1 mm. The otolith sits in a groove in the endolymph sac, indicated by the large triangle. It rests on its ventral edge (V) at the bottom of the groove, restricting the growth along this edge. The free growth edge is the dorsal edge (D), which is connected by a passage (P) to the atrium such that there is free flow of endolymphatic fluid between the sac and the semicircular canals. The sulcus groove (S) is on the inner side of the fish, and the anti-sulcul surface (A) faces towards the outside of the fish. Within the sulcus are the sensory kinocilia (K), or "hair cells," of the macula, which also contains proteinaceous material. A network of nerves and blood vessels (B) is present beneath the kinocilia that enter the endolymphatic sac at the sulcus. The sac is surrounded by the epidural fluid (E) of the brain cavity. The nucleus (N) is towards the anti-sulcul (A) surface in shallow water fishes, but in the middle for deeper water fishes (Gauldie and Nelson, 1990). Reproduced with the permission of Elsevier Limited (figure originally printed in *Comparative Biochemistry and Physiology*, Vol. 97A, p. 121).



to be the largest otoliths and are most often used in age estimation (Degens *et al.*, 1969).

The shape of otoliths varies between species and within a species (Nolf, 1985) reflecting both genetic and environmental influences (Torres *et al.*, 2000). This feature of otoliths has made them useful in taxonomy, food-web studies, and in archaeological and paleontological studies involving the reconstruction of paleoenvironments and paleofauna (Wright *et al.*, 2002). Otolith shape also plays an important functional role in determining the particular sound frequencies for which the otolith acts as a transducer (Gauldie and Nelson, 1990).

1.3 Otolith function

Otoliths in teleost fish are involved in mechanoreception, acting as electromechanical sound and displacement transducers that convert shear forces into electrical impulses by distorting the "hair cells" of the macula in the inner ear (Popper and Hoxter, 1981). Ciliary bundles are bent, stimulating a cranial nerve when there is relative motion between the sensory epithelium and the otolith (Wright *et al.*, 2002). The otoliths add mass to the gelatinous layer of the three otic sacs, increasing their sensitivity to gravitational and other linear acceleration forces (Ross and Pote, 1984). Two different pathways have been proposed for sound reaching the fish ear: direct and indirect stimulation (Popper and Lu, 2000). Direct stimulation is the result of density differences between the surrounding water and the fish body and otoliths. A fish body is approximately the same density of water and therefore moves with the water in response to an impinging sound field (Wright *et al.*, 2002). The otolith, however, is denser than the rest of the body, and so moves with a different amplitude and phase from the sensory macula and the body. Thus, the sound source directly stimulates the inner ear. Indirect stimulation is the result of otolith displacement caused by the vibrating walls of the swimbladder, which contains gas that is less dense than the body (Popper and Lu, 2000).

1.4 Otolith formation

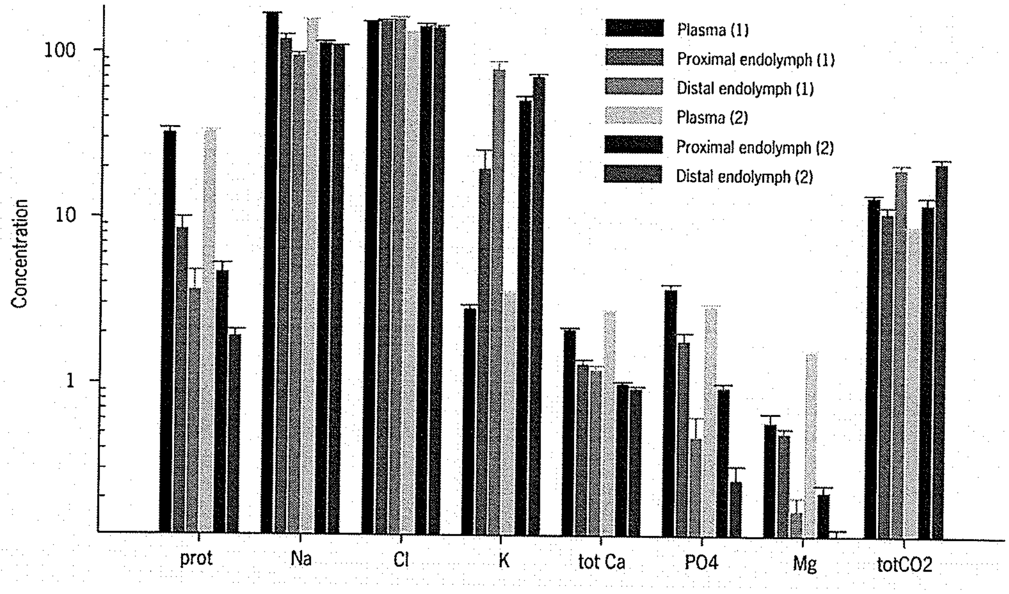
As with other biominerals, such as brachiopod and mollusc shells, otoliths are composite materials consisting of inorganic crystals and organic molecules such as lipids, polysaccharides, and proteins, collectively known as the organic matrix (Sarashina and Endo, 1998). The formation of otoliths is the result of molecular interactions at inorganic-organic interfaces (Mann *et al.*, 1993), whereby calcium carbonate is deposited onto an organic-matrix template (Degens *et al.*, 1969). Deposition of calcium carbonate may be initiated by a Ca^{2+}-nucleating protein, such as phosphophoryn. The otolith grows or accretes by the addition of concentric layers of proteins and calcium carbonate, resulting in a structure somewhat comparable to that of an onion. Interactions between the organic and inorganic components determine the shape of an otolith (Gauldie and Nelson, 1990). The mechanism for otolith growth, although not fully understood, differs from other biomineralization processes in two ways (ibid). Otolith formation is an acellular process in that the otolith epithelium is not in direct contact with the region of calcification (Figure 1.2; Campana 1999). As a result, the calcification process is heavily dependent upon the composition of the endolymphatic fluid surrounding the otolith (Thresher, 1999).

Few studies have been done on the fluid and organic components of otoliths, despite their obvious importance in otolith growth and composition. However, some generalizations about the chemistry of endolymph can be drawn from such studies. When compared to blood plasma, endolymph is rich in K^+ and low in Na^+ (Payan *et al.*, 1999).

In a comparison using whole blood samples, Melançon *et al.* (2009) determined that metal concentrations (Na, K, Rb, Mg, Ca, Sr, Ba, Mn, Fe, Zn, Pb) in wild lake trout and burbot endolymph were similar to those found in whole blood samples, with the exception of Mg and Fe being enriched in the blood. The total Ca concentration of endolymph is approximately 1-2 mM and it has relatively low protein content (Figure 1.3). Payan *et al.* (1999) noted that the principal components of endolymph have concentration gradients that probably act as driving forces in the biomineralization process and are able to generate a heterogeneous distribution of some elements on the surface of the growing otolith. In contrast to higher vertebrates, the endolymph pH in teleosts is more alkaline than the blood plasma (Payan *et al.*, 1998). Although not completely understood, a key physical regulating factor in the calcification process of otoliths is the pH of the endolymph, which is determined by the concentration of bicarbonate ions in the endolymph (Payan *et al.*, 1998). Proton secretion through the saccular epithelium reduces alkalinity in the endolymph, which then reduces the rate of calcification (Payan *et al.*, 1997), which is also a function of temperature (Campana, 1999). However, a solely inorganic process cannot account for many of the features of biomineralization in general, or otolith growth in particular (Wheeler and Sikes, 1984). Indeed, “it is now recognized that the endolymph proteins play a pivotal role in calcium carbonate precipitation and inhibition” (de Pontual and Geffen 2002, p. 251).

The organic matrix of otoliths is composed largely of a keratin-like protein, called otolin, which is rich in aspartate and glutamate residues (Degens *et al.*, 1969). The total protein content of otoliths has been divided into water-soluble proteins and water-insoluble proteins (Asano and Mugiya, 1993). The water-soluble proteins are calcium-

Figure 1.3: Ionic, total CO_2, and protein concentrations of plasma and saccular endolymph in trout (1) and turbot (2). Concentrations are in mM for all constituents except for proteins, which are in g/l (de Pontual and Geffen, 2002). Reproduced with the permission of Ifremer-IRD (figure originally printed in *Manual of Fish Sclerochronology*, p. 252).



binding glycoproteins and appear to be the most influential in regulating the rate of calcification, possibly through inhibiting crystal nucleation (Asano and Mugiya, 1993).

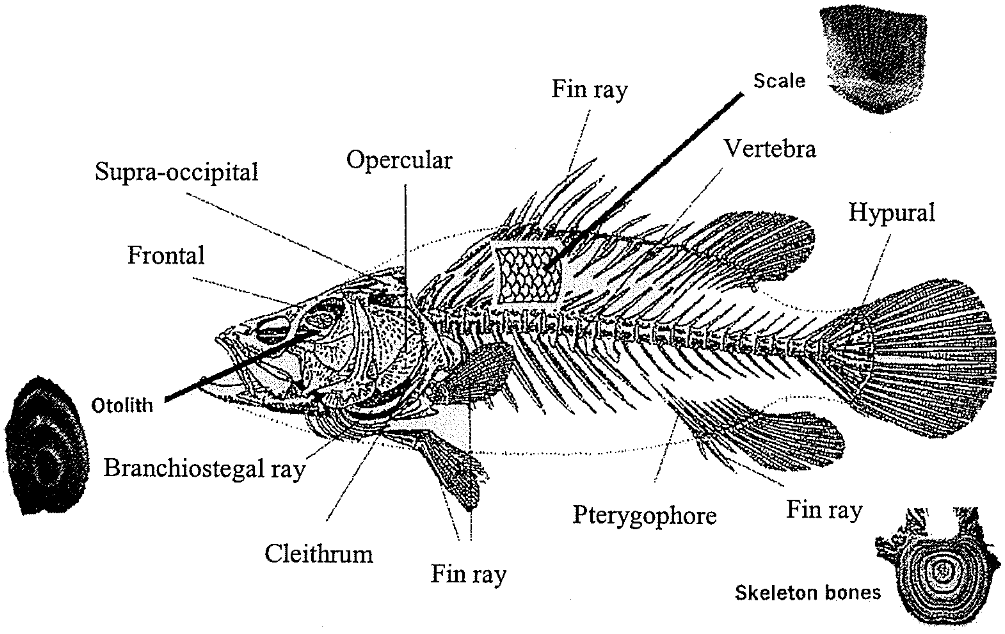
1.5 Growth increments in otoliths

Daily, seasonal, or annular growth patterns in calcified structures are common in a number of aquatic phyla (Campana and Thorrold, 2001). Daily growth bands are not as common as annular patterns and are restricted to species in which the depositional environment of the structure can be controlled by the organism without subsequent resorption (Campana and Thorrold, 2001). Otoliths contain many growth patterns at different levels of resolution, from diurnal to annular (Wright *et al.*, 2002). The presence of easily discernable daily increments in otoliths provides an accurate and precise method of age estimation of most larval and juvenile fish (Campana and Neilson, 1985). Seasonal increments in otoliths are often visible as bands of differing opacity, owing to their different ratios of calcium carbonate to protein matrix (Wright *et al.*, 2002). Seasonal zones also differ with respect to the width of primary increments and the thickness and size of aragonite crystals (Morales-Nin, 1987). Annual increments, also referred to as annular marks, rings, or annuli, are often interpreted as comprising an opaque and a translucent seasonal zone. Thickness of annuli can be up to a few hundred microns wide, but typically are between 40 and 50 microns (Wright *et al.*, 2002).

1.6 Elemental uptake

Teleost fish contain several calcified structures that can be used for sclerochronological studies, the main three being otoliths, scales, and bones (Figure 1.4; de Pontual and Geffen 2002). Of these structures, otoliths are unique in that they, unlike skeletal calcium, are acellular and considered to be metabolically inert so that any

Figure 1.4: Various calcified structures that can be utilized for sclerochronological studies, and the three main types of structures: otolith, scale, and skeleton (de Pontual *et al.*, 2002). Reproduced with the permission of Ifremer-IRD (figure originally printed in *Manual of Fish Sclerochronology*, p. 20).



elements or compounds accreted onto their growing surface are permanently retained (Campana and Neilson, 1985). This, along with the fact that otoliths grow continually from before time of hatch to the time of death, in principle indicates that otoliths may contain a complete record of both temperature variations and composition of the ambient water (Campana, 1999). Otoliths are therefore extremely useful in age estimation and environmental reconstructions. Despite complications in interpretation due to physiological filters, numerous examples of successful reconstruction of the life history of fish exist, including temperature history (Patterson *et al.*, 1993), detection of anadromy (Halden *et al.*, 2000), and use as a natural tag (Campana *et al.*, 1995). How and where elements are incorporated into otoliths is crucial for the aforementioned applications of otolith microchemistry. Otolith formation, being an acellular process, is completely dependent on the endolymph (Campana and Neilson, 1985). However, the translation of environmental factors into otolith composition is a complex process involving three stages of exchange: external medium (water and food) to blood plasma, blood plasma to endolymph, and endolymph to otolith. The current state of knowledge on these stages in otolith formation is summarized below.

1.6.1 Exchange from external medium to blood plasma

Elements are exchanged from the environment to the blood plasma via the surrounding water or the animal's diet (de Pontual *et al.*, 2002). Processes of elemental uptake at this stage depend on a large number of factors. Abiotic characteristics of the environment play a role; factors such as pH, salinity, dissolved oxygen, and temperature determine the concentration of free ions available for uptake (ibid).

In freshwater fish, the inorganic components in the plasma are mainly derived from the surrounding waters, via the gills (Simkiss, 1974). Uptake of major metal ions, such as Ca and Na, and non-metallic ionic species, such as sulphate and phosphate, is highly regulated and occurs through active transport pumps (de Pontual *et al.*, 2002). Transition metals, such as copper, zinc, and iron, are essential for the health of fish, forming integral components of proteins involved in all aspects of biological function (Bury *et al.*, 2003). Acquisition of these elements occurs via the gills as well as the intestine (ibid). Trace metal uptake depends on the relative ambient ionic concentrations and may be species and environment specific. The process is regarded as passive, not requiring expenditure of energy, and dependent on the affinity of water-soluble ions with organic ligands present in the membrane of the exchange surfaces. Melançon *et al.* (2009) calculated partition coefficients for several metals (Na, K, Rb, Mg, Ca, Sr, Ba, Mn, Fe, Zn, Pb) and determined that Mg, Sr, and Ba had the lowest uptake from water to blood.

Some elements, including micronutrients and contaminants, are at least partly supplied by the diet. Indeed nutritive metal uptake is believed to be dominated by gastrointestinal uptake and supplemented by waterborne sources (Bury *et al.*, 2003). A generalization of incorporation pathways for all elements is currently not known. For example, studies on Sr distribution in otoliths have shown that this element is assimilated from both food and water (Farrell and Campana, 1996), as well as from water only (Hoff and Fuiman, 1995).

1.6.2 Exchange from blood plasma to endolymph

The relationship between blood plasma and endolymph chemistry has not been extensively studied, and there are limited publications on the trace element content in the endolymph. A recent study on endolymph composition determined that endolymph and whole blood samples from wild lake trout and burbot have similar metal concentrations, except that Mg and Fe were enriched in the blood (Melançon *et al.*, 2009). Another study indicated that, while plasma and endolymph compositions vary on a daily cycle, the ionic gradients within the endolymph are maintained (Edeyer *et al.*, 2000). The mechanisms for transport of various elements through the saccular epithelium are still debated. It is likely that active and regulated ionic transports occur through the interface at the saccular epithelium. Studies on Sr/Ca ratios in plasma and endolymph suggest that these elements are transported into the endolymph by a particular route through the cells (Mugiya and Yoshida, 1995). Interestingly, Melançon *et al.* (2009) determined that wild lake trout and burbot endolymph compositions had few significant differences, with the exception of K, Mg, and Ba, from the same location.

1.6.3 Exchange from endolymph to otolith

The effect of endolymph compositional variations on the composition of the otolith has not been clearly established, and studies on this topic are difficult due to several factors. For example, temporal resolution differs for measuring endolymph composition, which can be measured instantaneously, and otolith composition, which is integrated over a period that depends on otolith growth rate. However, in a recent study by Melançon *et al.* (2009), trace metal concentrations of water and blood, endolymph, and otoliths of two freshwater species were compared. Although few significant differences existed between endolymph of lake trout and burbot, significant differences existed between their aragonitic otoliths. These differences were interpreted to be the result of different crystallization processes in the species, or the presence of different proteins that selectively influenced elemental incorporation in the otoliths.

Element-incorporation processes for otoliths have not been studied in detail. Elements may be incorporated within a crystal, adsorbed onto a crystal surface, or directly bonded to the organic matrix polymers. The two main methods of incorporation of trace metals within a crystal are by direct substitution for Ca^{2+} or by becoming entrapped within the crystal lattice as a crystal inclusion (Fritz *et al.*, 1990; Geffen *et al.*, 1998). Inorganic carbonate minerals accept a wide range of trace metals in their structure, including Sr, Mg, Mn, Fe, Cu, Co, Ni, Zn, Rb, Li, and rare earth elements (Reeder, 1983). In aragonitic molluscan shells, the orthorhombic crystal lattice structure allows for the substitution of divalent (e.g., Mg^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+}) and small monovalent cations (e.g., Li^{+}) (Onuma *et al.*, 1979). Larger monovalent cations (e.g., Na^{+}, K^{+}, and Rb^{+}), trivalent cations (e.g., Al^{3+}, Cr^{3+}, and Sc^{3+}), and anions (e.g., Cl^{-} and Br^{-}) can also be incorporated into carbonate shells as separate mineral phases entrapped as impurities during calcification or by adsorption onto organic matter in the shell (ibid). The substitution of monovalent cations for Ca^{2+} in biogenic carbonates may involve coupled substitution within the crystal, alter the mineral structure, or indicate some accommodation and charge-balance exchange with the protein (Halden and Friedrich, 2008).

Not much is known about trace elements that could be bonded to the organic matrix, though the topic has received some attention in recent years. Miller *et al.* (2006) developed a protein extraction procedure that allows for the observation of metal-protein binding in otoliths. The use of this solution on cod otoliths, enabled the determination that large portions of Cu and Zn present in the otoliths were associated with the protein phase, whereas Mn is either weakly bound to or not associated with the protein matrix. In a study on trout sampled near coal mining operations, Palace *et al.* (2007) suggest that selenium detected in the otoliths may be incorporated into the protein by two seleno-amino acids, both of which are present in otolin.

1.6.4 Element variations controlled by environmental availability

Elements that are likely to vary depending on their availability in the environment are identified based on distribution coefficients and comparisons between water, blood plasma, and otolith compositions (Campana, 1999). Distribution coefficients between water and otolith (D_e) are useful indicators of elements that are highly physiologically regulated; such elements are discriminated for or against at one or more of the interfaces: gills, intestine, saccular epithelium, and otolith. Distribution coefficients may be calculated by:

$$D_e = (\text{element/Ca})_{\text{otolith}} / (\text{element/Ca})_{\text{water}}$$

with element and Ca in molar concentrations. Very low distribution coefficients (<0.05) are characteristic for elements such as Na, K, and Cl. D_{Sr} is approximately 0.14 and for many trace elements, such as Mn, the distribution coefficient is greater than 0.25, and may even approach 1.

Comparisons between compositions of water, blood plasma, and otolith can provide more information as to the effect of environmental availability on metal uptake in otoliths (Campana, 1999). When normalized to Ca, such comparisons show inconsistent relationships for Mg, Cu, P, and Na, but greater consistency for elements such as Sr, Zn, Pb, Mn, Ba, and Fe, indicating that the relative environmental abundances of these latter elements may be well reflected in the otoliths. Campana (1999) also noted that Li, Cd, Ni, and other less abundant elements may well respond to environmental availability. However, these distinctions are speculative and complicated by the fact that some trace elements are involved in fish metabolism as essential micronutrients, or are toxic, or both. Zinc, for example, is known to be an essential micronutrient involved in the formation of bone and cartilage in fish, but it becomes toxic at high concentrations. As such, Zn uptake by otoliths may reflect changes in environmental bioavailability or fish metabolism (Halden *et al.*, 2000).

These stages of translation of an element from the environment to the otolith are complex and involve biological processes to varying degrees. One of the main processes involved is the ability of organisms to moderate their internal environments in response to changing external environments.

1.7 Osmotic and ionic regulation in teleost fish

Like all multicellular animals and plants, the osmotic and ionic concentrations of fish cells are relatively well buffered against changes in external salinity because of the presence of an extracellular fluid (ECF), the solute concentrations of which are maintained through the physiological processes described below (Evans, 1979). However, as these mechanisms are not perfect, there is additional need for cellular regulation by the plasma membrane (Evans, 1979). Almost all fish and most marine vertebrates maintain the Na^+ and Cl^- osmolality of their body fluids equivalent to approximately 30% of that in sea water. They therefore have body fluids whose solute concentration is different from that of their environment, and energy must be used in the homeostatic control of water and ion balance. The concentration of solutes in the internal fluids of a freshwater fish is much higher than that of freshwater, and consequently the fish constantly gains water and loses salts. Saltwater teleost fish have osmoregulatory problems opposite to those of freshwater species. Internal fluids are lower in total solutes than seawater, and as a result, the fish lose water and gain salts, specifically NaCl. Extracellular osmoregulation by fish is therefore the use of epithelial-based physiological mechanisms to offset or balance net passive osmotic and ionic movements (Evans, 1979).

Teleost fish in freshwater are adapted to compensate for this endosmosis through three routes of organ systems that work to achieve the proper water and solute balance: the digestive system takes up ions from food, the respiratory system (gills) actively takes up ions, and the renal (kidney) system works to produce large amounts of dilute urine (Figure 1.5; Evans 1979). They also limit their drinking rate to relatively low values (ibid).

Gills are important mechanisms for the uptake of ions, although the mechanism is not yet fully understood (Karnaky, 1998). Currently, it is believed that the inward movement of Cl^- is coupled to the outward movement of bicarbonate ions through a mechanism in the mitochondrial-rich cells (MRCs; Figure 1.6). The uptake of Na^+ was previously believed to be linked to the elimination of waste products, such that as Na^+ cations move inward, hydrogen or ammonia ions produced in metabolism may move outward, maintaining electrical neutrality (Mitchell *et al.*, 1988). However, more recent studies propose that Na^+ is attracted inward by a negative potential across the outer cell membrane created by H^+-ATPase (enzymes that catalyze adenosine triphosphate) in the apical membrane of the gill epithelia cells (Karnaky, 1998).

The kidneys of freshwater bony fish act as the principal route of water excretion, producing a dilute urine (Evans, 1979). The morphology of the teleost kidney allows

Figure 1.5: Osmoregulation in freshwater bony fishes. Freshwater fishes such as this perch gain water across their gills and the general body surface by osmosis. Excess water is discarded as urine that is hypoosmotic to body fluids. Chloride-absorbing cells in the gills actively transport salts into the body fluids (Mitchell *et al.*, 1988). Reproduced with the permission of Pearson Education, Inc. (figure originally printed in *Zoology*, p. 151).

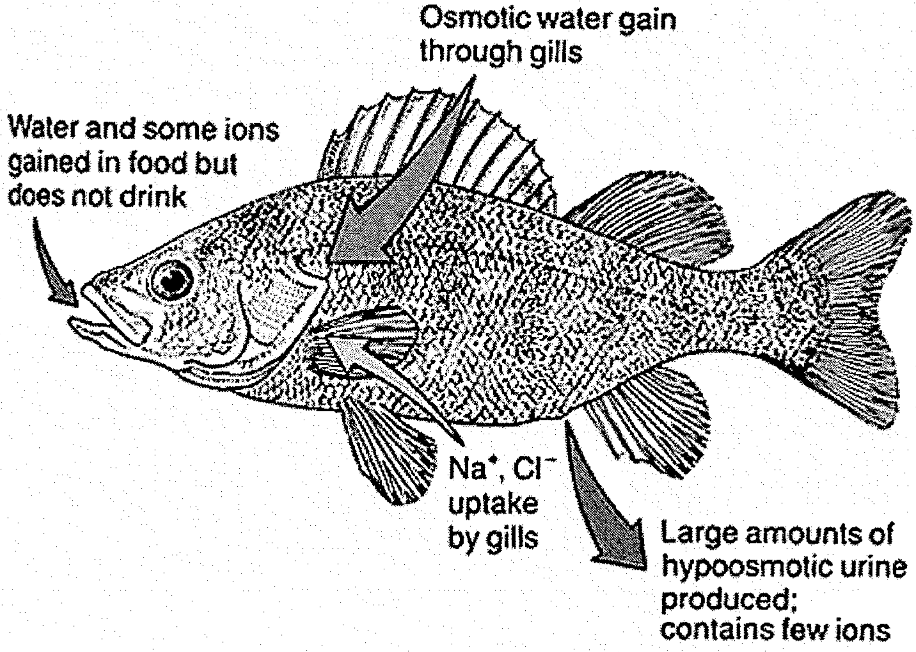
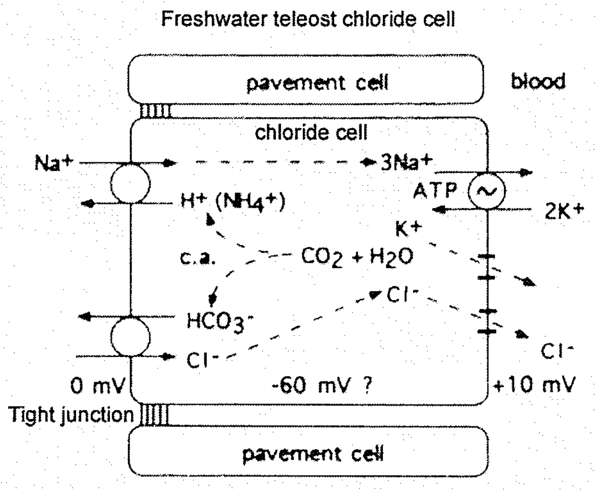


Figure 1.6: Older model for ion uptake mechanism in freshwater teleost gill epithelium. Newer models use the terminology “mitochondrial-rich cells” or “MRCs” instead of “chloride cells.” Note the coupled transport and co-transport of Cl^- and HCO_3^- and N^+ and H^+. Active transport represented by solid arrows, passive diffusion represented by dashed arrows (Marshall, 1995). Reproduced with the permission of Elsevier Limited (figure originally printed in *Cellular and Molecular Approaches to Fish Ionic Regulation*, p. 3).



almost all of the NaCl to be absorbed (Karnaky, 1998). The urinary bladder provides a secondary processing of urine and uptake for ions, for which several mechanisms have been described (ibid).

1.8 Literature review

1.8.1 History

Otoliths have been used as age indicators since the first observation of annuli in 1899 (Reibish, 1899). The discovery of daily growth increments (Pannella, 1971) helped propel the interpretation of their microstructure into the mainstream of fish biology. Since then, research involving otoliths has evolved and expanded, particularly over the last decade, largely owing to technological advances in data acquisition (Begg *et al.*, 2005). Primary publications reporting research on, or application of, otoliths have increased exponentially since 1980 to an average rate of approximately 200 papers per year (Campana, 2005). The focus of otolith research has shifted from largely annual age and growth research to detailed studies focused on chemistry and microchemistry. Recent trends mirror advances in technology and have expanded in innovative ways, including studies of population dynamics, species identification, tracer applications, and environmental reconstructions. A summary of some of the major fields of otolith research follows, including otolith microchemistry as it applies to environmental reconstructions.

1.8.2 Annual age and growth

Historically, otoliths were mainly used in studies of age and growth, and these studies continue to be the majority of otolith-related publications today. This topic encompasses a broad suite of problems, including the use of annual growth patterns for the estimation of longevity and growth rate of a population or species, development of ageing methods, and age validation (Francis and Campana, 2004; Laidig *et al.*, 2003; Wilson and Nieland, 2001). These types of studies are the foundation from which all other otolith research fields have stemmed, and such information forms the basis for most comparisons of growth rate and survival among environments and populations, fish stock assessments, and life-history studies (Campana and Thorrold, 2001).

Several recent studies have focused on developing automated techniques for acquiring age and growth data, which are of key importance for fisheries research in terms of stock assessment and marine ecology issues (Fablet and Le Josse, 2005; Troynikov and Robertson, 2005). Possibilities include deploying numerical reconstruction to the age composition using information from age-dependent measurements, such as fish length and otolith weight distributions, and the use of statistical learning techniques as applied to images of otoliths.

Other studies in this category report both the development and validation of an ageing method, followed by its application to a population for estimation of longevity and growth rate. For example, one study compared ages derived from whole and thin-sectioned otoliths, then applied several analyses to validate the accuracy of the method across all age groups (Dwyer *et al.*, 2003). Another study marked Arctic grayling in Alaska with oxytetracycline, and recaptured marked fish over the succeeding four years (DeCicco and Brown, 2006). Fluorescent marks were visible in thin-sectioned otoliths from 15 of the 16 recaptured fish, and annuli that were visible beyond the mark accurately recorded the passage of years between mark and recapture. Although uncommon, studies using known-age fish have the advantage of allowing specific recommendations to be made concerning optimum age interpretation approaches

(Buckmeier, 2002).

Major advances in this research category center on improved or more rigorous methods for age validation. Successful use of a novel otolith marker (strontium chloride) in a large-scale tag-recapture study of southern bluefin tuna was recently demonstrated (Clear *et al.*, 2000). The applicability of bomb radiocarbon for validating the ages of long-lived species around the world was broadened when radiocarbon histories for the northwest Pacific (Kerr *et al.*, 2004) and northeast Atlantic (Kalish *et al.*, 2001) demonstrated that a bomb signal in a given year was similar in other areas around the world. The largest methodological advance is considered to have been the development of an improved radiochemical assay for ^{226}Ra, which improved the precision of radiometric age estimations (Andrews *et al.*, 1999).

1.8.3 Tracer applications, trace elements, and elemental fingerprints

Natural tracer applications have become a very active area for research over the past 10 to 12 years (Campana, 2005). The approach is based on natural structures or chemical features formed in response to environmental or genetic factors, leaving a permanent natural marker record in the otolith. Thus, the marker serves as a natural tag or tracer of that same group of fish throughout its life. Although most of the recent research efforts have been focused on chemical tracers, alternative markers, such as those owing to unusual microstructural growth patterns formed in the early life history, have also been used (Quinn *et al.*, 1999). Otolith shape, although not a permanent marker, has been used successfully to distinguish among populations (Begg *et al.*, 2001).

Strontium is the most widely used element in tracer studies (Daverat *et al.*, 2005; McCulloch *et al.*, 2005; Tzeng *et al.*, 2005). Assays of Sr:Ca along otolith transects are a common means of reconstructing migration routes among environments with different salinities (Howland *et al.*, 2001). Otolith Sr:Ca ratios were used to determine migration histories of American eels in an eastern Canadian coastal stream that is impounded at the head of tide (Cairns *et al.*, 2004). In studies where the objective has been to distinguish among groups or populations of a species, elements other than Sr have been used. For example, distinct elemental fingerprints were detected in juvenile yellow perch growing up in different wetland nurseries (Brazner *et al.*, 2004). Otolith elemental fingerprints were also used to track seasonal migrations of redfish in and around the Gulf of St. Lawrence (Campana *et al.*, 2007). Even greater discrimination is achieved in studies that combine trace element data with stable isotopes (Thorrold *et al.*, 2001).

A logical direction for future developments in tracer research is the use of tracers in identifying or classifying a group of fish's breeding group, or source population. An increasing number of studies have been successful in identifying unknown fish in this manner, basing their classifications on maximum likelihood statistical methods and careful sampling of all possible source groups (Campana, 2005). One such study collected and analyzed juvenile snapper otoliths from estuaries for comparison to the juvenile region of adult otoliths (Gillanders, 2002). In this manner, a distinct chemical signature of each estuary was established and used to identify the nursery or recruitment estuary of adult fish, which will aid in the management of fish stocks. In a similar way, stable strontium isotopes are valuable markers for freshwater fish in that such isotopes vary considerably and consistently among freshwater drainages, a variation that is reflected in the otolith composition. As a result, the movement patterns and origin of individual fishes can often be reconstructed with high fidelity (Hobbs *et al.*, 2005; Milton and Chenery, 2003). Campana *et al.* (2000) used whole otolith Li, Mg, Mn, Sr, and Ba as elemental fingerprints of cod otoliths as a reflection of the physical and chemical characteristics of the ambient water. They concluded that although the use of elemental fingerprints as natural tags is not suited to all stock mixing situations, suitable elemental fingerprints can be determined through knowledge of existing biological and environmental information. The present study takes this elemental fingerprint application a step further, using the chemical signature of the environment as it relates to the surrounding geology. Suites of elements leached from the surrounding rocks and minerals have been detected in otoliths, indicating that otoliths can retain elemental fingerprints related to the known geology. In such a way, it may be possible to use otolith microchemistry to track where and when fish come into contact with contamination from mine tailings.

Although tracer applications account for most of the research on trace elements in otoliths, there is a considerable amount of research effort focused on the factors that influence the uptake and incorporation of such elements. Several studies have examined the relationship between water composition and the resulting composition of the otolith, concluding that the incorporation of selected trace elements was influenced by only water composition (Dorval *et al.*, 2007; Elsdon and Gillanders, 2003). The incorporation of certain elements into otoliths is the combined result of water composition and dietary intake (e.g., Mn, Zn).

1.8.4 Environmental reconstruction

A long-standing goal of fisheries science has been to take advantage of the understanding of the environmental factors that influence the elemental and isotopic compositions of otoliths to reconstruct the previous environmental history of the fish (Campana, 2005). Experiments designed to constrain environmental influences on otolith composition continue to demonstrate an effect, but also show a significant effect from interplay between factors, such as temperature and salinity, which complicates the extraction of such environmental information (Elsdon and Gillanders, 2002). Stable isotope ratios have been used to reconstruct the record of temperature variations (specifically oxygen isotope ratios; Gao *et al.*, 2001), differentiate among groups of fish (Edmonds and Fletcher, 1997), infer metabolic history (Schwarcz *et al.*, 1998; Weber *et al.*, 2002), and reconstruct migration history (Hobson, 1999; Kennedy *et al.*, 2002).

Trace elements are often considered to be excellent pollution indicators, given their relatively high concentrations in industrial effluent (Phillips and Rainbow, 1993). Accordingly, trace element composition of soft tissues of aquatic organisms is used routinely to monitor pollution (Lohan *et al.*, 2001; Storelli and Marcotrigiano, 2005). Calcified tissues in organisms such as bivalves and corals preserve a longer record of exposure, and thus are preferred for use where available (Reichelt-Brushett and McOrist, 2003; Zeng *et al.*, 2004). A similar precedent for the use of otoliths as environmental indicators has been set, although in some of the initial reports the link between otolith microchemistry and pollution was not obvious (Geffen *et al.*, 1998; Hanson and Zdanowicz, 1999). For example, Geffen *et al.* (1998) suggested that for lead, physiological mechanisms operate in the fish to regulate it once it enters the body. Once it enters the body, at high enough concentrations, the lead is sequestered or in some way removed from circulation such that it does not reach the otolith. However, more recent studies, present research included, have begun to find links between trace element chemistry of the environment and that of otoliths (Arai *et al.*, 2007; Friedrich and Halden, 2005; Halden *et al.*, 2005; Palace *et al.*, 2007). Several trace elements have been used for such studies, including zinc, copper, lead (in combination with other metals), lithium, cesium, and selenium, and elevations in their concentrations have been interpreted as indicating when the fish came in contact with effluents or runoff from mine tailings. Such observations provide the basis for the current study.

1.9 Thesis objectives

A major portion of Manitoba's economy depends on the resource, extractive, and power generation industries. Indeed, many northern communities depend on such industries for their survival. In today's socio-economic climate, resource industries, particularly the mining industry, are under pressure to extract minerals in the most cost-effective way possible, and to do so in such a way that does not lead to degradation of the environment. Interdisciplinary research focussed on the sustainable development of Manitoba's resources will integrate environmental imperatives and the remediation of the legacy of orphaned tailings left by past mining activity. The development and expansion of EEM programs require the development of long-term monitoring techniques that offer temporal trends of current, recent, and historic levels of contaminants in the environment.

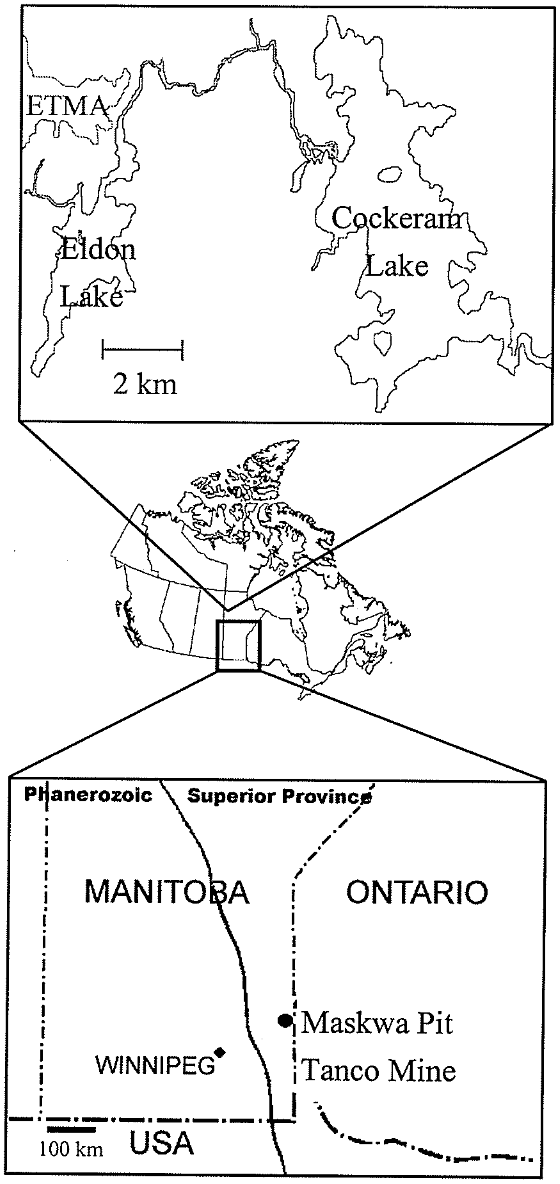
In recent years, researchers have identified certain biominerals as potential recorders of global and environmental changes, including scleractinian corals (Reichelt-Brushett and McOrist, 2003), the Asian clam (Zeng *et al.*, 2004), and limpets (Storelli and Marcotrigiano, 2005). Strontium levels in otoliths have been used in many studies to determine migratory behaviour of fish and past temperature conditions of the environment. However, the mineral portion of otoliths has the ability to incorporate a wide range of trace elements, including rare earth elements and heavy elements, such as mercury and lead. When coupled with the annular structure of these bones, the microchemistry of otoliths has the potential to record changes in the fish habitat, and provide insight on how the trace element chemistry of the environment can impact an organism. In this regard, it will be necessary to distinguish natural from anthropogenic changes in the environment.

Considerable work using microbeam techniques has been directed at understanding trace element distribution in fish otoliths. The majority of this work has focused on Sr, and how it may be used as a proxy for water temperature variations and delineating migratory behaviours. However, the inorganic portion of otoliths has the capability to incorporate a range of trace elements, and otoliths are not considered to be subject to resorption, hence only ontogenetic and environmental factors should cause changes to their chemical composition (Campana *et al.*, 1999; Halden *et al.*, 2000). As such, otoliths have the potential to contain a complete record of past conditions to which the fish was exposed, and analysis of these records should provide an insight into short-term environmental changes, on the order of a few tens of years. Archived otoliths have the potential to add historical insight into past and changing environmental conditions. However, the uptake of trace elements into the otoliths is a complex process that may be influenced by the habitat. Thus, the overall objective of this project was to investigate the relationship between otolith microchemistry and the geochemistry of the rocks comprising the watershed, and establish how chemical trends in the otoliths may act as records of changes in lakes impacted by mining activity. Three, geologically different sites in Manitoba were chosen for this study on the basis of the breadth of knowledge of the surrounding geology, their known geochemical characteristics, and their proximity to a body of freshwater. The sites were the Maskwa pit, Eldon and Cockeram Lakes, and the area surrounding the Tanco pegmatite mine near Lac du Bonnet (Figure 1.7).

The Maskwa pit is an abandoned nickel-copper (Ni-Cu) open-pit mine that has been stocked with arctic char (*Salvelinus alpinus*). It provided a unique opportunity to study the effects the geochemistry of an environment has on otoliths. In this setting, the char were not able to migrate out of the system, nor were other populations able to enter, thus providing a geographically closed system with a known source of metals, specifically Ni, Cu, and chromium (Cr), an ideal setting for examining a link between geology and otolith microchemistry. The material presented in chapter 2 on the Maskwa pit arctic char was written with the intent to submit to the journal of Environmental Earth Sciences and was submitted for publication on April 20, 2009. I completed all of the analyses outlined in this chapter (Appendix A) and wrote the full manuscript.

The second site chosen was the area adjacent to base metal mining operations and corresponding mine tailings near Lynn Lake, Manitoba. Eldon and Cockeram Lakes are linked via Lynn River, which flows directly past the tailings management area of the mine, which has high concentrations of Cu, lead (Pb), and zinc (Zn). These lakes are part of an open system in which fish are free to migrate, providing an ideal situation for examining if otolith microchemistry can record fish movements into and out of mine tailings-affected areas. The material presented in chapter 3 on Eldon and Cockeram lake otoliths was written with the intent to submit to Environmental Science and Technology journal and was submitted for publication on June 30, 2009. I completed all of the analyses outlined in this chapter (Appendix B) and wrote the full manuscript with

Figure 1.7 Location maps of the three, geologically distinct study areas in Manitoba.



guidance and feedback from my advisor, who is a co-author on the manuscript.

The last area chosen is near the Tanco pegmatite mine, which produces tantalum, cesium, and lithium. This area encompassed several sampling locations, sampled over a period of several years to provide detailed spatial as well as temporal trends. Otoliths were collected at different distances from the mine: Bernic Lake and the Tailings Management Area (TMA), both of which are in direct contact with mining activity; Bird River upstream from the Bernic Lake outlet; Lac du Bonnet and Bird River downstream from the Bernic Lake outlet; and Booster and Birse Lakes, which acted as control sites being parts of different watersheds. The material presented in chapter 4 on the Tanco area otoliths was written with the intent to submit to Environmental Science and Technology journal and was accepted for publication on February 26, 2008. I completed all of the analyses outlined in this chapter (Appendices C-J) and wrote the full manuscript with guidance and feedback from my advisor, who is a co-author on the manuscript, and feedback from anonymous reviewers.

Otolith analyses were done using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), which can detect a broad suite of elements at low detection limits and is capable of resolving micron-scale annuli. A variety of species were analyzed to determine what elements are being incorporated into otoliths and in what concentrations. Comparisons were made between sampling sites to resolve spatial variations in otolith composition, and between different species within the same sites to establish any potential influence of dietary sources on otolith microchemistry. Elemental substitutions in otoliths were compared to the annular structure to establish temporal chemical trends.

This research is the first extensive look at the relationship between otolith microchemistry and the geology of the habitat. Each site used in this study is proximal to mining activity and has a habitat with unique geology that provides a distinct suite of elements to the environment. Ultimately, the findings from this research may reveal if otolith microchemistry may be used as a proxy for monitoring short-term environmental changes in lakes. The results will lead to a better understanding of the impact mining has on the local environment and fauna, which can assist in conservation efforts, as well as rehabilitation and reclamation of affected areas. This technique may be further developed into a pro-active method of monitoring short-term changes in the environment, and this knowledge can lead to the shaping of policies on acceptable levels of trace elements in the environment through the development of better sampling and monitoring programs.

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Chapter 2 Base metal uptake in otoliths of Arctic Char (*Salvelinus alpinus*) from the Maskwa pit, Manitoba, Canada: Insight into the possibility of mine site reclamation using a fish-stocked lake

2.1 Abstract

Otoliths from arctic char (*Salvelinus alpinus*) recovered from the waterbody formed from an abandoned open-pit, nickel-copper mine contain a trace element record related to the geology of the immediate watershed, past mining activity in the area, and the fish's diet. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses across the annular structure of the otoliths detected trace amounts of nickel, copper, and chromium believed to be related to the metal-bearing, mafic-ultramafic minerals in the pit. Oscillatory strontium, barium, and zinc profiles may reflect changing water temperature, diet, or fish metabolism. Lead was detected in very low levels and may be related to anthropogenic influence. This closed lake system provides a unique opportunity to study an introduced exotic species in a setting where neither migration nor recruitment have been possible. The fish have successfully occupied the lake and continue to breed despite the influence of the surrounding rocks and local contamination. The chemical record retained within otoliths provides a method of monitoring the level of trace elements affecting fish on a yearly basis, and may be regarded as a useful assessment tool for examining the exposure of wild organisms to trace elements.

2.2 Introduction

To protect and manage aquatic biota, especially fish and fish habitat, discharge regulations have been established for a wide variety of wastewaters or effluents under terms of the *Canadian Fisheries Act*. To date, regulations exist for the pulp and paper industry (Walker *et al.*, 2002) and the metal mining industry (Dumaresq *et al.*, 2002). The adequacy of effluent regulations is routinely assessed by conducting Environmental Effects Monitoring (EEM) studies at locations where regulated effluents are discharged. The effect of effluents on local organisms is debated as uncertainty continues to exist regarding residence time of wild organisms in the exposure areas, recruitment, and extent of exposure. EEM studies require the development of assessment techniques for the determination of wild organisms' exposure to trace elements and the influence this contact has on the local fauna. Contaminants in muscle or visceral tissues can be useful indicators of recent exposure, however, they do not provide temporal trend data and metabolism can redistribute or eliminate contaminants (Palace *et al.*, 2007). In recent years, much microbeam analytical research has focused on trace element distributions in biominerals and how they may aid in reconstructing past environments (Arai *et al.*, 2007b; Friedrich and Halden, 2008; Halden and Friedrich, 2008; Palace *et al.*, 2007; Ranaldi and Gagnon, 2008a; Saquet *et al.*, 2002). Calcium carbonate biominerals in particular have been extensively studied as these minerals accept a wide range of trace elements, including Sr, Mg, Mn, Fe, Cu, Co, Ni, Zn, Rb, Li, and rare earth elements, into their crystal structure (Reeder, 1983).

Otoliths are calcium carbonate structures in the inner ear of teleost fish that assist in detecting sound and are used for balance and orientation (Popper and Hoxter, 1981). Typically, they consist of aragonite deposited in daily and yearly increments in a protein matrix (Degens *et al.*, 1969), and have been used to determine age and life history events of fish and fish populations. During formation, trace levels of numerous elements may be incorporated into either the organic or inorganic portion. In contrast to muscle or visceral tissues, otoliths are metabolically inert and, therefore, only ontogenetic and environmental factors should cause changes to their chemical composition (Campana, 1999). As such, otoliths retain a complete chemical record of the fish's life. Coupling this record to the annular structure of otoliths adds a time scale to the chemistry, affording a unique opportunity to provide information on environments the fish have occupied, changes in those environments, and any history of exposure to pollutants. Specifically, if a link exists between the microchemistry of otoliths and the geochemistry of the surrounding environment, otoliths can provide an assessment tool for the impact of historic or active mining activities on fish populations, either as part of background geochemical or environmental surveys, or in the form of on-going monitoring programs and fisheries management.

Several studies have pointed to a link between the environment, particularly the geochemistry of a watershed, and the microchemistry of otoliths (Friedrich and Halden, 2008; Halden and Friedrich, 2008; Palace *et al.*, 2007). These studies were done in natural, open systems. The purpose of this study is to examine if there is a link between otolith microchemistry and the geochemistry of the watershed through the analysis of a suite of otoliths obtained from fish in a closed system. The Maskwa pit is the result of open pit, nickel-copper mining activities that have since ceased. Currently, the closed mine is water filled and was stocked with arctic char (*Salvelinus alpinus*), though it is not known when the fish were introduced. Having been extensively studied as a potential source of Ni, Cu, Cr, and PGE, much is known about the geochemistry of the rocks of the area, and on-going environmental monitoring has provided information about the water chemistry, essentially the fish's immediate environment. A suite of elements (Cr, Ni, Cu, Zn, Sr, Ba, and Pb) was analyzed across the annular structure of char otoliths (i.e., life history of the fish) to delineate chemical signals from the geology.

2.3 Study Area and Geologic Setting

The Maskwa nickel deposit is located in southeast Manitoba, Canada, 160 km northeast of Winnipeg (Figure 2.1). It lies within the Archean Bird River Sill (Figure 2.2), which is an approximately 20-km-long, east-striking, mafic-ultramafic complex (Theyer, 2000). The Maskwa deposit has been a Ni, Cu, and Cr exploration target since the early 1900s (Cerny, 1989). An open pit mine was developed and operated in the mid-1970s at Maskwa, which was preceded by an underground mine that operated at the nearby Dumbarton site from August, 1969 until December, 1974 (Coats *et al.*, 1979). Over 30 million pounds of Ni and nearly 1.5 million pounds of Cu were mined from the Maskwa and Dumbarton properties (Stansell and Theyer, 2005). The open pit mine was closed with appropriate rehabilitation methods for the time and gradually filled naturally with water to form the current lake (Ian Ward, Mustang Minerals Corp., personal communication, 2009). The closed pit is 300 by 100 meters and is approximately 52 meters deep. A preliminary dissolved oxygen profile completed in the fall of 2006 suggested that the lake was anoxic (less than 5 mg/L) below 11.5 m depth, and levels dropped to less than 1 mg/L below 13 m depth (Dave Tyson, Wardrop Engineering Inc., personal communication, 2009). Future plans by Mustang Minerals Corp. are to reopen the mine with a larger pit as a nickel source in 2011 and operate for at least 7 years with an annual extraction of one million tonnes of ore plus waste rock.

Figure 2.1: Location of the Maskwa nickel deposit in southeast Manitoba, Canada.

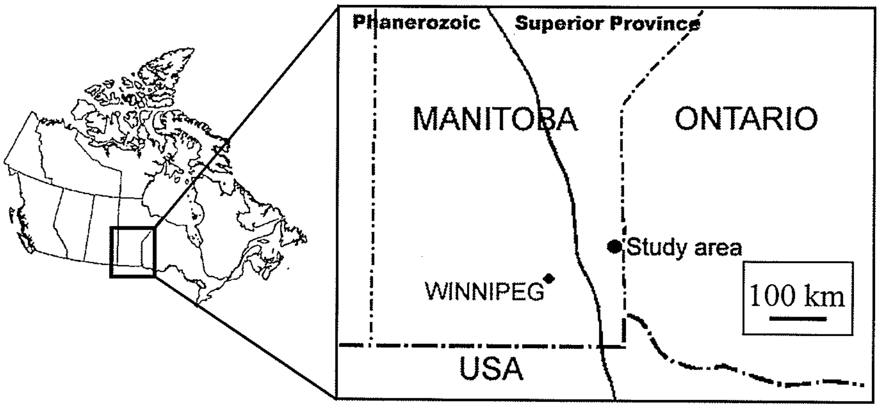
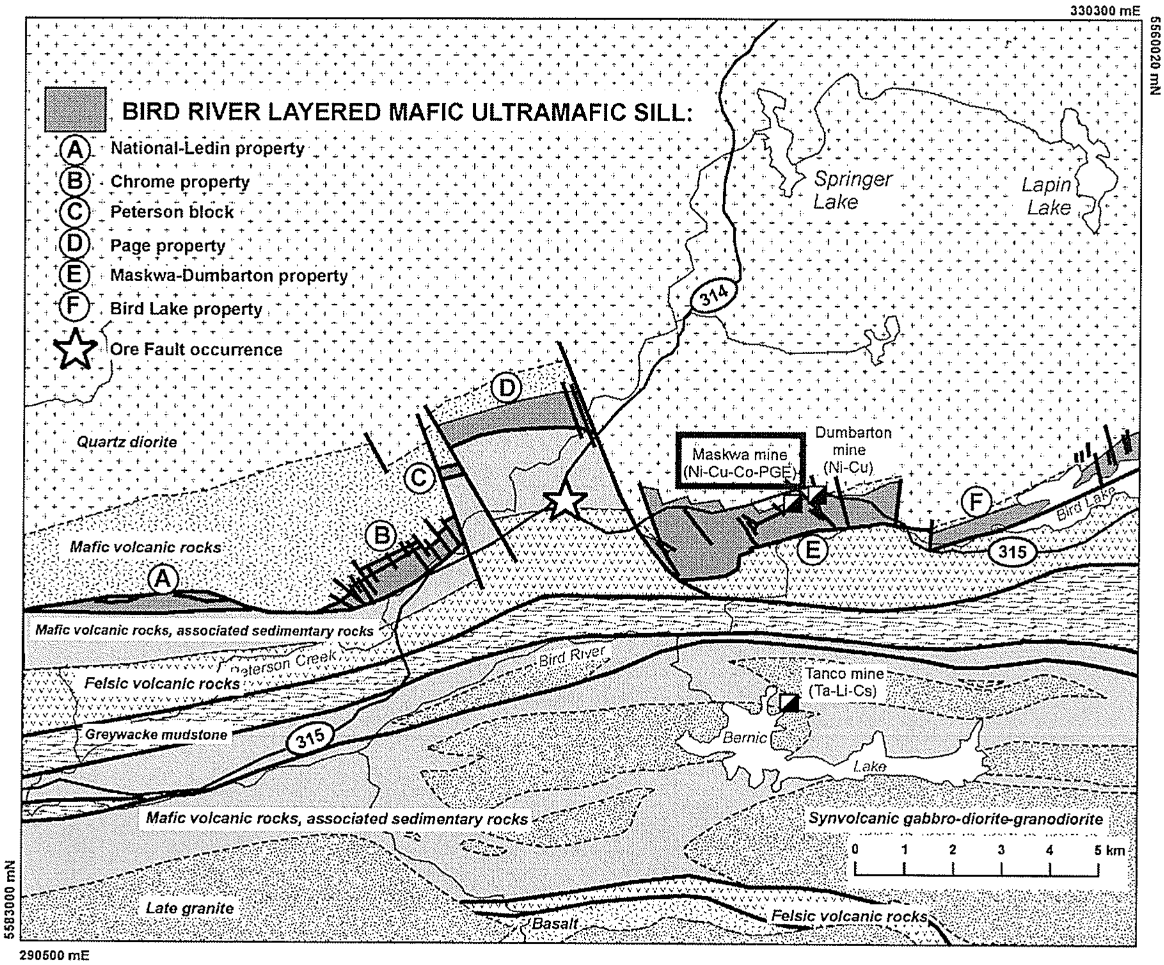


Figure 2.2: Simplified geology of the Bird River greenstone belt, showing the location of the Bird River Sill and the Maskwa open-pit mine (Theyer, 2000). Reproduced with the permission of the Government of Manitoba (figure originally printed in Theyer (2000) as Figure GS-27-1).



Mineralization at Maskwa occurs in the metaperidotite basal unit of the Bird River sill, a layered and differentiated ultramafic to gabbroic body that intrudes into the greenstone belt (Coats *et al.*, 1979). Sulphide mineralization is considered to have formed as magmatic segregation in the intruding magma, settling towards the base of the sill, close to the feeder source (ibid). The deposit is a low-grade disseminated sulphide zone consisting of marcasite-pyrite (FeS_2), violarite ($FeNi_2S_4$), pentlandite ($(Fe, Ni)_9S_8$), pyrrhotite ($Fe_{1-x}S$), and chalcopyrite ($CuFeS_2$) in a matrix of talc, carbonate, chlorite, and serpentine minerals (ibid). Historic production of Ni and Cu from the open pit came predominantly from an oxidized assemblage of marcasite, pyrite, violarite, and chalcopyrite. Chromite ($FeCr_2O_4$) layers occur in the peridotite units of the ultramafic series (Theyer, 2000).

2.4 Materials and Methods

Sixteen arctic char were collected from the Maskwa pit by gill netting in August of 2007 as part of an environmental survey of the area by Wardrop Engineering Inc. The sample set contained male and female specimens that were both mature and immature and ranged in age from 5 to 9 years. Fork lengths ranged from 34 to 56 cm, and wet weights ranged from 400 to 1650 g. To prepare for microbeam analysis, sagittal otoliths were embedded in epoxy resin and cut transverse to create a dorso-ventral cross section through the core of the otolith and expose all annuli. The posterior half of each cut otolith was re-embedded in a 25-mm Lucite microprobe mount, ground, and polished. Prior to analysis, samples were rinsed with double distilled water and allowed to air dry.

Whereas X-ray emission analysis of trace elements in otoliths has been done using proton-inducted X-ray emission (PIXE) and electron microprobe analysis (EMPA), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) can detect a broader suite of elements with better sensitivity and low detection limits. The micron-scale resolution of the LA-ICP-MS resolves the annular structure of otoliths, adding a time scale to the microchemistry. LA-ICP-MS analyses were done using a Thermo Finnigan Element 2 ICP-MS coupled to a Merchantek LUV 213 Nd:YAG laser. Table 2.1 summarizes the instrument parameters used during analysis. Running conditions used to optimize sensitivity and resolution of the annular growth features in these samples included a 30-μm-diameter beam traveling 2 μms^{-1}. Calcium as 56 wt% CaO was used as an internal standard, and the external calibration was done using NIST glass 610 with the nominal values reported by Pearce *et al.* (1997). Line scans were run across the otolith surface from core to edge, perpendicular to annuli in time-resolved or scanning mode. Standard analyses were collected prior to each analytical run. Measured trace element concentrations, standard deviations, and detection limits were processed using GLITTER software (van Achterberg *et al.*, 2001) and exported to Excel for final presentation.

2.5 Results

Table 2.2 summarizes trace element concentrations from the Maskwa pit arctic char otoliths. Chromium, Ni, and Cu were analyzed to determine if the otoliths contain a chemical signature that may be related to the geochemistry of the surrounding environment. Chromium and Ni were detectable in all samples, with concentrations ranging from 3 to 42 ppm and 1 to 6 ppm, respectively. Copper was detectable above background levels in only some of the samples. Where signatures were resolved, it ranges

Table 2.1: LA-ICPMS operating conditions and data acquisition parameters for otolith analysis.

ICPMS	
Forward power	1303 W
Gas flows	
Plasma (Ar)	16 L/min
Auxiliary (Ar)	0.80 L/min
Sample (Ar/He)	0.89/0.335 L/min
Shield electrode	Used for analysis

LA	
Repetition rate	20 Hz
Pre-ablation warm-up	~120 sec
Pulse duration	5 ns
Spot size	30 μm
Power	80%
Incident pulse energy	~0.020 mJ
Energy density on sample	~6.22 Jcm^{-2}
Laser scan speed	2 μms^{-1}

Data Acquisition	
Data acquisition protocol	Time resolved analysis
Scanning mode	BScan and EScan
Detector mode	Analog and counting
Isotopes determined	^{53}Cr, ^{60}Ni, ^{65}Cu, ^{66}Zn, ^{88}Sr, ^{137}Ba, ^{208}Pb
Dwell time (segment duration)	0.3 ms
Magnet settling time	0.001-0.3 ms
Time/Pass	1.7 s
Runs/Passes*	1000-1 (17m 09s)

*pass is a measurement cycle through the mass spectrum; 1 pass collected 1000 times producing 1000 blocks of data per sample

Table 2.2: A summary of the trace element concentrations (in parts per million) in arctic char otoliths from the Maskwa pit. Typical 1σ error values are given for elements that were relatively flat, and did not have oscillatory signatures.

	Cr	**Ni**	**Cu**	**Zn**	**Sr**	**Ba**	**Pb**
Concentration range	3.44 - 41.73	1.05 – 6.31	0.56 – 3.43	5.08 - 174.75	113.29 - 523.48	1.21 - 43.33	0.07 - 2.18
Average Detection Limit	0.46	0.53	0.56	4.35	43.80	0.20	0.07
Typical 1σ Error	6.76	1.18	0.97	N/A	N/A	N/A	0.04

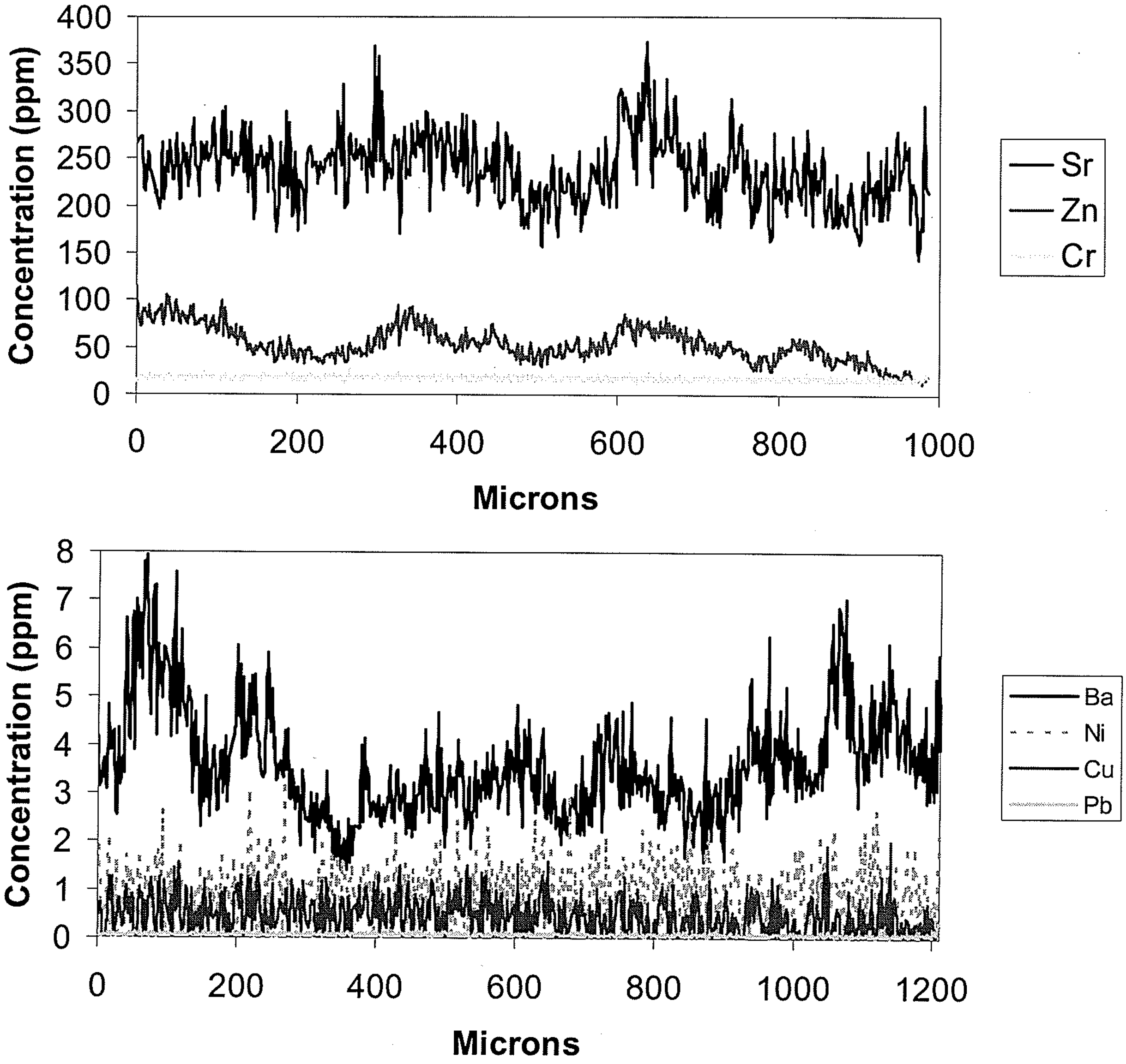
from 0.5 to 3 ppm. Zinc, Sr, and Ba were analyzed for comparison with other suites of otoliths as well as for signatures relating to diet. All three were detected in all samples. Zinc levels range from 5 to 175 ppm, Sr from 113 to 523 ppm, and Ba from 1.2 to 43 ppm. Lead was analyzed as an indicator of either Pb-bearing minerals or anthropogenic influence. It was detected in most samples at levels up to 2.2 ppm.

The chemical profiles in Figure 2.3 are representative of what a typical chemical signature is from the Maskwa pit arctic char. Chromium, Ni, and Pb profiles are relatively flat with approximate means of 13, 1.3, and 0.1 ppm, respectively. Copper may or may not be present in uniform concentrations around 0.5 ppm. Zinc, Sr, and Ba are ubiquitous and all show oscillatory patterns. Zinc concentrations are highest in the core, between 100 and 150 ppm, after which levels oscillate on a yearly basis with an overall decrease in Zn concentration with age. A typical Sr profile is oscillatory and ranges from 200 to 300 ppm. Oscillations in Ba concentrations are not uniform among the fish, but typically stay within the range of 3-10 ppm.

2.6 Discussion

Environmental Effects Monitoring (EEM) for Canadian metal mines was initiated in 1993 to assess the health of fish and their habitats potentially impacted by mining effluents (Dumaresq *et al.*, 2002). All mines regulated under the Metal Mining Effluent Regulations (MMER) are required to conduct EEM, the objective of which is to evaluate the effects of mining effluent on the aquatic environment, specifically fish, fish habitat, and the use of fisheries resources. Although these general criteria have been established, consensus on which methods provide the most practical and reliable results for a given

Figure 2.3: Representative LA-ICPMS spectra showing trace element concentrations in parts per million (ppm) *versus* distance in microns (μm) across the otolith from core to rim.



exposure scenario is a subject of discussion (Courtenay *et al.*, 2002; Palace *et al.*, 2005; Palace *et al.*, 2007). Specifically, considerable debate has occurred with respect to appropriate fish sampling methods for the analysis of effects. Fish population surveys are done to evaluate effects on fish, and benthic invertebrate community surveys are done to evaluate effects on fish habitat (Dumaresq *et al.*, 2002). To evaluate effects on the use of fisheries resources, fish tissue analyses are required. However, muscle and visceral tissues are good indicators of recent contaminant exposure only, due to metabolic transformation and tissue re-compartmentalization of trace elements (Palace *et al.*, 2007). Otoliths are metabolically inert and, as such, contain a complete chemical history of exposure.

Several recent studies have demonstrated a link between otolith microchemistry and proximity to mineral deposits. Friedrich and Halden (2008) demonstrated a link between local geology near rare element pegmatite mining activity and the microchemistry of otoliths from fish of the surrounding area. Otoliths obtained from water bodies adjacent to, or downstream from the mine contained Li, Cs, and Rb in elevated levels, elements that are known to be in abundance in the pegmatite. Otoliths obtained from water bodies upstream from the mine and from lakes in a different watershed, however, did not contain Li or Cs, and contained lower levels of Rb, suggesting a direct correlation between the geology and mining activity of the area and the microchemistry of otoliths. Halden and Friedrich (2008) reported significantly elevated concentrations of Cu, Pb, and Zn in one otolith from Lake Athapapuskow, which is adjacent to Cu, Pb, and Zn mining and smelting activities in Flin Flon, Manitoba. They concluded that this sudden increase in concentration is a record of the fish coming into contact with tailings effluence or atmospheric fallout. Palace *et al.* (2007) provided the first determinations of selenium in the otoliths of rainbow trout captured from a site receiving runoff with elevated selenium from a coal mine operation. Annular concentrations of selenium in the otoliths indicate that fish from the mine-impacted system are recent immigrants from nearby reference streams not receiving selenium-bearing effluent.

Otoliths are considered to serve as natural markers provided that the chemical environment influences the rate of trace element incorporation into the growing otoliths (Campana, 1999). For certain elements, such as Ni and Cr, there is no evidence that fish physiology and/or biological processes influence their uptake and, therefore, their incorporation into the otolith structure is dependent mostly on the concentrations available in surrounding water (Arslan, 2005). Most previous investigations of Ni in otoliths were whole-otolith studies that focused on marine species, and reported concentrations from 0.02-9.5 ppm (Ahmad and Al-Ghais, 1997; Arslan, 2005). Similarly, the majority of previous studies on Cr in otoliths has been on whole otoliths from marine fish, reporting concentrations in the range of 0.23-1.8 ppm (Arai and Hirata, 2006; Arai *et al.*, 2007a). One study used laser spot analyses across the life history transect of chum salmon otoliths and reported a range of Cr values from 3.8-68.1 ppm, concluding that element ratios have the potential to aid in distinguishing between salmon spawning sites and habitats (Arai *et al.*, 2007a).

The present study provides a unique opportunity to study the microchemistry of otoliths from fish living within a closed system exposed to the effects of base metal mining, and is the first to analyze this group of base metals, namely Ni, Cu, and Cr, across the entire life history transect of fish from freshwater. Given that the fish were obtained from a well-constrained setting, of which much is known about the geochemical character of the watershed, it is most likely that the metal-bearing, mafic-ultramafic rocks are the ultimate source of the base metals in the otoliths, in particular sulphide minerals bearing Ni (pentlandite and violarite) and Cu (chalcopyrite), and layers of chromite. Oxidation of these minerals exposed at the surface is a likely mechanism that would release these elements into the water in the pit. This link has implications for elemental fingerprinting using otoliths. In cases where the geology of habitats is sufficiently different as to provide the environment with a unique suite of elements, the trace element chemistry of otoliths may be used in distinguishing between such habitats.

Studies of Pb in otoliths in both natural and laboratory settings have found that elevated levels do not correlate with pH or salinity, suggesting that otoliths may serve as indicators of Pb contamination (Ranaldi and Gagnon 2008; Geffen et al 1998; Kock et al 1996). In a study of black bream (*Acanthopoagrus butcheri* Munro) from the Swan River estuary in Australia, Pb concentrations of the marginal regions (edge) of otoliths ranged from 0.14-0.38 ppm in the contaminated sites, compared with an average of 0.04 ppm in the reference site (Ranaldi and Gagnon 2008). The high Pb concentrations were attributed to urban drainage discharge, traffic emissions, and subsequent runoff from roads. Lead concentrations in otoliths from the Maskwa pit arctic char range from 0.07-2.18 ppm. The source of lead may be anthropogenic, such as leaded gasoline used during mining operations, or a natural occurrence of Pb in the area. Analyses of mineralized rocks from the Bird River Belt indicate Pb concentrations up to 48 ppm (Gilbert, 2006). Lead isotope ratio analyses would help distinguish between these two potential sources.

In this unusual situation, where an exotic species has been introduced to a closed lake, there has been no recruitment of fish from other environments. The relatively flat base metal signatures in the otoliths indicate that these char have retained a chemical signature from the Maskwa pit for their entire lives. The fish, which ranged in age from 5 to 9 years, have successfully occupied the lake and continued to breed despite the influence of the surrounding rocks and local contamination. Water chemistry data for the Maskwa pit were collected in 2006 by Wardrop Engineering, Inc. (Table 2.3). The values of trace elements in the water are to be expected given natural leaching of metals such as Ni and Cu from the surrounding geology as well as past mining activity.

Strontium and Ba signatures are oscillatory but are not necessarily in phase with one another. Oscillations in otolith Sr have been used in previous migration studies to distinguish anadromous from non-anadromous behaviour (Halden *et al.*, 1995; Halden *et al.*, 1996). In the Maskwa pit arctic char, Sr concentrations typically vary between 200 and 300 ppm, levels that are expected in a freshwater lake. The char do not migrate in or out of the Maskwa pit, which is reflected in the relatively consistent Sr concentrations across all annuli. Uptake of Sr into otoliths is a function of many factors, and the minor oscillations may reflect changing water temperature, diet, or fish metabolism. Barium uptake in otoliths has been shown to be related to both the ambient water composition (Bath *et al.*, 2000) and diet (Buckel *et al.*, 2004). As these samples were collected from a small closed system, it is hypothesized that the periodic distribution of Ba in the otoliths represents a dietary signature.

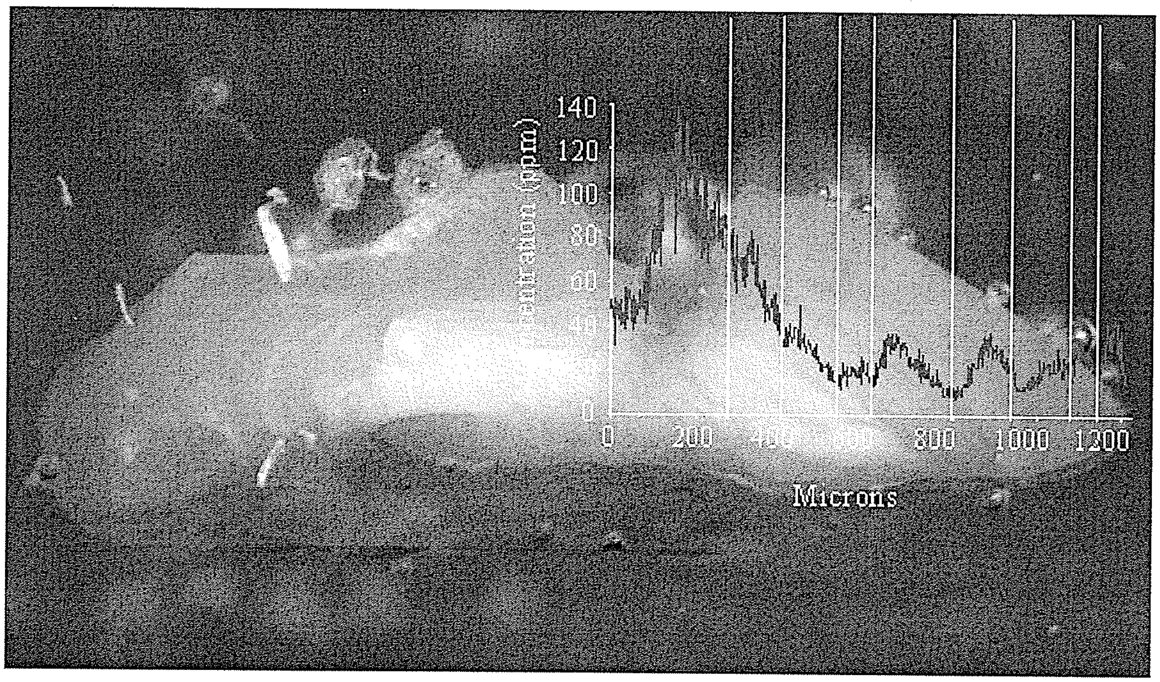
Distribution of Zn in Maskwa pit arctic char otoliths is oscillatory, corresponding to the annular structure of the otoliths (Figure 2.4), which indicates that Zn uptake by the

Table 2.3: Water chemistry data (concentrations in parts per million) for the Maskwa pit, provided by Wardrop Engineering, Inc (see also Appendix K). Samples were collected over 3 days in 2006 at a depth of 1 m. Samples for dissolved metals analyses were unacidified and passed through a 0.45 micron membrane filter. Samples for total metals analyses were unfiltered and digested with acid (Dave Tyson, Wardrop Engineering Inc., personal communication, 2009).

	Ca	**Cr**	**Ni**	**Cu**	**Zn**	**Sr**	**Ba**	**Pb**
Dissolved metal	56.6	<0.0002	0.0807	0.0037	<0.0005	0.164	0.0348	0.00004
Total metal	57.0	0.0007	0.0909	0.0040	0.0013	0.174	0.0382	0.00011

fish follows a yearly pattern, and there is an overall decrease of Zn content with age. These observations are consistent with those of Halden *et al.* (2000), where similar oscillatory Zn was detected in non-anadromous arctic char from Lake Hazen. The dissolved load of Zn in the Maskwa pit water is an order of magnitude lower than the total Zn concentration (Table 2.3), indicating that much of the Zn available to fish may be associated with particulate and organic materials, which are included in the latter form of water analysis. Zinc is known to be an essential micronutrient that is involved in various metabolic pathways, but becomes toxic at high concentrations (Watanabe *et al.*, 1997). For metabolic purposes, fish can derive Zn from dietary sources, via the gastrointestinal tract, as well as from the water, via the gills (Watanabe *et al.*, 1997). A recent study of pink snapper otoliths demonstrated that dietary Zn was the major source of Zn incorporated into the otoliths (Ranaldi and Gagnon, 2008b). Zinc availability for incorporation into an otolith therefore depends upon the uptake of the element into organisms of the arctic char diet, such as insects, crustaceans, and snails. However, the ultimate source of Zn in an environment is the lithosphere, particularly those rocks comprising the surrounding watershed. In the case of Maskwa, the adjacent Dumbarton Deposit (Figure 2.2) is a likely source of Zn-bearing sulphides (Duguet *et al.*, 2005), as is the Ore Fault property (Figure 2.2), which contains Zn in the form of sphalerite (Ritchie, 1972). The significance of the oscillatory signature is likely a reflection of Zn availability to the fish either within its local environment or through changes in metabolism. Correlations between Zn periodicity and the annular structure may provide temporally

Figure 2.4: Overlay of LA-ICPMS Zn spectrum on an image of a Maskwa pit arctic char otolith. The laser scan that produced the element trace shown lies directly under the *x* axis of the plot. Vertical lines represent position of annuli along laser trace.



constrained information on habitat, fish behaviour, or nutrient supply (Halden *et al.*, 2000). In such cases where a correlation does indeed exist and Zn varies with a yearly periodicity, it may be a method of chemically based age determination.

A typical signature for fish living in the Maskwa pit was determined by compiling chemical data from the suite of otoliths (Figure 2.3). This establishes a local baseline chemical record that could be used to identify periods when signatures vary from the norm and can function as a bio-monitoring tool for changes in the environment affecting fish. Otoliths offer a method for monitoring the level of trace elements affecting fish on an annual basis. As such, otolith microchemistry may be considered a useful assessment tool for monitoring the exposure of wild organisms to trace elements in lacustrine environments. Analysis of otolith microchemistry of fish from environments impacted by mining activity will determine what constitutes a typical chemical signature from the area, thus providing a baseline record against which any further analyses may be compared to determine any anomalous signatures. Development of this technique and database of yearly chemical data will aid in understanding the impact mining has on fish in the local aquatic environment, and can assist in conservation efforts as well as rehabilitation and reclamation of affected areas. The link between the microchemistry of otoliths and the geochemistry of the surrounding environment provides an assessment tool for the impact of mining activity on fish populations, either as part of background geochemical or environmental surveys, or in the form of on-going monitoring programs and fisheries management, and can help address the issue of remediating orphaned tailings. One of the challenges facing mining companies today is how to restore the environment after mining activity has ended. In many instances, particularly after open-pit mining, creating a stocked fishing lake may be a viable option for restoring the resulting excavation. Continued sampling of the fish and otoliths from the Maskwa pit will allow for on-going monitoring and provide useful insight into the feasibility of creating and maintaining a stocked lake after mining activity has ceased. To expand knowledge on the topic further, the initiation of similar monitoring programs where other stocked lake settings occur is recommended.

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Chapter 3 Determining exposure history of northern pike (*Esox lucius*) and walleye (*Sander vitreus*) to tailings effluence using trace metal uptake in otoliths

3.1 Abstract

Determining the effects of mining activity on fish populations is complicated by the uncertainty of fish residency in an affected area. Otoliths are considered to be metabolically inert and can contain complete chemical records of environments in which the individual has lived. When coupled with the annular structure, otoliths provide temporal information to the history of exposure to pollutants. Northern pike (*Esox lucius*) and walleye (*Sander vitreus*) otoliths collected from two lakes adjacent to base metal mine tailings effluence at Lynn Lake, Manitoba, Canada, were analyzed using laser ablation inductively coupled plasma mass spectrometry to determine background levels of trace metals. The presence of overlapping Zn, Cu, and Pb anomalous peaks above background levels in some of the fish otoliths is interpreted as a record of elevated levels in the environment. These otoliths provided a record of the history of fish movement into and out of the affected area.

3.2 Introduction

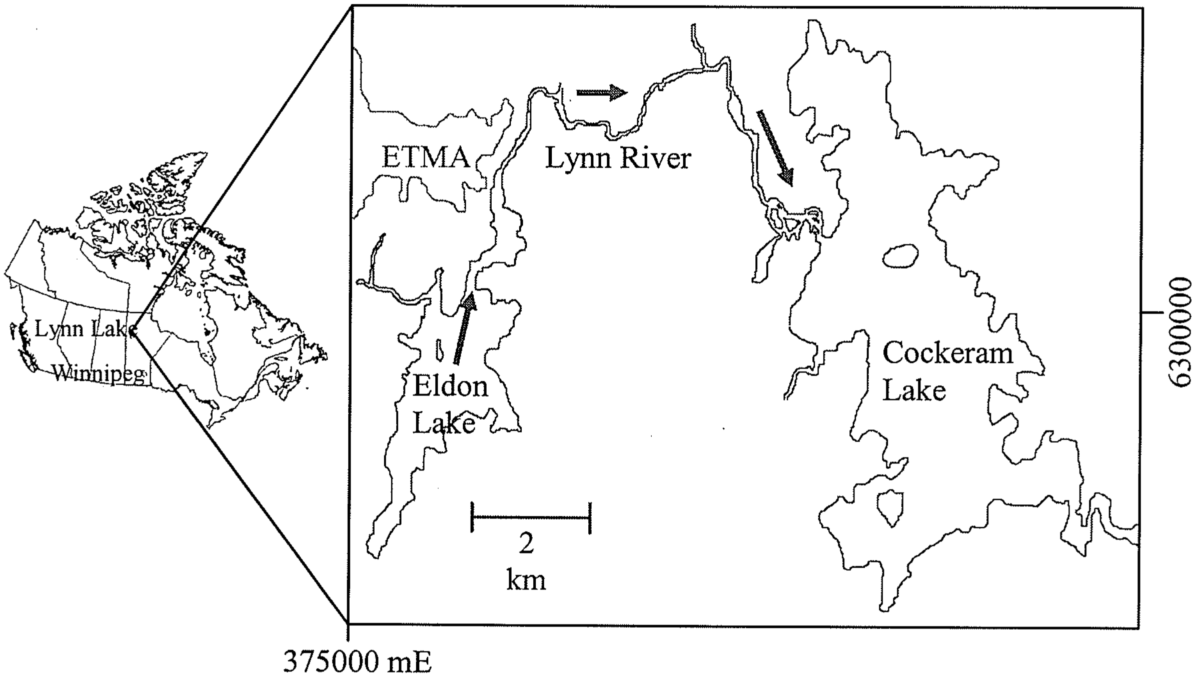
Otoliths are calcified structures located in the inner ear of teleost fish, composed of layers of aragonite in a protein matrix deposited continuously throughout the lifetime of the fish (Degens *et al.*, 1969). Both the inorganic portion (Reeder, 1983) and the protein matrix (Hüssy *et al.*, 2004) have the capacity to incorporate a broad range of trace elements, many of which can now be detected at the low parts per million (ppm) to parts per billion (ppb) level. Periodic changes in trace metal concentrations in the environment may influence the amounts available for incorporation into the otolith through food or ambient water (Campana, 1999). Unlike many biominerals, otoliths are acellular and metabolically inert, offering a permanent record of the bioavailability of certain metals (Campana and Neilson, 1985). Numerous studies have used chemical analysis of otoliths as a proxy for water temperature variations, to distinguish migratory from non-migratory behaviour, and for stock discrimination (Campana *et al.*, 2000; Campana *et al.*, 1995; Kalish, 1989; Milton *et al.*, 2008; Radtke, 1989). An area of application that has received by comparison less attention is the assessment of environmental pollution and the impact mine tailings have on fish populations. Several recent studies have examined the link between the chemistry of the environment, particularly the geochemistry of a watershed, and the microchemistry of otoliths in lakes near mining operations (Friedrich and Halden, 2008; Halden and Friedrich, 2008; Palace *et al.*, 2007). Coupling annular structure to the chemical record of otoliths can provide a chronologic record of the environmental history of the individual fish, particularly where the bioavailability of specific metals can be linked to spatial or temporal variations, forming the basis for an expanding branch of otolith microchemistry studies.

To be able to interpret changes in the environment from the record, it is necessary to establish what constitutes normal or expected variations in otolith microchemistry for a given environment or species. This study is an examination of northern pike (*Esox lucius*) and walleye (*Sander vitreus*) otoliths from the vicinity of mine tailings using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). A suite of trace elements (Mn, Ni, Cu, Zn, Sr, Cd, Ba, and Pb) was analyzed across the annular structure of the otoliths to determine what constitutes a typical chemical signature in the area for these two fish species, and to identify any periods where the chemistry might be considered anomalous.

3.3 Study Area and Geologic Setting

The town of Lynn Lake, Manitoba is approximately 1100 km northwest of Winnipeg (Figure 3.1), in an area that is underlain by Precambrian Wasekwan volcanic and sedimentary rocks, with amphibolite and basic igneous intrusions that consist of gabbro and norite (Davies *et al.*, 1962). Sulphide mineralization occurs as massive and disseminated deposits consisting of pyrrhotite [$Fe_{(1-x)}S$], pendlandite [$(Fe, Ni)_9S_8$], and chalcopyrite [$CuFeS_2$] (ibid). Small amounts of pyrite [FeS_2] and trace amounts of sphalerite [ZnS] are associated with the sulphide deposit (Pinsent, 1980; Ruttan, 1955). The Lynn Lake nickel mine was operated by Sherritt-Gordon from 1953 to 1976, during which time over 20 million tonnes of Ni-Cu ore was produced and approximately 21.8 million tonnes of tailings were generated (Acres International Ltd., 1986). The tailings pile in the East Tailings Management Area (ETMA) consists of pyrrhotite, chalchopyrite, pentlandite, and pyrite, and have been oxidizing for over 30 years (Gunsinger *et al.*, 2006). Surface acid mine drainage seepage into Lynn River from the tailings slimes has been documented (ibid). In recent years, a number of rehabilitation activities have been completed, including the installation of a trial permeable reactive barrier to treat contaminated groundwater and construction of a diversion to divert clean rain and melt water around the ETMA (Government of Manitoba, 2009). Ongoing remediation activities include revegetation trials, reviewing options for covering the tailings, installation of an engineered wetland to remove contaminants from the ETMA runoff,

Figure 3.1: Map of Eldon and Cockeram Lakes also showing position of Lynn River and the East Tailings Management Area (ETMA) at Lynn Lake. Direction of flow indicated by blue arrows.



relocation of the solid waste facility, and implementation of the ETMA rehabilitation plan (ibid).

Eldon Lake is situated southeast of the town of Lynn Lake and drains northeast into Lynn River at the ETMA. The river flows past the ETMA and into Cockeram Lake, which is approximately 5 km east of Eldon Lake.

3.4 Materials and Methods

Fish were collected from Eldon and Cockeram Lakes in August, 2008, as part of a Lynn River health survey by TetrES Consultants, Inc (Winnipeg, MB). Otoliths were obtained for microchemical analysis from three northern pike and three walleye from Eldon Lake, and three northern pike from Cockeram Lake. The sample set contained mature male and female specimens that ranged in age from 7 to 16 years. To prepare for microbeam analysis, sagittal otoliths were embedded in epoxy resin and cut in a transverse plane to create a dorso-ventral cross section through the core of the otolith, exposing all annuli (yearly growth increments). The posterior half of each sectioned otolith was re-embedded in a 25-mm Lucite microprobe mount, and ground and polished. Prior to analysis, samples were rinsed with double distilled water and allowed to air dry. Laser ablation-ICP-MS analyses were done using a Thermo Finnigan Element 2 ICP-MS coupled to a Merchantek LUV 213 Nd:YAG laser. Running conditions were set to optimize sensitivity and resolve annular growth features in the otoliths, and included a 30 μm-diameter beam travelling 2 μms^{-1} (Table 3.1). Calcium at 56 wt% CaO was used as an internal standard, and the external calibration was done using NIST glass 610 with the nominal values reported by Pearce *et al.* (1997). Line scans were run across the otolith

Table 3.1: Analytical instrument parameters used during analysis.

ICPMS	
Forward power	1303 W
Gas flows	
Plasma (Ar)	16 L/min
Auxiliary (Ar)	0.80 L/min
Sample (Ar/He)	0.89/0.335 L/min
Shield electrode	Used for analysis

LA	
Repetition rate	20 Hz
Pre-ablation warm-up	~60 sec
Pulse duration	5 ns
Spot size	30 μm
Power	75%
Incident pulse energy	~0.020 mJ
Energy density on sample	~6.22 Jcm^{-2}
Laser scan speed	2 μms^{-1}

Data Acquisition	
Data acquisition protocol	Time resolved analysis
Scanning mode	BScan and EScan
Detector mode	Analog and counting
Isotopes determined	^{55}Mn, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{88}Sr, ^{114}Cd, ^{137}Ba, ^{208}Pb
Dwell time (segment duration)	0.3 ms
Magnet settling time	0.001-0.3 ms
Time/Pass	1.7 s
Runs/Passes*	1000-1 (17m 09s)

*pass is a measurement cycle through the mass spectrum; 1 pass collected 1000 times producing 1000 blocks of data per sample surface from core to edge, perpendicular to annuli in time-resolved or scanning mode. Standard analyses were collected prior to each analytical run. Measured trace element concentrations, standard deviations, and detection limits were processed using GLITTER software (van Achterberg *et al.*, 2001) and exported to EXCEL for final presentation.

3.5 Results

Nickel, Cu, and Zn were analyzed to determine if the otoliths contain a chemical signature that may be related to the geochemistry of surrounding environment. Zinc may also serve as a signature relating to diet, as may Ba and Mn. Lead was included as a potential indicator of the deposit, as it commonly occurs with Cu and Zn in sulphide minerals and oxidation of galena (PbS) is assumed to be the source of Pb in the ETMA (Gunsinger *et al.*, 2006). Cadmium is a trace metal that is toxic to aquatic animals at low concentrations that may be an indicator of anthropogenic influence (Canadian Council of Ministers of the Environment, 2002). However, the source of Cd in pore waters of the ETMA is considered to be Cd substituting for Zn in sphalerite (Gunsinger *et al.*, 2006), a mineral which occurs in trace amounts in the ore (Ruttan, 1955). This suite of elements analyzed in northern pike and walleye otoliths from fish in Eldon and Cockeram Lakes provide information on what characteristic chemical signatures are for the two species in the Lynn River area. Table 3.2 summarizes trace element concentration ranges from the otoliths.

Figure 3.2 is a representative laser scan of a northern pike otolith from the study area. These northern pike otoliths typically contain 250–650 ppm Sr in relatively flat profiles with occasional peaks, and 50–140 ppm Zn, which is highest in the core and decreases with age. Zinc signatures in northern pike contain periodic oscillations that

Table 3.2: Range of trace element concentrations (parts per million) in otoliths of northern pike and walleye from the study area. Typical 1σ error values are given for elements that did not produce oscillatory signatures.

	Mn	**Ni**	**Cu**	**Zn**	**Sr**	**Cd**	**Ba**	**Pb**
Northern Pike	0.18 – 186.50	0.00 – 1.76	0.00 – 2.91	0.32 – 165.10	123.90 – 1581.90	0.00 – 0.48	1.09 – 33.38	0.00 – 0.14
Walleye	0.05 – 6.23	0.07 – 1.63	0.07 – 2.59	0.05 – 2.25	118.28 – 566.50	0.00 – 0.46	0.86 – 10.15	0.00 – 0.11
Typical 1σ Error	N/A	0.29	0.36	N/A	N/A	0.08	N/A	0.011
Typical Detection Limit	0.05	0.13	0.15	0.06	0.03	0.05	0.01	0.01

Figure 3.2: Representative trace element distribution profiles from LA-ICP-MS line scans of northern pike otoliths from the study area. Smoothed lines in Ni, Cu, Cd, and Pb plots represent moving average trend line with a 25 point period.

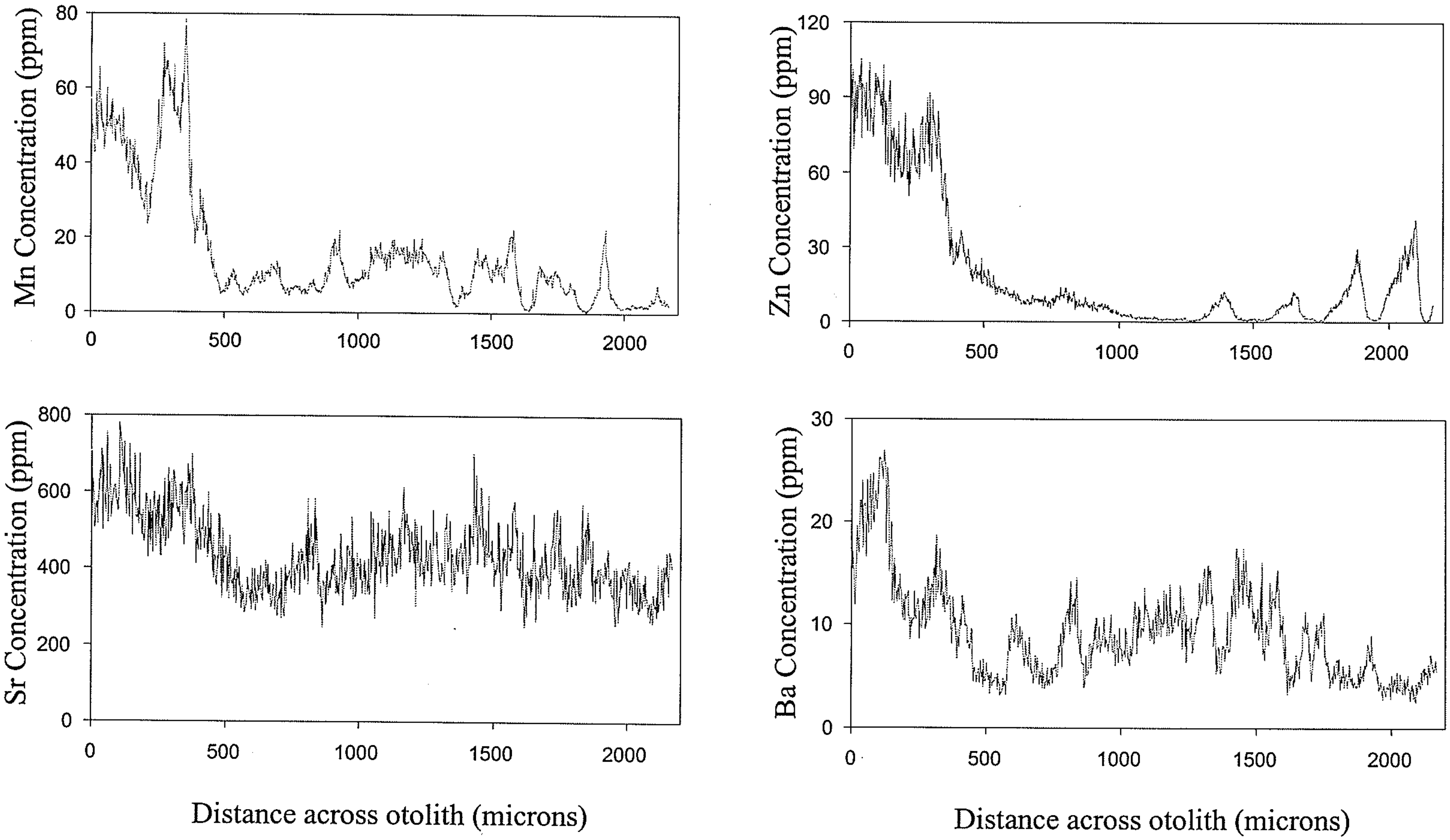
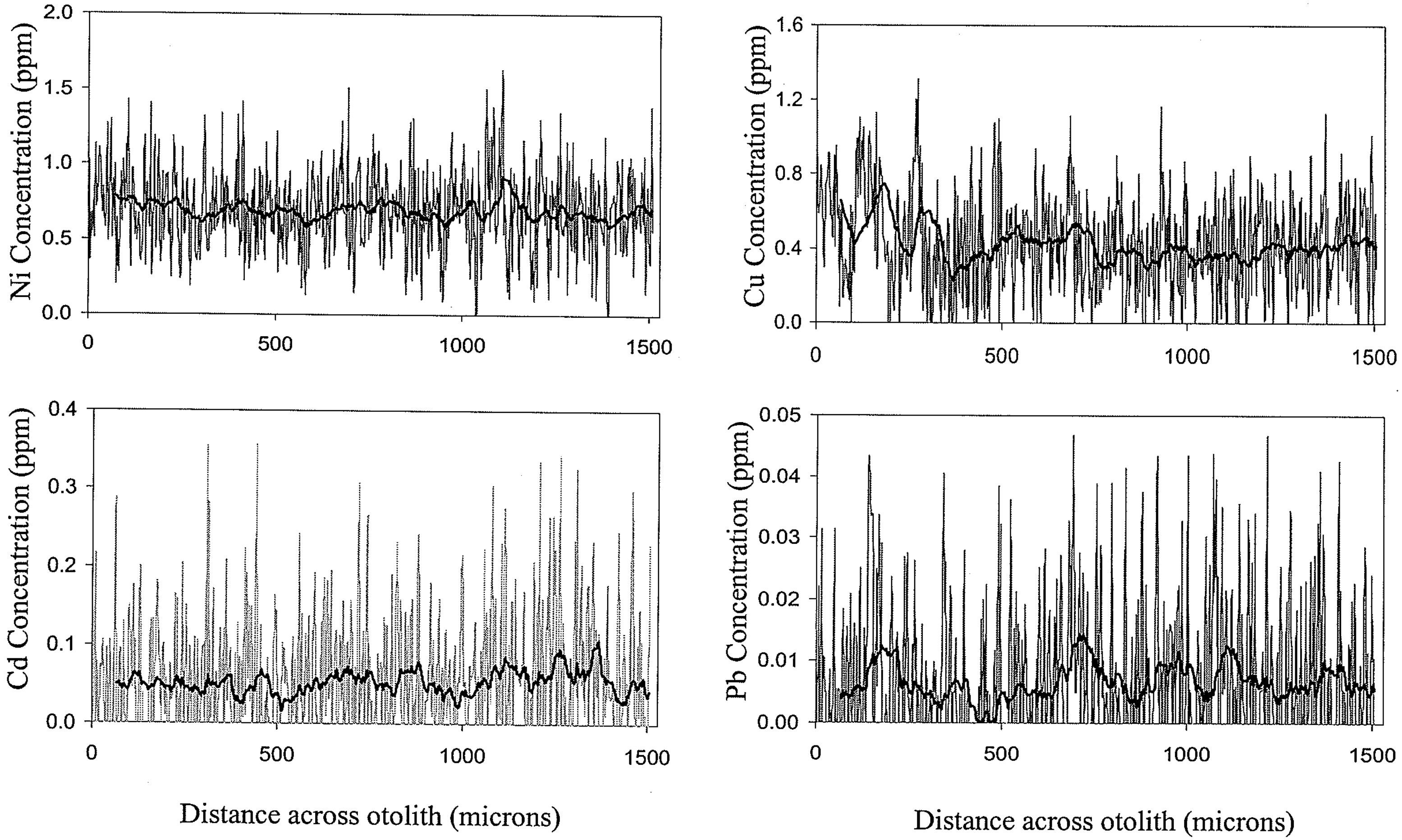


Figure 3.2 *continued*



correspond with the position of annuli (Figure 3.3). Manganese and Ba profiles are oscillatory, with maximum concentrations of approximately 185 and 30 ppm, respectively. Similar to Zn, Mn and Ba concentrations are usually highest in the core of the otolith and decrease to the edge, i.e. with age. Typical concentrations of the metals are 0.1–0.4 ppm Cu, 0.5 ppm Ni, 0.05 ppm Cd, and 0.01 ppm Pb, all of which produce relatively flat profiles. Walleye otoliths typically contain 120–550 ppm Sr and around 0.4 ppm Zn, both in relatively flat signatures (Figure 3.4). Manganese and Ba are oscillatory, but concentrations are an order of magnitude less than those in northern pike otoliths; typical Mn concentrations in walleye are less than 5 ppm, and Ba ranges from 1-10 ppm. Characteristic trace metal concentrations are 0.1 ppm Cu, 0.6 ppm Ni, 0.05 ppm Cd, and 0.01 ppm Pb.

A departure from these general patterns was observed in two walleye otoliths from Eldon Lake. Figure 3.5 shows the location of a laser line scan across an otolith of a walleye, estimated to be 5 years old. A Zn peak of about 1.2 ppm occurs approximately 170 microns along the laser traverse from the core. Overlaying Zn data with scans for Cu and Pb shows that elevated levels of Cu and Pb, 0.9 and 0.1 ppm, respectively, correspond to the Zn peak. Comparison with the optical image of the otolith indicates that the fish encountered slightly higher levels of these elements within the first year of life, possibly near the location of spawning.

3.6 Discussion

Although the majority of otolith chemistry studies focuses on Sr and how it may be used to distinguish migratory from non-migratory behaviour, otoliths have the capability to incorporate a wide range of trace elements that can provide information on a

Figure 3.3: Overlay of LA-ICP-MS Zn distribution profile on an image of a northern pike otolith from Cockeram Lake showing correlation between Zn peaks and position of annuli, represented by vertical bars.

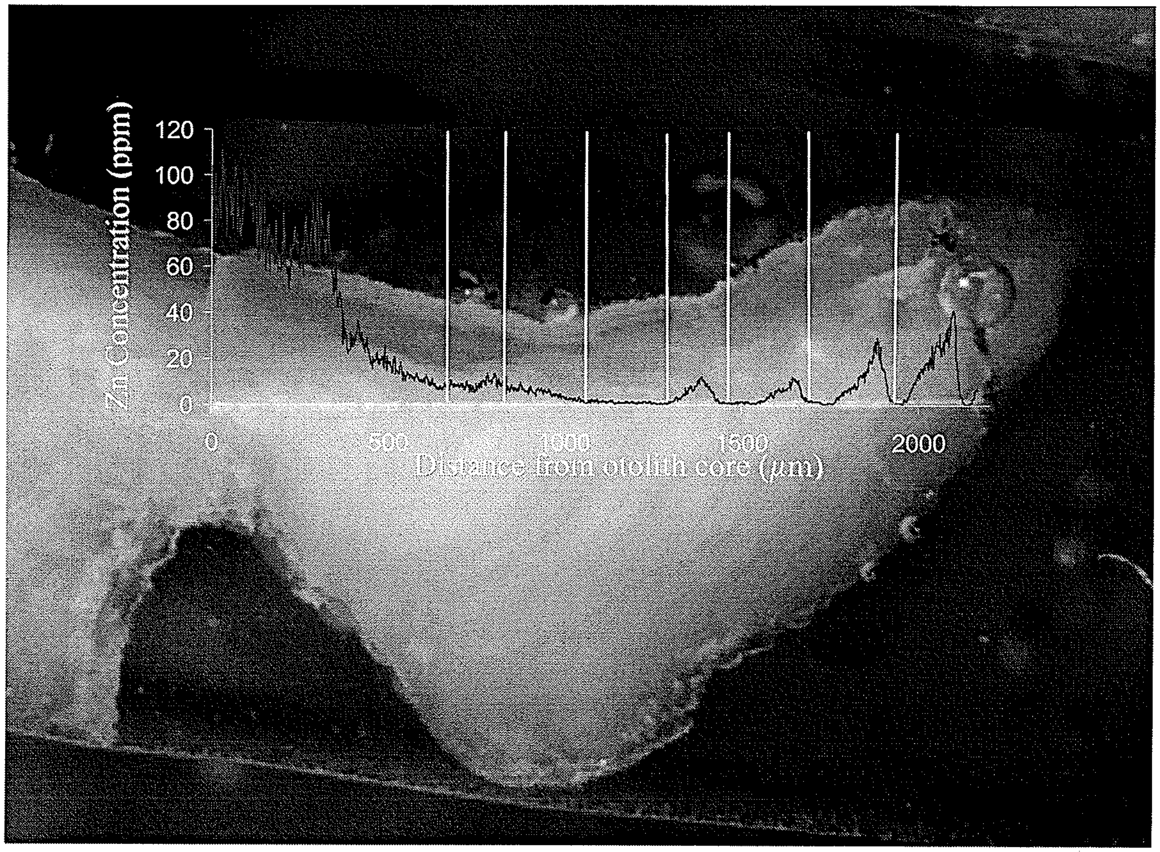


Figure 3.4: Representative trace element distribution profiles from LA-ICP-MS line scans of walleye otoliths from the study area. Smoothed lines in Ni, Cu, Cd, and Pb plots represent moving average trend line with a 25 point period.

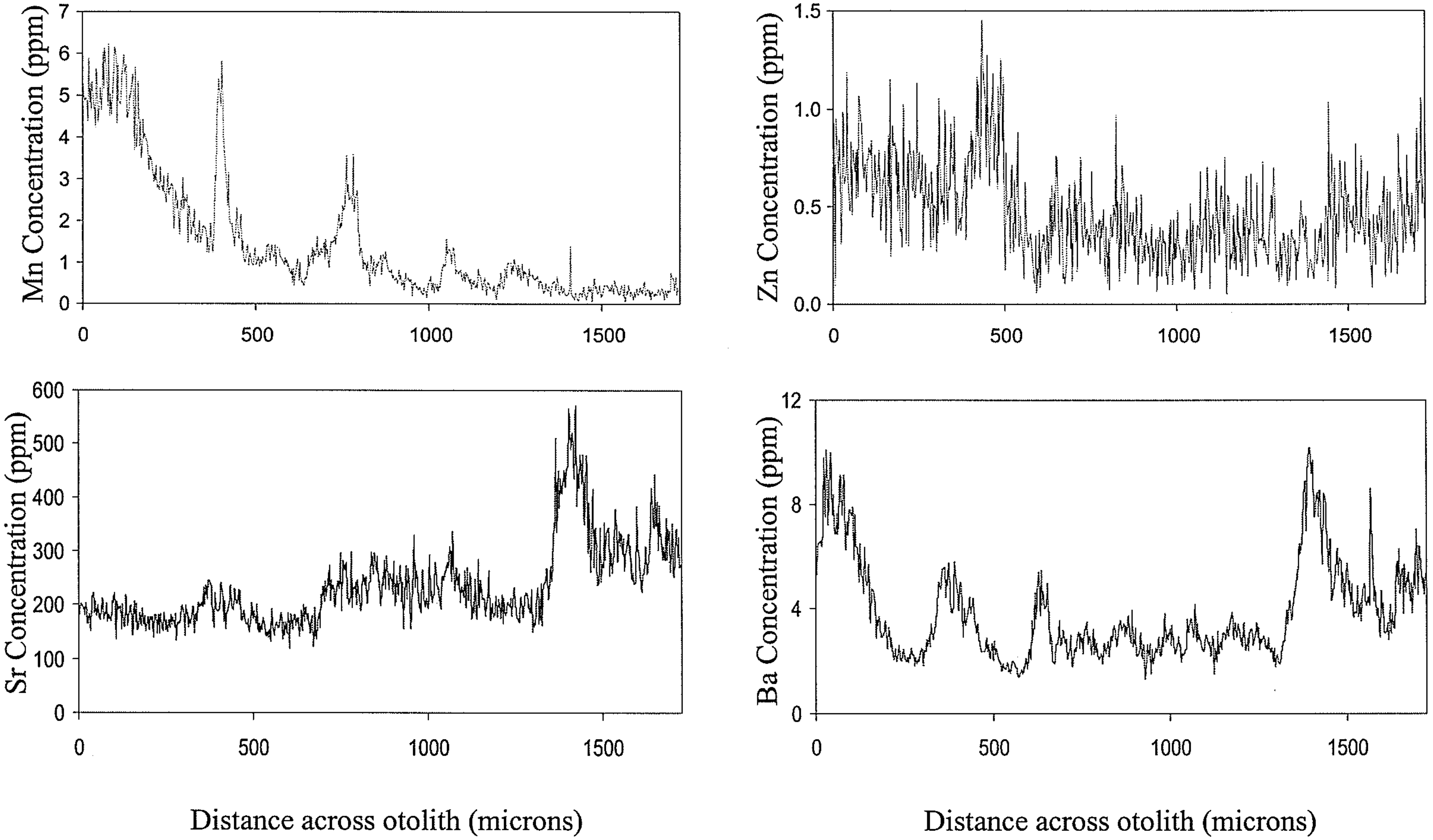


Figure 3.4 *continued*

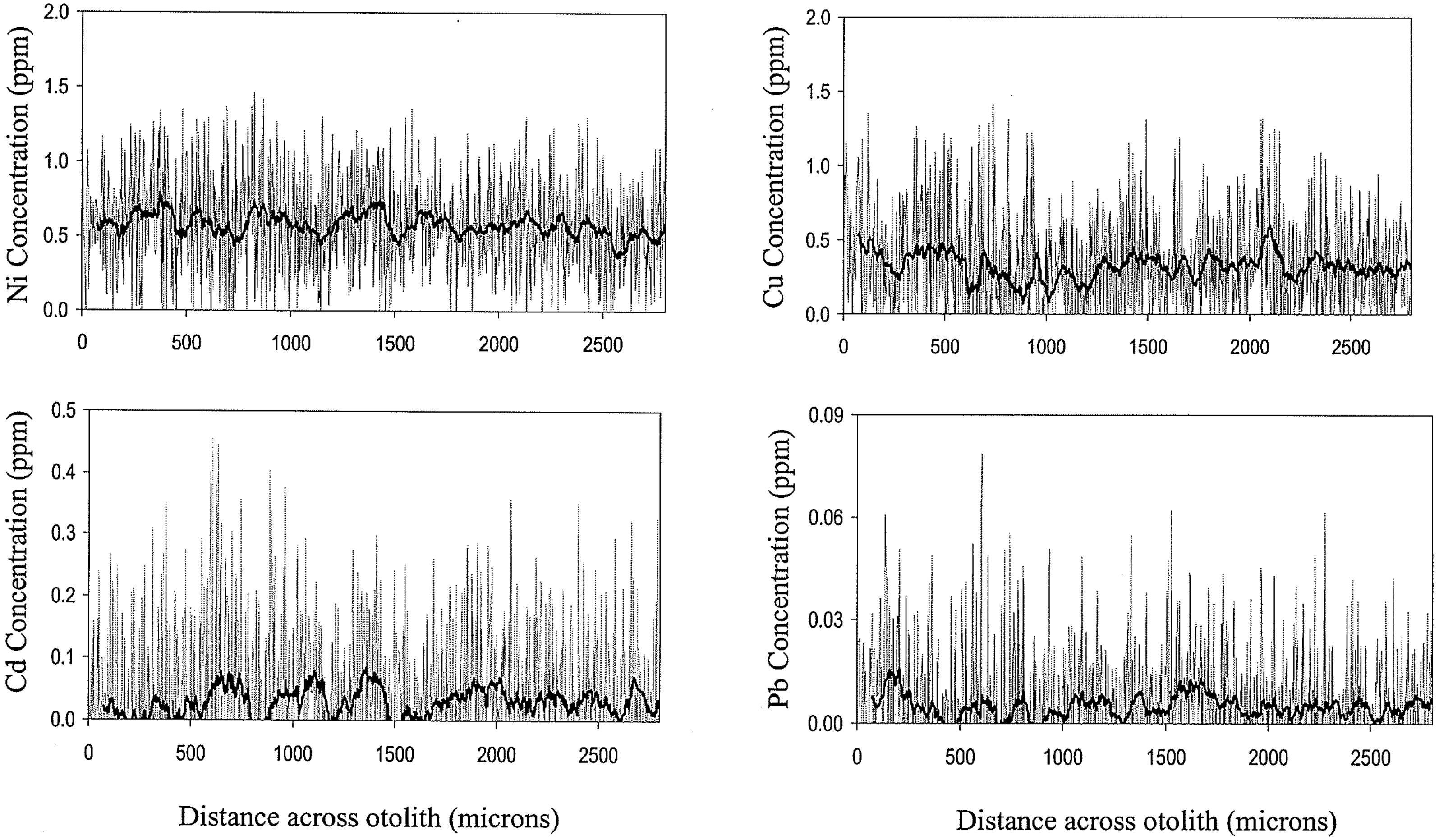
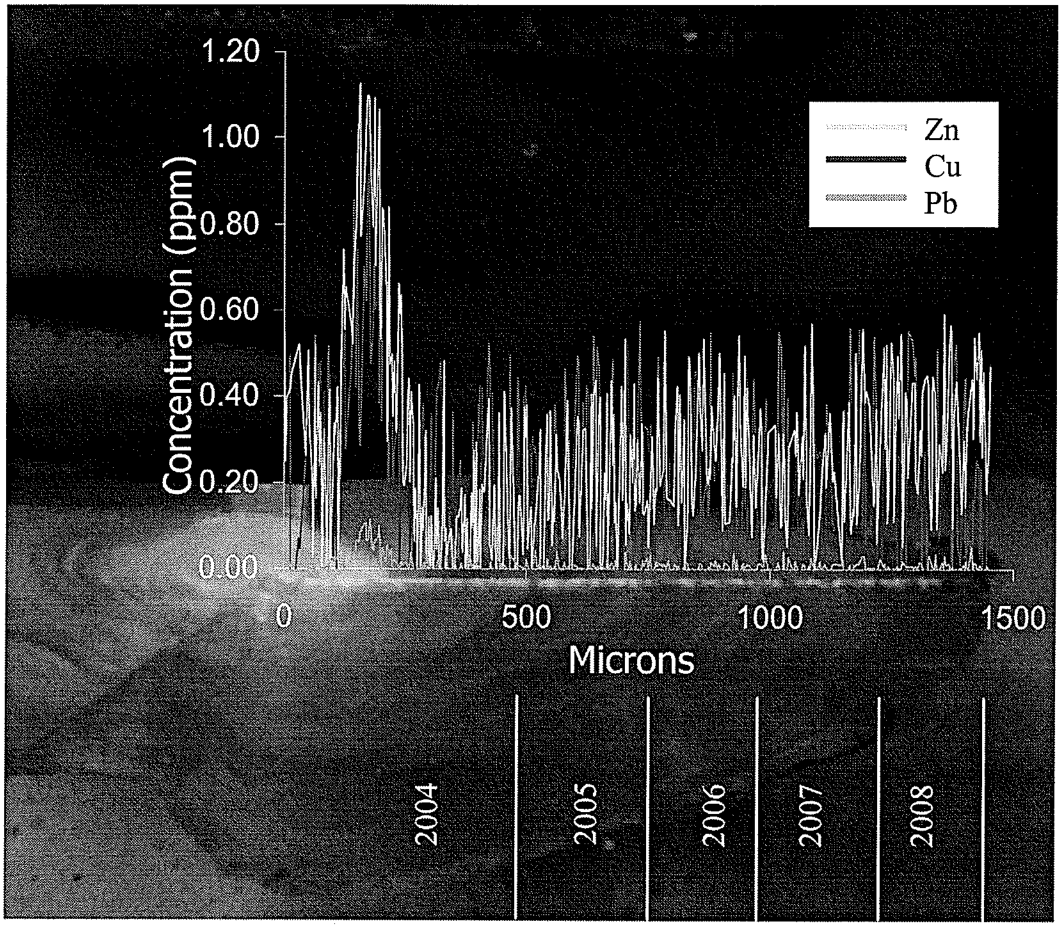
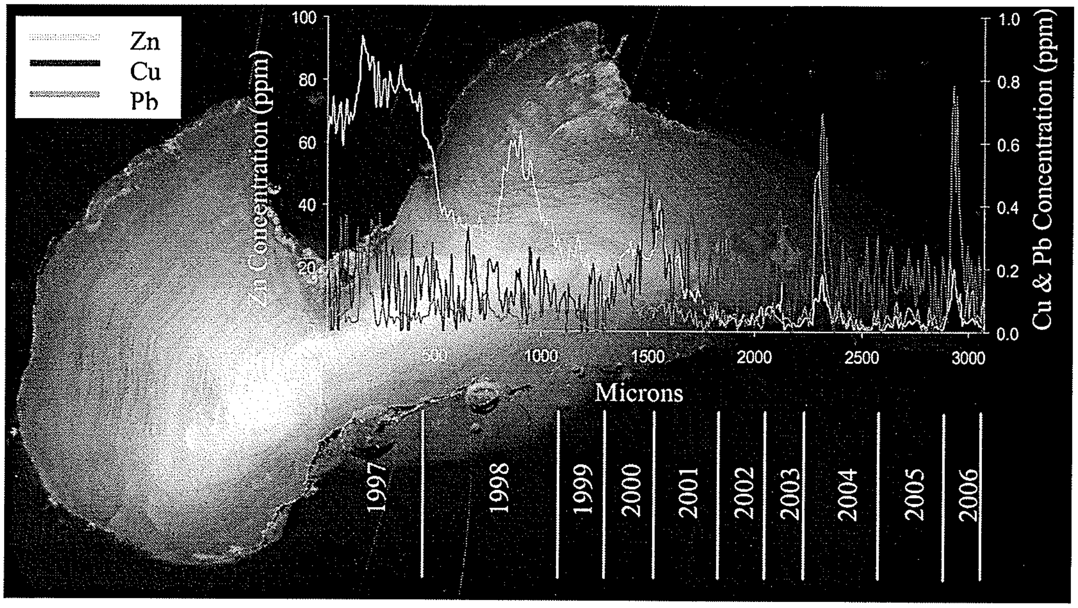


Figure 3.5: Overlay of LA-ICP-MS trace metals distribution profiles on an image of a walleye otolith from Eldon Lake. Years corresponding to each section of otolith were determined by assigning annual growth zones from the year of capture (2008) to the otolith primordia.



fish's environment and behaviour. Otoliths from Eldon and Cockeram Lakes give a general idea of what background signatures should be for metals in the area. Increased levels of Zn in otoliths are not uncommon (Friedrich submitted (see chapter 2), Halden and Friedrich, 2008; Halden *et al.*, 2000). Zinc is an important, biologically mediated element involved in various metabolic pathways, but becomes toxic at high concentrations (Watanabe *et al.*, 1997). Signals detected above these background levels may be related to diet or metabolism. Therefore, the identification of a Zn peak in an otolith laser trace may simply be indicative of ontogenetic change in the individual and is not in and of itself indicative of contamination. However, the coincidence of elevated levels of geochemically coherent Cu and Pb with the Zn peak strongly suggests a link to tailings effluence and could be regarded as an anomalous signature. The chemical profiles of the two Eldon Lake walleye indicate that these individuals encountered elevated concentrations of Cu, Pb, and Zn in a relatively sudden or different way from how they typically encounter these elements, as well as Ba, Mn, and Sr. Similar, anomalous Cu-Pb-Zn peaks were also found in 5 northern pike otoliths collected from Lynn River in 2006, one of which contained 2 separate anomalous peaks (Figure 3.6). Lake trout otoliths from Athapapuskow Lake, Manitoba contained anomalous Cu-Pb-Zn signatures that were attributed to the fish coming in contact with tailings effluence from Cu, Pb, and Zn mining activity occurring nearby in Flin Flon, Manitoba (Halden and Friedrich, 2008). In a laboratory study, Melançon (2008) injected yellow perch with Sr and Ba isotopes and found that enriched levels of the isotopes began to rise in otoliths in as little as hours to days after injection. This would suggest that wild fish coming in

Figure 3.6: Overlay of LA-ICP-MS trace metals distribution profiles on an image of a northern pike otolith from the Lynn River area showing anomalous peaks in 2004 and 2006. Years corresponding to each section of otolith were determined by assigning annual growth zones from the year of capture (2006) to the otolith primordia.



contact with elevated levels of trace elements in the environment might incorporate such signals into their otoliths within a relatively short period of time after exposure. Such a signal would appear as a sudden increase in concentration in comparison to any natural, annual periodicity to the signal, or above background levels.

Geochemical coherence of Cu, Pb, and Zn is to be expected in nature because these elements occur together in sulphide minerals. Such minerals are ubiquitous in rocks, and hence the environment, therefore it is reasonable to anticipate some level of these elements to be constantly present at background levels. The occurrence of corresponding elevated levels of these metals in both the Lynn River area and Athapapuskow Lake are above any background level or periodic signature of the fish. Both locations are in close proximity to mine tailings containing these elements, which are recognizable and identifiable as potential sources of the elevated concentrations. Anomalous peaks above background levels in otoliths provide a retrospective view of exposure to these elements. The time scale provided by otolith annuli allows not only the determination if fish are coming in contact with elevated levels of metals, but when contact has happened and how frequently (e.g., Palace *et al.*, 2007).

Defining variations in life history within a population using otolith microchemistry requires establishing a relationship to environmental parameters, without which interpretations are limited, and movements between different environments cannot be identified (Elsdon *et al.*, 2008). Concentrations of metals in Cockeram Lake are at background for the area (0.002 ppm Cu, <0.0001 ppm Pb, and 0.005 ppm Zn), similar to Eldon Lake (0.005 ppm Cu, <0.0001 ppm Pb, and 0.029 Zn). One location in Lynn River contains slightly higher levels of the metals: 0.010 ppm Cu, up to 0.001 ppm Pb, and

0.051 ppm Zn (Karen Mathers, TetrES Consultants, personal communication, 2009). High concentrations of these metals in pore waters from ETMA adjacent to Lynn River (Gunsinger *et al.*, 2006) can be identified as a likely source for the group of trace metals in this particular environment. This location has unique geochemical characteristics that appear to be reflected in the otolith microchemistry. In this case it is possible to describe the movement of contingents within this limited sample set with respect to the ETMA in terms of when and how often they are coming in contact with tailings effluence.

With the exception of the anomalous peaks described above, the majority of otoliths from Eldon and Cockeram Lakes contain concentrations of metals at low levels. Such levels indicate that the chemical signature from the mine is attenuated away from the mine, an observation that has been described in other otolith microchemistry studies. Friedrich and Halden (2008) described the decrease in alkali element signal with increasing distance from a rare element pegmatite mine. Saquet *et al.* (2002) observed highest Zn levels in fish captured at the outflow from a tailings dump, and lower levels in fish from farther away. These observations may aid in assessing the impact of mine tailings on fish populations and speak to the effectiveness of remediation attempts that have been made.

Although walleye and northern pike otoliths contain similar amounts of Ni, Cu, Cd, and Pb, a comparison of the two species from Eldon Lake shows that there are differences in the amounts of Zn and Mn, suggesting that these elements are recording something different. This may be a dietary signal or, in the case of Mn, variations in redox potential. Manganese signatures are similarly oscillatory in both species, however the concentration in the walleye is consistently an order of magnitude less than that in the northern pike. In walleye otoliths, Zn is present only at low levels, with no oscillations in the signals. Distribution of Zn in Eldon Lake northern pike is oscillatory and roughly corresponds to the annular structure of the otoliths, which indicates that Zn uptake by the fish is periodic on a yearly basis, and there is an overall decrease of Zn content with age. These patterns for Mn and Zn are consistent with walleye and northern pike from Booster Lake, Lac du Bonnet, and Bird River in southern Manitoba (Table 3.3). The similarity of these chemical traces from northern and southern Manitoba would suggest that these are characteristic signatures for these species, and point to dietary influence over these elements. Such information is imperative for determining background levels for environments. The northern pike Zn signatures are comparable to those found by Halden *et al.* (2000) and Friedrich (submitted; see chapter 2), where similar oscillatory Zn was detected in non-anadromous arctic char from Lake Hazen, Nunavut, and stocked arctic char in a closed open-pit mine in southeast Manitoba, respectively. For metabolic purposes, fish can derive Zn from dietary sources, via the gastrointestinal tract, as well as from the water, via the gills (Watanabe *et al.*, 1997). A dietary influence over otolith Zn concentration would therefore seem a likely explanation for the differences observed in the Eldon Lake walleye and northern pike. Although both piscavores, northern pike are the most dominant predator of walleye over most of its range.

Results in the literature on dietary uptake of trace elements in otoliths are inconsistent. In a laboratory setting, Bucket *et al.* (2004) determined that diet of juvenile bluefish affected levels of Sr and Ba in otoliths, but not Na, Mg, K, Ca, or Mn. In an experiment on European eel otoliths, food was found to have no significant influence on

Table 3.3: Comparison of average Zn and Mn concentrations (in parts per million) between northern pike and walleye otoliths from lakes in northern (this study) and southern Manitoba (Friedrich, unpublished data).

	Northern Manitoba		*Southern Manitoba*		
	Eldon Lake	*Cockeram Lake*	*Booster Lake*	*Bird River*	*Lac du Bonnet*
Zn					
Northern Pike	27.6 (± 0.8) (*n* = 3)	34.8 (± 0.9) (*n* = 3)	47.1 (± 0.6) (*n* = 7)	28.9 (± 0.4) (*n* = 5)	36.9 (± 0.6) (*n* = 7)
Walleye	0.37 (± 0.01) (*n* = 3)	Not available	0.26 (± 0.01) (*n* = 9)	0.93 (± 0.01) (*n* = 6)	1.55 (± 0.03) (*n* = 7)
Mn					
Northern Pike	6.66 (± 0.18)	20.85 (±0.68)	14.59 (± 0.15)	19.44 (± 0.52)	12.13 (± 0.23)
Walleye	0.83 (±0.02)	Not available	1.31 (± 0.02)	0.67 (± 0.02)	2.79 (± 0.10)

the incorporation of Na, Sr, Ba, Mg, Mn, Cu, or Y into otoliths (Marohn *et al.*, 2009). However, it has been argued that, although most animals accumulate metals more efficiently from water than from food, for many species the dosage is likely to be much greater from food because of its higher concentration (Ni *et al.*, 2000; Ward, 1989). Sanchez-Jerez *et al.* (2002) suggested that in seagrass systems, concentrations of Mn in the habitat and prey items influence the accumulation in otoliths. Laboratory studies of Zn uptake in pink snapper otoliths demonstrated that dietary Zn was the major source of Zn incorporated into otoliths (Ranaldi and Gagnon, 2008). Results from this study show that two species from the same habitat incorporate the same trace elements, but in different quantities. This would suggest at least a partial influence of dietary intake of certain trace elements in otoliths, in this case Zn and Mn. It would appear that the influence of diet and ambient water on otolith composition varies with location as well as with species. Ultimately, the source of Zn is the lithosphere and, in the case of Eldon Lake, the most obvious and proximal source is the mine tailings at Lynn Lake that contain Zn-bearing minerals. It is important to note that although anomalous signatures of Zn were identifiable in walleye from the 2008 sample set and in northern pike from 2006, the naturally low background levels in walleye otoliths made the identification of anomalous peaks much simpler. Comparison with Cu and Pb traces is recommended for determining anomalous peaks for the northern pike otoliths, as without the other traces, the anomalous Zn peaks could easily be mistaken for or masked by normal Zn oscillations. These factors will be important to bear in mind when using otolith microchemistry to set up monitoring programs.

The relationship between fish and their chemical environment is a complex one. Previous studies indicate that only selected trace elements in otoliths are influenced by water composition (Bath *et al.*, 2000; Elsdon and Gillanders, 2003), a relationship that is complicated by fish physiology and the habitat. Recent studies have examined the link between the geology of a habitat and otolith microchemistry (Friedrich submitted (see chapter 2), Friedrich and Halden, 2008; Halden and Friedrich, 2008) and confirmed that a link does indeed exists. The knowledge of that link is essential in creating environmental change monitoring programs. In today's socio-economic climate, resource industries are under pressure to extract resources in such a way that does not lead to degradation of the environment. Federal regulations are in place for the pulp and paper and metal mining industries to monitor discharge from a wide variety of wastewaters or effluents in order to protect and manage aquatic biota (Dumaresq *et al.*, 2002; Walker *et al.*, 2002). Assessing environmental change relies on monitoring physical, chemical, and biological parameters over extended periods of time. Detecting change is difficult in areas where baseline data is sparse or non-existent. Otoliths may prove to be essential in compiling baseline chemical data of an environment as they can preserve life-long records of trace elements in the environment. When coupled with the historical perspective that archived otoliths can provide, a database may be created of baseline chemical signatures for an area over a period of several decades. The knowledge of what a typical signature is will allow for the delineation of periods when the chemistry has varied from the norm, and assessment of overall environmental impact. As demonstrated by this research, such a database could provide a way to distinguish naturally occurring signals from those of an anthropogenic origin, and be used as a form of ongoing monitoring with systematic otolith sampling. In particular, otoliths provide a method for determining if fish have been exposed to tailings effluence, and how frequently exposure occurs, which can offer information on how a population as a whole may be affected.

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Chapter 4 Alkali element uptake in otoliths: A link between the environment and otolith microchemistry.

4.1 Abstract

Otoliths taken from fish in the vicinity of rare element pegmatites in eastern Manitoba, Canada, were analyzed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and found to contain lithium, sodium, rubidium, cesium, and strontium at levels ranging from a few ppm to a few 10s of ppm. In some otoliths, the concentrations varied in correspondence to the annular structure of the otoliths, suggesting a periodicity to their incorporation. This is the first reported detection of Rb and Cs in otoliths and the first resolution of periodic signals in these elements in otoliths. The correspondence between the elements in the otoliths and surrounding rocks suggests there can be a strong link between the microchemistry of a fish's otoliths and its environment, particularly where there are distinctive rocks. These elements may serve as natural markers in certain environments and may be used to characterize and monitor lacustrine environments over a period of time.

4.2 Introduction

Otoliths are hard calcareous structures in the inner ear of teleost fish that grow throughout the life of the fish and form part of the organs that sense position and motion (Degens *et al.*, 1969). They are composed of layers of calcium carbonate, typically aragonite, deposited annually in a non-collagenous organic matrix (Campana, 1999). Observed in reflected light, each layer is composed of a bright and a dark band, the bright band representing a period of summer growth, and the dark band corresponding to winter growth, when the nutrient supply is diminished (Degens *et al.*, 1969). Annuli also act as "information storage structures" that record the life-history of fish: annually-deposited aragonite layers indicate the age of the fish, the elemental composition of otoliths can provide information as to the past environmental conditions experienced by the fish, and quantitative trace element otolith composition can be used to deduce population structure and movement (Andrus *et al.*, 2002; Berg *et al.*, 2005; Laidig *et al.*, 2003).

In recent years, research on biominerals such as otoliths, teeth, and bone has increased with improvement of resolution and sensitivity of instrumental techniques, which has allowed for the analysis of a broader suite of elements and isotopes. Otolith trace element composition has been the focus of many studies, and strontium in particular has been well studied as a proxy for water temperature variations and as a method of establishing migratory behaviour of fish (Daverat *et al.*, 2005; Hobbs *et al.*, 2005; McCulloch *et al.*, 2005). However, the aragonite structure ($CaCO_3$) has the capacity to incorporate a wide range of other trace elements, including barium, transition elements, rare earth elements, and, as shown in this study, alkali elements. The incorporation of such elements into otoliths has the potential to record information about fish behaviour and diet, as well as on the local environment, including the surrounding geology. New insights are emerging into the role of biominerals as records of environmental change, as well as how the trace element chemistry of the environment can impact an organism (Dove and Kingsford, 1998; Milton *et al.*, 2005). The objectives of this study are to 1) analyze a suite of trace elements (Li, Na, Rb, Sr, Cs) across the annular structure of otoliths (i.e. life history of the fish); 2) compare and contrast trace element content with respect to time, species, and local geology; and 3) establish what constitutes a characteristic trace element pattern in otoliths for the region.

4.3 Study Area and Geologic Setting

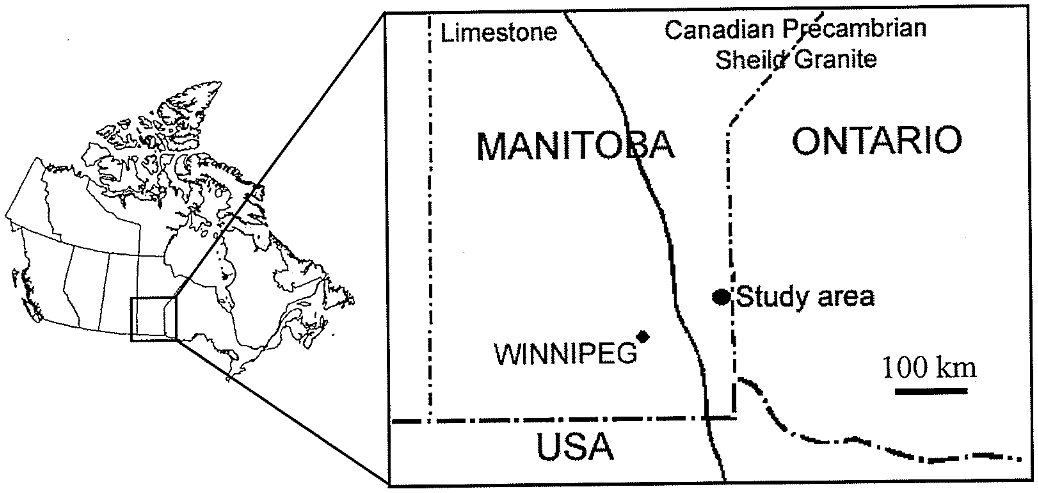
Samples were collected from lakes in the Lac du Bonnet region of southeastern Manitoba, Canada, close to the Manitoba – Ontario border, in the Canadian Precambrian Shield (Figure 4.1). The area is approximately 2.6 billion years old and lies within the Bird River greenstone belt (Cerny, 1989). An east-west trending suite of metamorphosed sedimentary and volcanic rocks underlie the belt that have been intruded by mafic to ultramafic rocks (Crouse and Cerny, 1979). Large plutonic masses of granitic rocks lie north and south of the belt, and there are many pegmatites hosting minerals of rare elements, of which the Tanco pegmatite is particularly distinct (Cerny, 1989).

The Tanco pegmatite is an igneous body and is believed to be the product of very advanced differentiation of granitic magma that was emplaced approximately 2.55 billion years ago (Cerny, 1982). It is classified as a relatively high temperature, low pressure lithium pegmatite and is famous for it's concentrations of tantalum, lithium, and cesium minerals (Crouse and Cerny, 1972). Tantalum primarily occurs in the minerals wodginite $Mn^{2+}(Sn, Ta)(Ta, Nb)_2O_8$, tantalite $(Fe, Mn)(Ta, Nb)_2O_6$, and microlite $(Ca, Na)_2Ta_2O_6(O, OH, F)$. Cesium is mined from pollucite $(Cs, Na)(AlSi_2O_6)\cdot nH_2O$, and this pegmatite contains over 80% of the world's known Cs/pollucite reserves. Lithium is found in spodumene $LiAlSi_2O_6$, which is used in the manufacturing of glassware and ceramics. The locality was chosen because a great deal is known about the unique mineralogy and geochemistry of the rocks.

4.4 Materials and Methods

Otoliths from northern pike (*Esox lucius*), walleye (*Stizostedion vitreum*), white suckers (*Catostomus commersoni*), and ciscos (*Coregonus artedii*) were collected and

Figure 4.1 Map of southeastern Manitoba showing the location of the study area in the English River gneissic belt of the western Superior Province of the Canadian Shield. Reproduced with permission of the Canadian Institute of Mining, Metallurgy and Petroleum (Figure originally printed in *CIM Bulletin*, Vol. 72, No. 802, p. 142).



archived in 1998 by TetrES Consultants, Inc. as part of a preliminary environmental study of the distribution of trace elements. This collection forms the basis of an on-going survey. Five locations were sampled: Bernic Lake (white sucker n=11, cisco n=10), Birse Lake (northern pike n=8, walleye n=4), the Tanco mine tailings management area (TMA; white sucker n=8), and Bird River up- (northern pike n=3, walleye n=3) and downstream (northern pike n=3, walleye n=3) from Bernic Lake (Figure 4.2). Birse Lake is outside the Bernic Lake watershed and is not in contact with the pegmatite and was therefore sampled to act as a control site. Sagittal otoliths were removed from the fish, embedded in epoxy resin, and cut transverse to create a dorso-ventral cross section through the core of the otolith and expose all annuli. The posterior half of each cut otolith was re-embedded in a 25 mm lucite microprobe mount, ground, and polished. Prior to analysis, samples were rinsed with DDW and allowed to air dry.

While X-ray emission analysis of trace elements in otoliths has been done using proton-induced X-ray emission (PIXE) and electron microprobe analysis (EMPA), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) can detect a broader suite of elements with better sensitivity and can detect Li. LA-ICP-MS analyses were done using a Thermo Finnigan Element 2 ICP-MS coupled to a Merchantek LUV 213 Nd-YAG laser. Table 4.1 summarizes the instrument parameters used during analysis. Running conditions used to optimize sensitivity and resolution of the annular growth features in these samples included a 30 μm-diameter beam traveling 2 μms^{-1}. Calcium as 56 wt% CaO was used as an internal standard, and the external calibration was done using NIST glass 610 with the nominal values reported by Pearce *et al.* (1997). Line scans were run across the otolith surface from core to edge, perpendicular to annuli

Figure 4.2 Map of the study area near the town of Lac du Bonnet in south eastern Manitoba showing the sample locations: Bernic Lake, Tailings Management Area (TMA), Birse Lake, and up- and downstream Bird River (Davies *et al.*, 1962). Scale 1:500 000. Reproduced with the permission of the Government of Manitoba (Figure originally printed in *Geology and mineral resources of Manitoba*, p. facing 38).

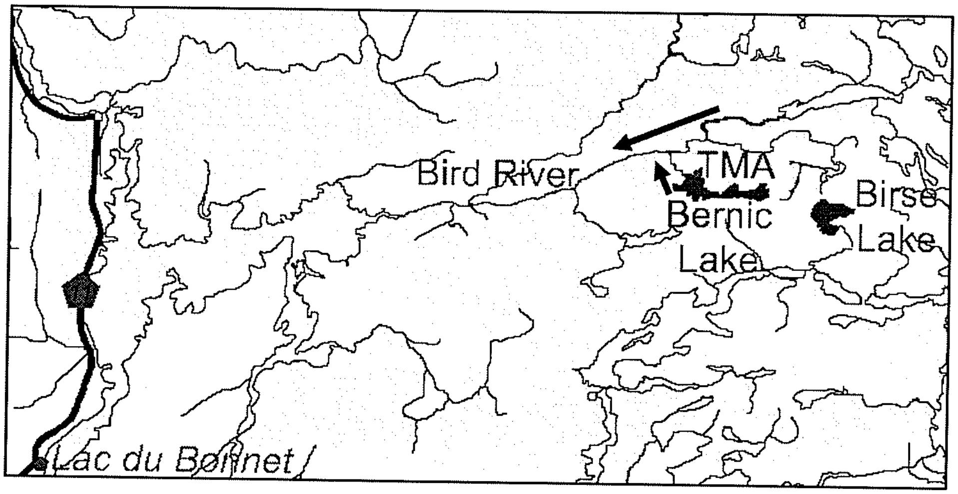


Table 4.1 LA-ICP-MS operating conditions and data acquisition parameters for otolith analyses.

ICPMS	
Forward power	1303 W
Gas flows	
Plasma (Ar)	16 L/min
Auxiliary (Ar)	0.80 L/min
Sample (Ar/He)	0.89/0.335 L/min
Shield electrode	Used for analysis

LA	
Repetition rate	20 Hz
Pre-ablation warm-up	~120 sec
Pulse duration	5 ns
Spot size	30 μm
Power	80%
Incident pulse energy	~0.020 mJ
Energy density on sample	~6.22 Jcm^{-2}
Laser scan speed	2 μms^{-1}

Data Acquisition	
Data acquisition protocol	Time resolved analysis
Scanning mode	BScan and EScan
Detector mode	Analog and counting
Isotopes determined	^{7}Li, ^{23}Na, ^{44}Ca, ^{85}Rb, ^{88}Sr, ^{133}Cs
Dwell time (segment duration)	0.3 ms
Magnet settling time	0.001-0.3 ms
Time/Pass	1.7 s
Runs/Passes*	1000-1 (17m 09s)

*pass is a measurement cycle through the mass spectrum; 1 pass collected 1000 times producing 1000 blocks of data per sample in time-resolved or scanning mode. Standard analyses were collected prior to each analytical run. Measured trace element concentrations, standard deviations, and detection limits were processed using GLITTER software (van Achterberg *et al.*, 2001) and exported to EXCEL for final presentation.

4.5 Results

Table 4.2 summarizes the trace element contents from otoliths analyzed in this study. Sodium, Rb, and Sr are found in substantial concentrations in all otoliths, the concentrations varying between sample sites as well as between species. The presence or absence of Li and Cs depends on location, and elevated levels of Li, Cs, and Rb were detected in areas proximal to the pegmatite. In fish taken from water bodies outside the Bernic Lake watershed, Li and Cs are below detection limits, approximately 2.9 and 0.1 ppm respectively. Representative chemical profiles from four of the sites are shown in Figure 4.3 and may be used to establish what constitutes a characteristic chemical pattern for each location, as described below. In cases where annular structures were visible on the otolith section, a link was made between such structures and the periodic nature of the chemical profiles (Figures 4.3 and 4.4). Some otolith sections did not have clear annular structures, but periodic variations were still present in the chemical profiles (Figure 4.3). Indeed, periodic patterns of all elements are evident in many samples, but there are differences in element concentration and correlations, also described below. Uptake of elements into the otolith structure varied with sample location as well as species.

Bernic Lake

All otoliths from Bernic Lake contain the entire suite of elements analyzed and fall within the following typical ranges: Li: 0.2-90 ppm, Na: 900-4300 ppm, Rb: 7-50 ppm, Sr: 200-1500 ppm, and Cs: 0.4-6 ppm. Four out of seven cisco samples from this site contain Na peaks that reach up to 8500 ppm. Rubidium and Cs concentrations are relatively consistent across species, whereas concentrations of Li, Na, and Sr are higher in cisco otoliths than in otoliths from white suckers.

Table 4.2 Summary of otolith trace element content in parts per million from the study area.

	Li	Na	Rb	Sr	Cs
Bernic Lake					
White Sucker	0.2 – 28	953 – 3838	7 – 34	202 – 773	0.4 – 4.8
Cisco	3 – 98	1234 – 8880	8 – 50	627 – 1528	0.4 – 6.4
TMA					
White Sucker	2.9 – 38	459 – 4614	8 – 83	212 – 839	1.7 – 26.3
Bird River – downstream					
Northern Pike	2.9 – 8	2254 – 4700	1 – 4	325 – 661	0.1 – 0.5
Bird River – upstream					
White Sucker	<2.9	1057 – 3355	0.2 – 2	192 – 636	<0.1
Northern Pike	<2.9	980 – 2867	0.15 – 3	203 – 746	<0.1
Birse Lake					
Walleye	<2.9	807 – 2808	0.15 – 2	94 – 218	<0.1
Typical Detection Limits	2.9	5.2	0.15	0.25	0.1
Typical 1σ Error	2	200	1	30	0.1

Figure 4.3 Representative line scans from the LA-ICP-MS showing trace element concentrations in parts per million (ppm) *versus* distance in microns (m) across otoliths from core to rim. Shading represents the best estimate of annuli based principally on reflected light microscopy. (a) Cisco otolith from Bernic Lake. (b) White sucker otolith from Tailings Management Area. (c) Northern pike otolith from downstream Bird River. (d) Northern pike otolith from upstream Bird River.

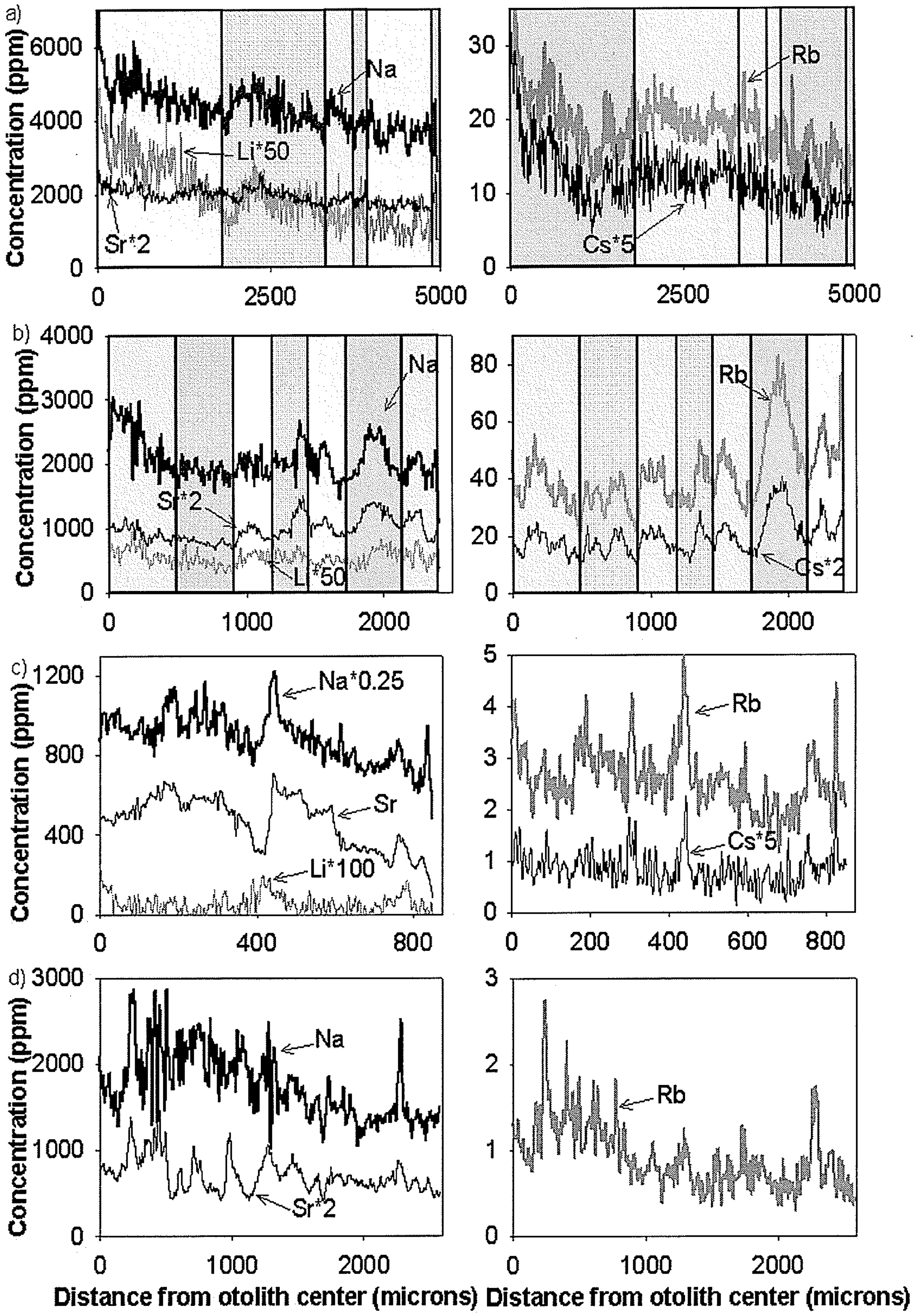
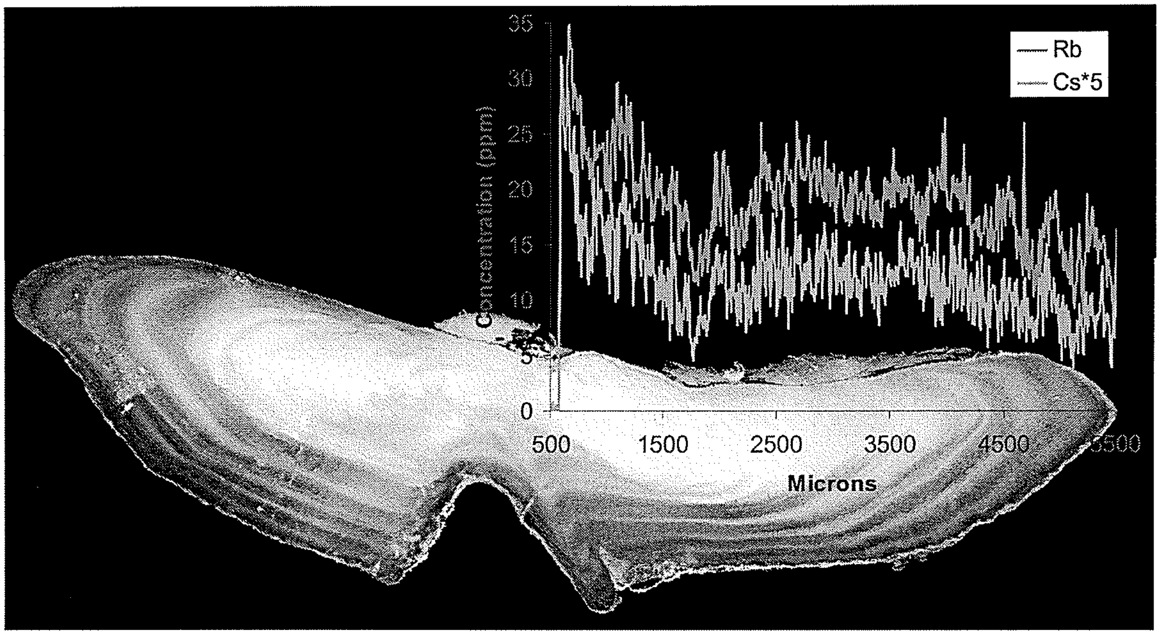

a)
Concentration (ppm)
6000
4000
2000
0
Na
Li*50
Sr*2
0
2500
5000
30
20
10
0
Rb
Cs*5
0
2500
5000
b)
4000
3000
2000
1000
0
Concentration (ppm)
Na
Sr*2
Li*50
0
1000
2000
80
60
40
20
0
Rb
Cs*2
0
1000
2000
c)
1200
800
400
0
Concentration (ppm)
Na*0.25
Sr
Li*100
0
400
800
5
4
3
2
1
0
Rb
Cs*5
0
200
400
600
800
d)
3000
2000
1000
0
Concentration (ppm)
Na
Sr*2
0
1000
2000
3
2
1
0
Rb
0
1000
2000
Distance from otolith center (microns)
Distance from otolith center (microns)

Figure 4.4 Overlay of LA-ICP-MS analyses on image of otolith from Bernic Lake. The laser scan that produced the element traces shown lies directly under the *x* axis of the plot.



Tailings Management Area (TMA)

As in Bernic Lake, all otoliths from the TMA contain all five elements. Typical ranges for the elements in otoliths from TMA are: Li: 3-35 ppm, Na: 450-4500 ppm, Rb: 8-80 ppm, Sr: 200-825ppm, and Cs: 2-26 ppm. Otoliths were only obtained from white suckers in this location, as no other species were caught.

Bird River Downstream

The chemical signature of samples from Bird River downstream from the Bernic Lake outlet is characterized by the presence of all five elements, in abundances that are less than those in Bernic Lake and the TMA. Typical concentration ranges in this sample location are: Li: 3-8 ppm, Na: 2200-4500 ppm, Rb: 0.8-4 ppm, Sr: 300-650 ppm, and Cs: 0.1-0.5 ppm. Northern pike was the only species captured from this site.

Bird River Upstream

Sodium, Rb, and Sr are ubiquitous in samples from upstream Bird River in concentrations in the ranges of 950-2500 ppm, 0.2-2.5 ppm, and 200-750 ppm, respectively. Concentrations from northern pike and white sucker otoliths are of similar magnitude. Lithium and Cs were below detection limits in all samples from this location.

Birse Lake

Birse Lake was sampled as a control lake, being in a different watershed as well as distant to the pegmatites and mining activity. Chemical signatures from the walleye captured in this location are characterized by Na in the range of 800-2800 ppm, Rb in the range of 0.2-2 ppm, and Sr in the range of 90-210 ppm. Similar to what was observed in samples from upstream Bird River, Li and Cs were below detection limits.

4.6 Discussion

In this and other studies (e.g., Halden *et al.*, 2005; Palace *et al.*, 2007) we have shown that the trace element signature in otoliths can be connected to the geological character of the sample location. Otoliths from the Lac du Bonnet region have also shown variations between different species of the same location.

Alkali Element Concentrations

Sodium levels average about 3000 ppm for marine fish (Secor *et al.*, 2002) and freshwater otoliths typically range from 2500-2600 ppm (Brazner *et al.*, 2004). Values detected in the Lac du Bonnet region fall within the range of 450-4500 ppm. However, some samples in this study show concentrations up to 8500 ppm. The incorporation of so much sodium raises several questions from a crystal chemical standpoint. If the Na^+ is substituting for Ca^{2+} in the aragonite structure, it must be coupled with the incorporation of another monovalent cation to maintain a neutral charge balance of the crystal, a phenomenon that is not uncommon in minerals. However, the incorporation of such high amounts of Na would clearly have an adverse effect on the structure of the crystal. It is possible that at least some of the Na is being incorporated into the protein matrix of the otolith. Resolution of this issue by means of protein analysis is part of this on-going study.

Detection of Rb, Cs, and Li indicates that these relatively rare elements are present and mobile in this particular environment. Lithium-, Cs-, and Rb-bearing minerals, including carbonates, are common in the surrounding rocks; moreover these minerals are easily weathered and, as such, would release elements to the aqueous environment. The presence of Li has previously been detected in cod otoliths from the

Gulf of St. Lawrence area, in amounts averaging from 0.6 to 1.0 ppm (Campana *et al.*, 2000). In this study however, we have detected Li in amounts >90 ppm. In addition to this, the incorporation of Li, as well as Rb and Cs, into the otolith structure is periodic, suggesting a seasonal or dietary control. It is apparent from the site-specific uptake of Li, Cs, and increased amounts of Rb that the most likely source is the Tanco pegmatite based on spatial distribution of elements and element association.

The pathway of these elements into the otolith structure is not well understood. Early studies stated that calcium deposited in otoliths comes predominantly from the surrounding water, via the gills, to the endolymphatic sac (Simkiss, 1974), with only a small proportion attributed to dietary sources (Ichii and Mugiya, 1983). These two major pathways have also been proposed as the mechanism of incorporation for trace elements (de Pontual and Geffen, 2002). It seems likely that the alkali elements detected in otoliths of this study have followed similar pathways. Indeed the data presented in Table 4.3 suggest that there is more than one process involved in trace element uptake into otoliths, although their relative roles as sources of such elements remains to be assessed.

Variations with Sample Location

In a comparison of white sucker otoliths from three samples sites (Bernic Lake, TMA, upstream Bird River), several observations can be made (Table 4.3). Concentrations of Na and Sr are about equal for all three locations, and although Rb is detectable in all three sites, the concentration of this element is an order of magnitude higher in the otoliths from Bernic Lake and Tanco Mine Area than in the otoliths from upstream Bird River. Lithium and Cs are below detection limits at upstream Bird River but are present in significant amounts at the other two sites. The strong correlation

Table 4.3 Comparison of otolith microchemistry (ppm) among locations and species.

	Li	Na	Rb	Sr	Cs
Upstream Bird River White Sucker	<2.9	1057 – 3355	0.2 – 2	192 – 636	<0.08
TMA White Sucker	2.9 – 38	459 – 4614	8 – 38	212 – 839	1.7 – 26.3
Bernic Lake White Sucker	2.9 – 28	953 – 3838	7 – 34	202 – 773	0.4 – 4.8
Bernic Lake Cisco	3 – 98	1234 – 8880	8 – 50	627 – 1528	0.4 – 6.4

between elements present in the otolith and proximity to the Tanco pegmatite indicate that otoliths are incorporating a chemical signature that reflects the geology of the local environment, either directly from the water or through food.

Variations with Species

Table 4.3 shows a comparison of otoliths from two different species from Bernic Lake; a cisco, which is a pelagic species feeding mainly on plankton, and a white sucker, which feeds on a variety of benthic organisms, such as insect larvae and small crustaceans. Both types of fish contain the same suite of elements, but these data show that the cisco otoliths contain higher concentrations of all five elements than do the otoliths from the white suckers. This suggests that otoliths may also incorporate a chemical signature related to the fish's diet.

In a recent study by Halden and Friedrich (2008) trout otoliths from an area near mining operations were found to contain periodic signatures of Cu, Pb, and Zn. Anomalous high-concentrations in individual annuli were believed to represent the fish moving into areas where levels of these elements are high, such as near the tailings. Similarly, Palace *et al.* (2007) concluded that annular concentrations of selenium in otoliths of rainbow trout indicated the fish had come in contact with selenium-bearing effluent from a coal mining operation. In this study, we have shown that otoliths collected from five sample locations have distinct trace element signatures that are highly correlated to the local geology, indicating that the chemical signature of otoliths vary on a local scale. In areas where mining is important to the local economy, specific suites of elements may be present in the environment, and otoliths may provide a method of determining and monitoring the impact on fish by acting as natural markers of the trace element chemistry of the environment.

A mechanism for understanding the concentration and periodic uptake of alkali element signals in otoliths remains to be established. However, by expanding the suite of elements analyzed in otoliths, there is the potential for a more detailed assessment of environmental changes experienced by the fish in this area. It should be possible to use these records to study the life histories of fishes and the environment during their lives. Areas with unique geology and geochemistry that contain a distinctive suite of elements, such as the Tanco pegmatite, are ideal for such studies.

4.7 References

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Chapter 5 Establishing a chemical baseline for the Tanco mine area

The utility of otolith microchemistry analysis as an assessment tool for environmental studies in areas affected by resource extraction requires the understanding of what might constitute a background or normal signal. This would necessitate a multi-year study with a broad distribution of sampling locations and designed to collect a variety of species with different feeding habits. Where present, the concentration of trace elements in otoliths can be tracked and used to establish a typical chemical profile for a particular species in a given area. Including archived otoliths in the assessment will expand the time frame of the chemical profiles making a longer historical perspective available, in some cases dating back more than 20 years. Baselines established in control sites can be used to define background levels for uncontaminated sites in a region, to which levels from sites adjacent to mining activity can be compared. The ultimate goal of such a study would be to determine if it is possible to reconstruct the chemical history of a lake using otolith microchemistry. Most fish sampling studies are designed to assess population dynamics. The multi-year scope and location distribution required is beyond the scope and resources available to this research.

Sampling and analytical work for this thesis included the area in the vicinity of the rare-element Tanco pegmatite mine in southeastern Manitoba, which encompassed the lake proximal to the mine and several lakes and rivers at some distance upstream and downstream. A complete description of the location, methods, materials, and results from a suite of otoliths collected in 1998 was presented in chapter 4. To distinguish between otolith microchemistry from the control sites and the sites adjacent to mining activity, a compilation of otolith chemistry data is presented in this chapter over the period from

1980 through 2008, in an attempt to show the progress of otolith microchemistry over a period of 29 years. The material presented in this chapter was written as a supplement to the information presented in chapter 4, to establish a broad temporal framework for the chemical information from which comparisons may be drawn.

5.1 Sampling

Chapter 4 describes the chemistry of a suite of otoliths collected in 1998 from five sample locations at and around the Tanco pegmatite mine. Whereas the majority of the fish were less than 10 years old, there were two 18-year-old individuals collected from Bernic Lake. To supplement this preliminary suite and expand the timeline, field sampling was completed from 2006-2008 (Table 5.1). Access to the 1998 upstream control site Birse Lake is limited, therefore Booster Lake was chosen as the control site as it too is upstream. No further samples were obtained from the TMA site, although many samples were collected from Bernic Lake. Samples were collected from Lac du Bonnet to represent downstream Bird River, and from Bird Lake to represent upstream Bird River.

5.2 Construction of temporal chemical trends

Whereas trace element patterns in otoliths have been shown to vary between sampling locations (chapter 4), the annular structure of otoliths provides a temporal information to trace element distribution. In order to determine baseline chemistry for the area, it was necessary to determine how trace element levels have fluctuated in the past. This required the determination of a mean concentration for each element in the otoliths for each year, both at the control sites and the site most proximal to the mine, Bernic Lake. As demonstrated in chapters 3 and 4, different species from the same location can incorporate different amounts of the same element; therefore, species were considered

Table 5.1 A summary of all samples collected from the area surrounding the Tanco pegmatite mine. Sampling years with an asterisk * denotes samples obtained through the archives of Manitoba Conservation at Lac du Bonnet. Sampling years followed by (T) denotes samples donated by TetrES Consultants, Inc. Species abbreviations are walleye (WA; *Sander vitreus*), northern pike (NP; *Esox lucius*), white sucker (WS; *Catostomus commersoni*), small mouth bass (SMB; *Micropterus dolomieui*), yellow perch (YP; *Perca flavescens*), silver redhorse (SR; *Moxostoma anisurum*), sauger (SAU; *Sander canadensis*), whitefish (WF; *Coregonus lavaretus*), cisco (CIS; *Coregonus artedii*), rock bass (RB; *Ambloplites rupestris*), black crappie (BC; *Pomoxis nigromaculatus*).

Sampling site and year	**Number of fish captured**	**Otolith time span**	**Species**
Booster Lake			
2008	15	1990-2008	WA, NP, WS, SMB
2007	10	1998-2008	WA, NP, SMB
2006	9	1998-2006	WA, NP, YP, SMB
2004*	5	1982-2004	WA
1995*	6	1987-1995	WA
Birse Lake			
1998(T)	13	1986-1998	WA, NP, SR
Bird Lake			
2008	10	1997-2008	WA, NP, SR, WS
2003*	5	1990-2003	WA, SMB
Bird River Upstream			
2006	5	1998-2006	NP, YP
1998(T)	7	1984-1998	NP, SR, WS
Lac du Bonnet			
2008	23	1994-2008	WA, SAU, NP, WF, CIS, YP, RB, SR, WS
2007	33	1996-2007	WA, SAU, NP, BC, WF, CIS, YP
2006*	4	1993-2006	WA
2005*	6	1993-2005	WA, SAU
2004*	5	1987-2004	WA
2003*	6	1999-2003	WA, SAU
2002*	6	1991-2002	WA, SAU
2001*	6	1987-2001	SAU
2000*	6	1979-2000	WA, SAU
1999*	1	1994-1999	WA
1998*	6	1993-1998	WA
1997*	6	1988-1997	WA, SAU
1996*	6	1984-1996	WA
Bird River Downstream			
1998(T)	6	1989-1998	WA, NP
Bernic Lake			
2008	91	1994-2008	NP, CIS, YP, WS
2006	3	2000-2006	YP
1998(T)	21	1980-1998	CIS, WS
TMA			
1998(T)	8	1989-1998	WS

separately. Plotting mean concentrations and standard deviations for each year produced temporal chemical trends for each species at the control sites and Bernic Lake.

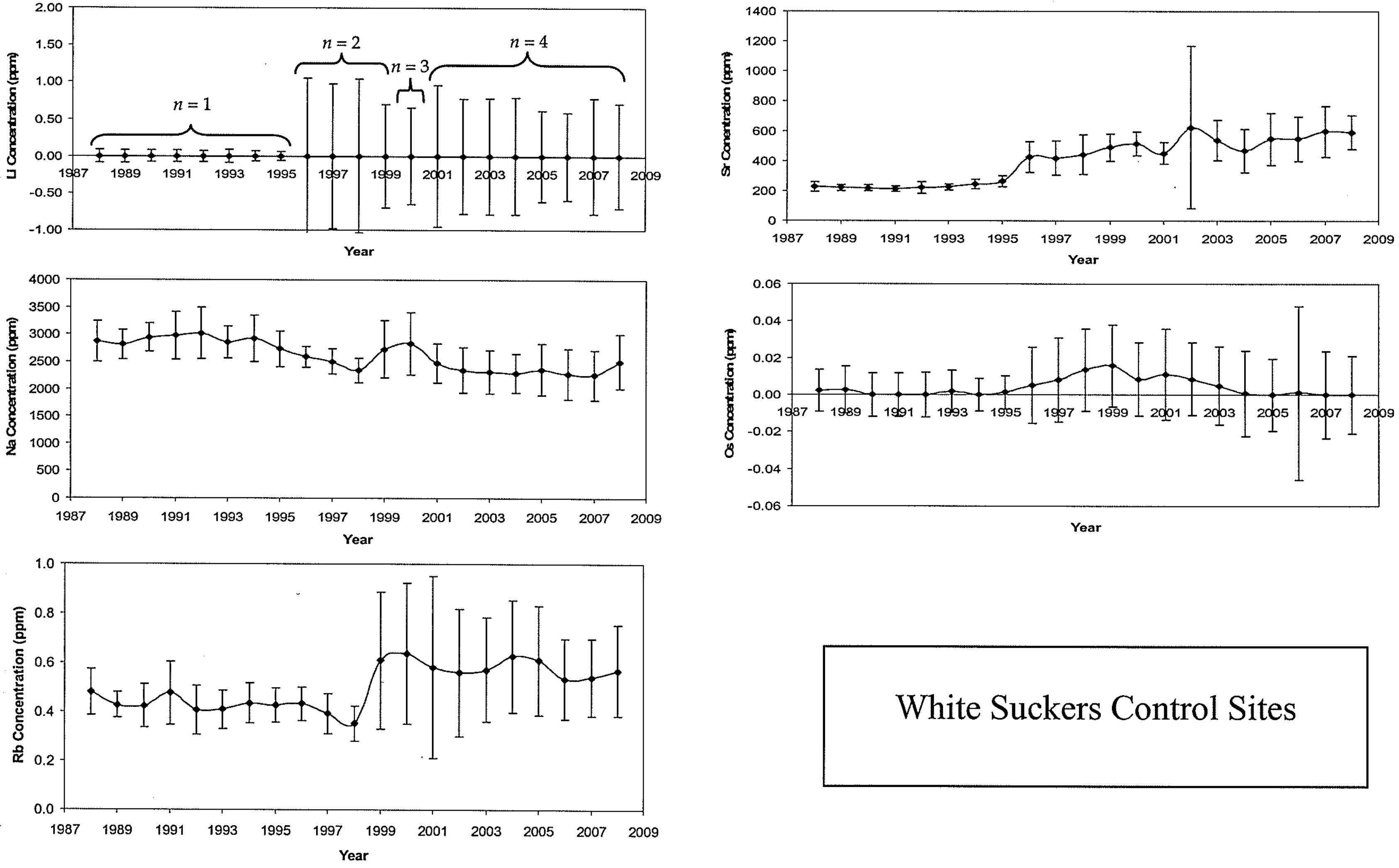
To determine the mean concentration for each year, the chemical distribution profiles of an otolith collected through use of the LA-ICP-MS were compared with an optical image of the sectioned otolith showing the laser ablation transect. LA-ICP-MS produces profiles that are plotted against distance across the otolith surface; therefore, by measuring the width of each annulus along the laser transect, a range of chemical data was assigned to each year. A mean concentration for each year, encompassing annuli from several fish, was calculated and plotted against time to produce a year-to-year trend of element concentrations.

The control sites Booster, Birse, and Bird Lakes were used to define background levels for Li, Na, Rb, Sr, and Cs in the region, and to compare with levels found in otoliths from Bernic Lake. Otoliths of northern pike and white sucker were chosen as they are resident to both Bernic Lake and the control sites, and they represent two different feeding habits, being piscivores and benthivores, respectively.

5.2.1 White suckers in the control sites

Five white sucker otoliths were used to construct a timeline for the background information from the control sites. One, ten-year-old sucker was obtained in Birse Lake in 1998, providing chemical data back to 1988. The remaining four white suckers were collected in 2008 from Booster and Bird Lakes, the oldest of which hatched in 1996. Combining data from all five samples produced a 21-year timeline of white sucker otolith chemical data, from 1988 to 2008 (Figure 5.1). Throughout this period of time, Li and Cs in these otoliths were consistently below detection limits. Sodium stayed in the range of

Figure 5.1 Mean concentrations (ppm) per year for white sucker otoliths from the control sites Booster, Birse, and Bird Lakes for the period 1988-2008. Error bars represent 1 standard deviation.

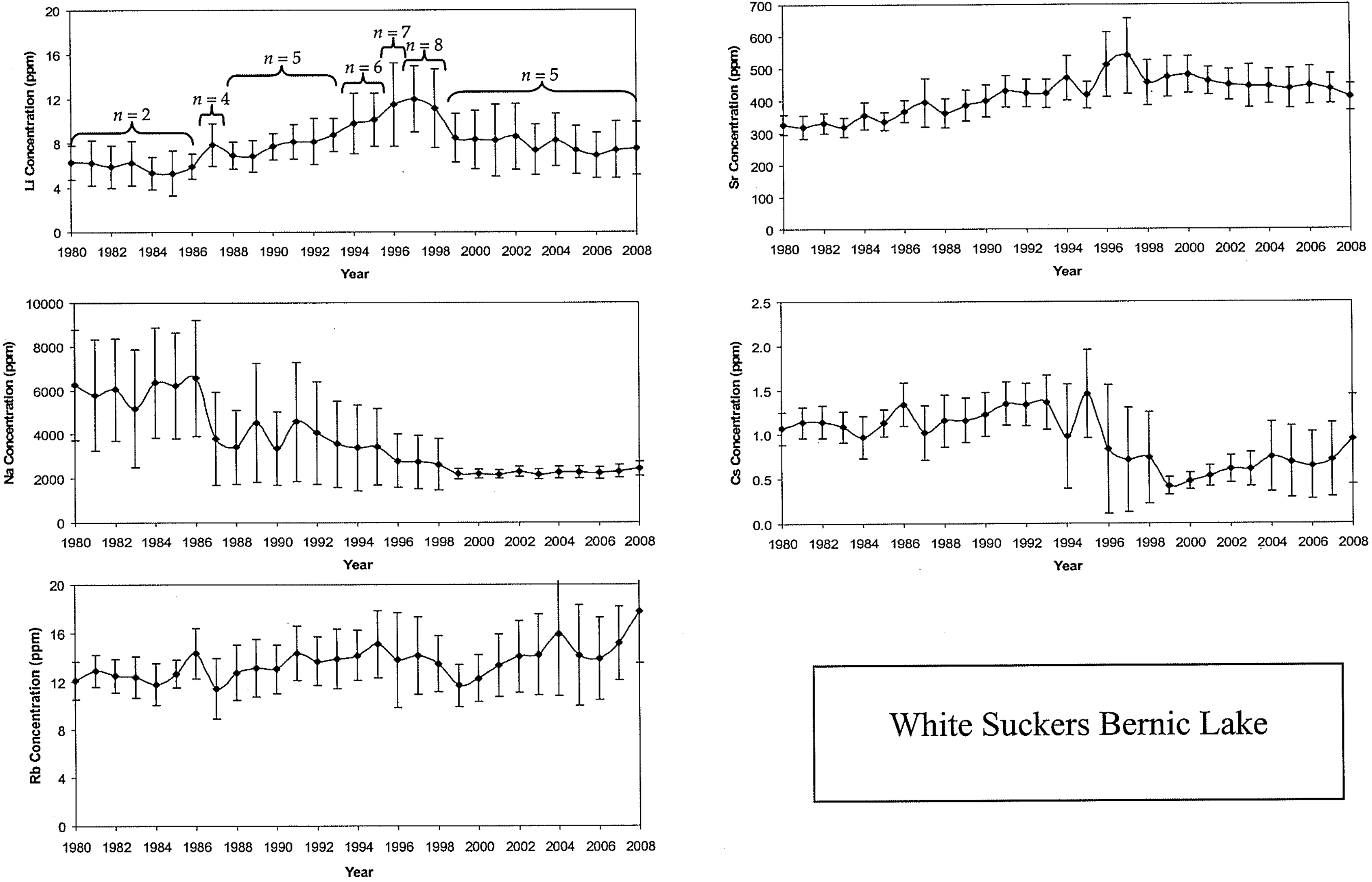


2000-3000 ppm, with a slight decrease in concentration with time. Rubidium concentrations were fairly consistent between 0.3 and 0.6 ppm. Strontium concentrations for the period 1988-1995 averaged 230 ppm. In 1996, Sr concentrations increased to more than 400 ppm, and levels remained that high through 2008.

5.2.2 White suckers in Bernic Lake

Ten white sucker otoliths from Bernic Lake were used to determine the history of chemical trends in the area immediately adjacent to mining activity. Five of the otoliths were collected in 1998, including two 18-year-olds that provided chemical data from 1980 to 1998. Five otoliths collected in 2008 that hatched prior to 1998 were chosen to overlap with the chemical data from the 1998 samples. Data from the two suites of otoliths provided 29 years of chemical information, from 1980 through 2008 (Figure 5.2). Lithium levels overall increased from around 6 ppm in 1980 to a maximum of 12 ppm in 1997, after which levels decreased to around 7 ppm. Sodium levels during the period 1980-1986 were significantly higher than the period 1999-2008, decreasing from just over 6000 to 2200 ppm, indicating an overall decrease in Na concentration with time. Rubidium levels have consistently been between 12 and 17 ppm. Strontium levels rose through the 1980s and 1990s from 325 ppm to a maximum of 540 ppm in 1997. From 1998 to 2008, Sr levels were fairly consistent, around 450 ppm. From 1980 through 1995, Cs levels in Bernic Lake white sucker otoliths were between 1.0 and 1.5 ppm, whereas in the period from 1996 to 2008, Cs levels were between 0.45 and 1.0 ppm.

Figure 5.2 Mean concentrations (ppm) per year for white sucker otoliths from Bernic Lake for the period 1980-2008. Error bars represent 1 standard deviation.



5.2.3 Northern pike in the control sites

Five northern pike otoliths from Booster and Bird Lakes collected in 2007 and 2008 were used to determine temporal chemical trends for the control sites. The oldest specimen hatched in 1995, providing 14 years of data (Figure 5.3). Lithium was below detection limits for the time span, and Na levels were fairly constant within the range of 2200 to 2700 ppm. Rubidium levels were below 1.0 ppm, with a maximum of 0.9 in 1996 and a minimum of 0.7 in the period 2000-2004. Strontium in the otoliths stayed within the range of 350-450 ppm, and Cs levels were at or below detection limits of 0.01 ppm.

5.2.4 Northern pike in Bernic Lake

Only two northern pikes were captured in Bernic Lake, both in 2008; one fish was 11 years old, and the other 9 years old. The otoliths from these two samples provide chemical trend data from 1998 through 2008 (Figure 5.4). Lithium levels ranged from a minimum of 3.8 ppm in 2000 to 7.3 ppm in 2003. Sodium and Rb levels across the 11 years were fairly constant, staying within the range of 2500-3200 ppm and 18-25 ppm, respectively. Strontium levels were typically around 330 ppm for the time frame, with the exception of two years; in 1998 and 2001, Sr concentrations in northern pike otoliths in Bernic Lake were just over 500 ppm. This was followed by an overall decrease in Sr levels during the period from 2001 to 2008. Cs levels ranged from 1.1 ppm in 2004 to a maximum of 1.8 ppm in 1999.

5.3 Determining background chemical levels

In order to develop otolith microchemistry as a tool for assessment in environmental monitoring surveys, it is essential to determine baseline data, which will serve as a comparison for areas where contamination is suspected. For the Tanco mine

Figure 5.3 Mean concentrations (ppm) per year for northern pike otoliths from the control sites Booster and Bird Lakes for the period 1995-2008. Error bars represent 1 standard deviation.

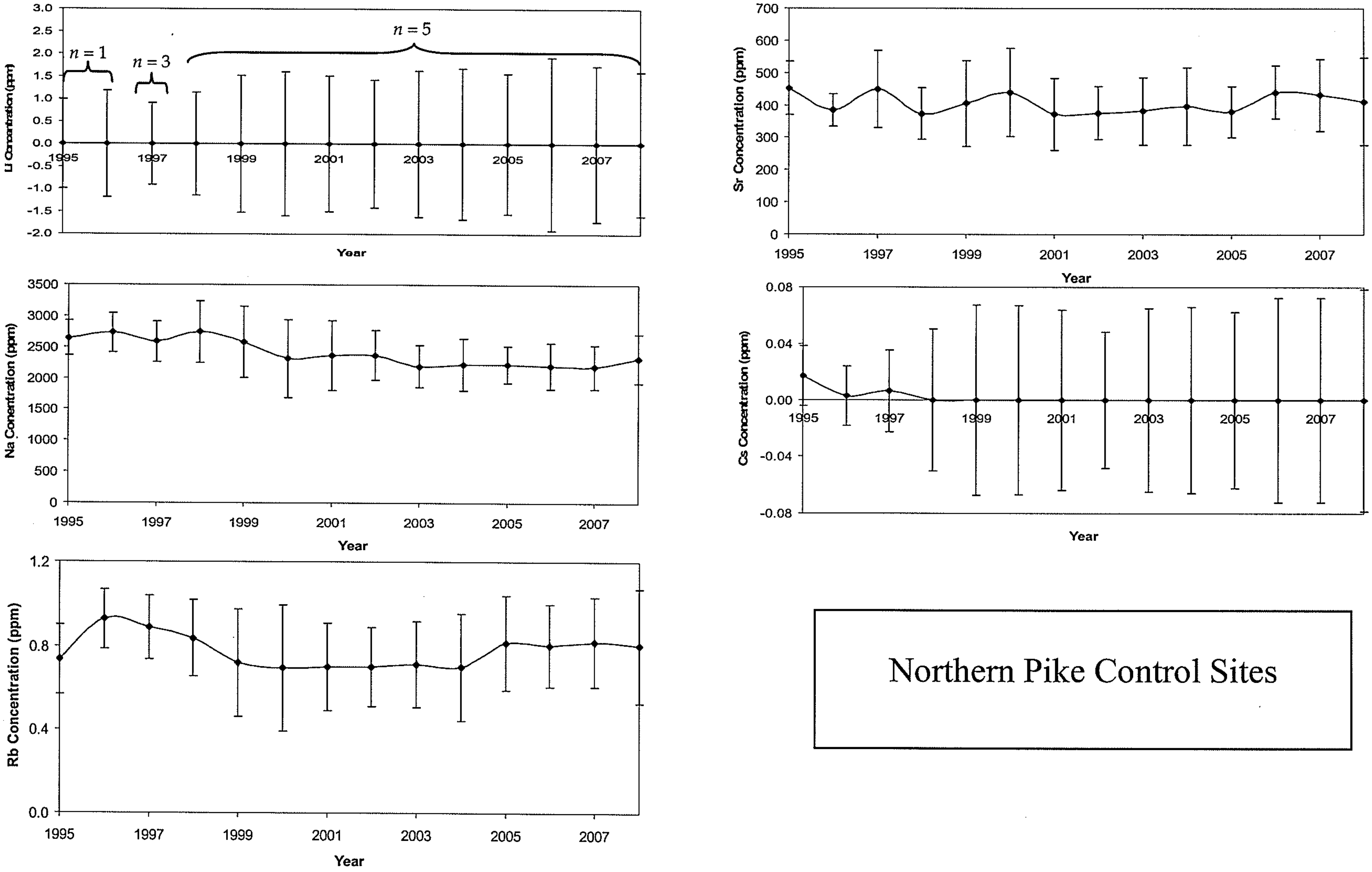
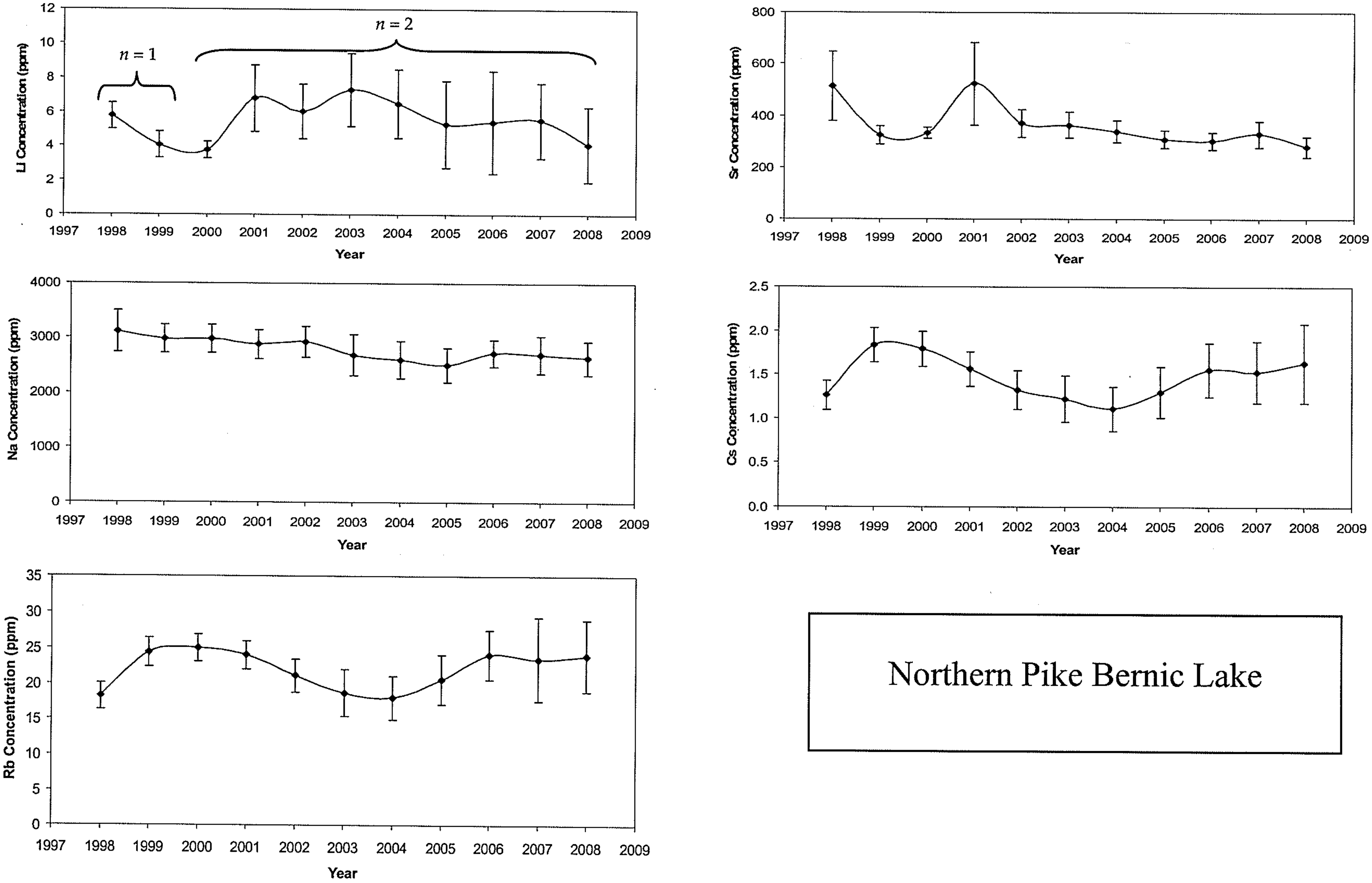


Figure 5.4 Mean concentrations (ppm) per year for northern pike otoliths from Bernic Lake for the period 1998-2008. Error bars represent 1 standard deviation.



area, the control lakes may be used to determine such a baseline for the area where similar geology exists, with the exception of the rare-element pegmatite. The temporal trend data produced by coupling LA-ICP-MS data to the annular structure of the otoliths from Bernic Lake can be a useful tool for monitoring changes within the lake itself in comparison with previous years, and a way of determining the success of tailings impoundment strategies. Temporal trend data for the control sites provides a baseline for comparison with trends determined for Bernic Lake; a comparison to the control site can establish what effects, if any, the mining activity has had on the fish of Bernic Lake or how Bernic Lake otoliths differ from other water bodies in the area.

Temporal trend data for white sucker and northern pike otoliths from the control sites indicate what baseline values are for the given elements in those species. With the exception of the variations noted above, most year-to-year fluctuations present are within one standard deviation, indicating that levels have remained fairly constant over the given time period. Comparing the levels detected in Bernic Lake otoliths to the background levels determined from the control sites indicates similarities as well as differences (Table 5.2). For both white sucker and northern pike otoliths, Na and Sr values from Bernic Lake are at or near background levels. However, levels of Li, Rb, and Cs differ between the sites. In Bernic Lake, Li and Cs in otoliths of both species are one to two orders of magnitude higher than background levels, and Rb is two orders of magnitude higher than background. A compilation of data from otoliths collected downstream from the mine site indicates that white suckers contain background levels of all five elements (Table 5.2). Downstream northern pike otoliths contain background levels of Na and Sr, but contain levels of Li, Rb, and Cs that are above background, but an order of magnitude

Table 5.2 Comparison of background concentrations of elements (ppm) from white sucker and northern pike otoliths to those from Bernic Lake and downstream from the mine.

	Li	**Na**	**Rb**	**Sr**	**Cs**
White Sucker Otoliths					
Background 1988-2008	<0.3	2000-3000	0.4-0.7	200-600	<0.01
Bernic Lake 1988-2008	7-12	2000-4000	12-16	400-500	0.5-1.5
Downstream 1994-2008	<0.3	2500-3000	0.4-0.7	200-300	<0.04
Northern Pike Otoliths					
Background 1998-2008	<0.3	2000-3000	0.7-0.8	350-450	<0.01
Bernic Lake 1998-2008	3-7	2500-3200	18-25	300-400	1-2
Downstream 1989-2008	<0.3-2.1	2000-3000	0.5-3.5	150-700	0.01-0.4

less than Bernic Lake levels. This emphasizes the need to consider species separately and speaks to the usefulness of otolith microchemistry as an indication of signature attenuation downstream from a mine site.

5.4 Summary

The reconstruction of the chemical history of Bernic Lake provides a year-by-year catalogue of information on changes and trends in otolith microchemistry as compared with background levels. The major findings are:

- Bernic Lake otoliths contain levels of Na and Sr similar to levels in the surrounding region;
- Bernic Lake otoliths contain significantly higher concentrations of Li, Rb, and Cs;
- white sucker otoliths collected from Lac du Bonnet, approximately 17 km downstream from Bernic Lake contain background levels of all 5 elements;
- northern pike otoliths collected from Lac du Bonnet contain background levels of Na and Sr;
- downstream northern pike otoliths contain levels of Li, Rb, and Cs an order of magnitude above background levels;
- the chemical signature in otoliths that is related to the geochemistry of the Tanco pegmatite is attenuated downstream;
- yearly chemical data provides information on fluctuating concentrations in both the control sites and in Bernic Lake;
- yearly chemical data provides an indication of overall trends of increasing or decreasing concentrations; and

- otoliths from species with different feeding habits should be considered separately to account for any dietary influence.

5.5 Conclusion

Comparing trace element levels in the environment adjacent to the Tanco pegmatite mine to background levels of the area indicate that otoliths in Bernic Lake have background levels of Na and Sr, and elevated levels of Li, Rb, and Cs. Statistically significant increases in Li, Rb, or Cs may be related to changes in production activity at the mine, or to higher than normal precipitation levels increasing runoff from tailings piles.

Determining background levels for elements in the environment is necessary in order to detect environmental contamination. Otoliths provide chemical information that, when coupled the annular structure, can increase the ability to detect current, recent, and historical levels of contamination. Temporal trend chemical data can provide a tool for monitoring trace element levels in the environment and may be used by mining companies to observe changes in those levels in relation to changes in mining activity or buffering efforts over a period of many years. Such a tool can be used to assess the impact of contamination at both the individual and population levels.

Chapter 6 Summary and Conclusions

Research on otolith microchemistry has expanded well beyond assessing migratory patterns to indicate stock and sub-population structure and mixing, temperature and salinity histories of oceans, and variability in life-history strategies (Thresher, 1999). The relationship between otolith composition and physiological and environmental conditions is a complex issue, compounded by fish metabolism and influences from the habitat. A better understanding of the influences over otolith microchemistry is needed to expand this tool to its fullest potential. In this vein, the aim of the work presented in this thesis was to determine if the geology of an area influences otolith microchemistry. This is the first systematic study of the link between the geochemistry of a habitat, particularly the geology of the watershed, and otolith microchemistry in lacustrine environments. Mining in Manitoba is currently centred on base metal and tantalum-lithium-cesium production. The work presented here spanned three types of major metal production in Manitoba: two base-metal mines producing Cu-Pb-Zn and Ni-Cu ores, and a Ta-Li-Cs mine. Each study area was influenced by current or recently abandoned mining activity, which had the potential to increase the availability of certain elements in the environment. In each case, a suite of elements was selected that would reflect the geologic character of the particular area, and in each case the suite of elements was detected in the otoliths.

Arctic char living in the Maskwa pit, as described in chapter 2, provided an opportunity to examine the potential link between mafic and ultramafic, Ni- and Cu-bearing rocks and otolith microchemistry. What made this opportunity more important was that the fish were geographically isolated, eliminating migration out of and recruitment into the system, two factors that complicate toxicology studies using wild fish. This setting was ideal for examining the link between geology and otolith microchemistry from a constrained site where past base-metal mining occurred. The presence of flat, uniform signatures of Ni, Cu, and Cr in the otoliths is consistent with there being a link between the geochemical character of the surrounding rocks and the chemistry of the otoliths. This study was the first of its kind to examine otolith microchemistry from an exotic species of fish that was introduced into a closed lake. The findings of this work have implications for the possibility of creating a fish-stocked lake in a pit lake setting after mining activity has ceased, and the usefulness of otoliths as a method of monitoring levels of trace elements affecting fish on a yearly basis.

The goal of the paper presented in chapter 3 was to explore the link between geology and otolith microchemistry in an unconstrained setting, and to explore the possibility of using otoliths to track movements of individuals in relation to mine tailings. Some of the otoliths from Eldon and Cockeram Lakes contain anomalous peaks of Cu, Pb, and Zn that, because of geochemical coherence, are reasonably linked to tailings effluence from the Lynn Lake mine. This work strengthened the hypothesis that the geochemistry of an area has an impact on otolith chemistry. The coincident Cu, Pb, and Zn peaks are regarded as evidence of times the individual came in contact with tailings effluence. This implies that otolith microchemistry may be useful in tracking the movements of individuals within a population in an area with unique geochemical characteristics. This work suggested that anomalous signatures might provide an idea on what proportion of a population has come in contact with contamination and how frequently contact occurs, providing important details about the environmental history of fish and the long-term effects of exposure to environmental contamination.

The site chosen for the paper presented in chapter 4 is influenced by rare element pegmatite mining, for the purpose of determining if the pegmatite and associated mining activities imparted a chemical signature to otoliths of fish from nearby waterways. In this regional study, various sites were chosen at different distances from the source rock and mine. The investigations determined that otoliths from fish caught water bodies adjacent to, or downstream from the pegmatite contain Li, Cs, and Rb, which are indicative of the Tanco pegmatite, whereas otoliths from fish caught upstream from the mine and from lakes in a different watershed in the area did not contain all of elements analyzed. It was also determined that these otoliths recorded the attenuation of the chemical signature from the pegmatite mine. The incorporation of alkali elements into otoliths provided additional questions in regards to the mechanism for element uptake. Substitution of monovalent cations for Ca^{2+} may alter the mineral structure, require coupled substitution, or indicate some accommodation and charge-balance potentially involving the otolin protein (Halden and Friedrich, 2008). This was the first detailed survey of its kind in a lacustrine environment, was the first study to resolve periodic signatures for Rb and Cs, and reported the highest levels of Li in otoliths. Whereas Campana *et al.* (2000) reported that trace elements, including Li, could be detected using isotope dilution ICP-MS, the objective of the present study was to test the uptake of alkali elements in the vicinity of known concentrations. This work indicated a direct correlation between the geology and mining activity of the area and the microchemistry of otoliths from fish living within surrounding lakes and rivers. This work suggested that otoliths might be used to monitor trace element levels in lakes adjacent to active mines, attenuation, and mitigation strategies, as well as assess what affects these trace element levels have on fish. For example, the incorporation of Na into some otoliths at levels similar to those seen in marine environments would likely place some strain on the osmoregulatory system and energy balance of the fish.

Chapter 5 was written as a supplement to the work presented in chapter 4 on the Tanco mine site. Chapter 4 presented work on a suite of otoliths collected in one year and focused on the spatial differences in otolith microchemistry with distance from the mine site. Detailed sampling at the various sites over several sampling seasons, combined with archived samples provided by Manitoba Conservation provided detailed temporal chemical trend data that was the focus of chapter 5. This is the most detailed work done to date resolving temporal trends of otolith microchemistry in relation to mining activity. The several decades of information presented in the form of timelines showed differences between different species at the same sites, and the same species at different sites over time. These trends may be used as a monitoring tool by the mine to assess how changes in mining activity are affecting the biota, as well as a method for monitoring the effectiveness of mitigation strategies for buffering mining output into the environment.

In general, this series of studies has found that otolith microchemistry:

- contains a complete chemical record of the life history of the fish that is directly related, at least in part, to the geochemistry of the watershed;
- may be used as a tool for monitoring trace element levels in lakes that have been restored after mining activity has ceased

- can be used as a record of fish movement, particularly when a fish had come in contact with mine tailings, delineating when and how often contact occurred;
- can be used as a measure of the attenuation of a chemical signature away from the source;
- may be used as a tool for monitoring trace element levels in water bodies adjacent to active mines as a means for examining the affects of mining effluence on the biota; and
- provide temporal information to the chemistry that offer an historical perspective to the trends that may be used in environmental assessments and monitoring strategies.

6.1 Future Considerations

An obvious area of application of otolith microchemistry is in assessing the impact of present mine tailings on fish populations, or as a method of determining pre-mining levels prior to mine development. This may be done in the form of ongoing monitoring studies, or as background geochemical or environmental surveys. Water quality studies and environmental contamination impact surveys rely on a combination of long-term measurements of the physical, chemical, and biological components of an environment at the ecosystem, community, population, and individual levels (de Pontual and Geffen, 2002). However, detecting environmental contamination is difficult in areas where baseline data are sparse or non-existent (ibid). Otoliths can preserve annual periodicity of a number of elements in life-long records that are intimately connected to their local environment. These records can provide information on life histories and environments in lakes and river systems. Archived sets of otoliths provide an historical perspective and have the potential to expand baseline data back several decades. In this regard, chemical analysis of otoliths can improve the detection of current, recent, and historical levels of contamination.

Recommendations for developing a monitoring strategy to include the use of otoliths.

Regulations and guidelines are currently in place for developing EEM programs. For environments effected by metal mining activity, studies are designed specifically for each site, as mine effluent quality is highly variable from site to site (Ribey *et al.*, 2002). The main focus of EEM programs in metal mining areas are to determine if there is an effect on fish, if the effect is mine-related, what the magnitude and geographic extent of the effect is, and if the mine-related cause of the effect is known (ibid). To address these questions, a link needs to be established between the changes in the fish (how the effect has manifested) and the effluents. In this regard, otoliths can provide such information, as demonstrated in the work presented in this thesis. Adapting current monitoring strategies to include the use of otoliths can very easily be accomplished simply by the collection of otoliths from individuals already being sampled for fish survey requirements. A few considerations for developing an otolith-based monitoring program are given below.

Selecting sampling sites for otolith studies can parallel those chosen for EEM studies that examine tissue contamination. When selecting sampling locations, it is important to take into consideration the species that are present, their mobility (to predict any mixing of populations or if movement between two locations is possible), and their abundance to ensure that similar species may be sampled at each location for ease of comparison, given that different species from the same location can produce different otolith chemical traces (chapters 2 and 4). At least one reference area should be carefully chosen where the geological character of the watershed is similar, with the exception of exposure to mine effluent. Such a reference site should be upstream from the exposure area or in an adjacent area in cases where migration or mixing of populations is possible. Within the exposure area, one sampling site should be as proximate to the discharge area as possible to determine the likely maximum levels of trace element concentrations in the otoliths. Additional sampling sites within the exposure area should be sampled to provide spatial trend data, and to determine the geographic extent of the effects and attenuation of the effluent signal at an interval that reflects the needs of the study. It is suggested here that at least two downstream sites are sampled, as attenuation of a chemical signature may not necessarily have a linear relationship to distance. At each sampling location, it is recommended to collect water samples to provide for a comparison with otolith chemistry.

Guidelines for EEM studies in metal mining-affected areas suggest sampling of two sentinel (characteristic of the environment) species that are sexually mature, where available (Ribey *et al.*, 2002). These species should be of high abundance, to enable long-term monitoring, and their diet should be known. For food chain bioaccumulation, a long-lived predatory fish is recommended, specifically a piscivore, whereas for population surveys, benthivores that feed at the water-sediment interface where metals accumulate are preferred, particularly small-bodied fish, which typically have smaller home ranges (ibid). As demonstrated by the work in this thesis, different species from the same location can contain different levels of trace elements in their otoliths. One explanation for these differences within a location is that otoliths can record dietary signatures in their chemistry. Therefore, for otolith studies, it is recommended to select species with different feeding habits. An ideal situation for southern Manitoba lakes would include one benthivorous species, such as white suckers, one species that feeds on both benthos and fish, such as perch, and one piscivorous species, such as walleye or northern pike. Obviously, the selection of species will be site-specific depending on which species are resident.

In selecting species for monitoring trace elements in the environment through otolith microchemistry, it is important to consider their sensitivity to the given effluent. For example, in chapter 4 it was demonstrated that walleye and northern pike both contain anomalous, correlated peaks of Cu, Pb, and Zn. However, walleye naturally contain much lower amounts of Zn that did not produce oscillations corresponding to ontogenetic changes. As a result, the typical Zn profile for a walleye is less than 5 ppm and relatively flat. This made the identification of anomalous peaks much easier. In contrast, northern pike from the same location contained very high levels of Zn in their otolith cores, after which levels decreased with age, although yearly oscillations were still present. Such natural variation in Zn concentrations in northern pike otoliths could easily mask anomalous signatures. As a result, a comparison with Cu and Pb traces is necessary for distinguishing anomalous peaks. In such cases as these, the naturally low background levels of Zn in walleye otoliths make them a more sensitive marker for anomalous Zn concentrations.

To determine the health of fish populations in EEM programs, the optimal sentinel species would have an intermediate life span, one that is long enough to show responses, but not too long to obscure impacts (Munkittrick, 1992). For otolith-based studies, long-lived fish are ideal as they can provide historic perspective to chemical data, and younger fish, particularly those that are sexually immature or even young of the year, can establish chemical data that represents the year of sampling only, and one that is not affected by ontogenetic changes associated with sexual maturity. For otolith studies, it is recommended to sample a range of fish ages to provide for comparisons between the young and old, which represent comparisons between current trace element levels with historic ones.

When setting up EEM programs, a sample size of 20 mature males and 20 mature females from 2 sentinel species in each area is recommended where such sampling mortality will not adversely affect the population (Ribey *et al.*, 2002). These sample numbers provide a statistically significant characterization of the population averages. Studies have shown that there is little change in the 95% confidence limits with sample sizes higher than these (Munkittrick *et al.*, 1991). Similarly, in setting up otolith-based monitoring studies, these numbers should be employed to establish baseline chemistry for the area. A range in ages would be preferable so that any ontogenetic changes in chemistry may be identified. Both water and otolith samples should be collected over a period of several years, to provide temporal trend data and to build a database of chemical information from which a typical chemical signature may be constructed for an area. Compiling data in a GIS database would provide for effective graphic representation of temporal and spatial trends. For a more complete idea of what constitutes the typical signature, recently collected otoliths should be compared with archived samples, which provide information on historic levels of trace elements in otoliths. Once the baseline chemistry has been established, it will be possible to separate naturally occurring signals from those with an anthropogenic origin. The identification of anthropogenic influence can provide information on fish movement with respect to tailings effluence, and any affects that non-lethal exposure can have. The temporal and spatial scales of compositional variations of both water an otoliths are needed to build a complete picture of the environment and contamination. The continued monitoring of an area may use reduced numbers of individuals once the baseline has been established, depending on the requirements of the study design. From this point, otolith microchemistry may be routinely assessed as part of an ongoing environmental assessment.

Recommendations for furthering knowledge of trace element uptake in otoliths.

The interaction between a fish and the environment is complex. Whereas some geochemical coherence can be anticipated and we have some understanding of the trace element substitutions possible in aragonite, much remains to be understood about the details of substitution, otolith growth mechanisms, and the pathways by which elements are deposited in otoliths. There is also a need for more research on the biological barriers that fractionate metals from the water to the otolith. The usefulness of otolith microchemistry applications depends on our understanding of the processes of otolith formation, all of which effectively control otolith composition.

A set of data has begun to emerge from the literature in recent years on Mn uptake in otoliths and how it may be related to diet and/or redox potential. In suboxic environments, microbes reduce solid Mn oxides to soluble Mn (II) (Lasslet, 1995). Increased Mn:Ca levels detected in Atlantic croaker (*Micropogonias undulates*) otoliths collected from the Neuse River, North Carolina are believed to be related to reducing conditions in the bottom sediments during hypoxic events (Thorrold and Shuttleworth, 2000). They suggested that the reduction of particulate MnO_x increases the bioavailability of dissolved Mn to croaker otoliths, making otoliths a potential proxy for hypoxic conditions in estuaries. Differences in Mn uptake in northern pike and walleye otoliths from Eldon Lake, Manitoba may indicate that oscillatory Mn was a record of dietary signatures (chapter 3). It is evident from these and similar studies that trace elements in otoliths potentially reflect different physical and chemical parameters of the environment as well as the physiology of the fish. Further work on the uptake of Mn, and indeed other trace elements, in otoliths will provide information on the mechanisms controlling their uptake as well as details on what parameters these signals are reflecting.

The relative roles of ambient water and diet as sources for element uptake in otoliths are a topic of ongoing study (Buckel *et al.*, 2004; Marohn *et al.*, 2009; Ranaldi and Gagnon, 2008; Sanchez-Jerez *et al.*, 2002). At present, it is difficult to generalize about the pathways of all elements (de Pontual and Geffen, 2002). Laboratory studies have been performed for a small portion of trace elements where fish were fed metal-contaminated food versus fish held in contaminated water. These studies typically use bulk analytical techniques or do not present the results with any temporal trend data (e.g., Ranaldi and Gagnon, 2008). However, these studies, along with those using direct injection into the fish, are important in understanding the pathway by which metals are incorporated into otoliths. As such, they should be expanded upon to examine pathways for other elements, and presented along the time scale that otoliths provide. This time scale will offer information on the amount of time that elapses between contact with elevated levels of trace elements and when the signal is recorded in otoliths. This will aid in understanding anomalous levels of trace elements resolved in wild fish otoliths.

Determining element pathways in wild fish otoliths is challenging in that there are many uncontrolled variables in a natural environment. However, it may be possible to use stable carbon isotopes to discuss the likelihood of element uptake being related to diet. Plants and living organisms within a lake system will preferentially incorporate the lighter ^{12}C isotope, enriching the ambient water in the heavier ^{13}C isotope. The carbon isotopic composition of otoliths is in equilibrium with the dissolved inorganic carbon (DIC) of the endolymph, which is influenced by ambient water and diet, and may therefore record dietary shifts of the fish (Schwarcz *et al.*, 1998). Depending on the pathway through which C is incorporated into the otolith, the $\delta^{13}C$ will be relatively high, if the C is derived from the ambient water, or relatively low, if C is derived from dietary sources. A comparison of the fluctuations of $\delta^{13}C$ values across an otolith transect to fluctuations in trace element concentrations may provide information on if the trace element in question is derived from water or diet. Such isotopic variations may be determined with Secondary Ion Mass Spectrometry (SIMS) where spot analyses can be used to determine the isotopic ratios of individual annulus.

Otoliths can incorporate a wide range of trace elements, which poses many additional questions and challenges as to the nature of the uptake of these elements. In inorganic carbonates, substitution for Ca^{2+} is a common phenomenon, particularly among the divalent cations. For other cations, or for elements substituting in large quantities, their incorporation may distort the crystal structure of the mineral or may require coupled substitution to maintain charge balance. Alternatively, some trace elements may be incorporated into the protein matrix. The analysis of otolith proteins has been very limited, given the amount of soluble and insoluble proteins in otoliths is only 1-5% by weight (Pote and Ross, 1991; Tomas *et al.*, 2004). Until recently, decalcification techniques using EDTA caused leaching of metals loosely bound to the proteins (Borelli *et al.*, 2001). However, a new technique has been developed that stops the decalcification reaction prior to demetallation of the proteins, allowing the extraction of intact metal-protein complexes (Miller *et al.*, 2006). These extracted proteins may be analyzed for bulk metal concentrations, without interference of the calcium carbonate structure and any metals contained within. Such analyses would provide information on some of the physical controls of trace element uptake in otoliths at the site of otolith formation.

In terms of analytical advancements for the benefit of otolith microchemistry studies, there is a need for the development of a certified otolith reference material for the LA-ICP-MS. The lack of such a material has necessitated the use of glass-based standards. Glass standards have very different ablation characteristics than do real otoliths, which result in poor sensitivity curves (Campana, 1999).

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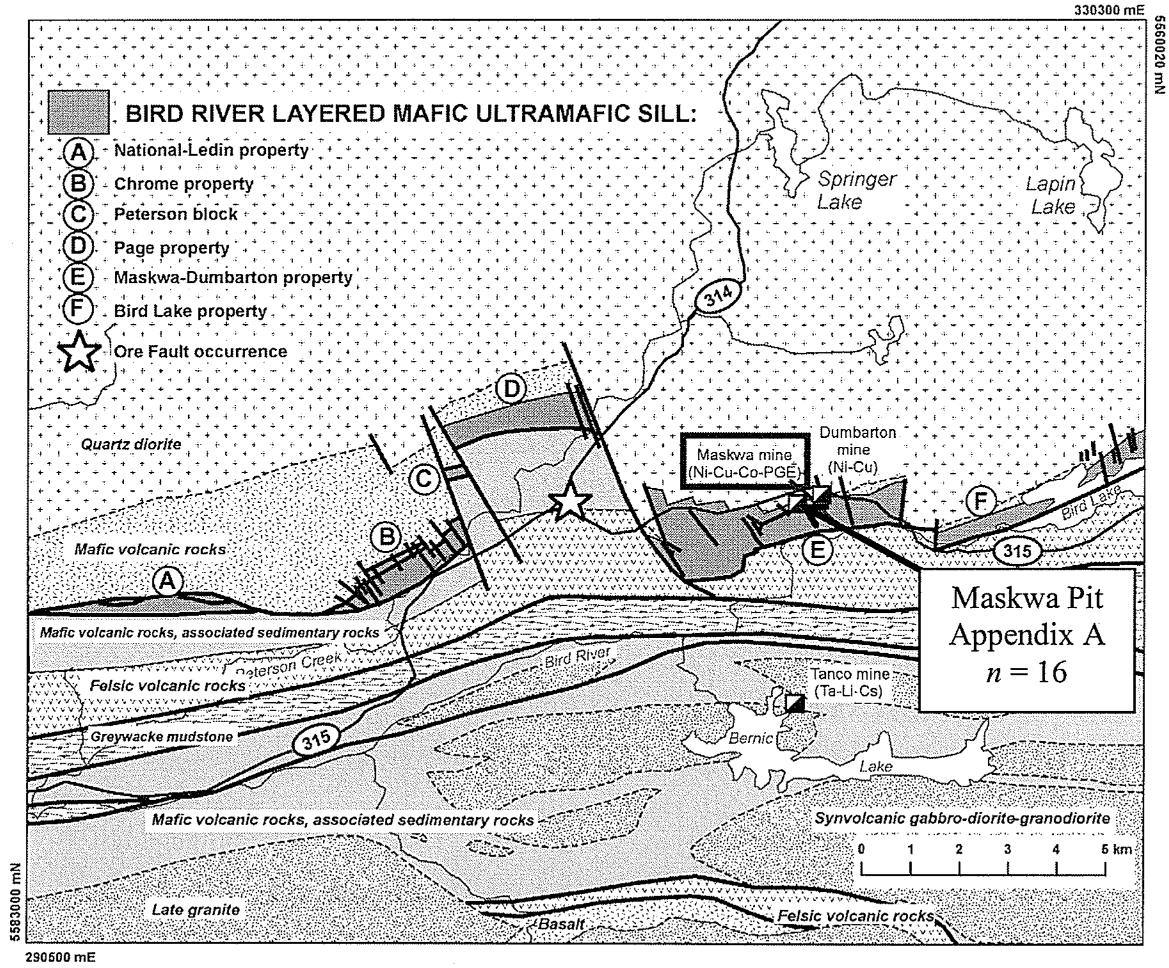
Appendix A: LA-ICP-MS data for Maskwa pit otoliths



Appendix A LA-ICP-MS data for Maskwa Pit otoliths

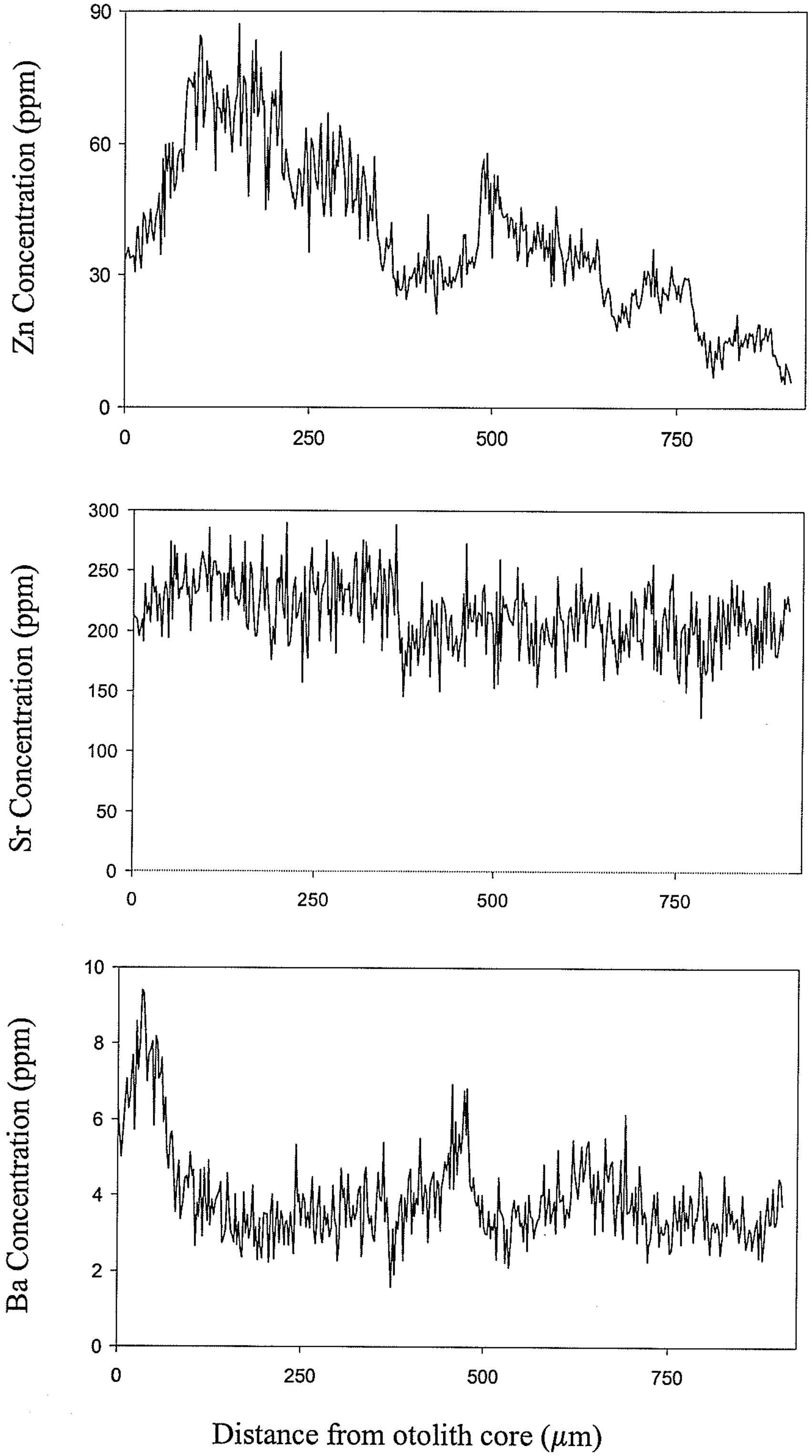
Species: Arctic Char (*Salvelinus alpinus*)

Captured: 2007 (Wardrop Engineering, Inc.)

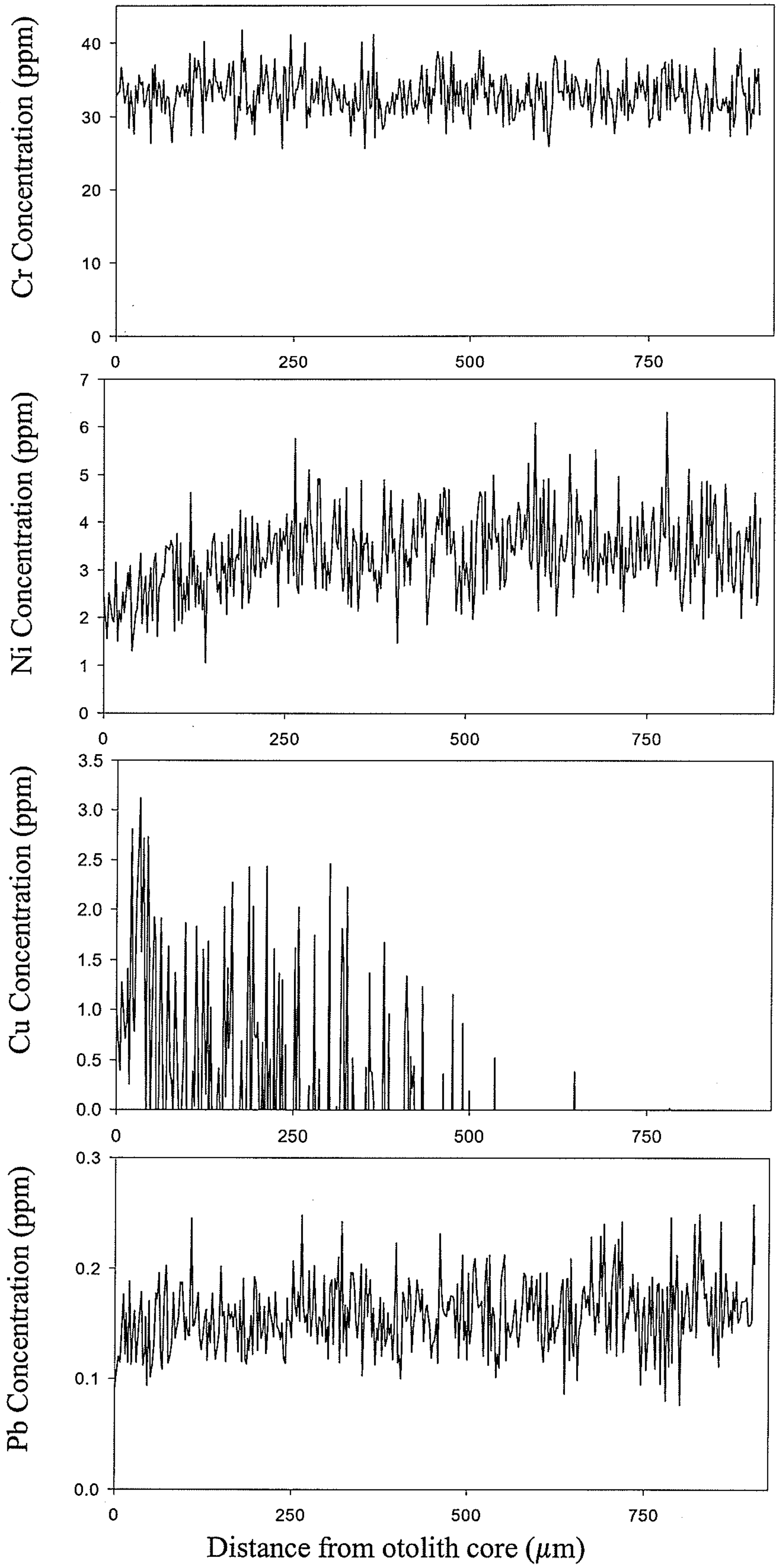
Isotopes	$\mathbf{Cr^{53}}$	$\mathbf{Ni^{60}}$	$\mathbf{Cu^{65}}$	$\mathbf{Zn^{66}}$	$\mathbf{Sr^{88}}$	$\mathbf{Ba^{137}}$	$\mathbf{Pb^{208}}$
Typical Detection Limit	0.45	0.52	0.87	6.86	70.39	0.32	0.18
Typical 1σ Error	6.76	1.18	0.97	30.01	37.20	1.29	0.04

Sample Number	***Fork Length (cm)***	***Wet Weight (g)***	***Sex, Maturity***	***Age***
182	36.0	425	N/A	5
183	39.8	625	N/A	9
184	36.3	460	N/A	9
185	41.6	630	N/A	9
186	37.9	409	N/A	8
187	34.1	470	N/A	9
188	44.2	630	Male, immature	9
189	34.5	460	Male, immature	6
190	56.0	1650	Male, mature	7
191	48.5	1250	Male, mature	7
192	42.0	680	Male, immature	9
193	43.2	750	Female, mature	9
194	38.0	518	Female, mature	6
196	37.7	455	Unknown, immature	6
199	35.7	452	N/A	6
200	41.1	581	Female, immature	8

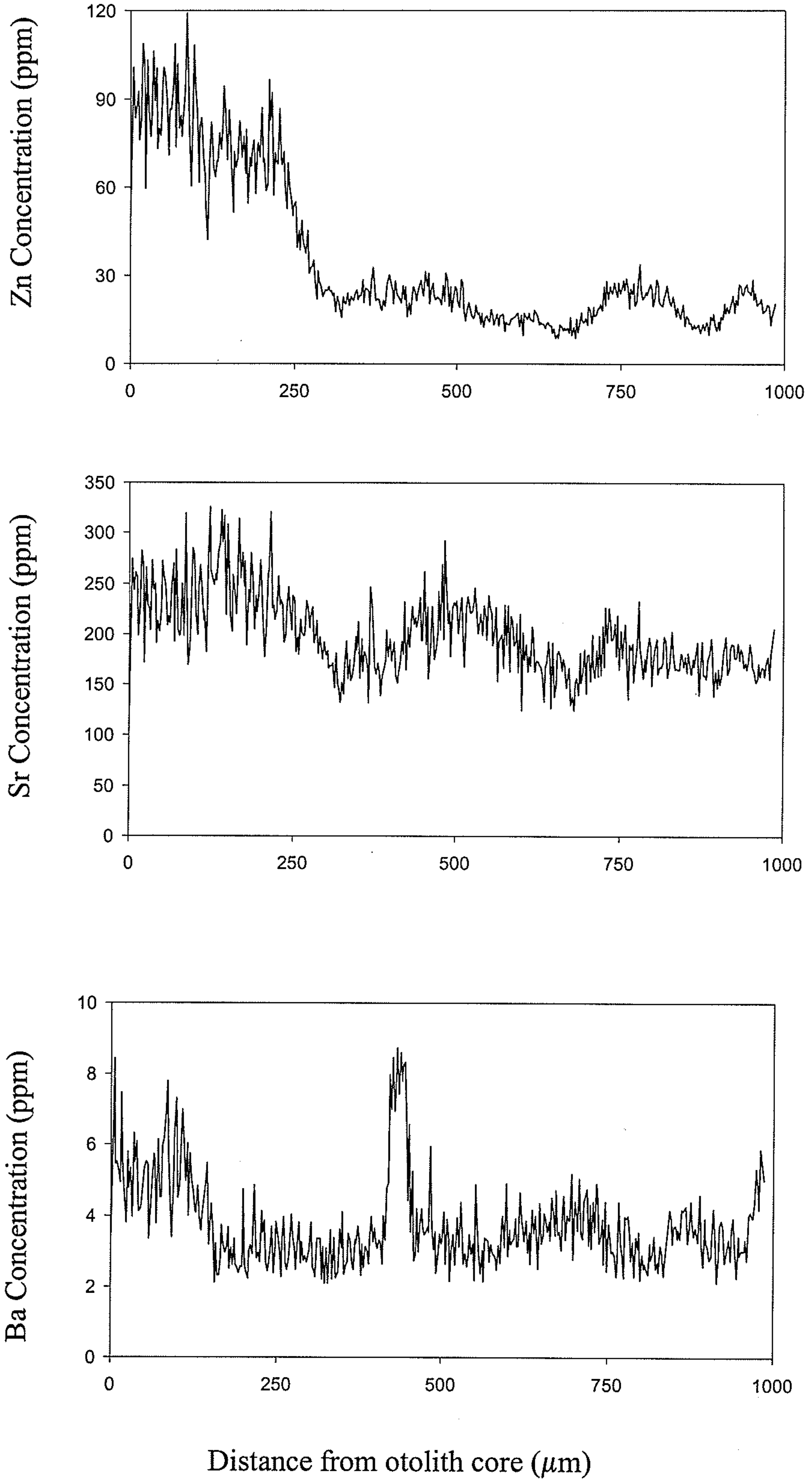
Maskwa_182


Zn Concentration (ppm)
90
60
30
0
0
250
500
750
Sr Concentration (ppm)
300
250
200
150
100
50
0
0
250
500
750
Ba Concentration (ppm)
10
8
6
4
2
0
0
250
500
750
Distance from otolith core (μm)

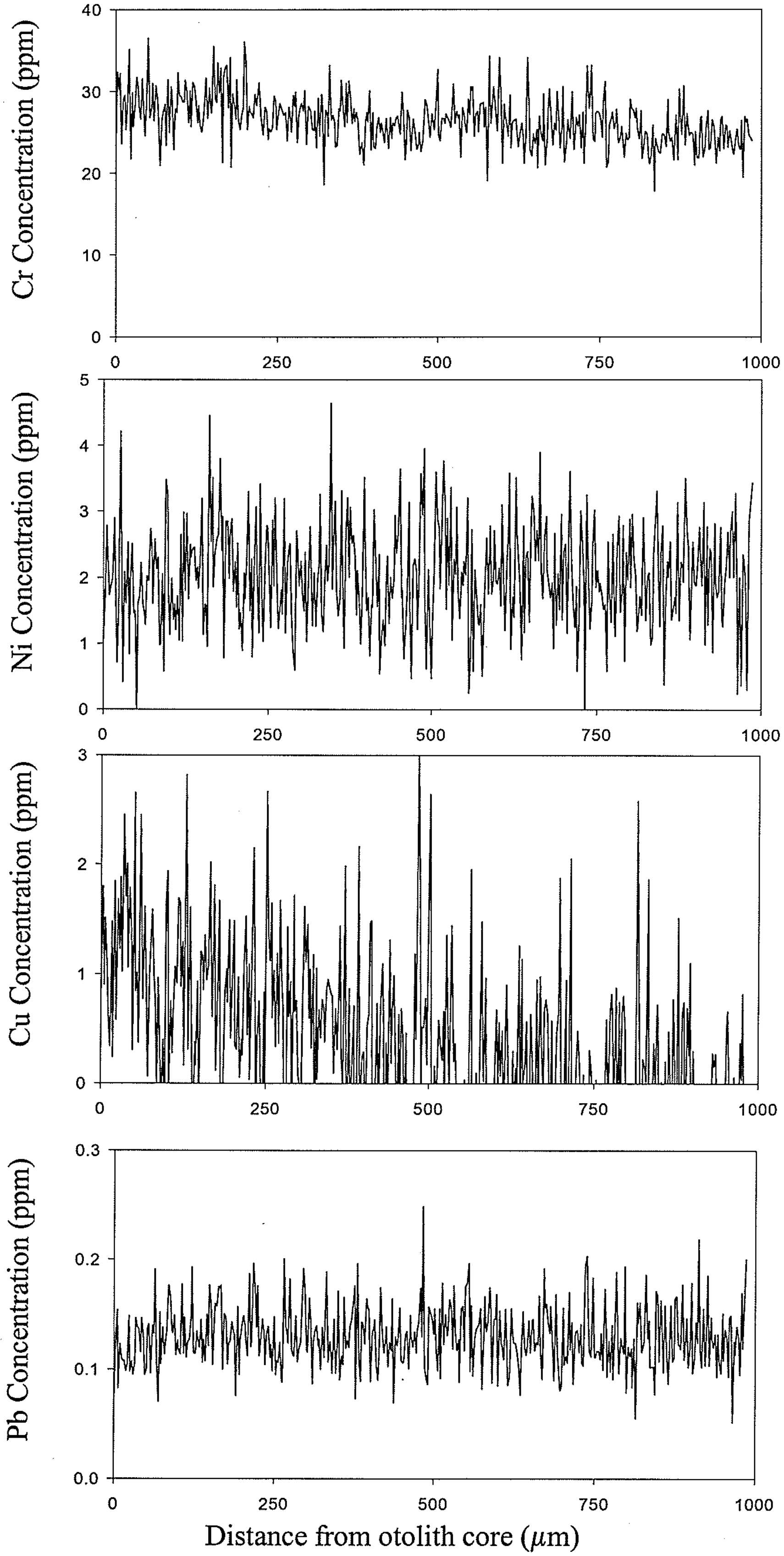
Maskwa_182 *continued*



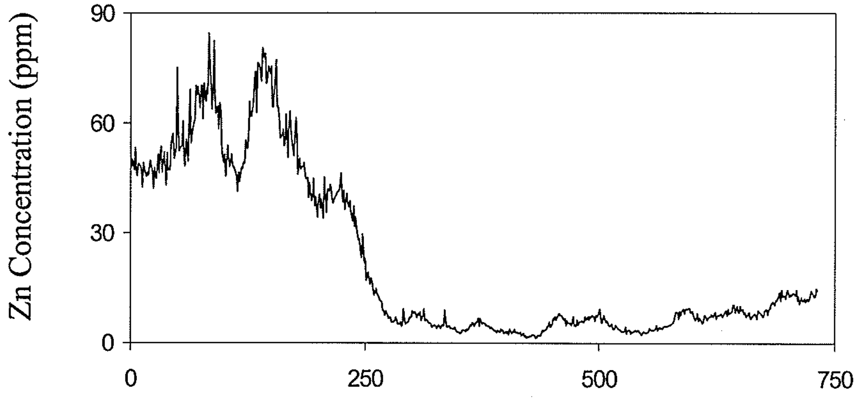
Maskwa_183

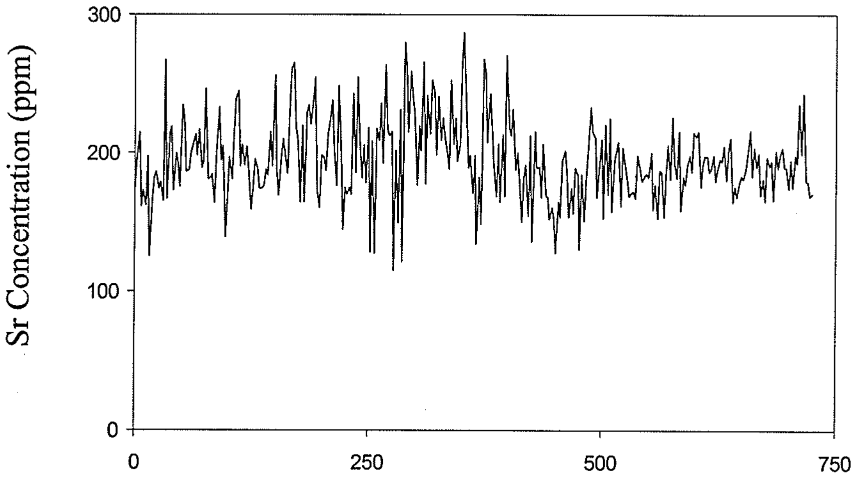

Zn Concentration (ppm)
120
90
60
30
0
0
250
500
750
1000
Sr Concentration (ppm)
350
300
250
200
150
100
50
0
0
250
500
750
1000
Ba Concentration (ppm)
10
8
6
4
2
0
0
250
500
750
1000
Distance from otolith core (μm)

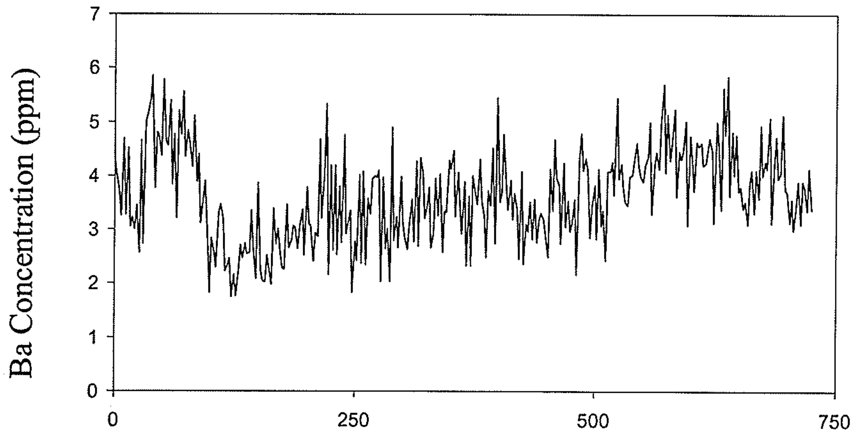
Maskwa_183 *continued*



Maskwa_184

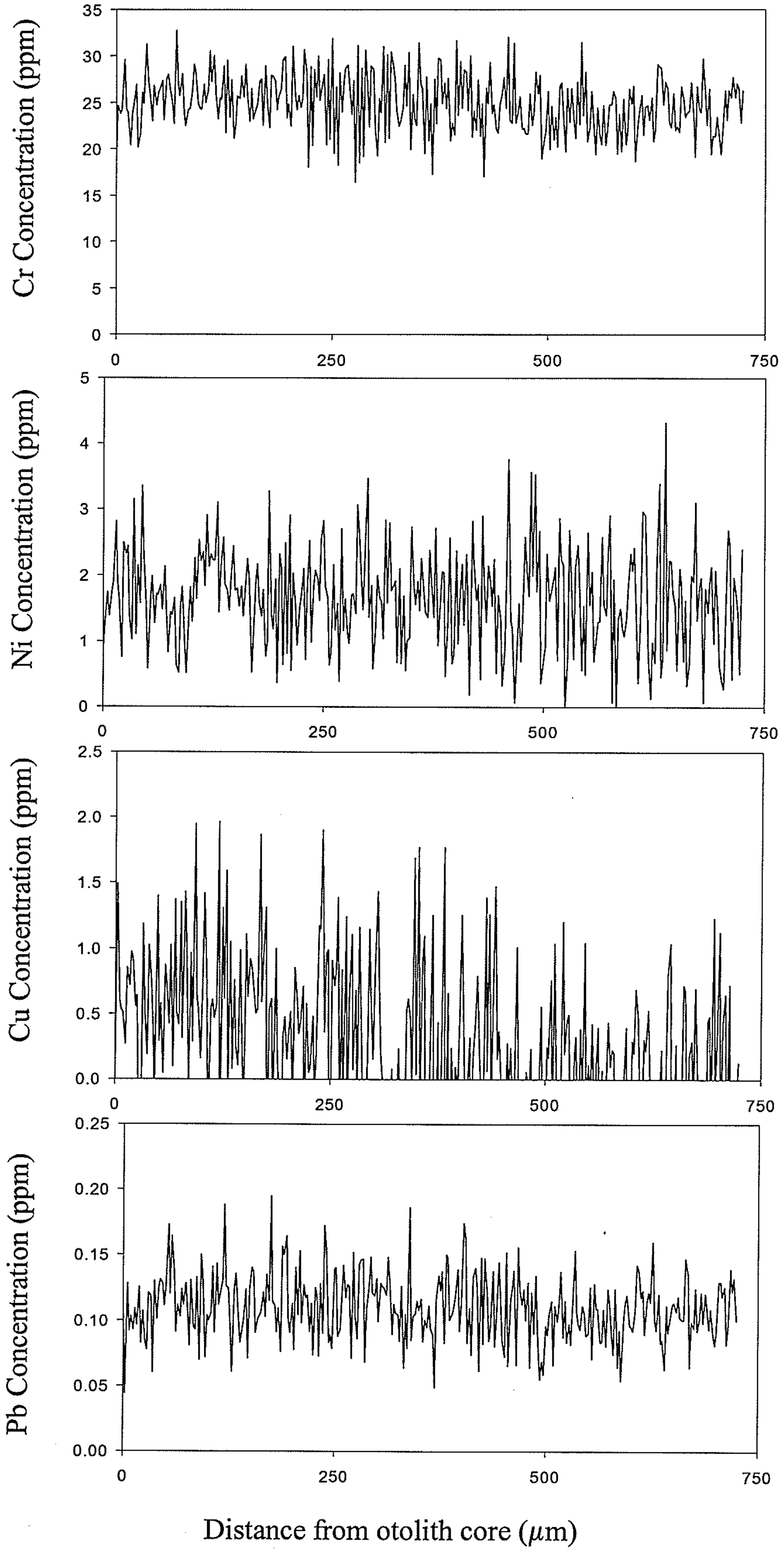




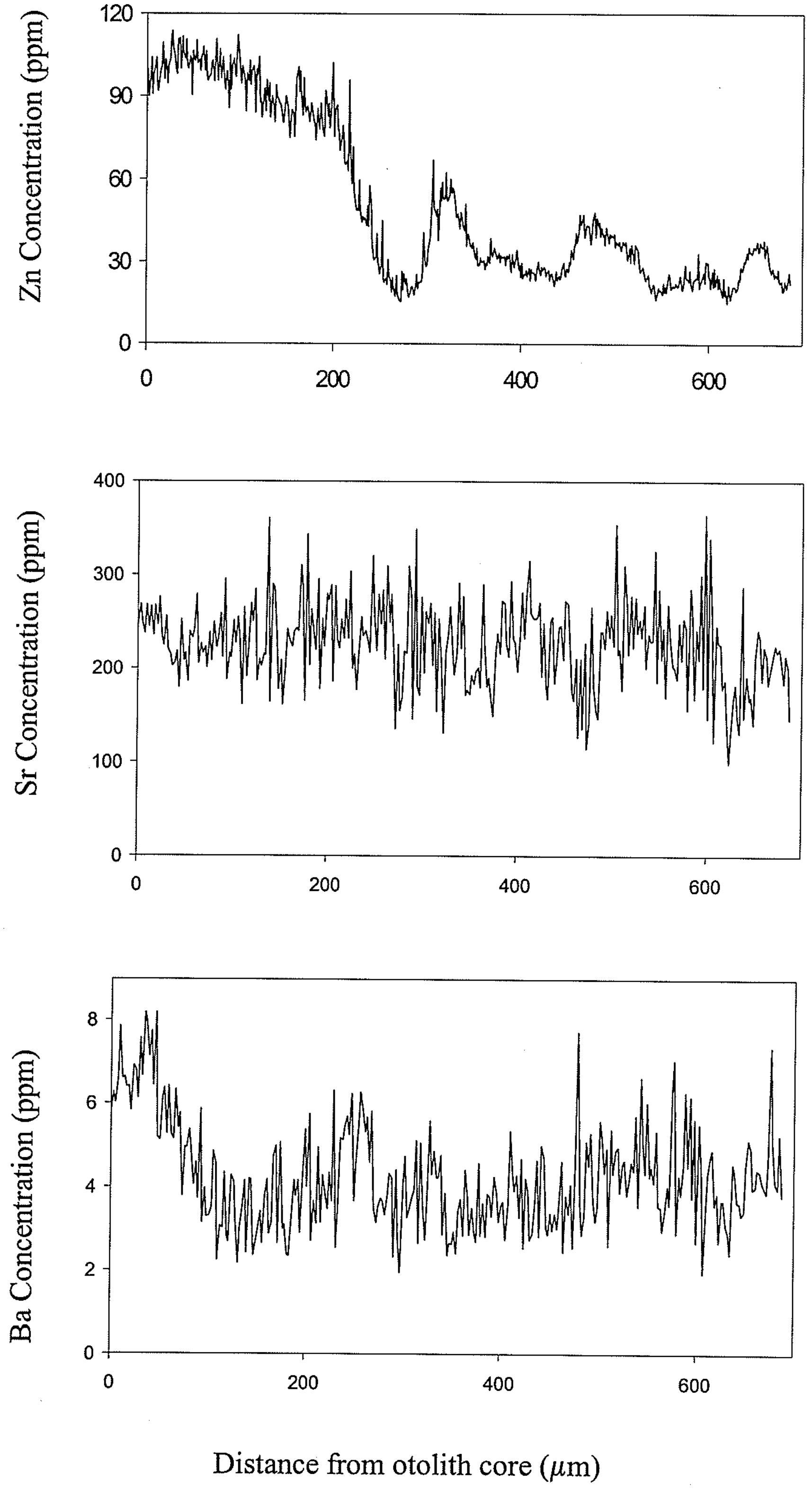


Distance from otolith core (μm)

Maskwa_184 *continued*

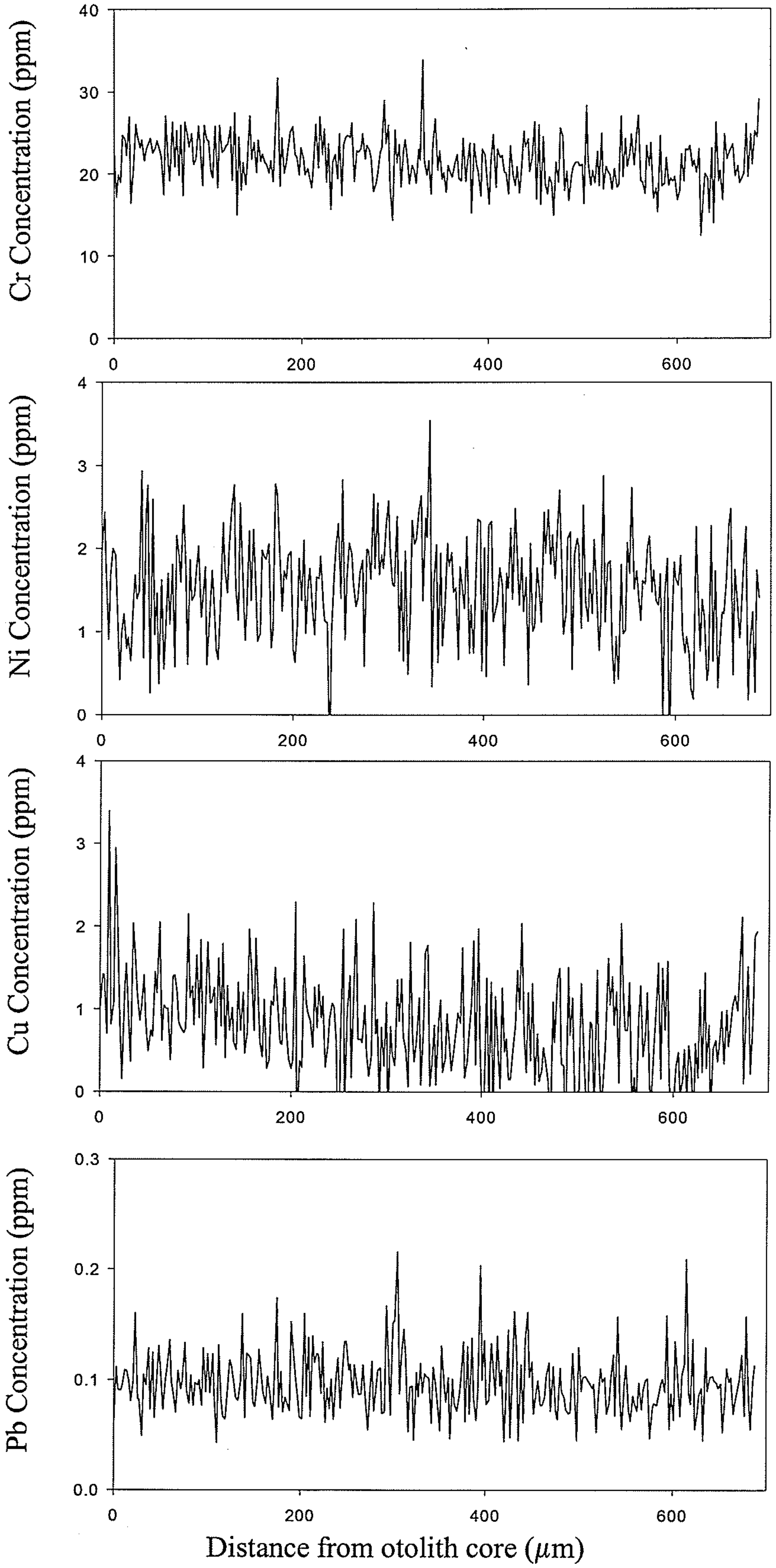


Maskwa_185

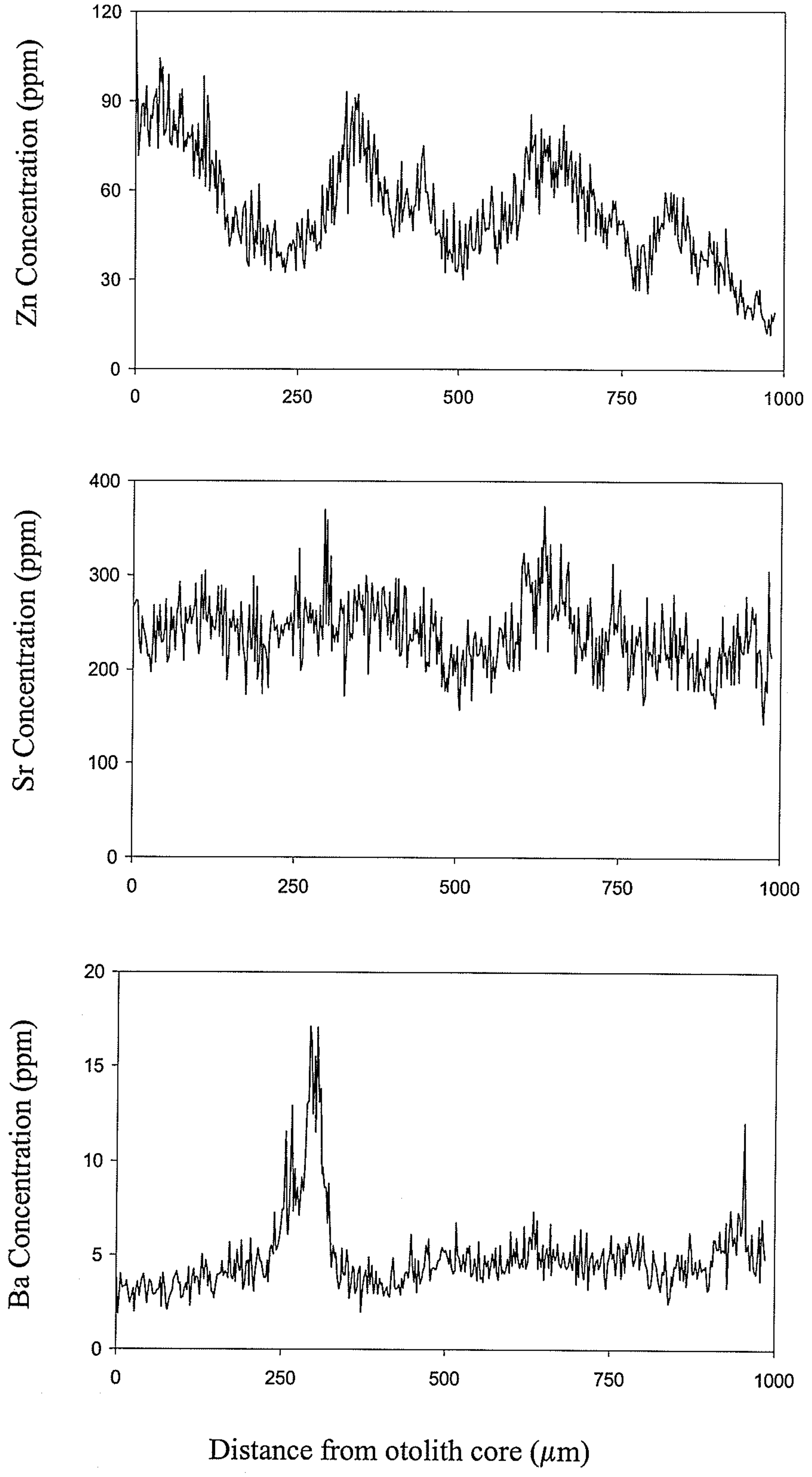


Zn Concentration (ppm)
120
90
60
30
0
0
200
400
600
Sr Concentration (ppm)
400
300
200
100
0
0
200
400
600
Ba Concentration (ppm)
8
6
4
2
0
0
200
400
600
Distance from otolith core (μm)

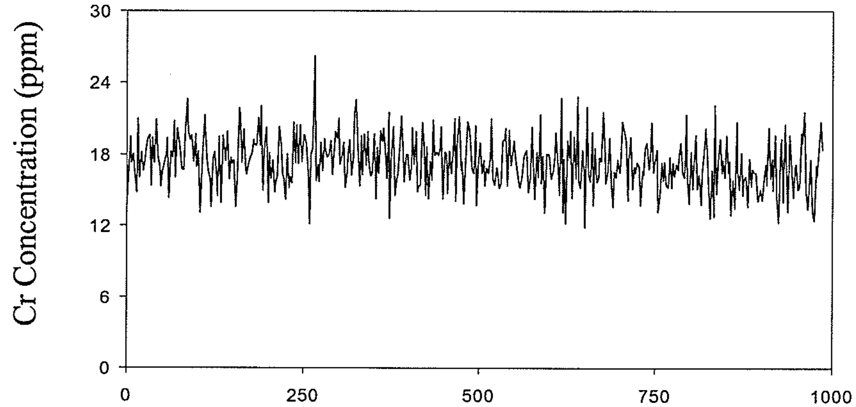
Maskwa_185 *continued*

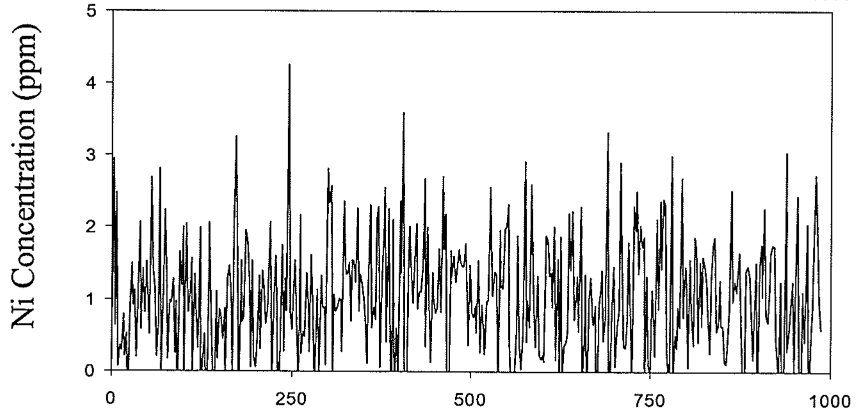


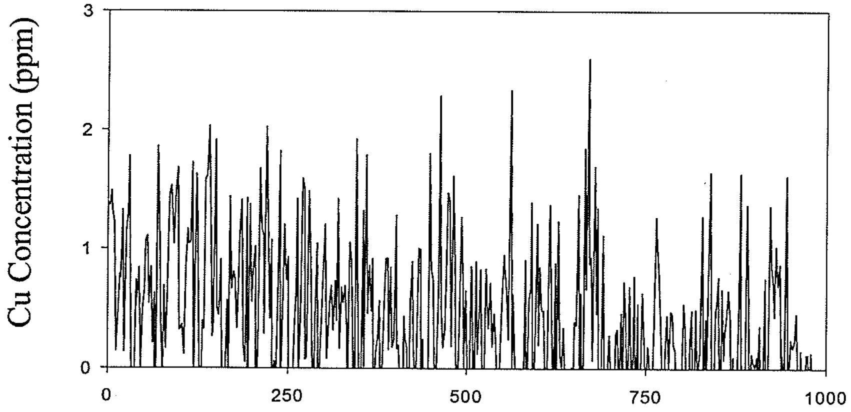
Maskwa_186

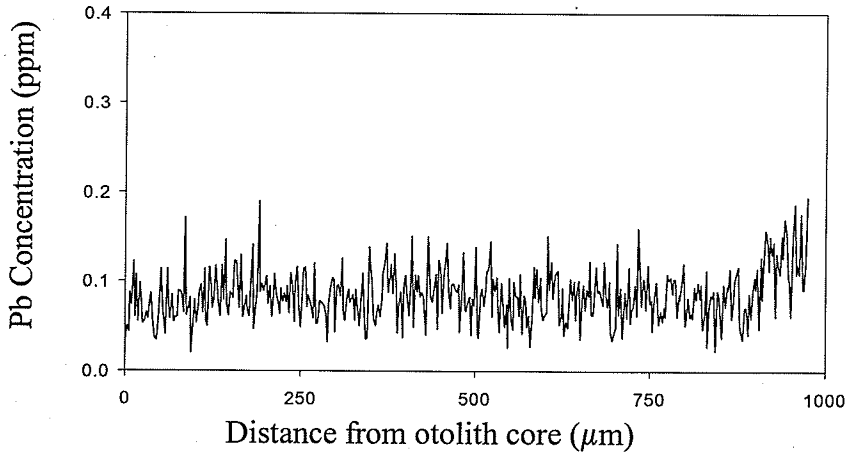

Zn Concentration (ppm)
120
90
60
30
0
0
250
500
750
1000
Sr Concentration (ppm)
400
300
200
100
0
0
250
500
750
1000
Ba Concentration (ppm)
20
15
10
5
0
0
250
500
750
1000
Distance from otolith core (μm)

Maskwa_186 *continued*

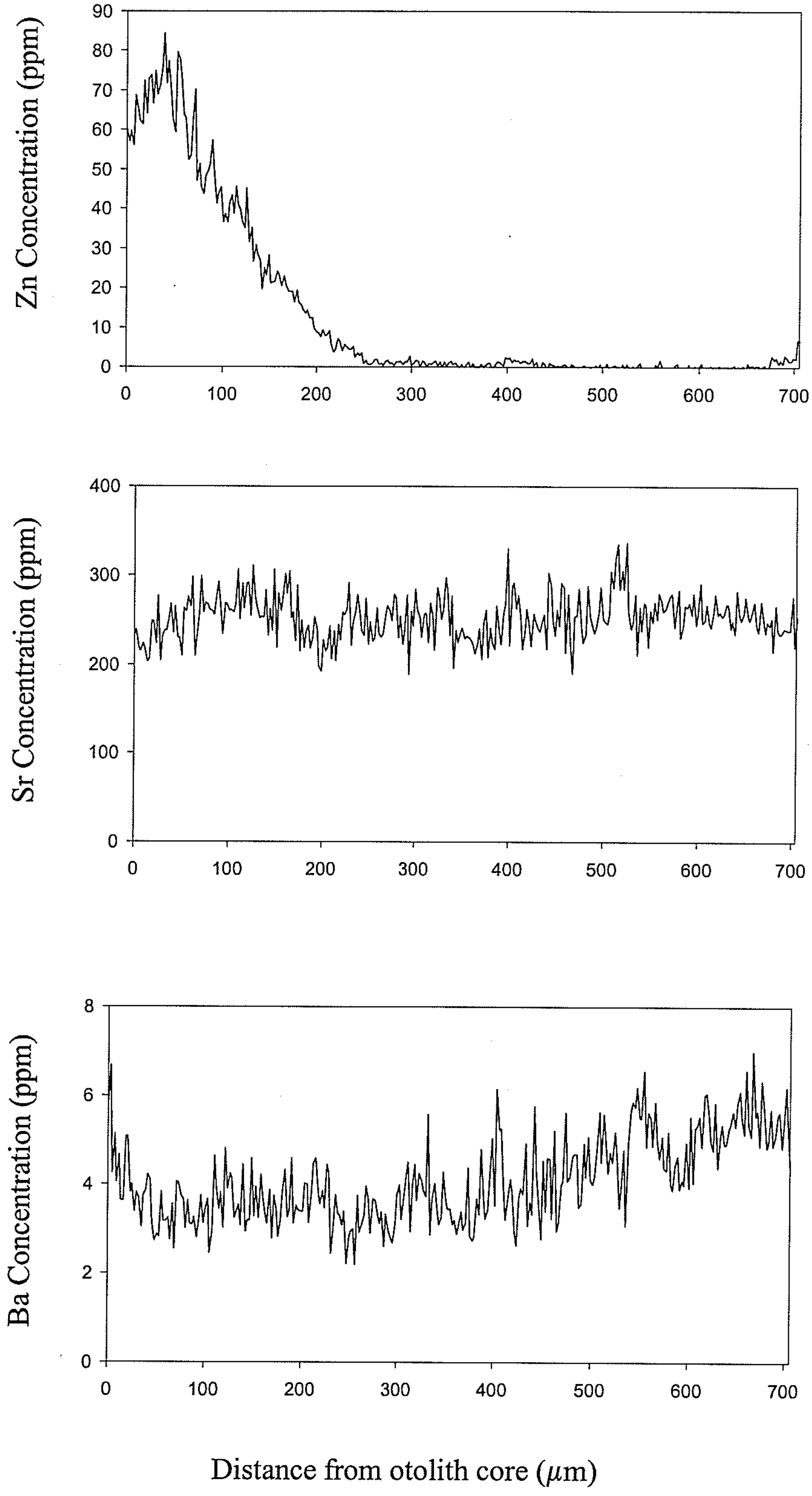




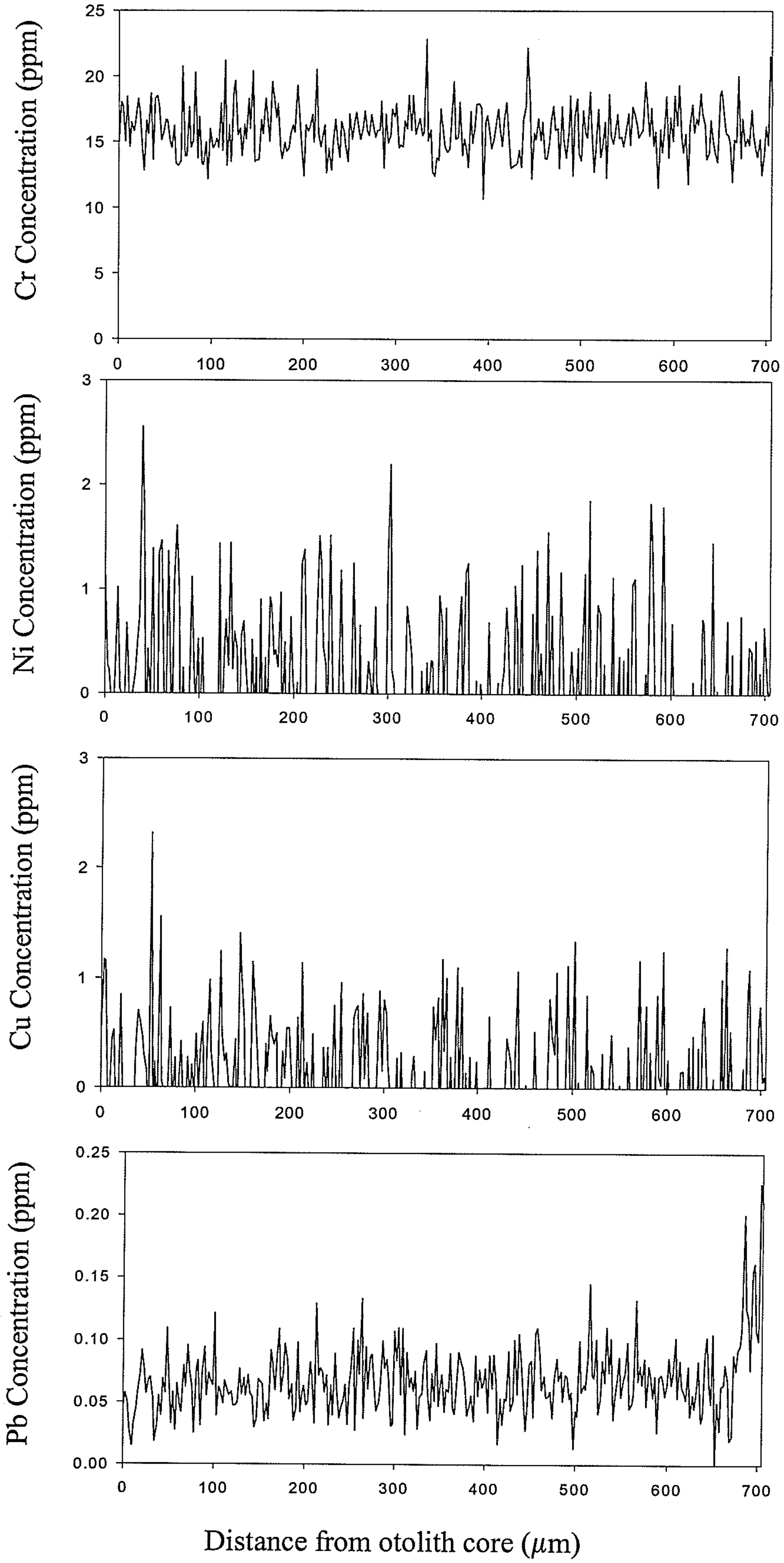




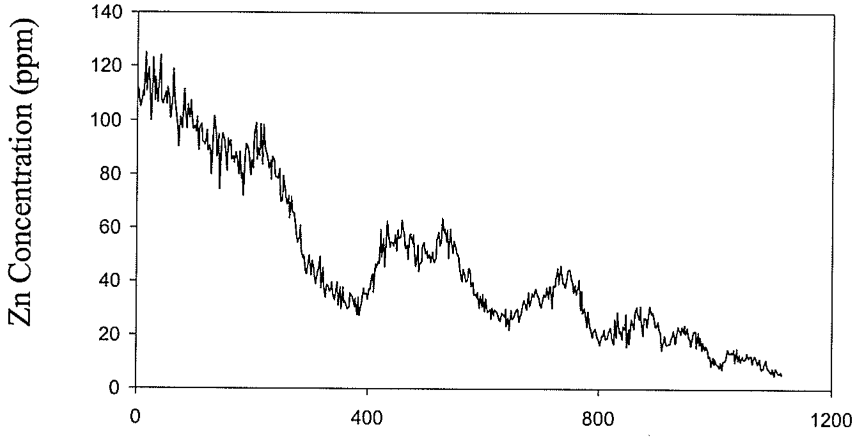
Maskwa_187

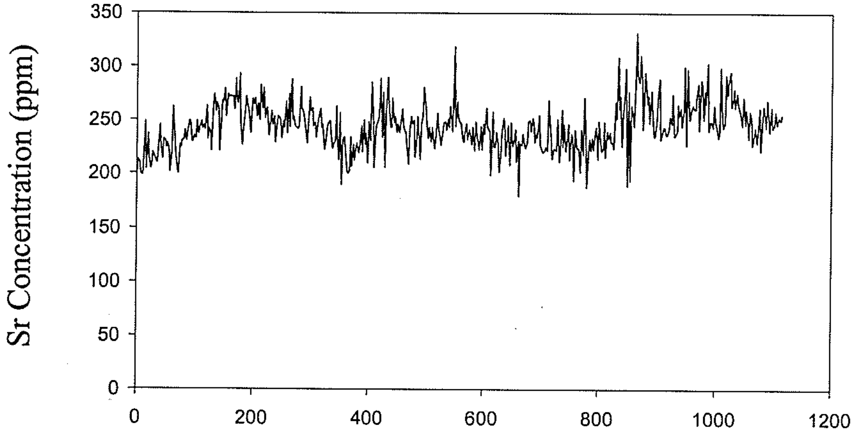

Zn Concentration (ppm)
0
10
20
30
40
50
60
70
80
90
0
100
200
300
400
500
600
700
Sr Concentration (ppm)
0
100
200
300
400
0
100
200
300
400
500
600
700
Ba Concentration (ppm)
0
2
4
6
8
0
100
200
300
400
500
600
700
Distance from otolith core (μm)

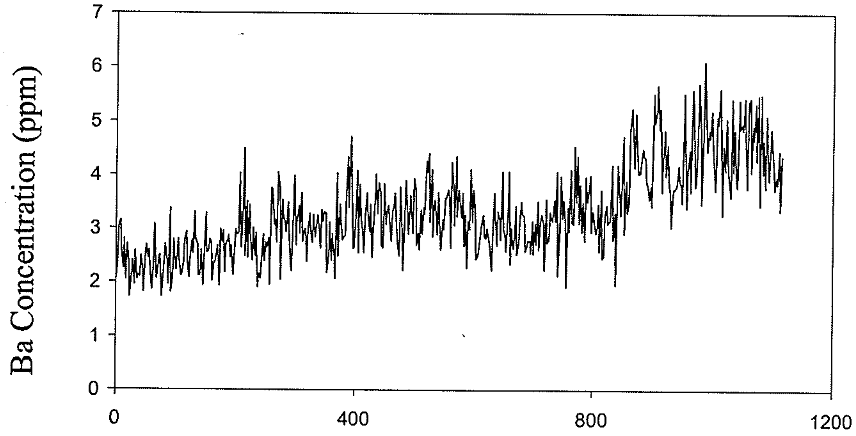
Maskwa_187 *continued*



Maskwa_188

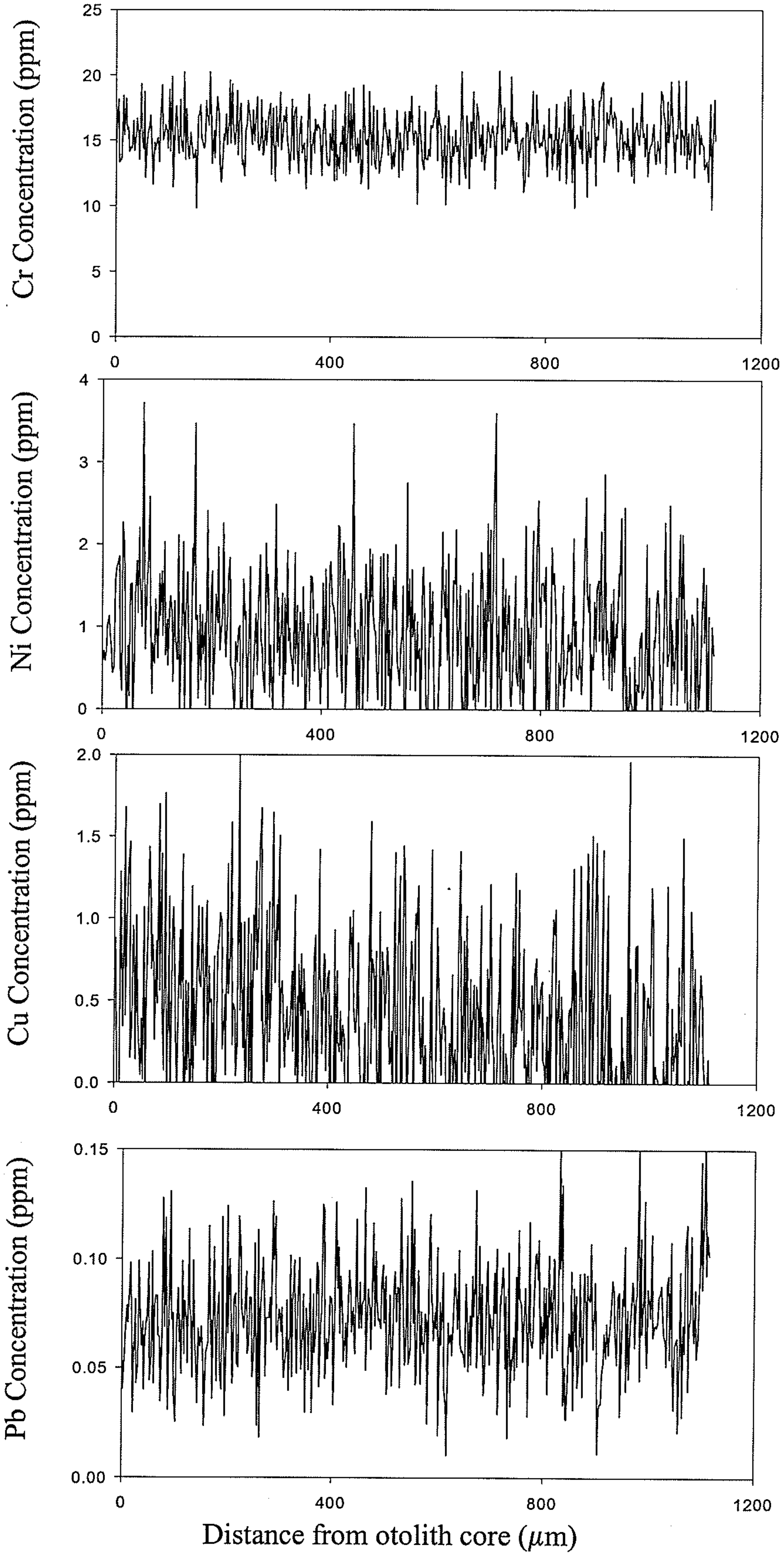




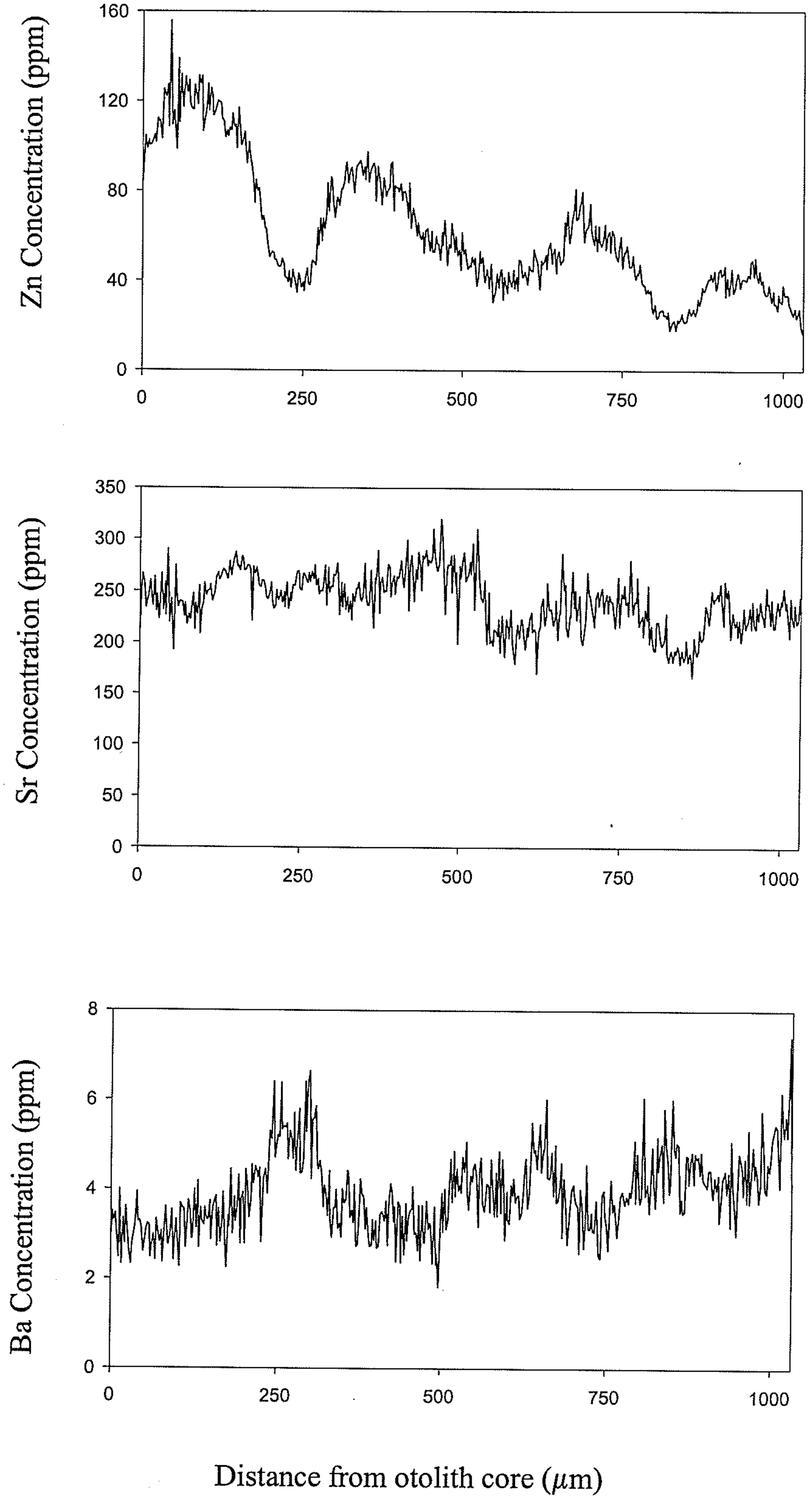


Distance from otolith core (μm)

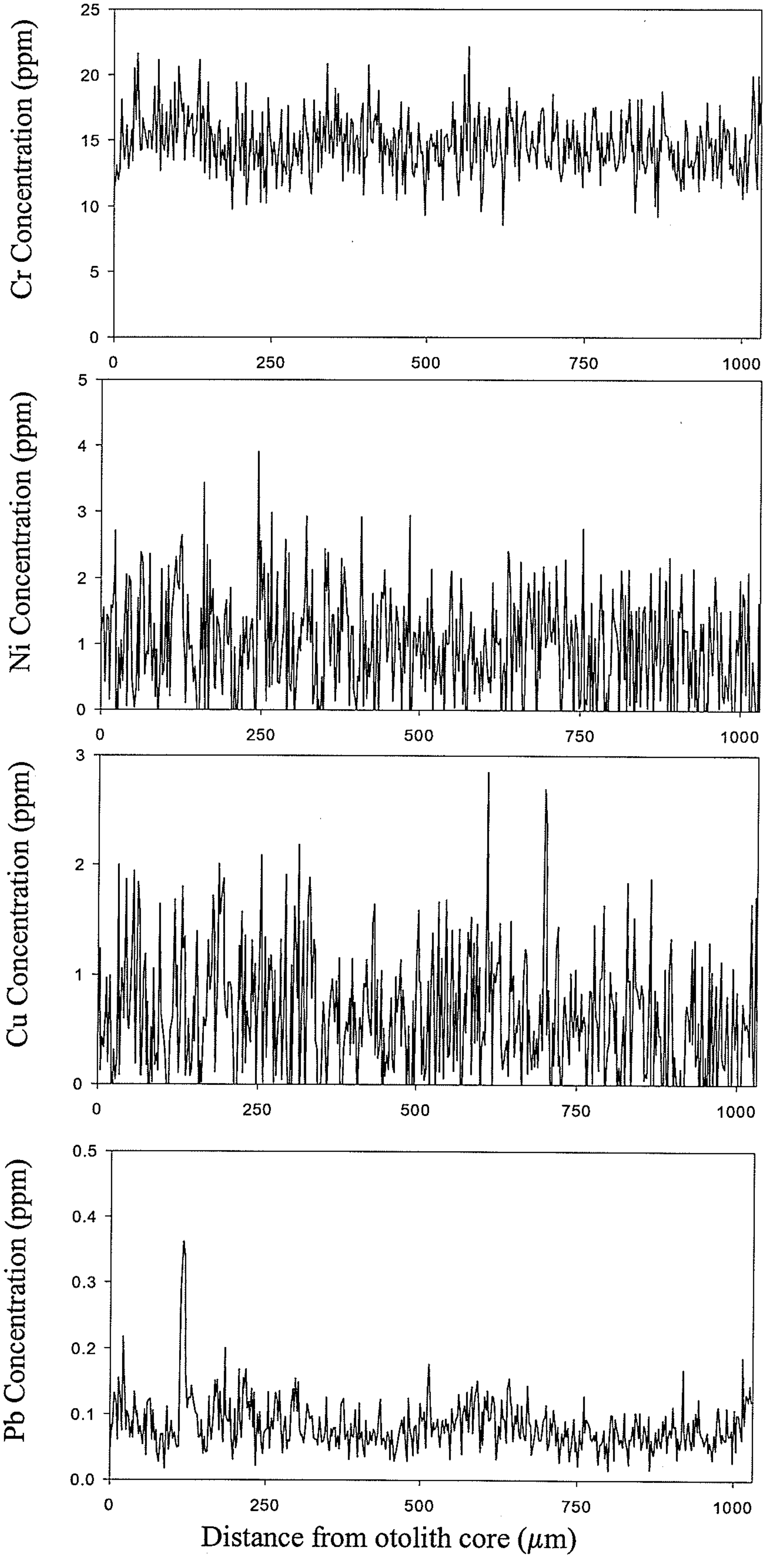
Maskwa_188 *continued*



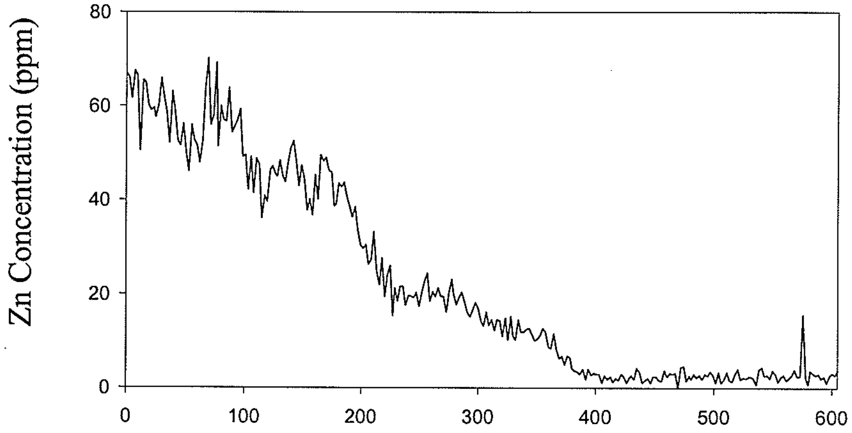
Maskwa_189

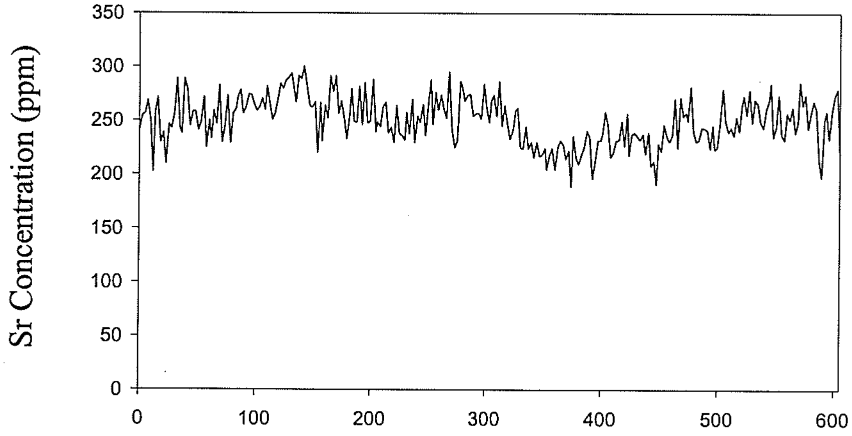

Zn Concentration (ppm)
160
120
80
40
0
0
250
500
750
1000
Sr Concentration (ppm)
350
300
250
200
150
100
50
0
0
250
500
750
1000
Ba Concentration (ppm)
8
6
4
2
0
0
250
500
750
1000
Distance from otolith core (μm)

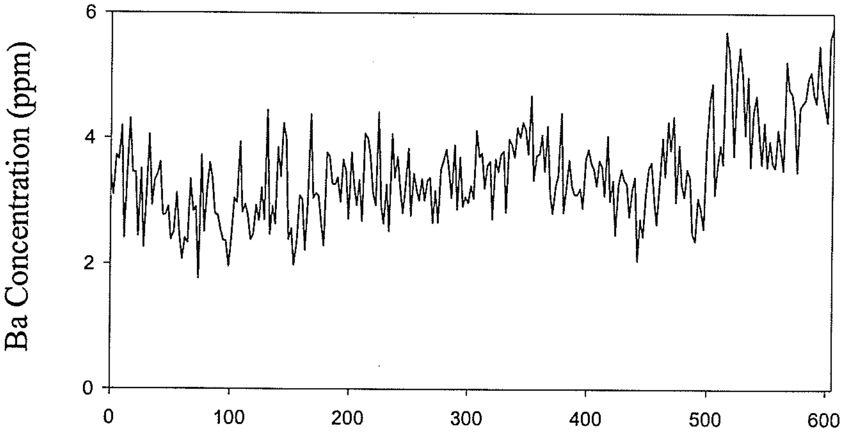
Maskwa_189 *continued*



Maskwa_190

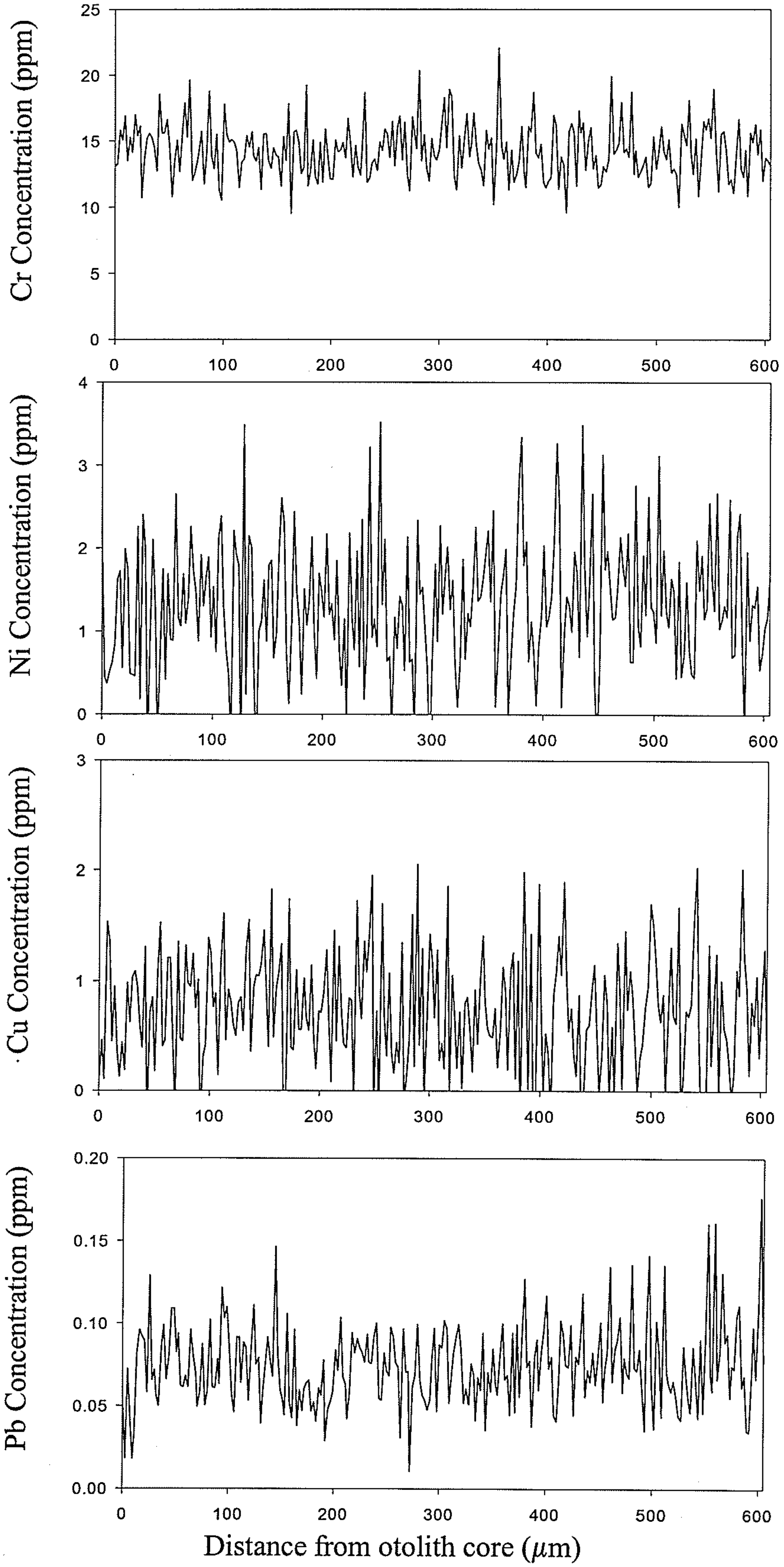




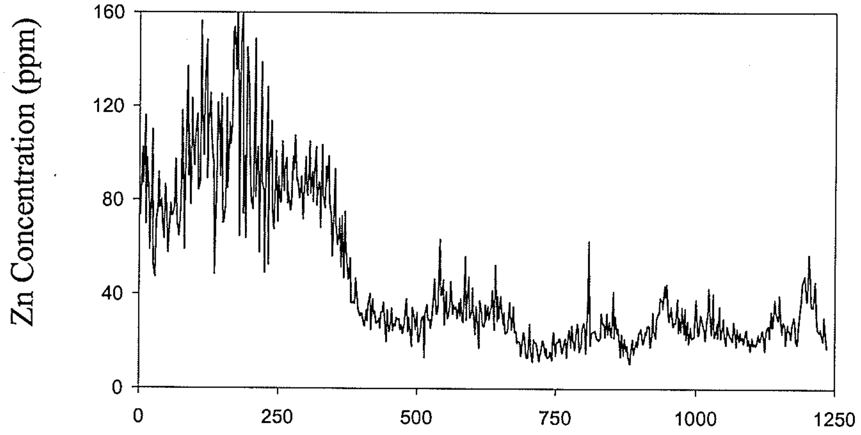


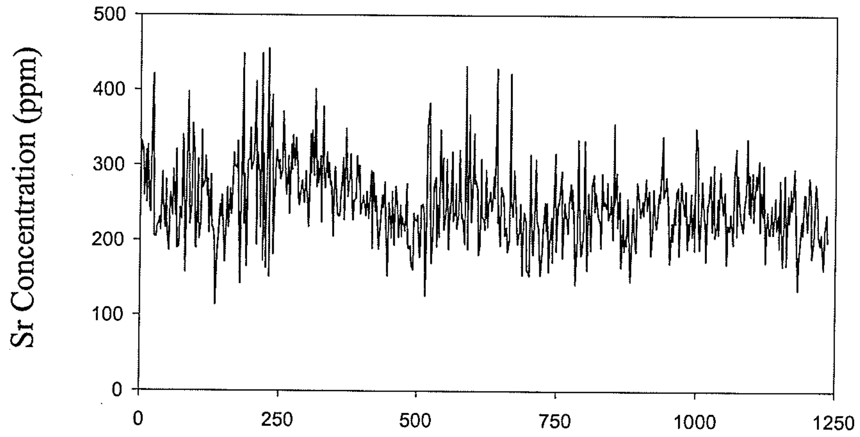
Distance from otolith core (μm)

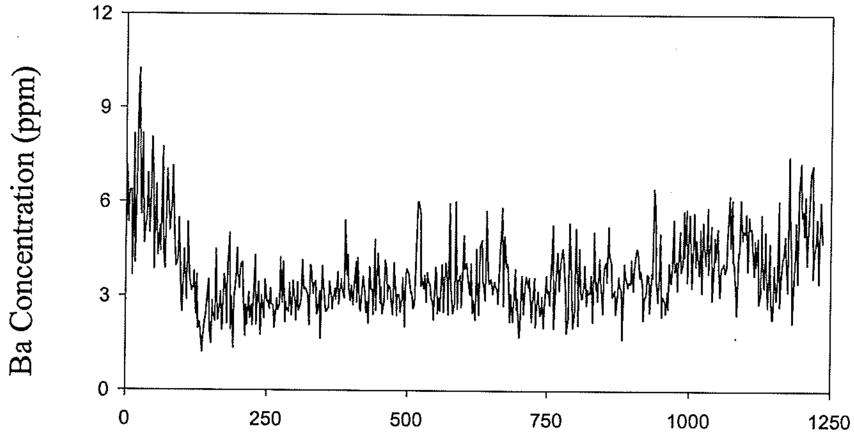
Maskwa_190 *continued*



Maskwa_191

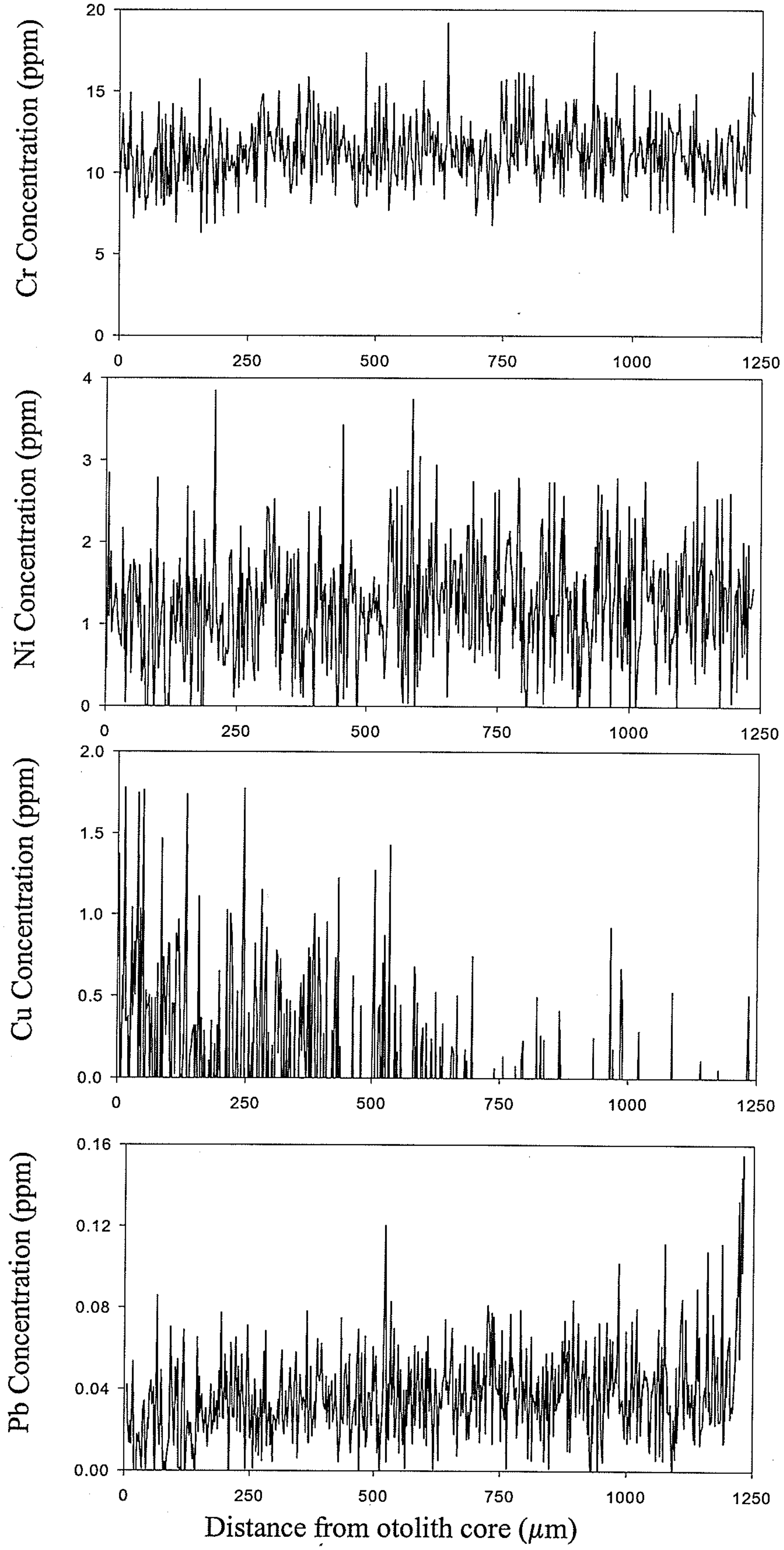




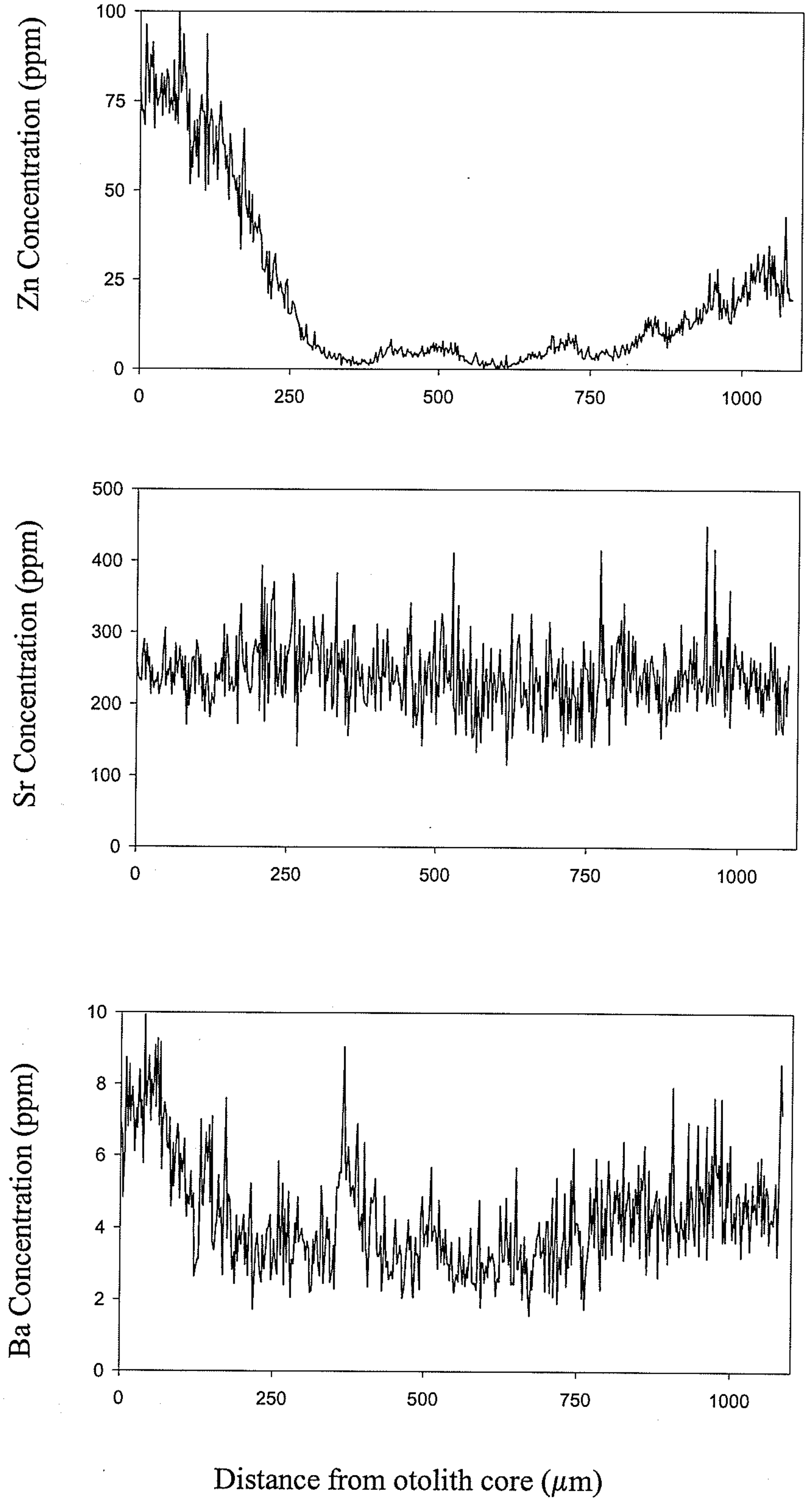


Distance from otolith core (μm)

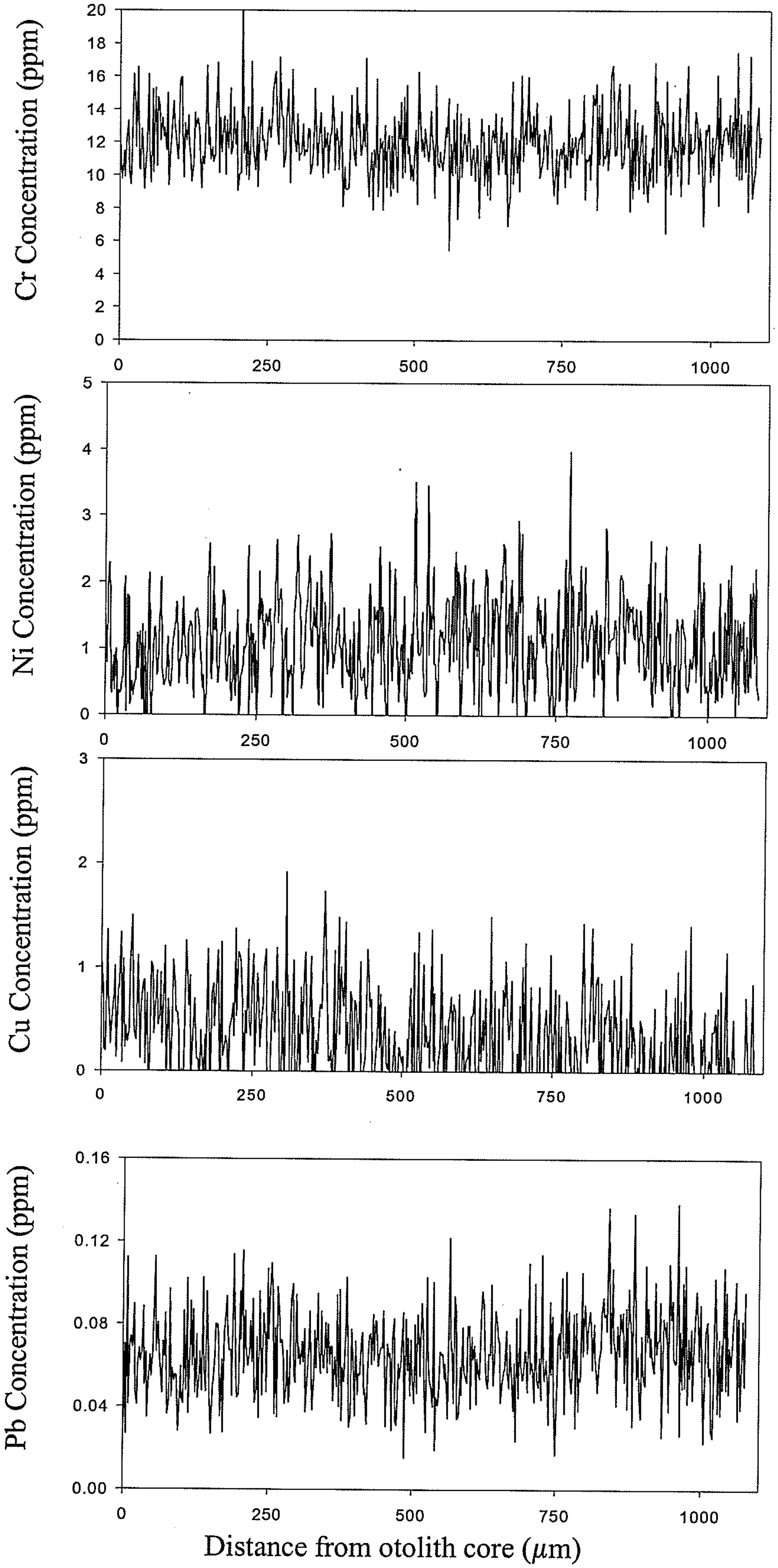
Maskwa_191 *continued*



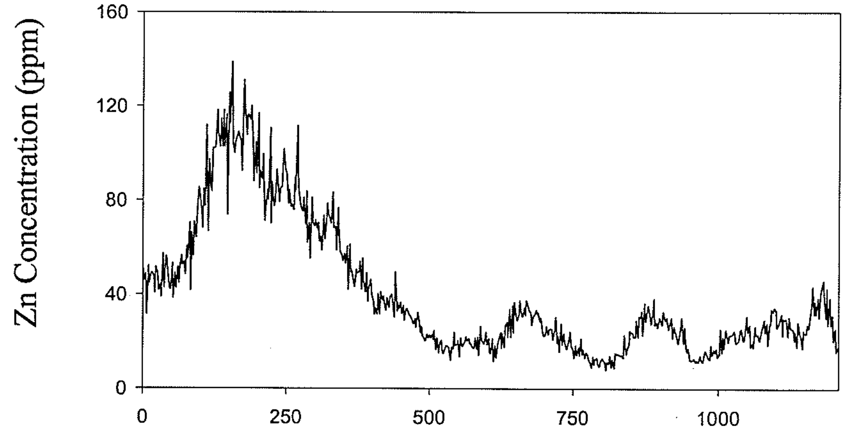
Maskwa_192

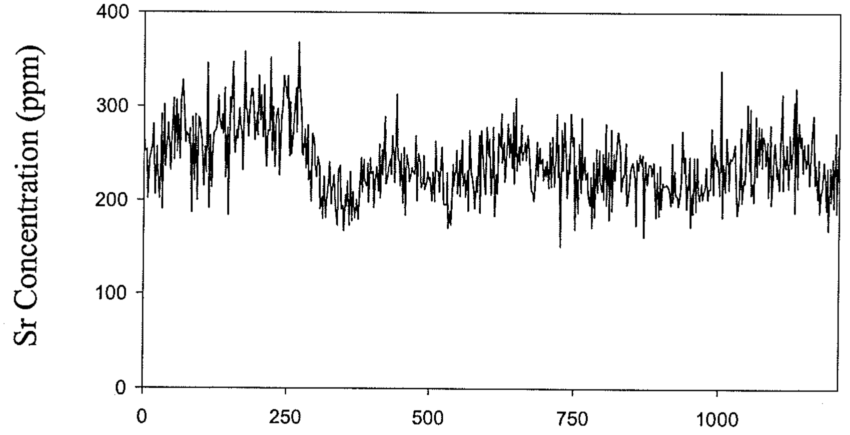

Zn Concentration (ppm)
100
75
50
25
0
0
250
500
750
1000
Sr Concentration (ppm)
500
400
300
200
100
0
0
250
500
750
1000
Ba Concentration (ppm)
10
8
6
4
2
0
0
250
500
750
1000
Distance from otolith core (μm)

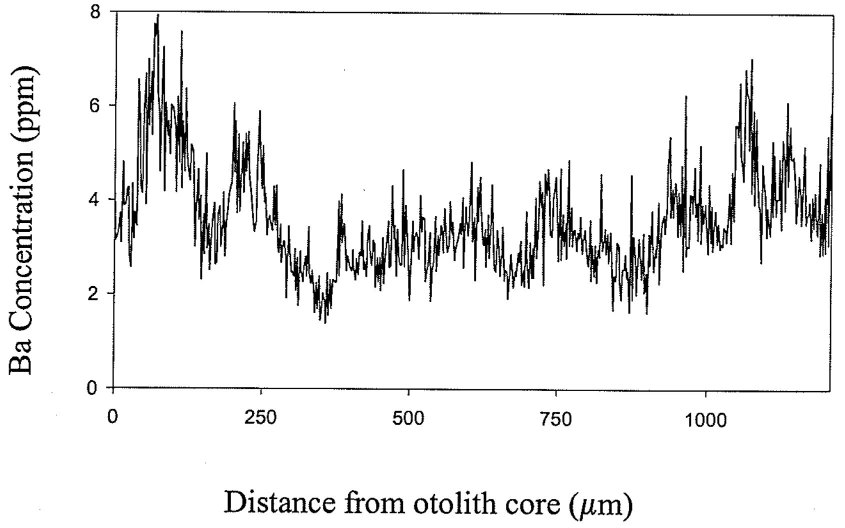
Maskwa_192 *continued*



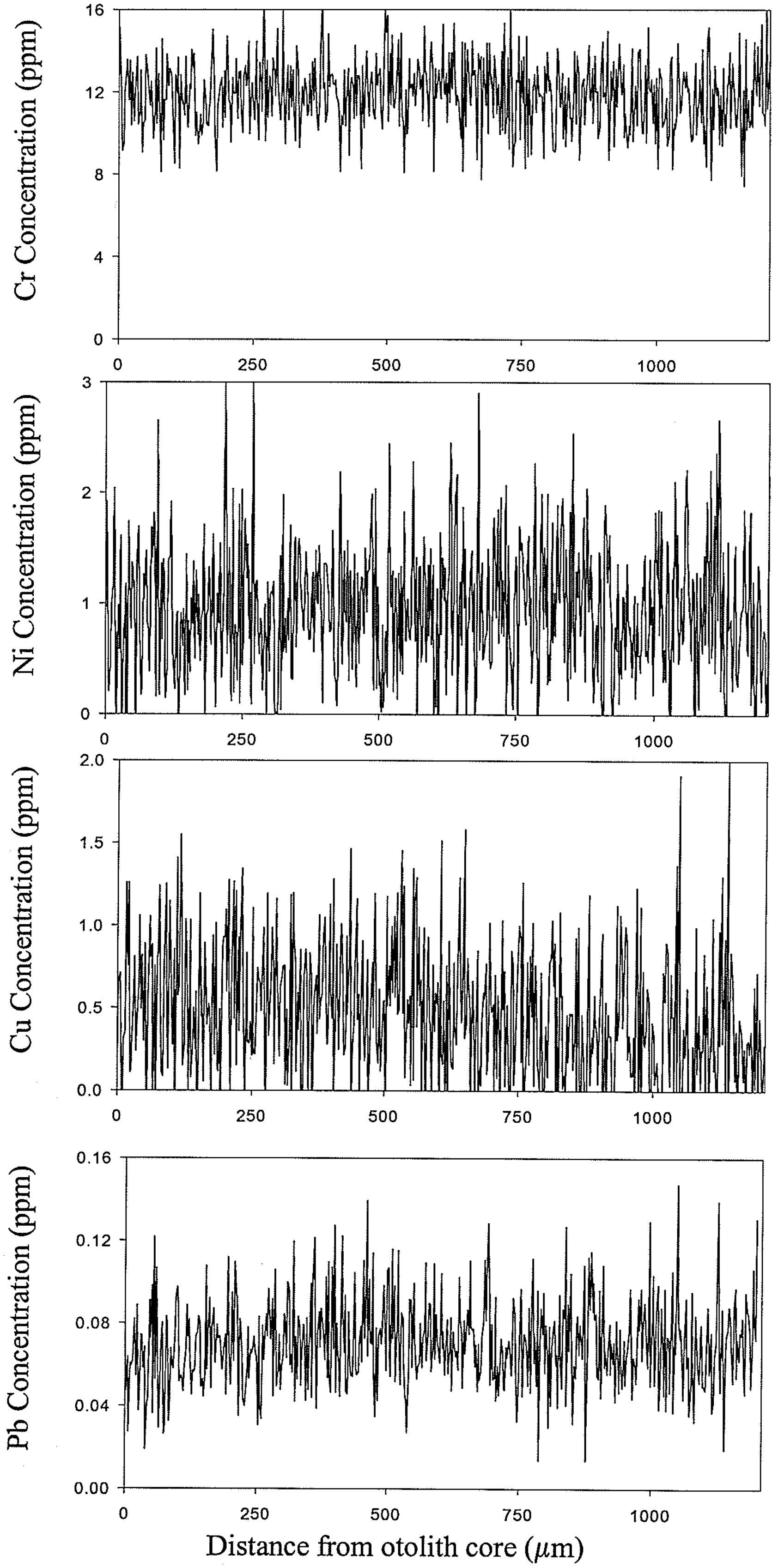
Maskwa_193


Zn Concentration (ppm)
160
120
80
40
0
0
250
500
750
1000

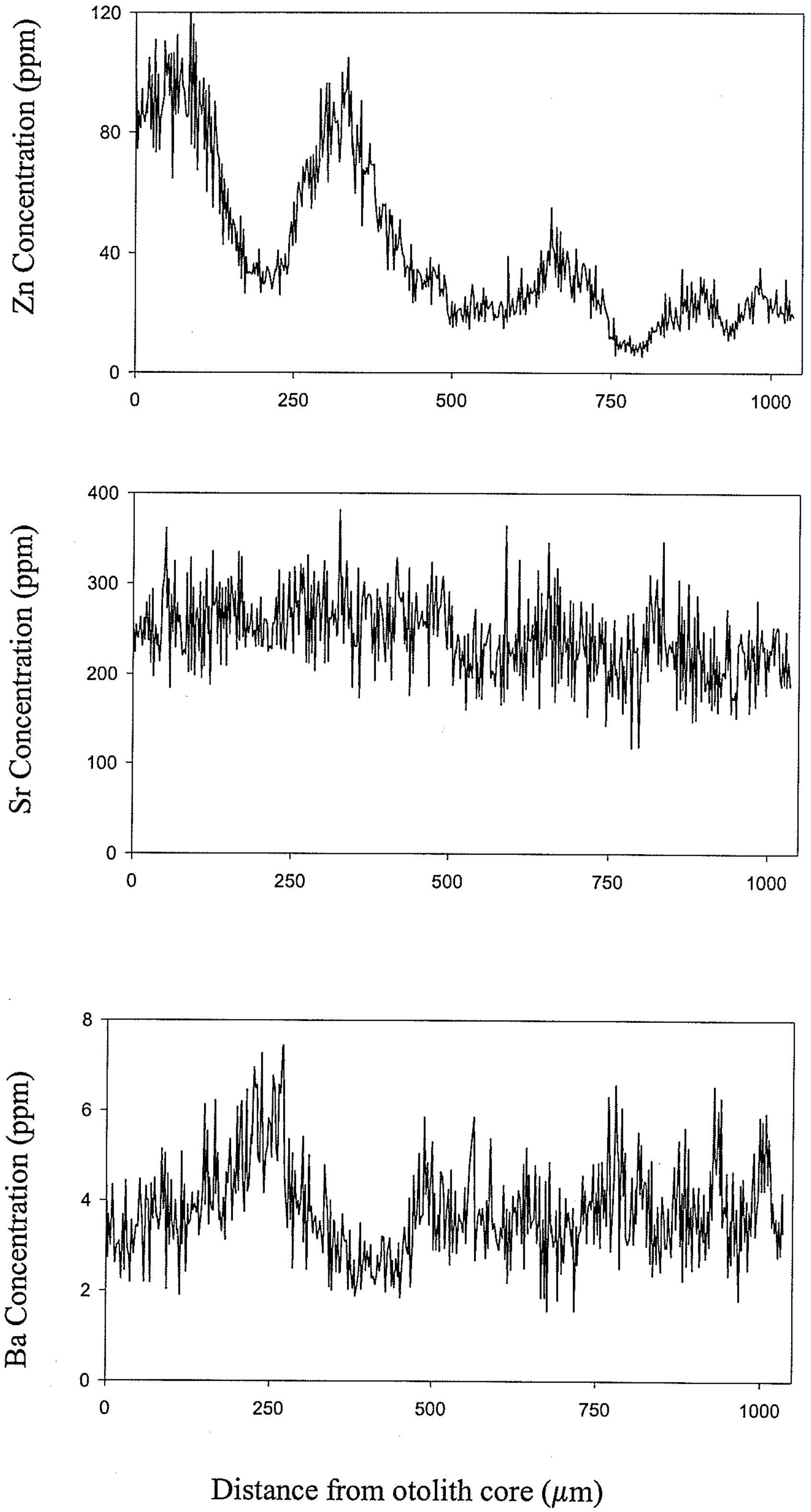

Sr Concentration (ppm)
400
300
200
100
0
0
250
500
750
1000


Ba Concentration (ppm)
8
6
4
2
0
0
250
500
750
1000
Distance from otolith core (μm)

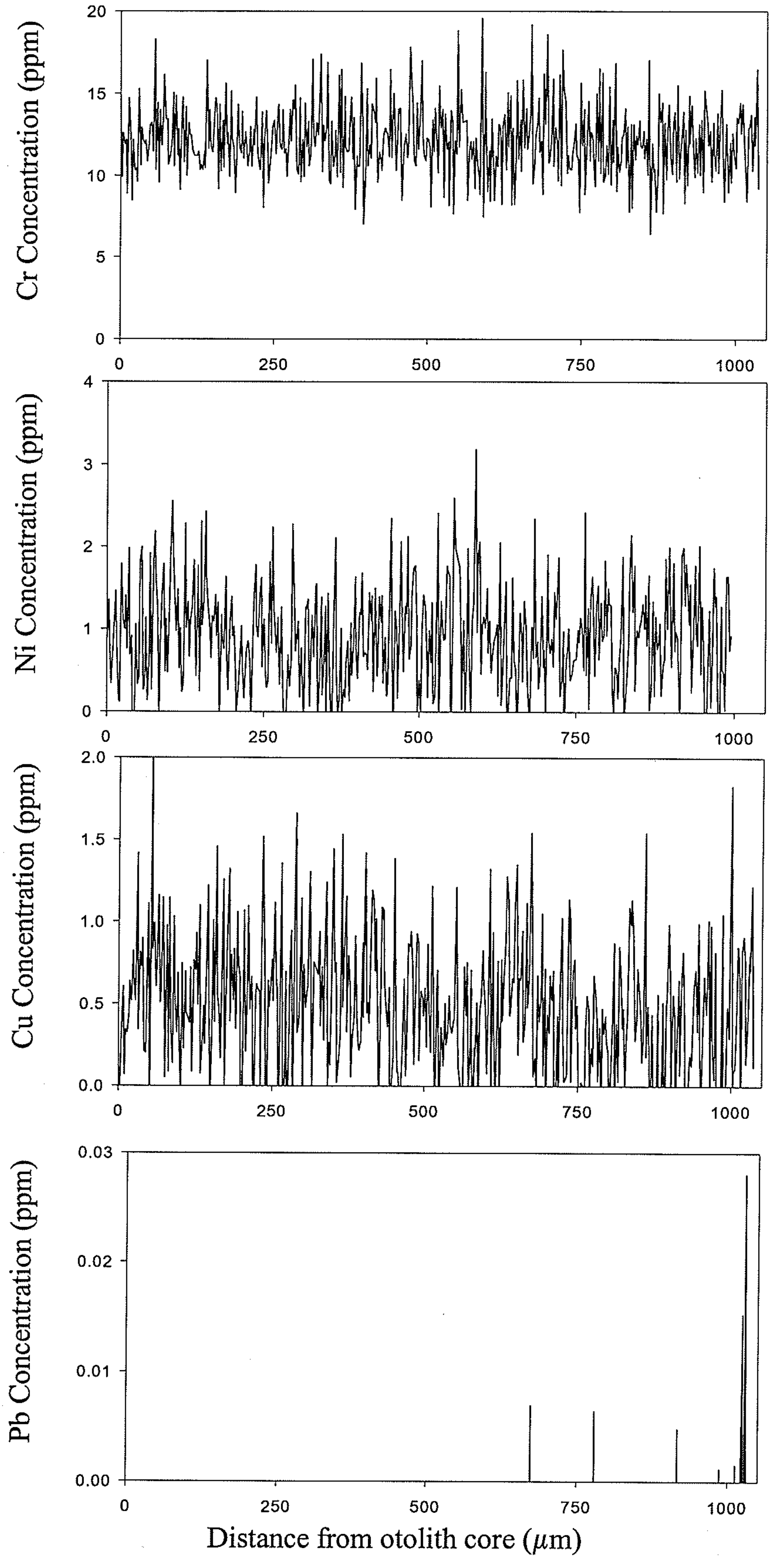
Maskwa_193 *continued*



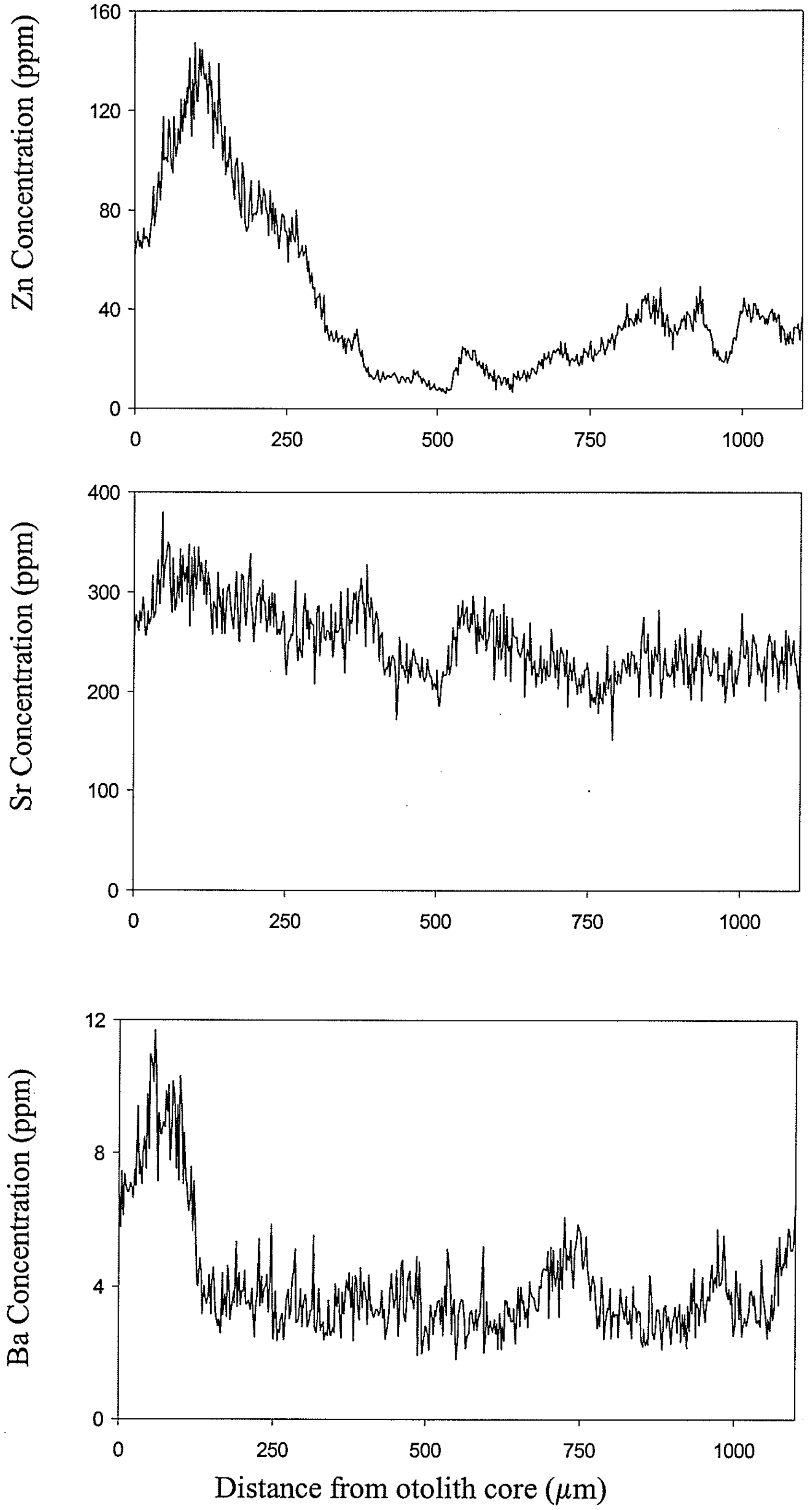
Maskwa_194


Zn Concentration (ppm)
120
80
40
0
0
250
500
750
1000
Sr Concentration (ppm)
400
300
200
100
0
0
250
500
750
1000
Ba Concentration (ppm)
8
6
4
2
0
0
250
500
750
1000
Distance from otolith core (μm)

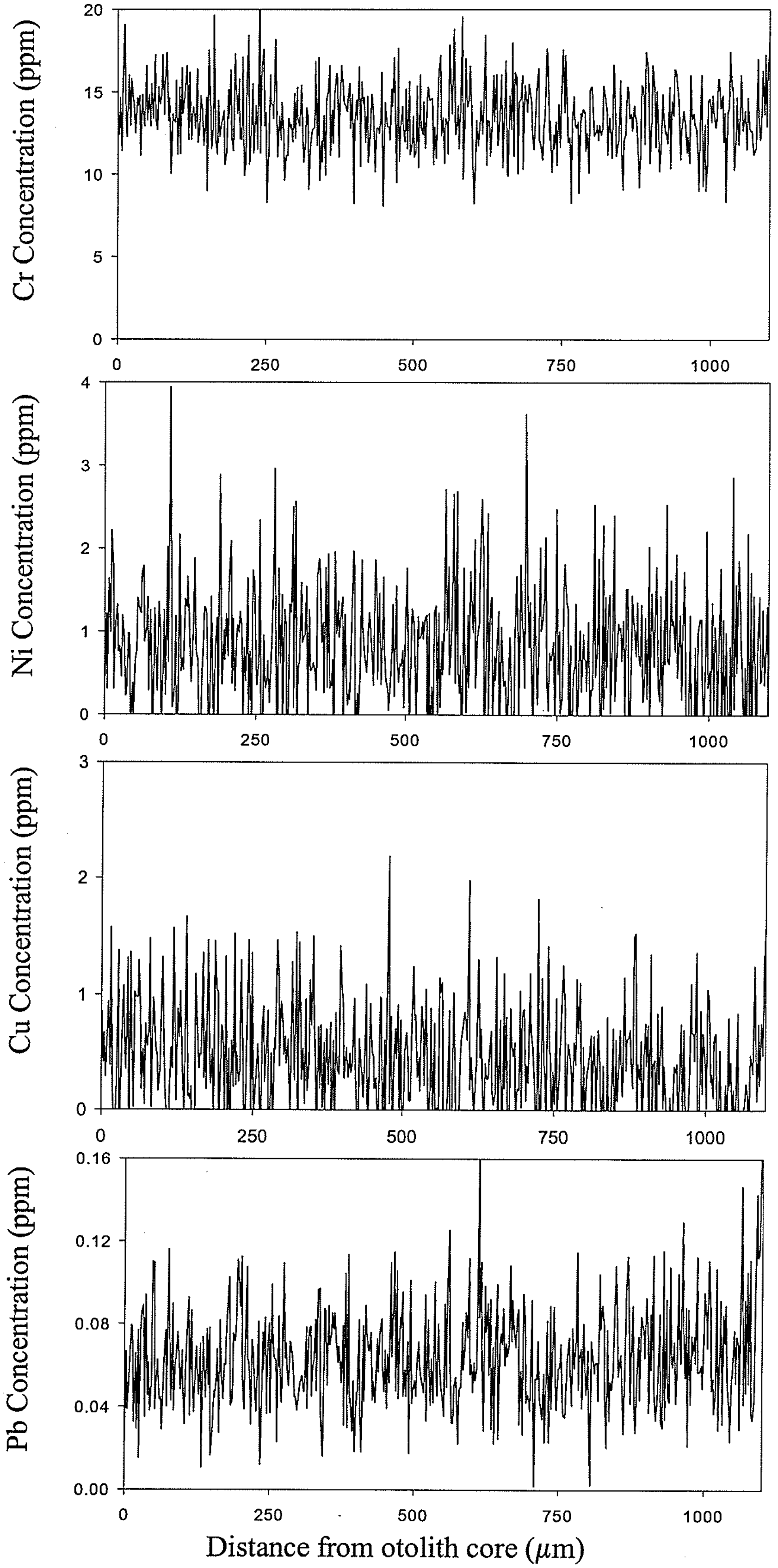
Maskwa_194 *continued*



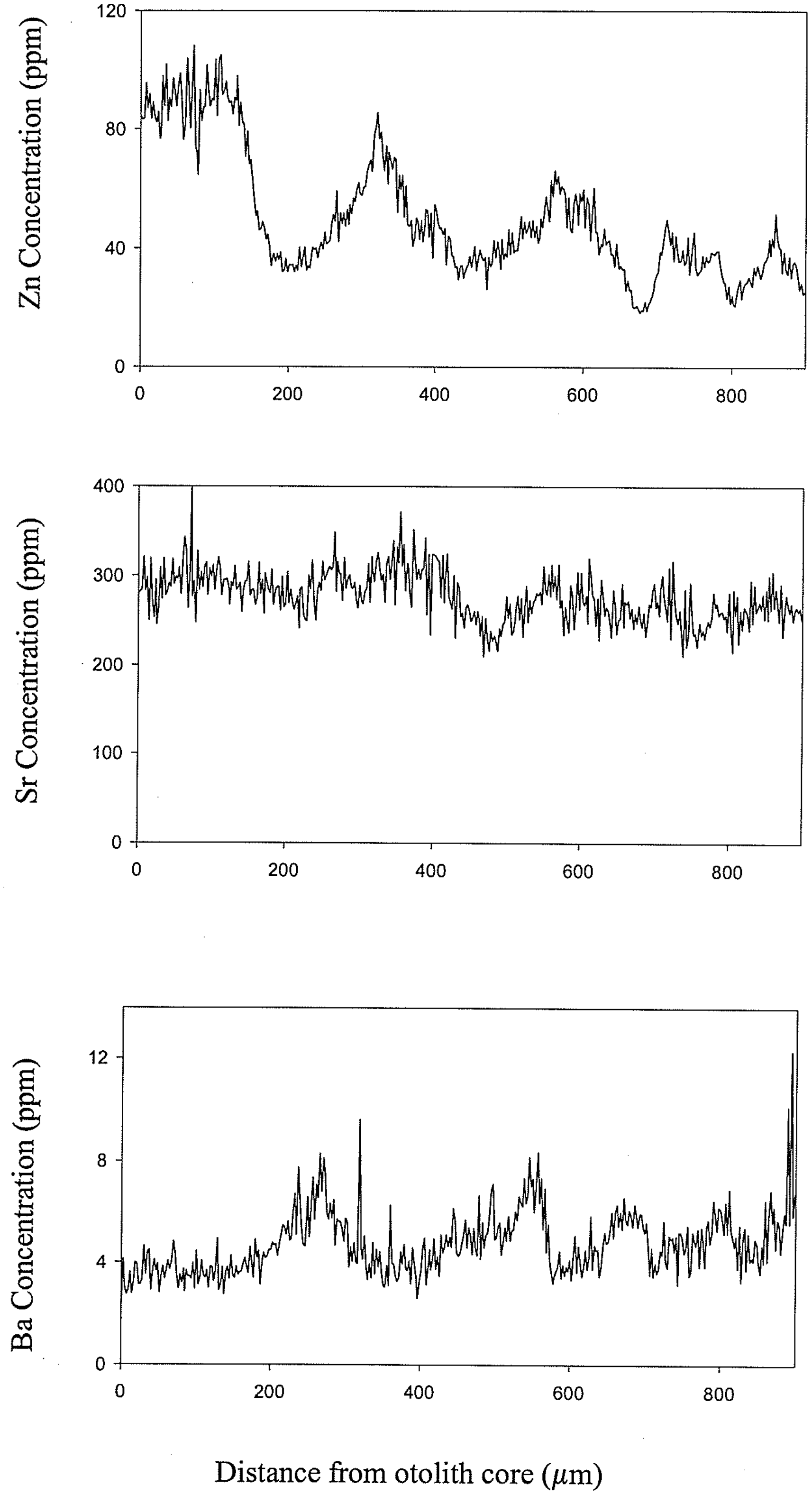
Maskwa_196


Zn Concentration (ppm)
0
40
80
120
160
0
250
500
750
1000
Sr Concentration (ppm)
0
100
200
300
400
0
250
500
750
1000
Ba Concentration (ppm)
0
4
8
12
0
250
500
750
1000
Distance from otolith core (μm)

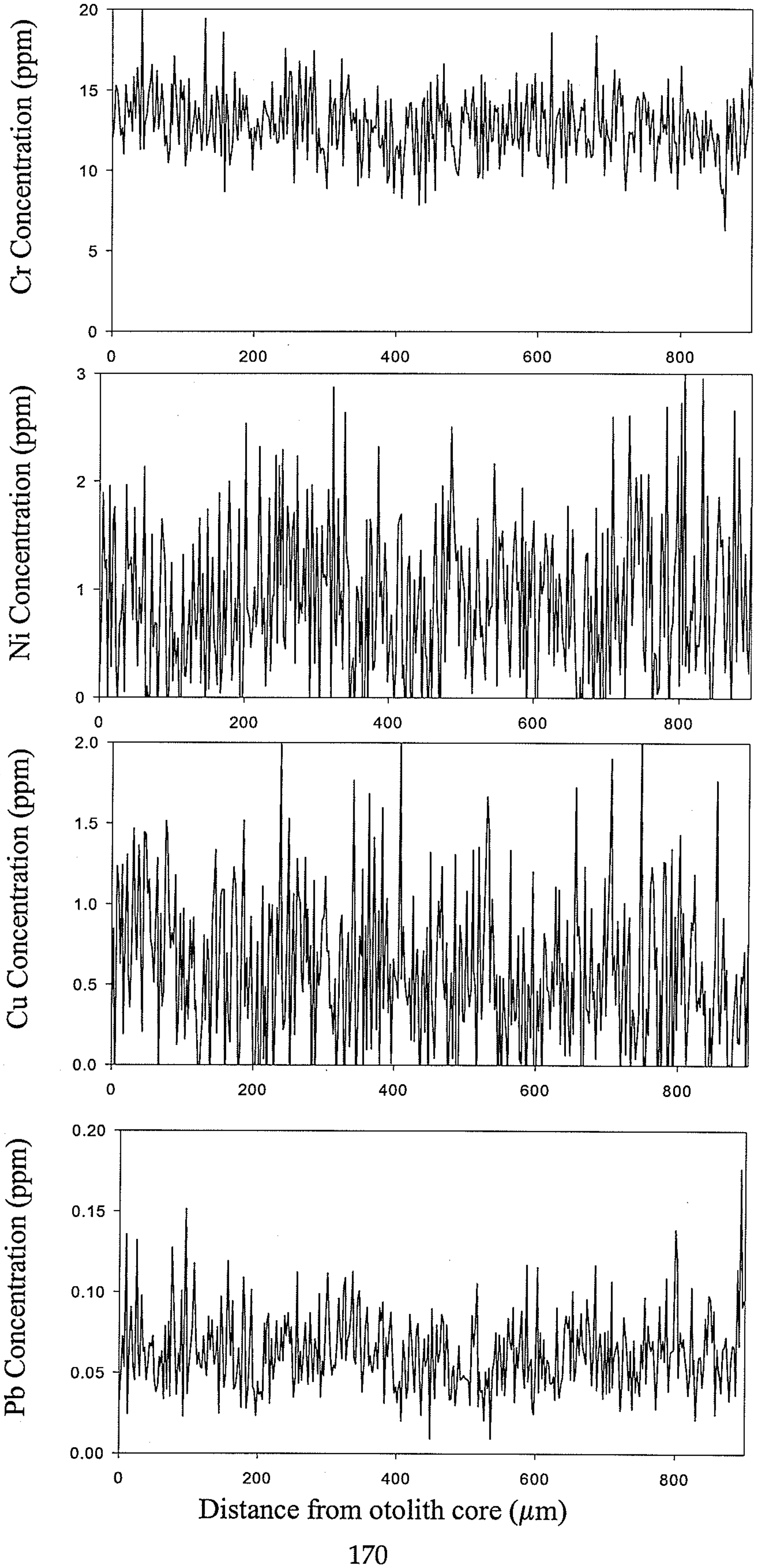
Maskwa_196 *continued*



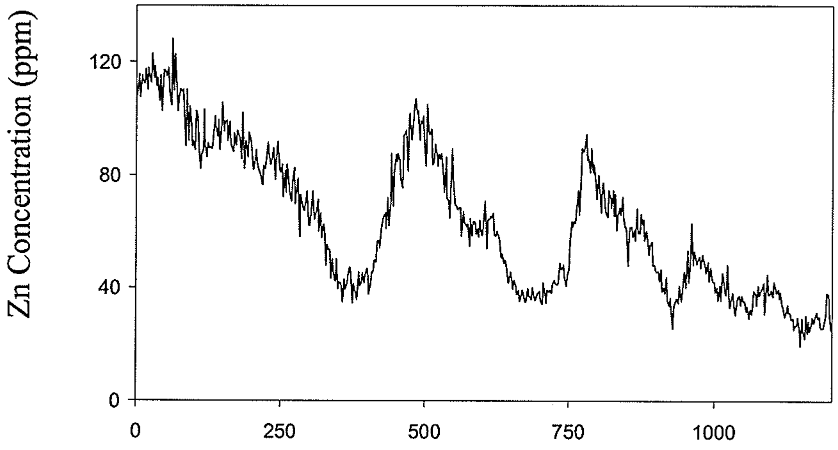
Maskwa_199

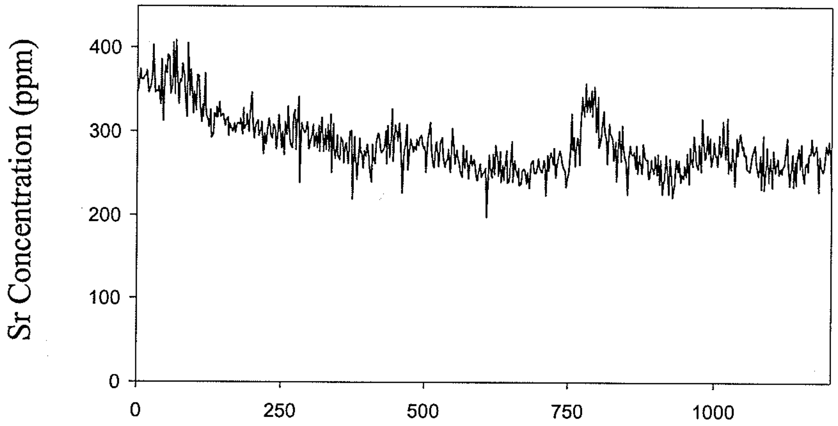

Zn Concentration (ppm)
120
80
40
0
0
200
400
600
800
Sr Concentration (ppm)
400
300
200
100
0
0
200
400
600
800
Ba Concentration (ppm)
12
8
4
0
0
200
400
600
800
Distance from otolith core (μm)

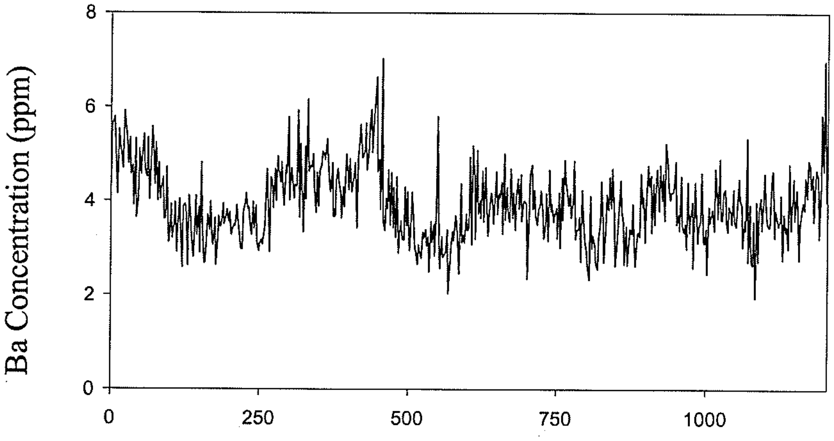
Maskwa_199 *continued*



Maskwa_200

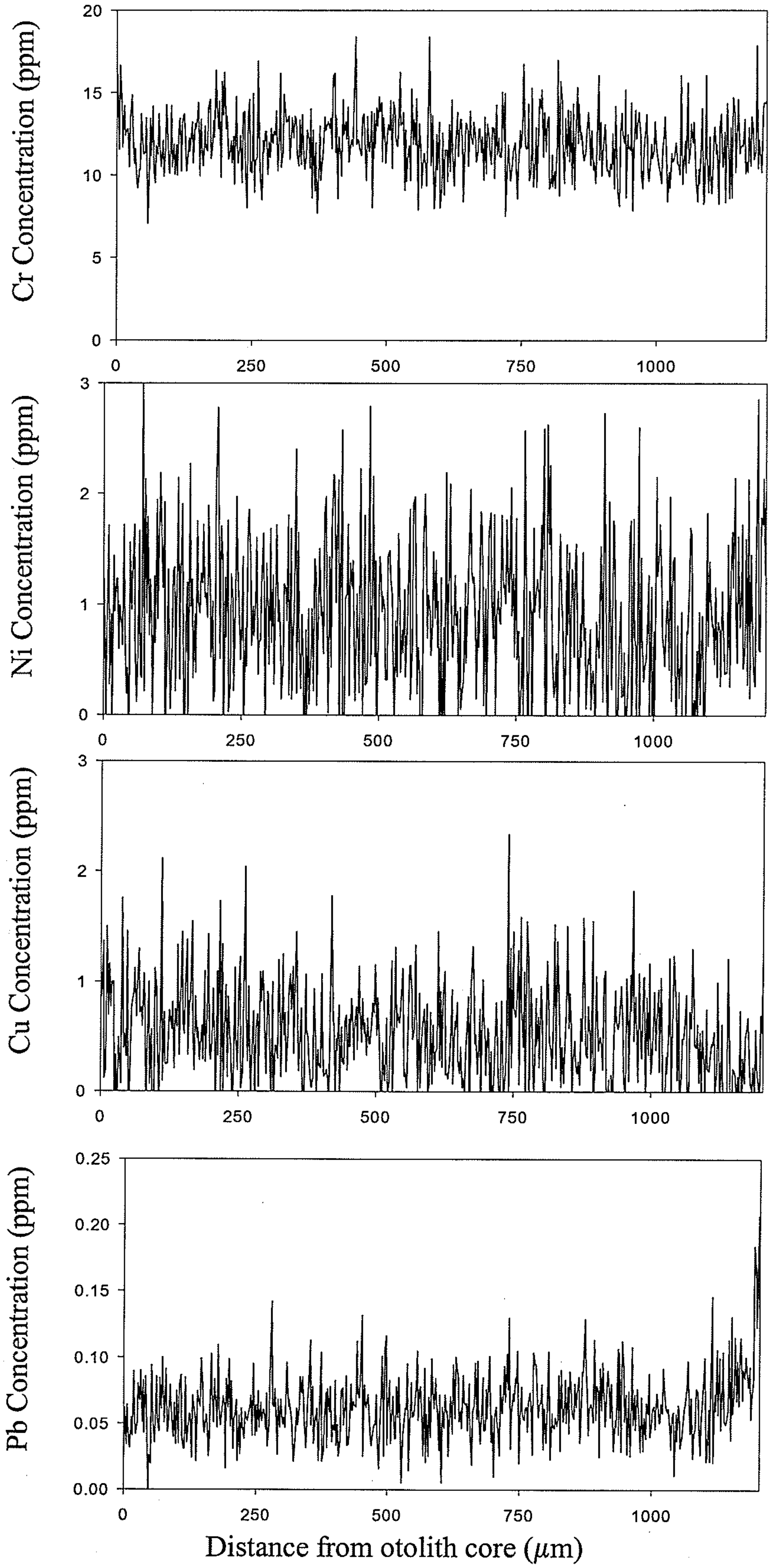




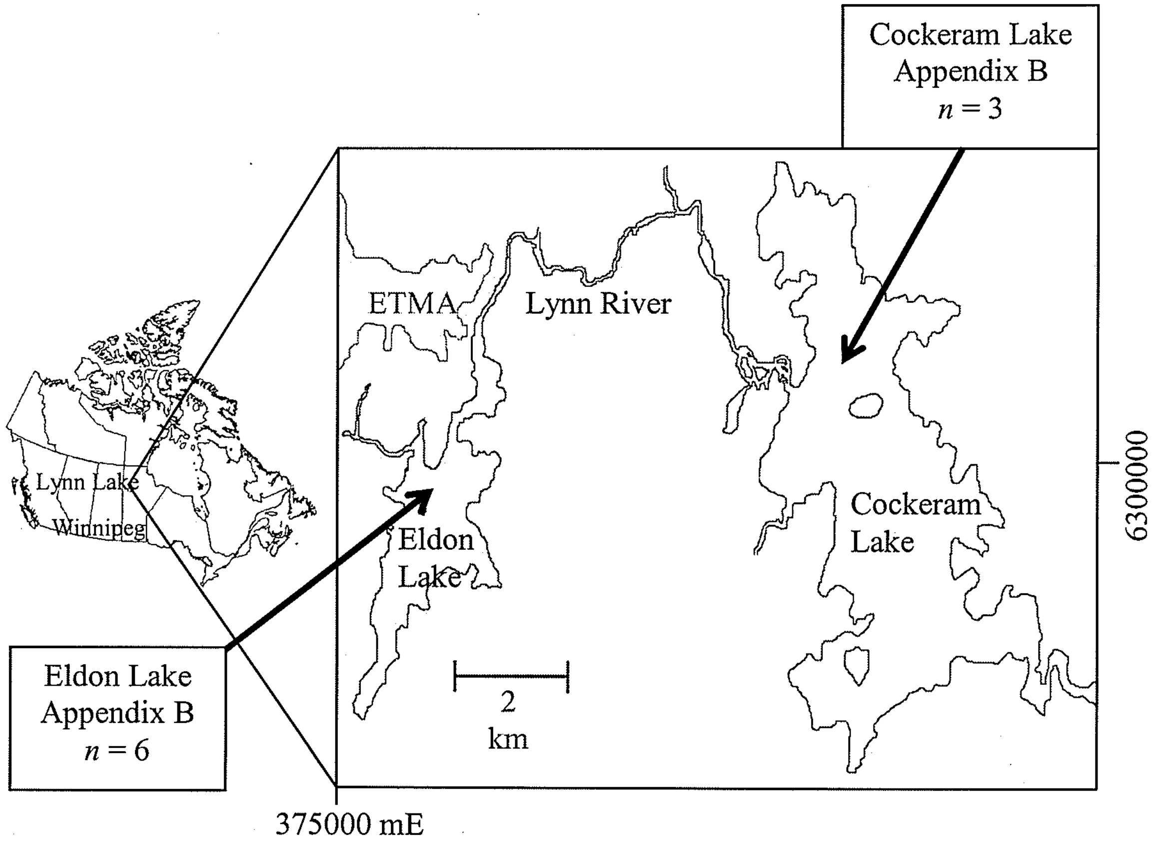


Distance from otolith core (μm)

Maskwa_200 *continued*



Appendix B: LA-ICP-MS data for Lynn Lake otoliths



Appendix B LA-ICP-MS data for Lynn Lake otoliths

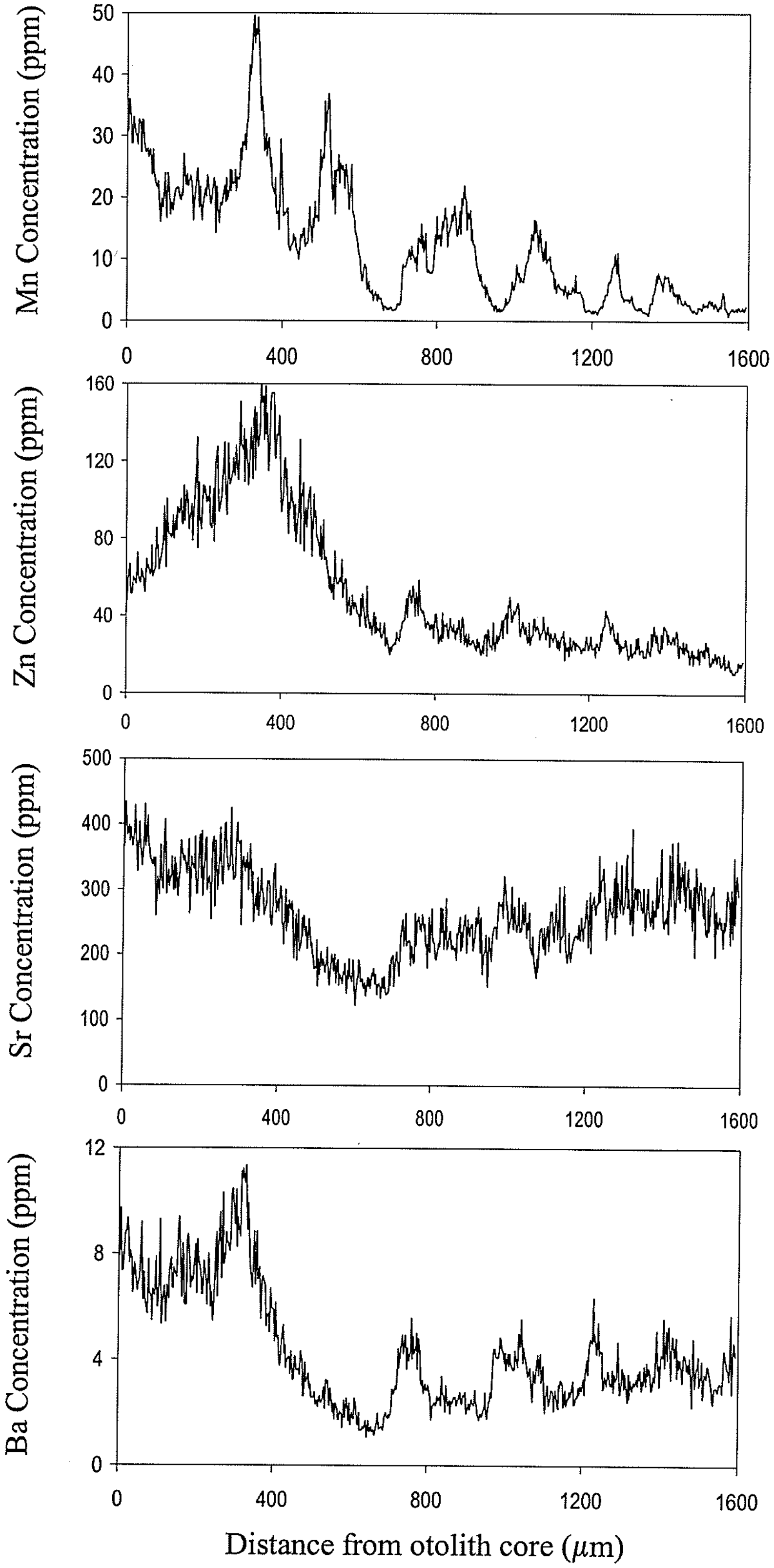
Species: Walleye (*Sander vitreus*), Northern Pike (*Esox lucius*)

Captured: 2008 (TetrES Consultants, Inc.)

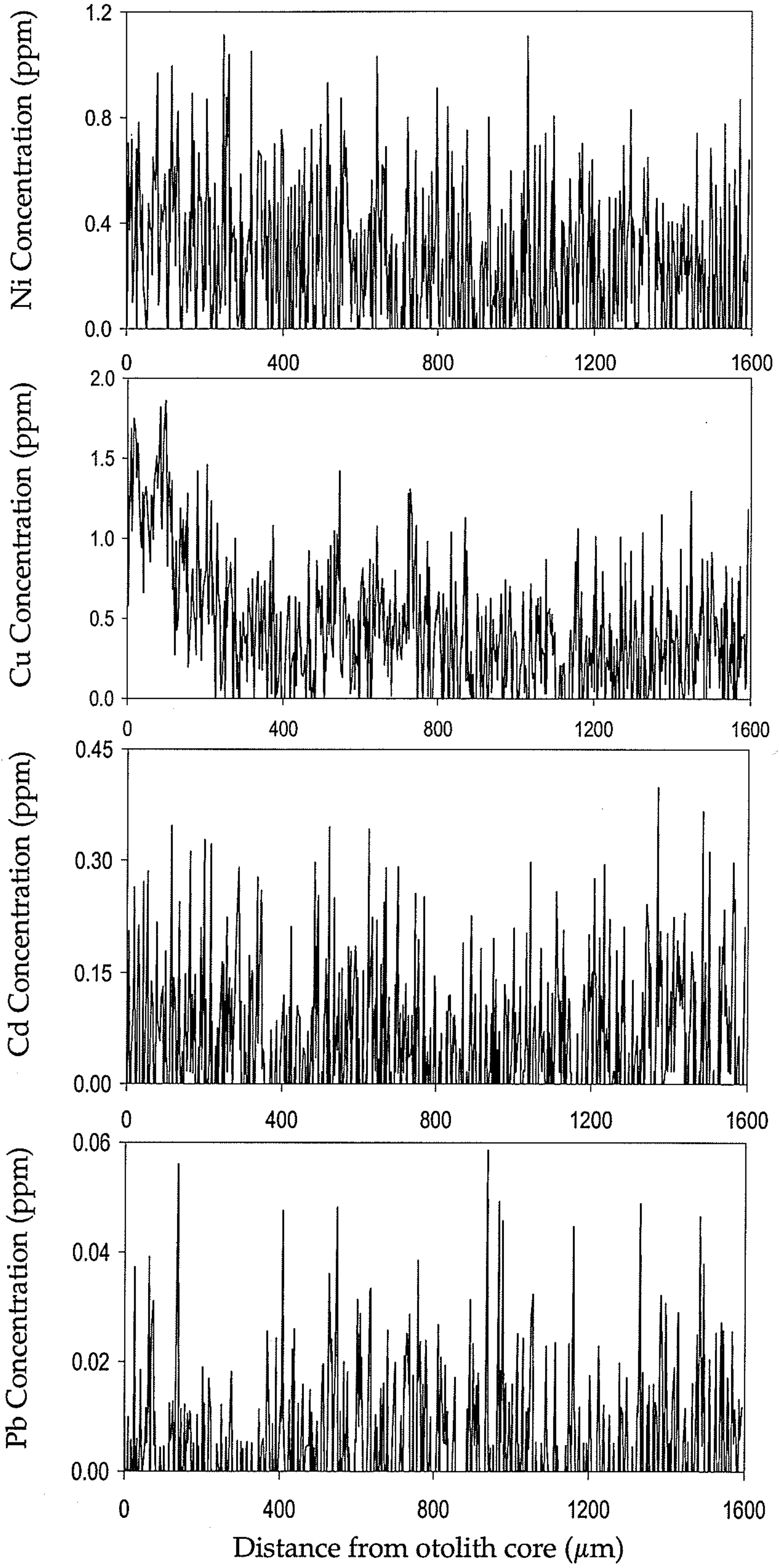
Isotopes	**Mn^{55}**	**Ni^{60}**	**Cu^{63}**	**Zn^{66}**	**Sr^{88}**	**Cd^{114}**	**Ba^{138}**	**Pb^{208}**
Typical Detection Limit	0.05	0.13	0.15	0.06	0.03	0.05	0.01	0.01
Typical 1σ Error	N/A	0.29	0.36	N/A	N/A	0.08	N/A	0.011

Sample Number	***Species***	***Sampling Location***	***Age***
01	Northern Pike	Eldon Lake	8
02	Northern Pike	Cockeram Lake	8
03	Walleye	Eldon Lake	9
06	Walleye	Eldon Lake	5
07	Northern Pike	Eldon Lake	12
08	Walleye	Eldon Lake	6
12	Northern Pike	Eldon Lake	8
14	Northern Pike	Cockeram Lake	8
16	Northern Pike	Cockeram Lake	6

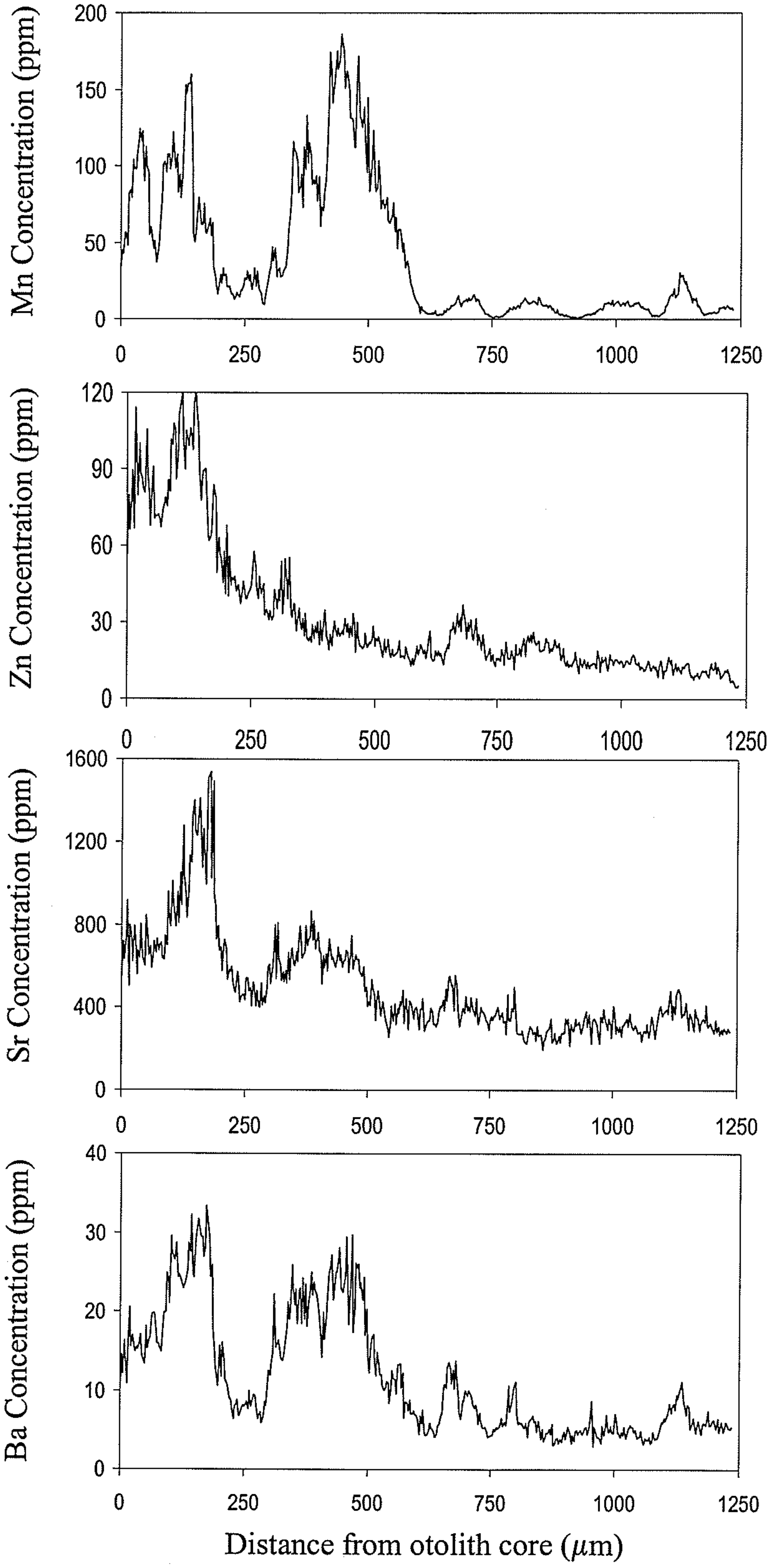
Lynn08_01


Mn Concentration (ppm)
50
40
30
20
10
0
0
400
800
1200
1600
Zn Concentration (ppm)
160
120
80
40
0
0
400
800
1200
1600
Sr Concentration (ppm)
500
400
300
200
100
0
0
400
800
1200
1600
Ba Concentration (ppm)
12
8
4
0
0
400
800
1200
1600
Distance from otolith core (μm)

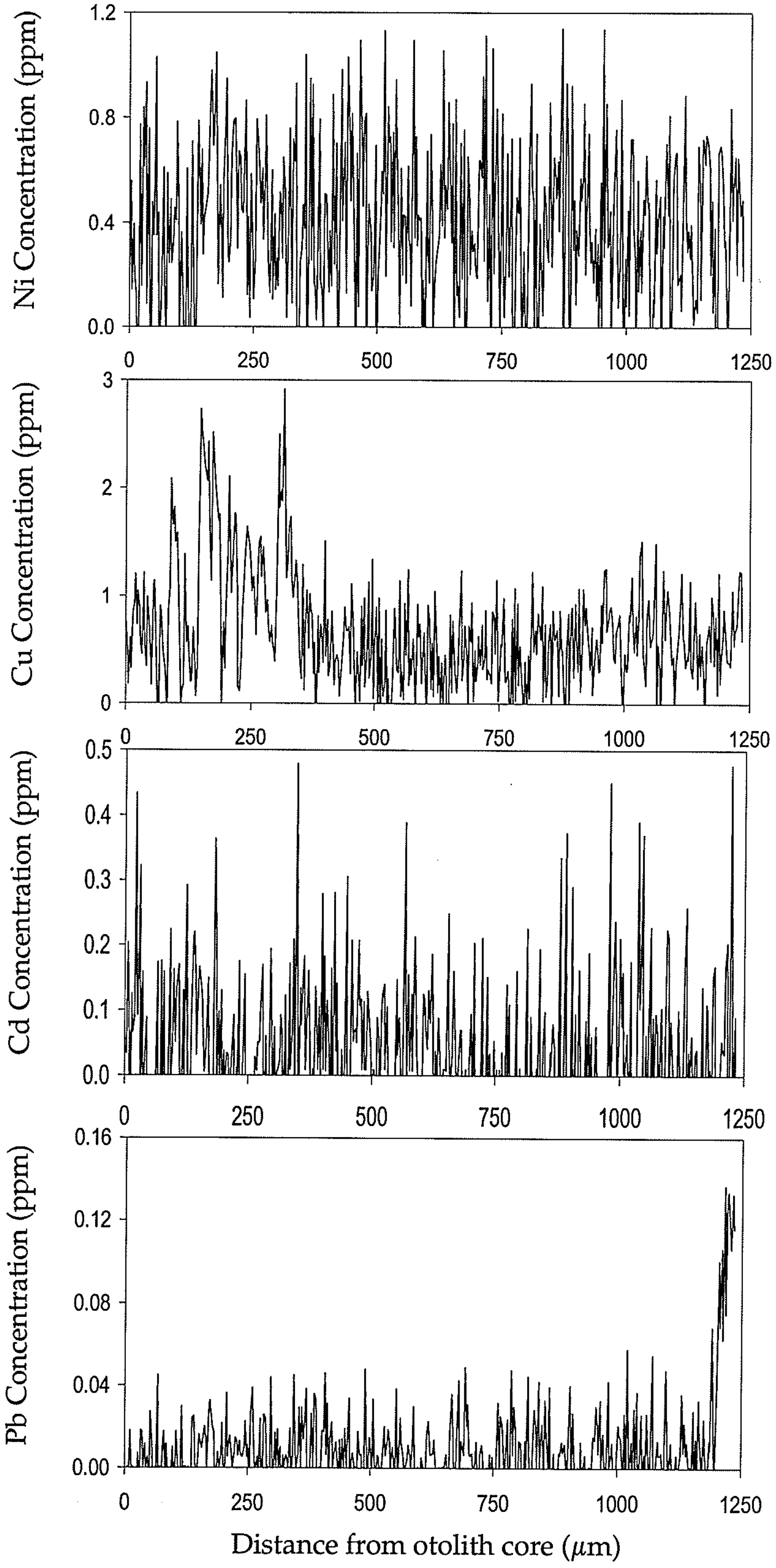
Lynn08_01 *continued*



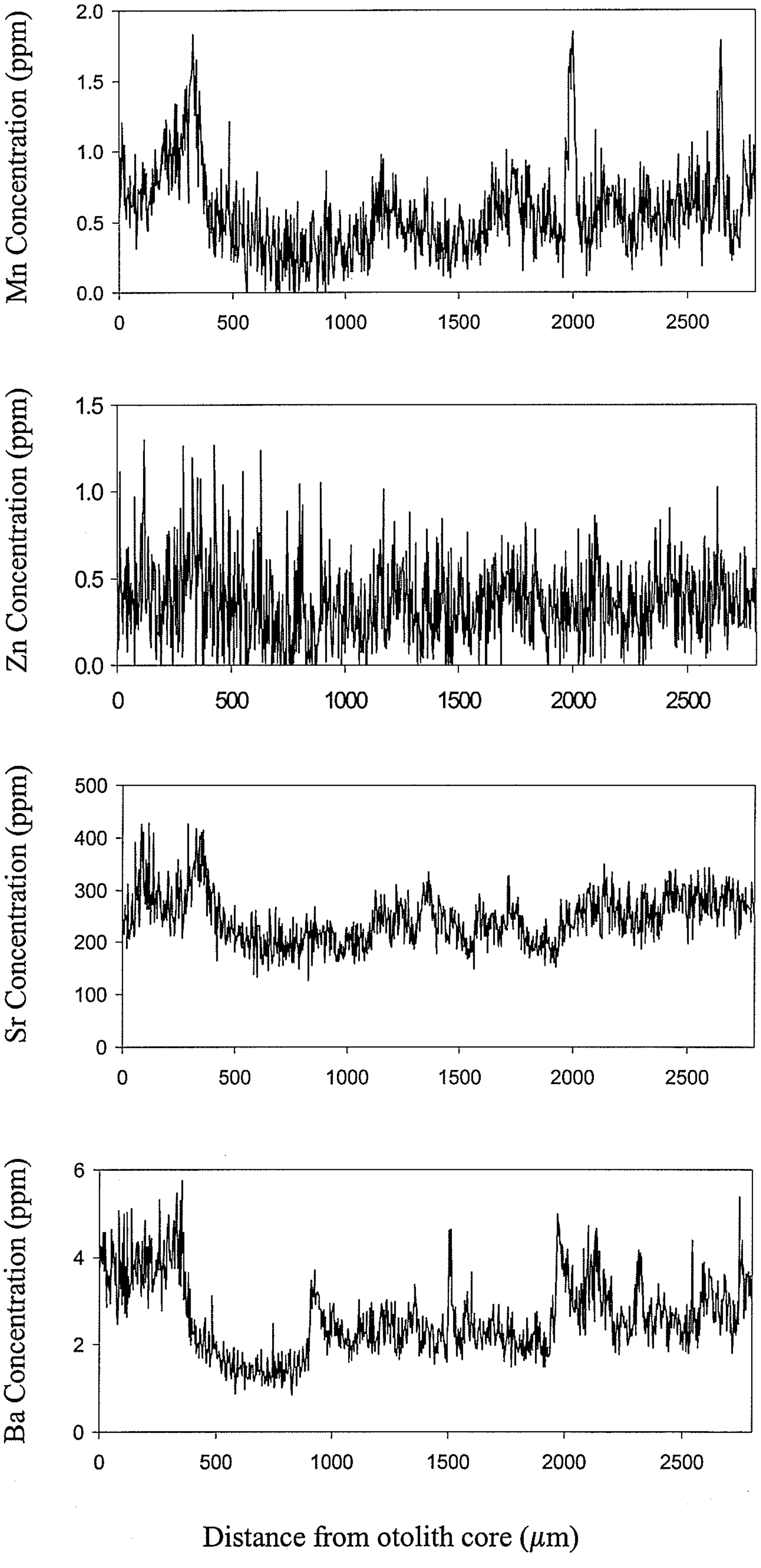
Lynn08_02


Mn Concentration (ppm)
200
150
100
50
0
0
250
500
750
1000
1250
Zn Concentration (ppm)
120
90
60
30
0
0
250
500
750
1000
1250
Sr Concentration (ppm)
1600
1200
800
400
0
0
250
500
750
1000
1250
Ba Concentration (ppm)
40
30
20
10
0
0
250
500
750
1000
1250
Distance from otolith core (μm)

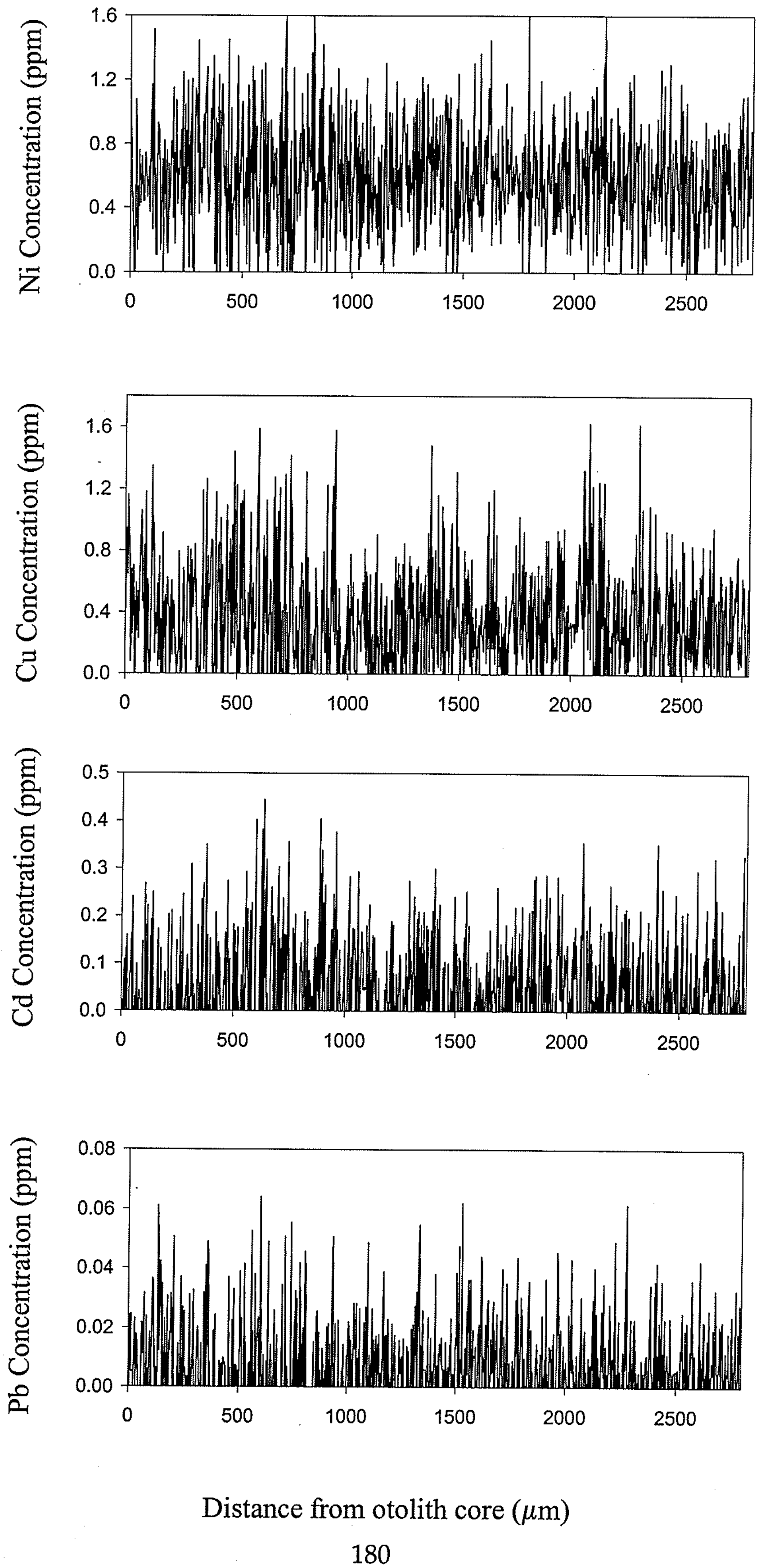
Lynn08_02 *continued*



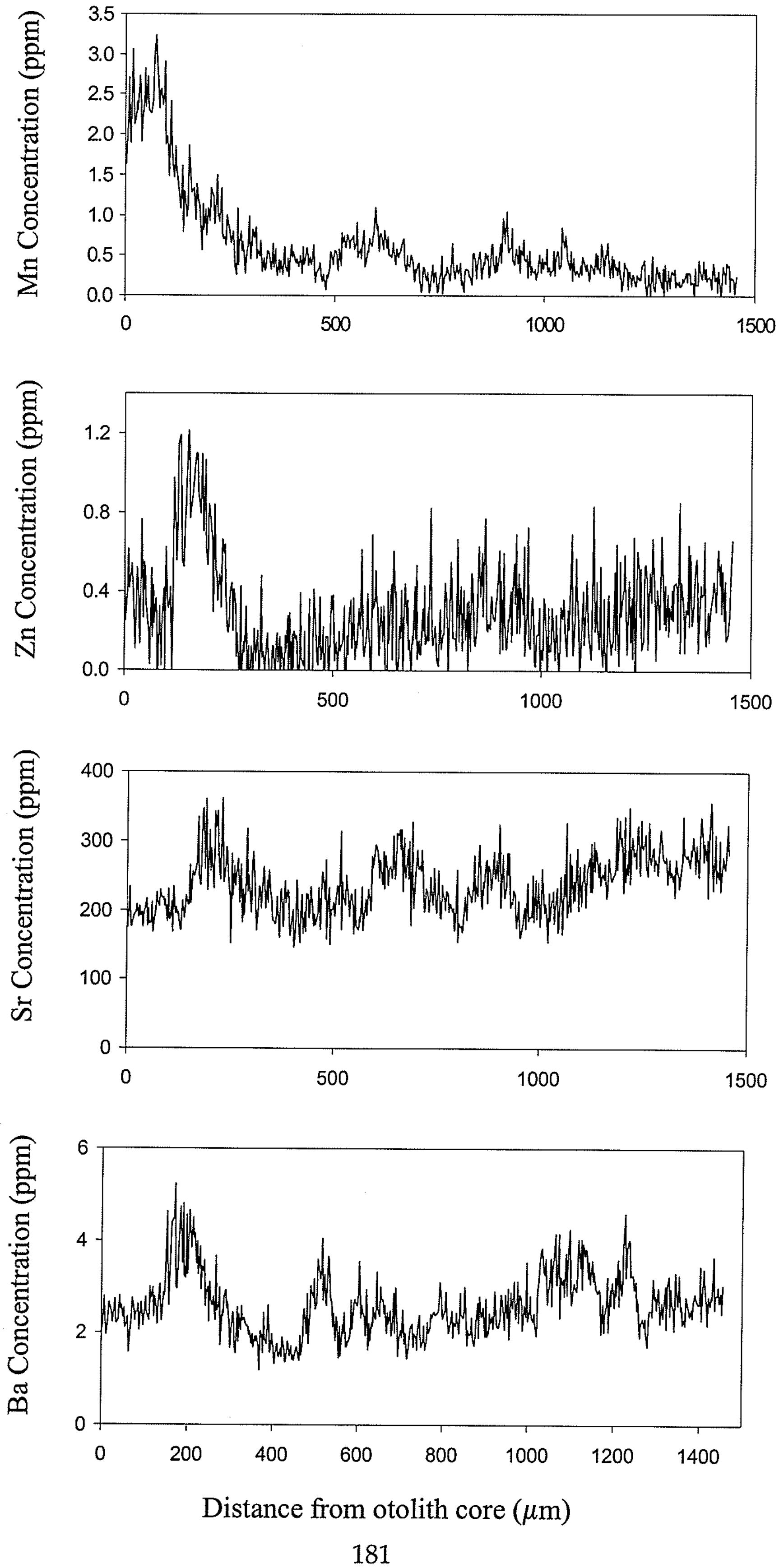
Lynn08_03


Mn Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
2500
Zn Concentration (ppm)
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
2500
Sr Concentration (ppm)
500
400
300
200
100
0
0
500
1000
1500
2000
2500
Ba Concentration (ppm)
6
4
2
0
0
500
1000
1500
2000
2500
Distance from otolith core (μm)

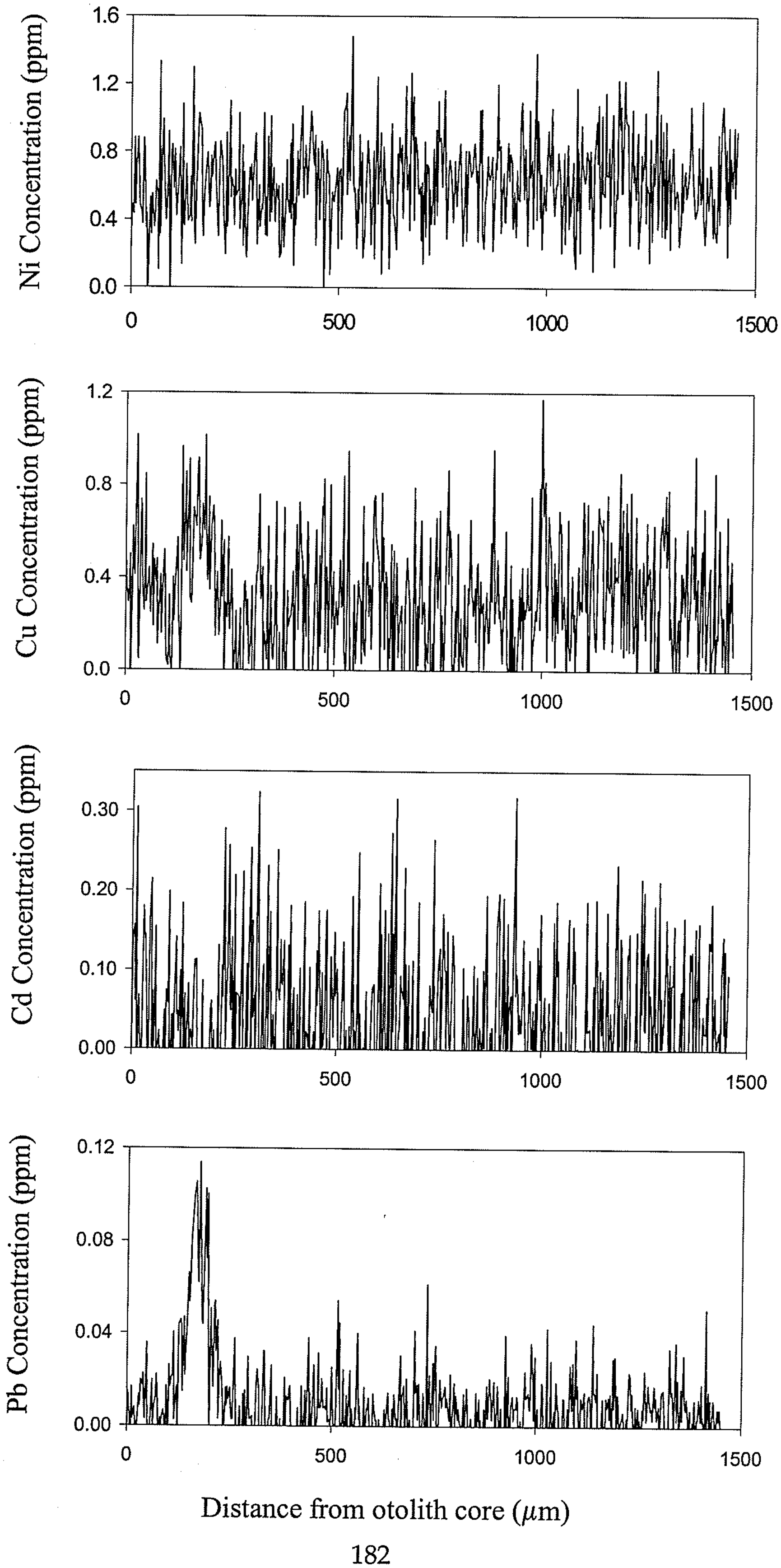
Lynn08_03 *continued*



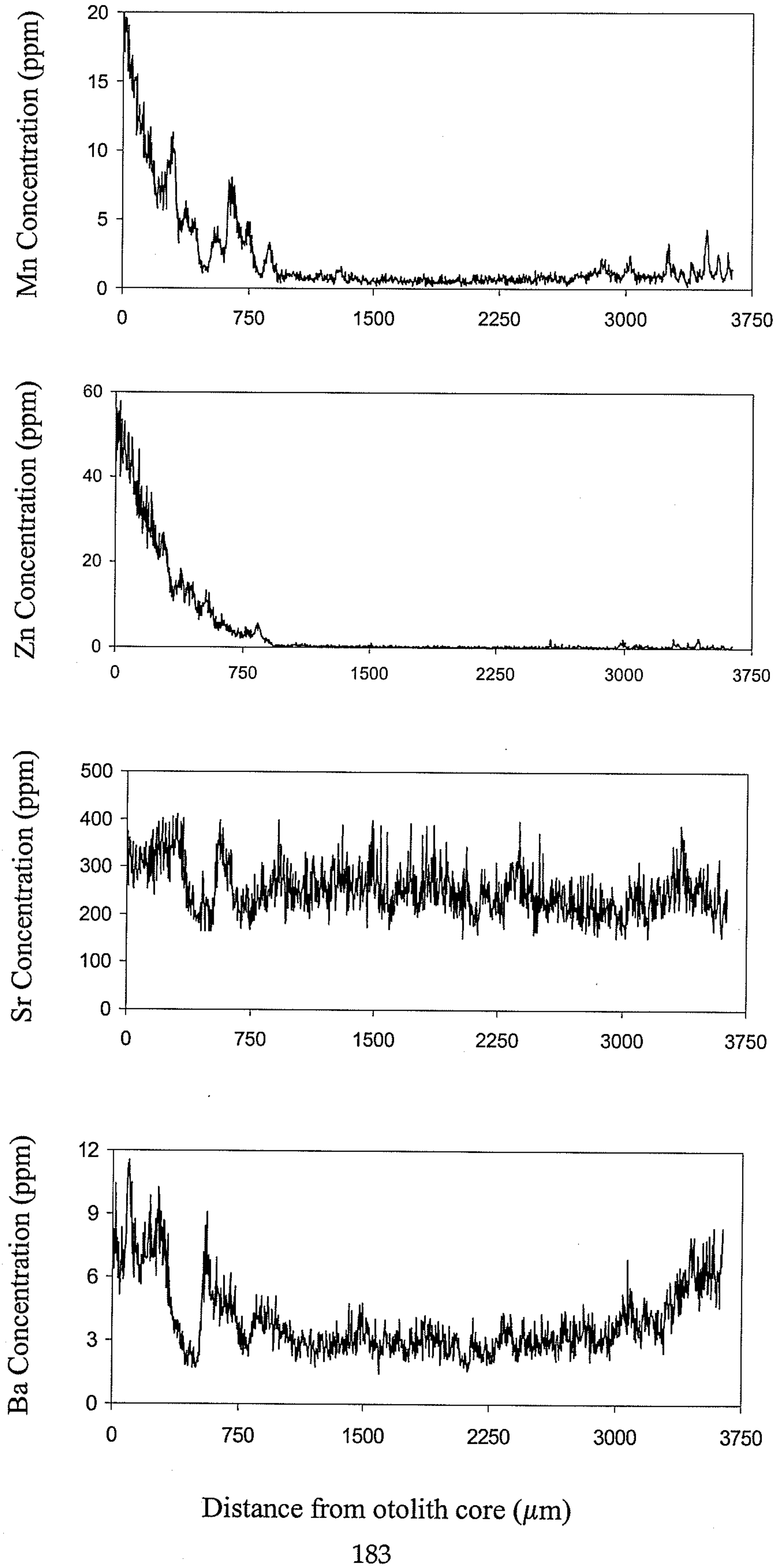
Lynn08_06


Mn Concentration (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
Zn Concentration (ppm)
1.2
0.8
0.4
0.0
0
500
1000
1500
Sr Concentration (ppm)
400
300
200
100
0
0
500
1000
1500
Ba Concentration (ppm)
6
4
2
0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (µm)

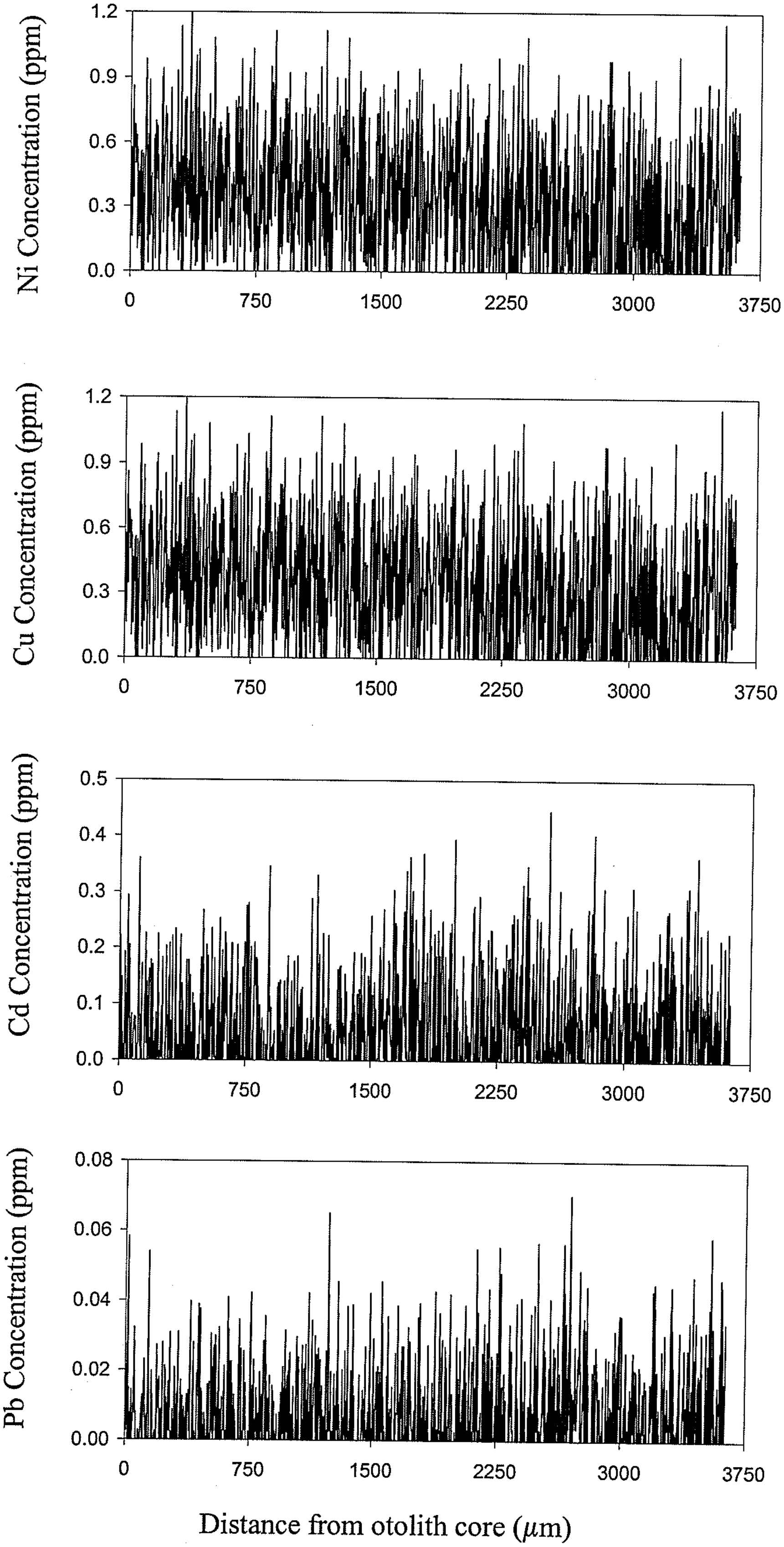
Lynn08_06 *continued*



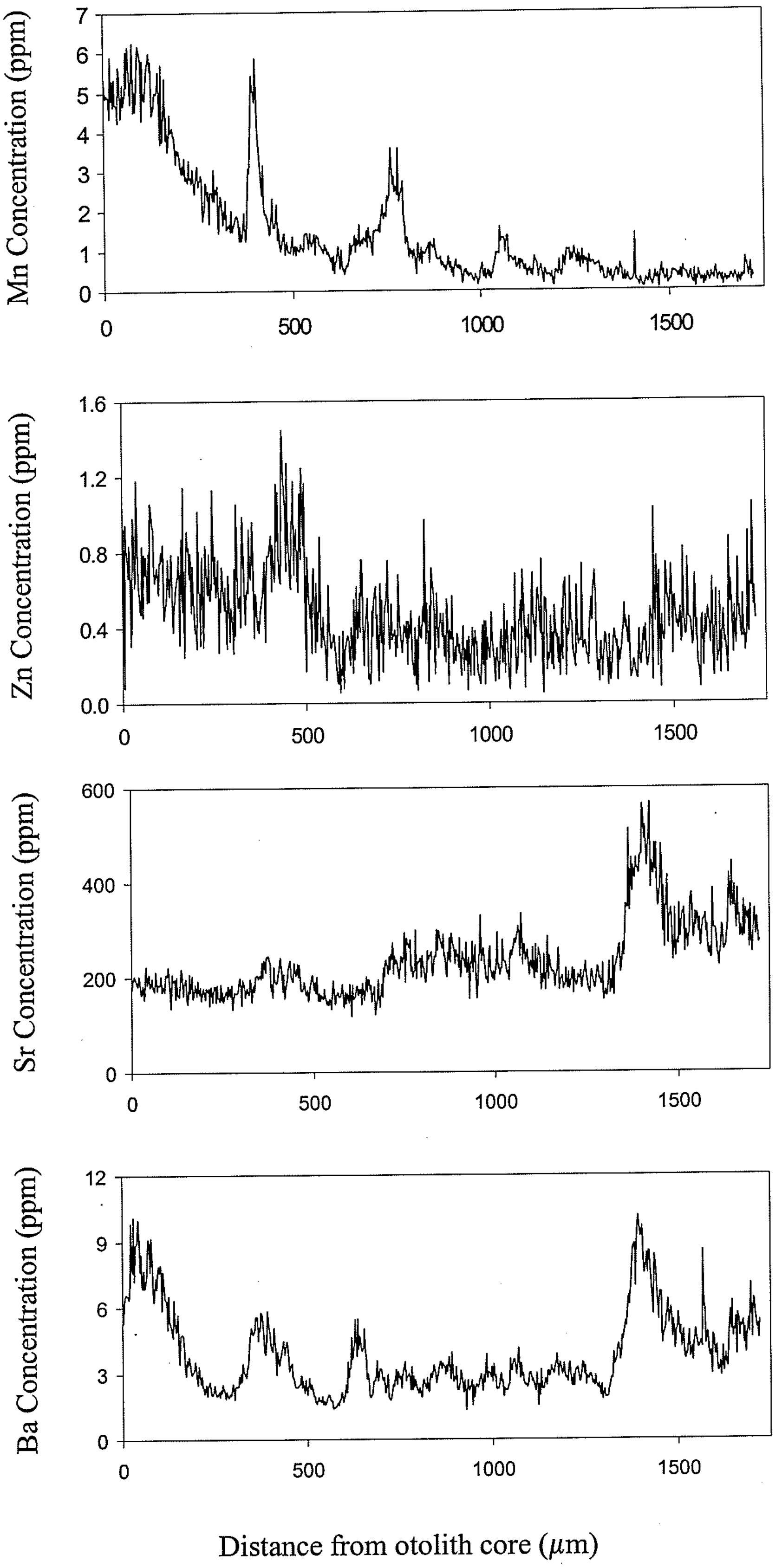
Lynn08_07


Mn Concentration (ppm)
0
5
10
15
20
0
750
1500
2250
3000
3750
Zn Concentration (ppm)
0
20
40
60
0
750
1500
2250
3000
3750
Sr Concentration (ppm)
0
100
200
300
400
500
0
750
1500
2250
3000
3750
Ba Concentration (ppm)
0
3
6
9
12
0
750
1500
2250
3000
3750
Distance from otolith core (μm)

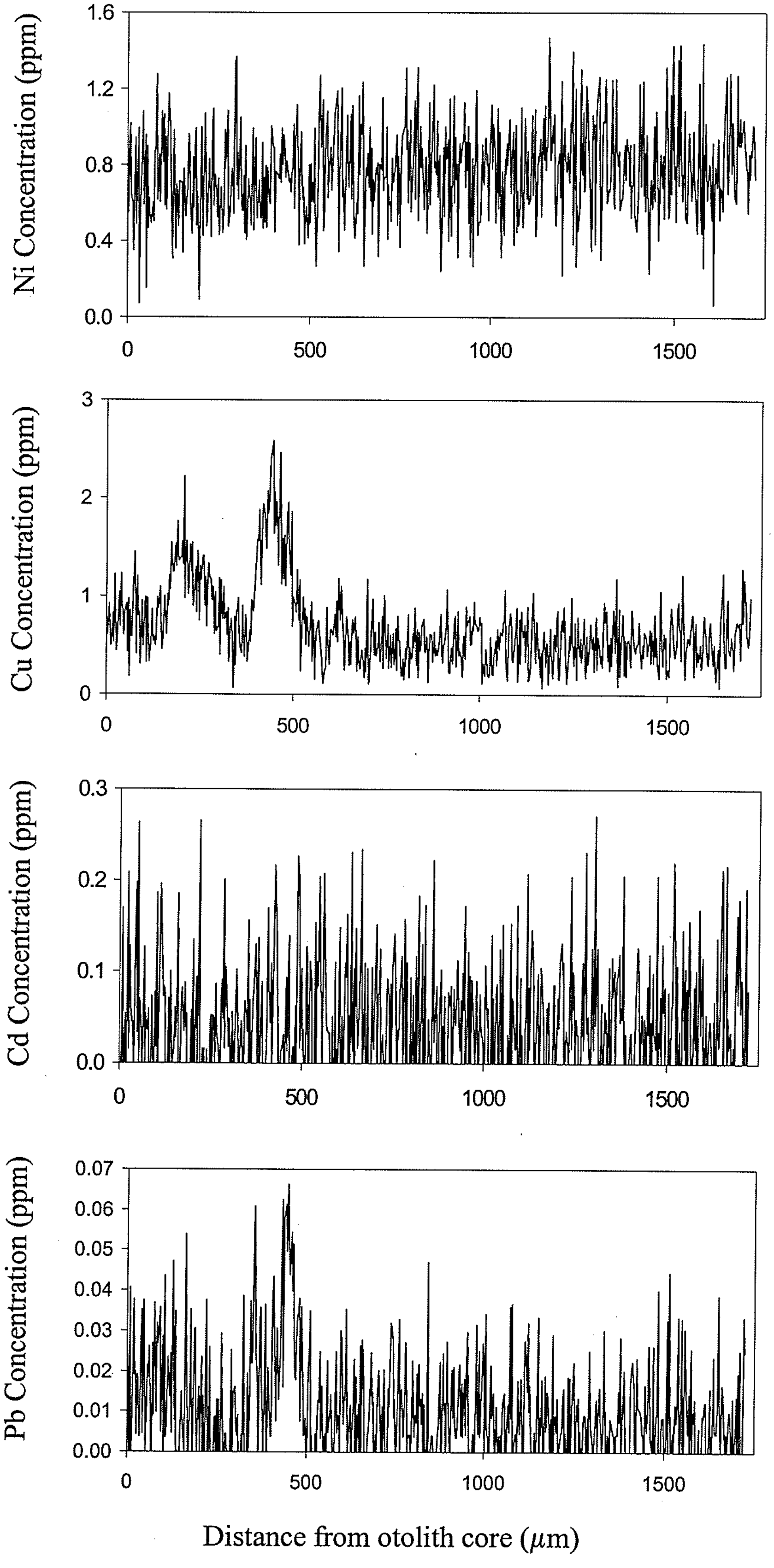
Lynn08_07 *continued*



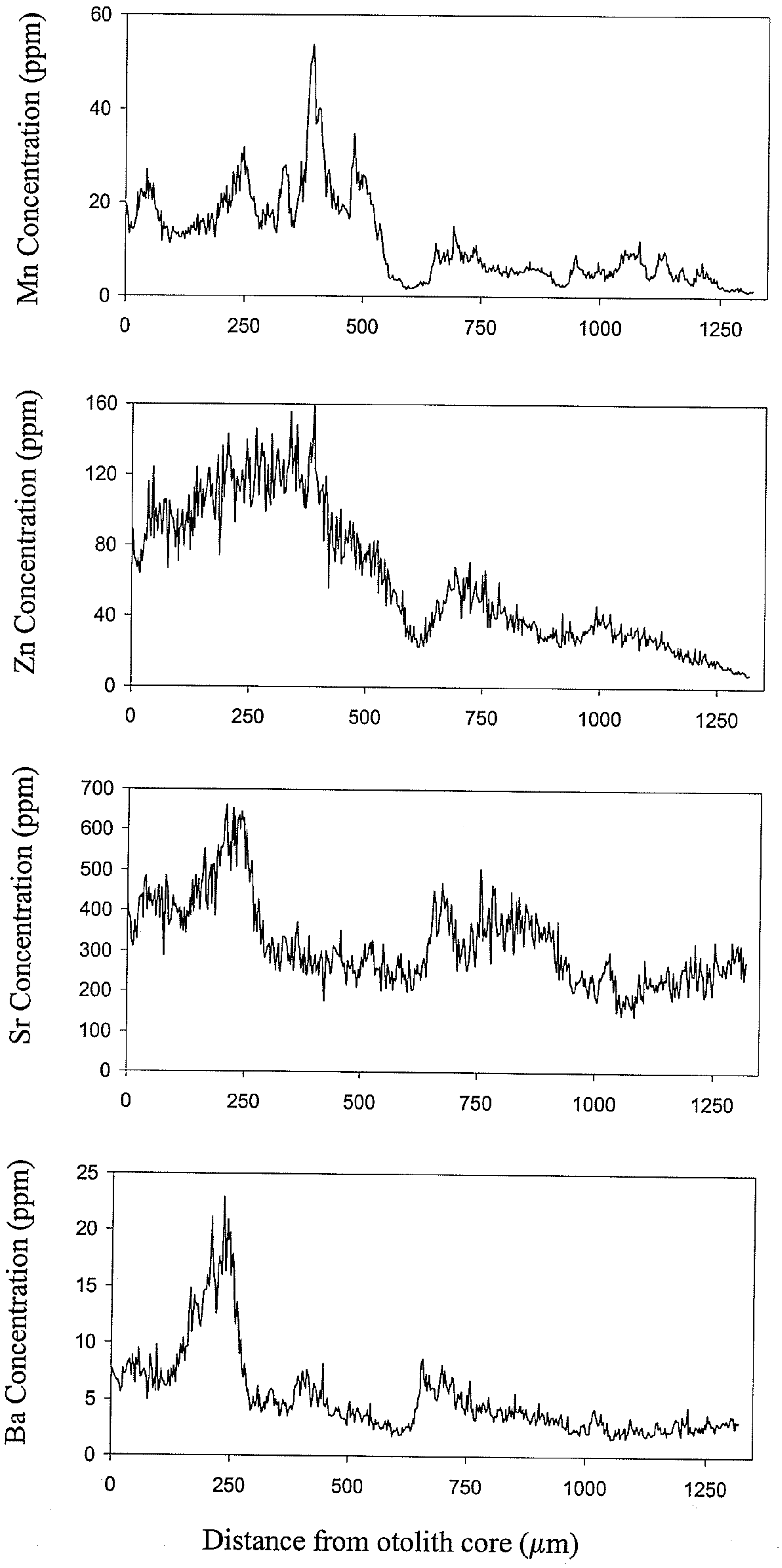
Lynn08_08


Mn Concentration (ppm)
7
6
5
4
3
2
1
0
0
500
1000
1500
Zn Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
500
1000
1500
Sr Concentration (ppm)
600
400
200
0
0
500
1000
1500
Ba Concentration (ppm)
12
9
6
3
0
0
500
1000
1500
Distance from otolith core (μm)

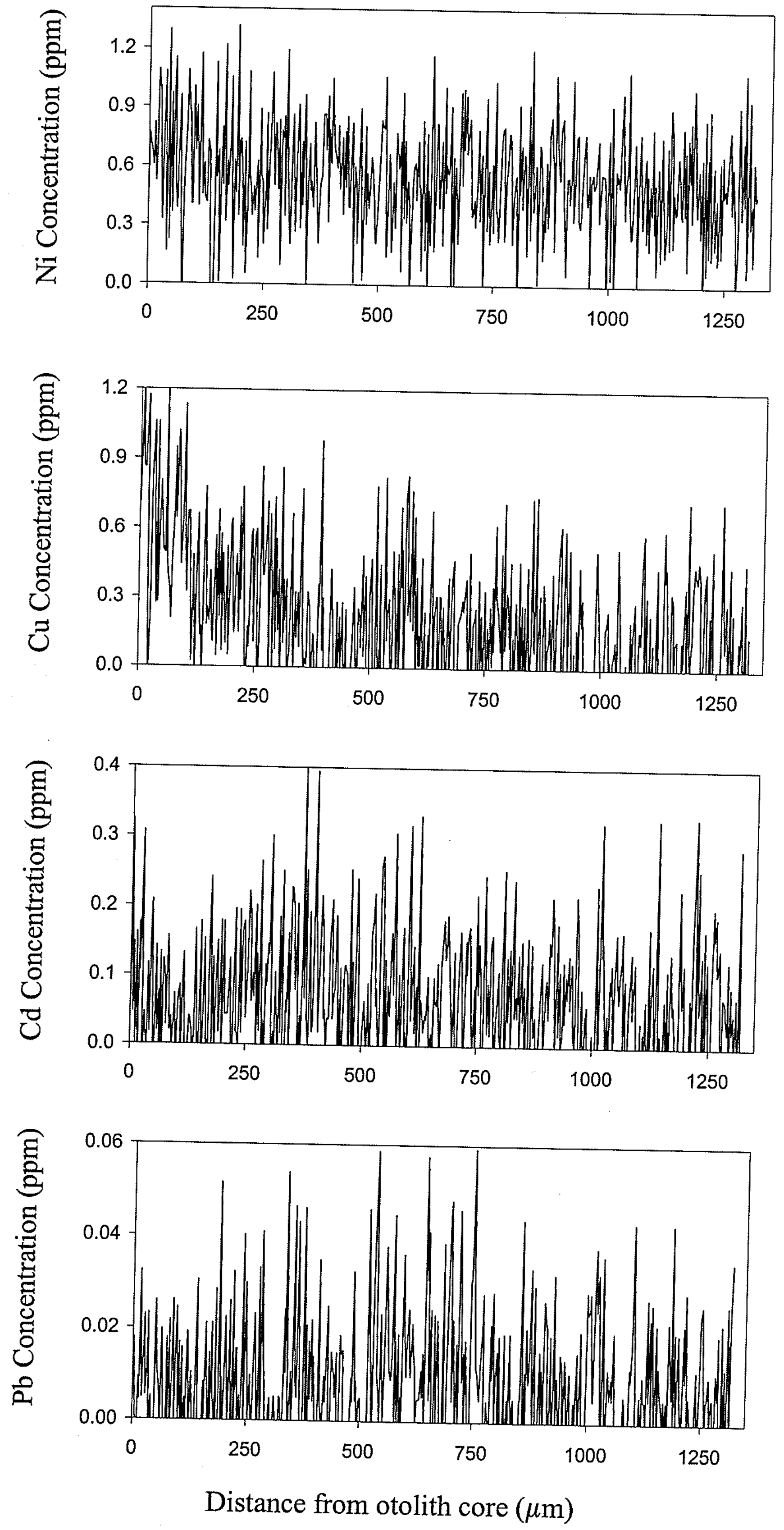
Lynn08_08 *continued*



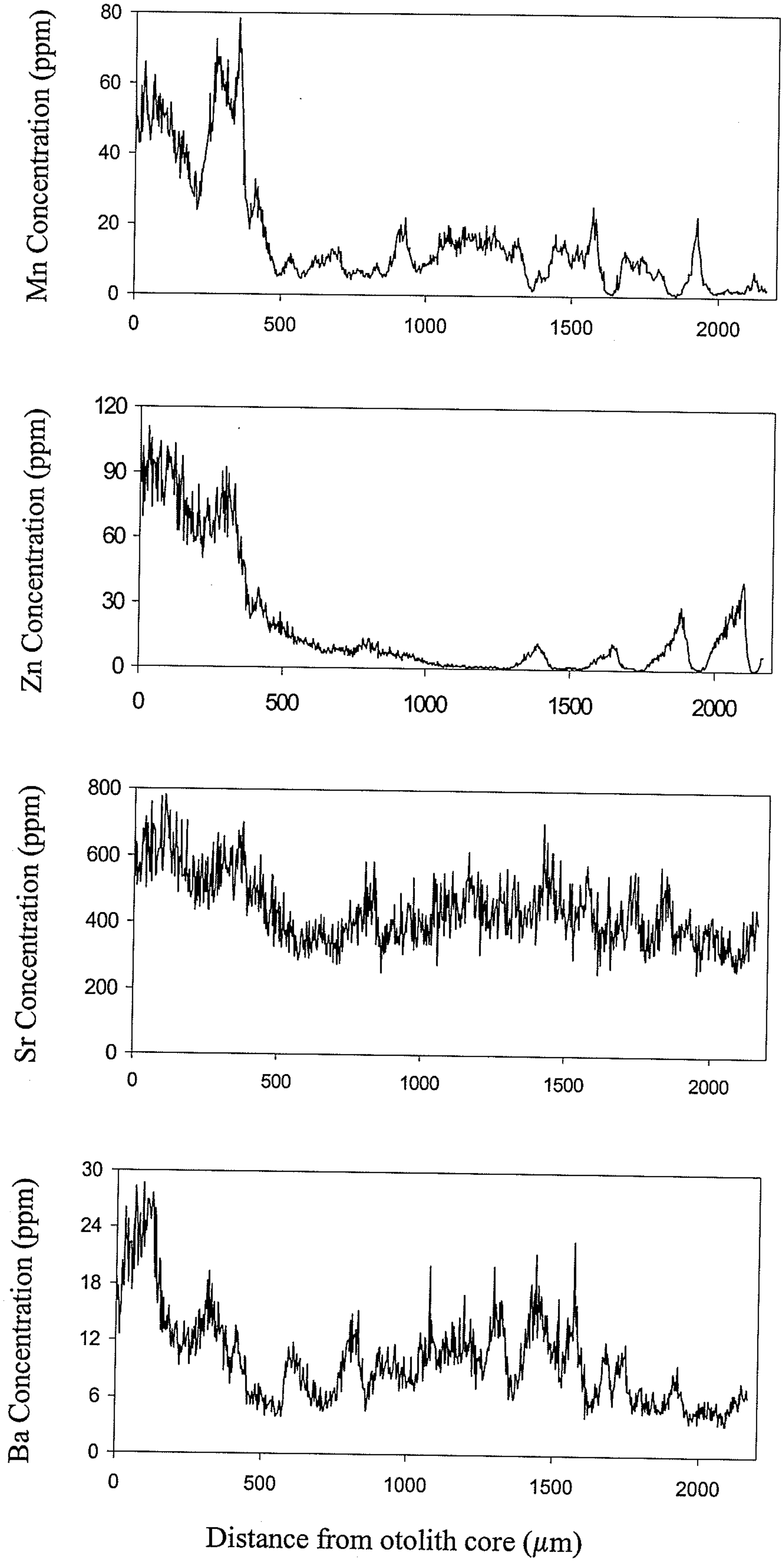
Lynn08_12


Mn Concentration (ppm)
60
40
20
0
0
250
500
750
1000
1250
Zn Concentration (ppm)
160
120
80
40
0
0
250
500
750
1000
1250
Sr Concentration (ppm)
700
600
500
400
300
200
100
0
0
250
500
750
1000
1250
Ba Concentration (ppm)
25
20
15
10
5
0
0
250
500
750
1000
1250
Distance from otolith core (μm)

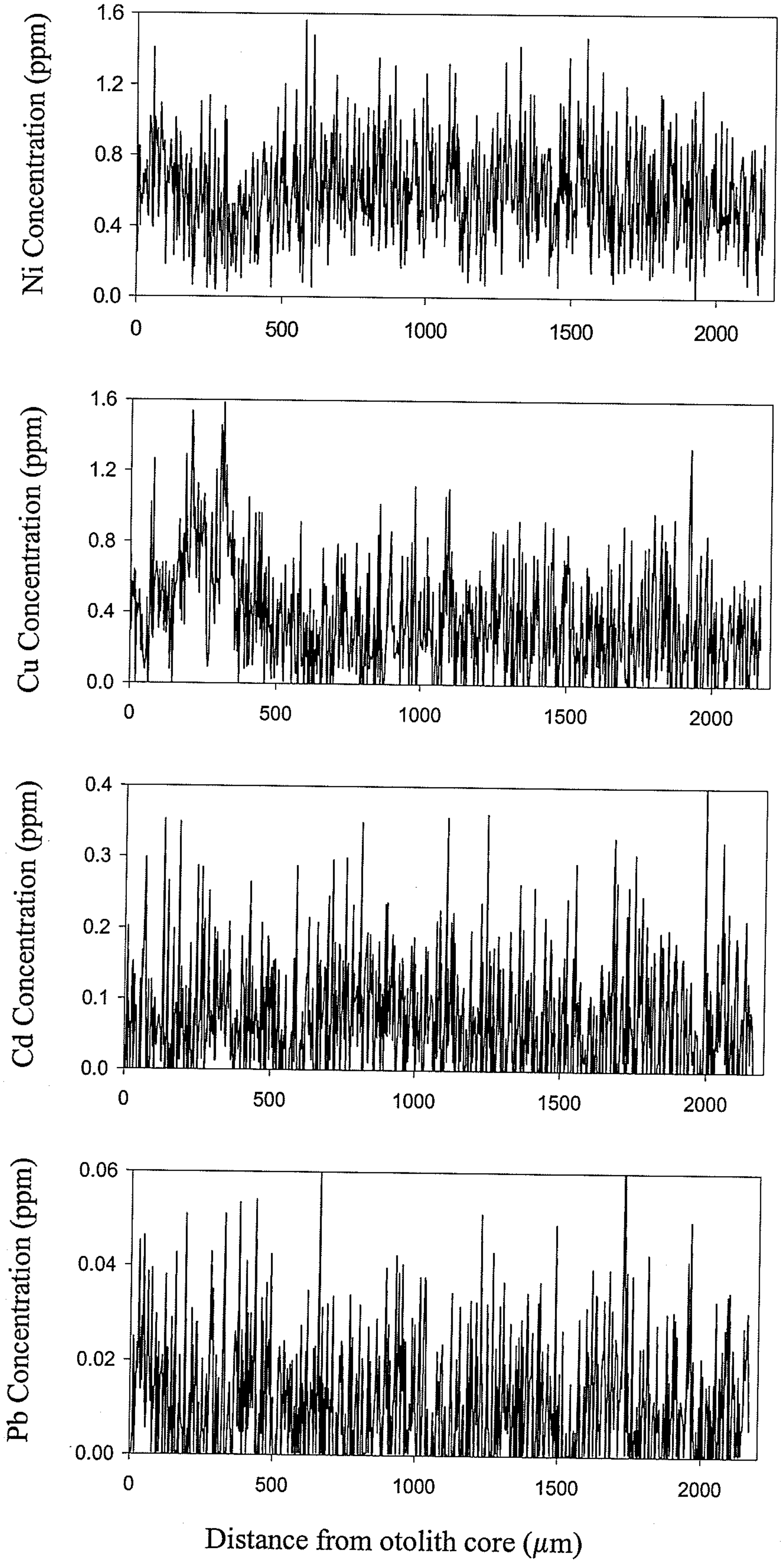
Lynn08_12 *continued*



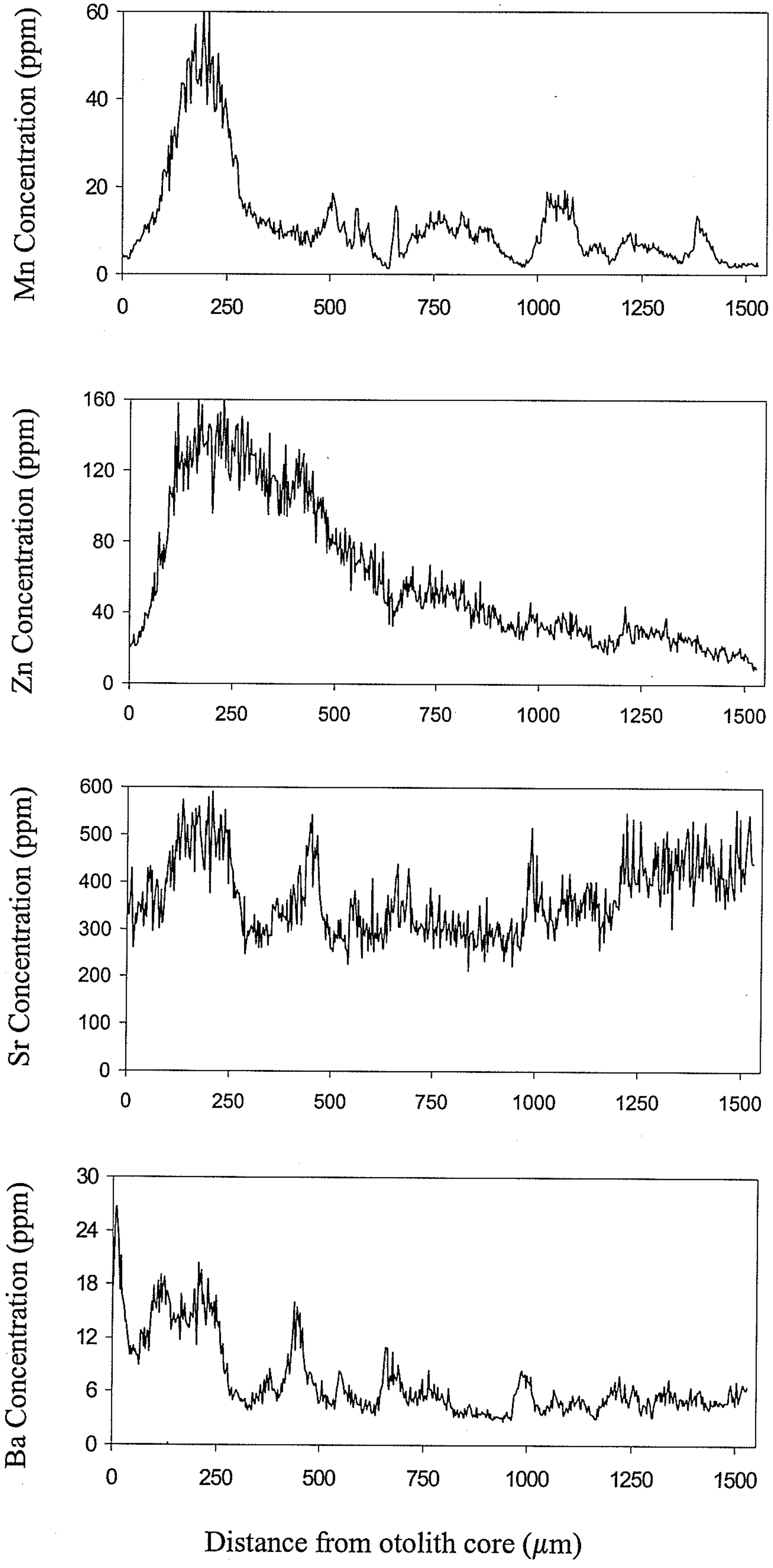
Lynn08_14


Mn Concentration (ppm)
80
60
40
20
0
0
500
1000
1500
2000
Zn Concentration (ppm)
120
90
60
30
0
0
500
1000
1500
2000
Sr Concentration (ppm)
800
600
400
200
0
0
500
1000
1500
2000
Ba Concentration (ppm)
30
24
18
12
6
0
0
500
1000
1500
2000
Distance from otolith core (μm)

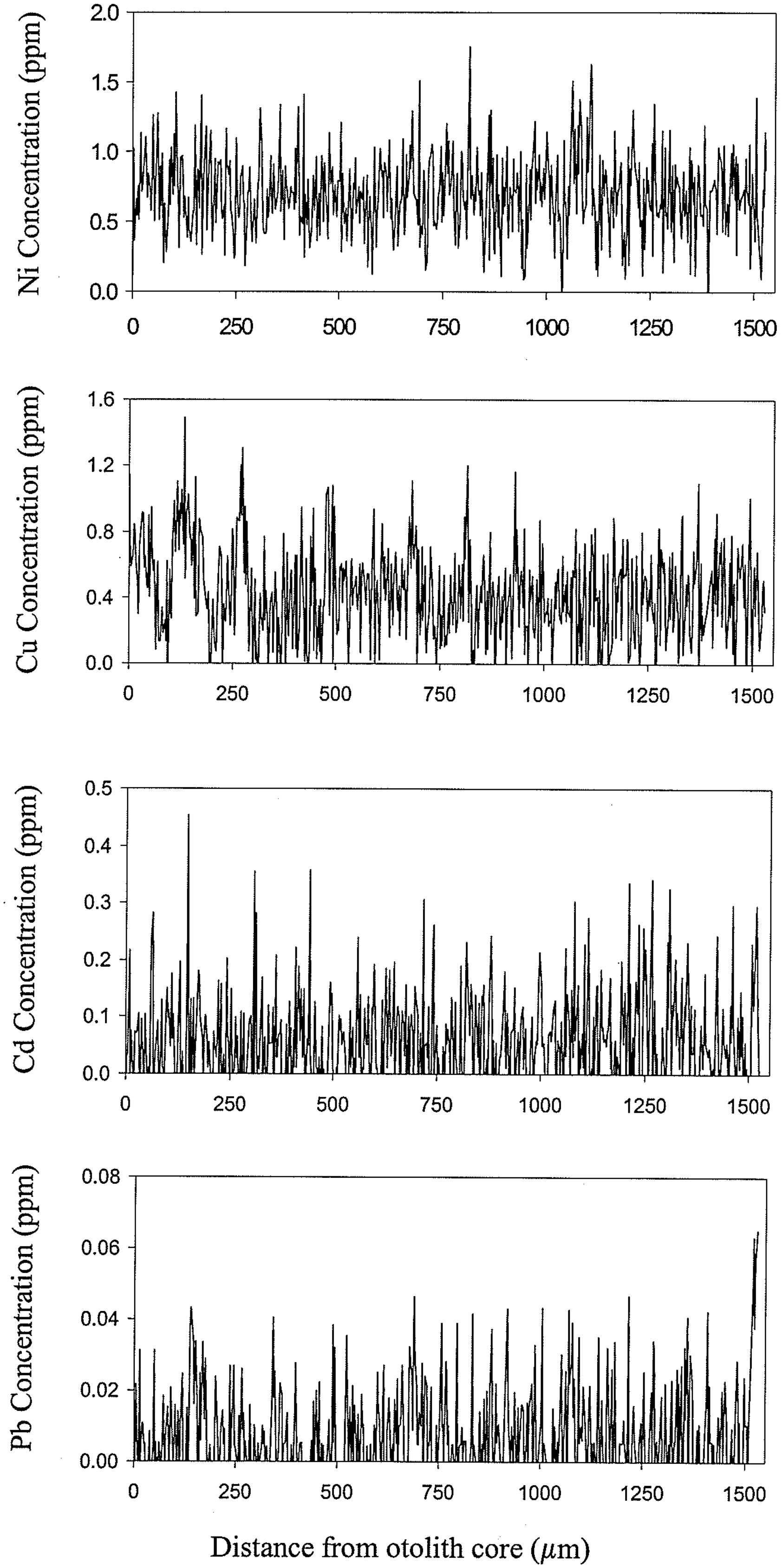
Lynn08_14 *continued*



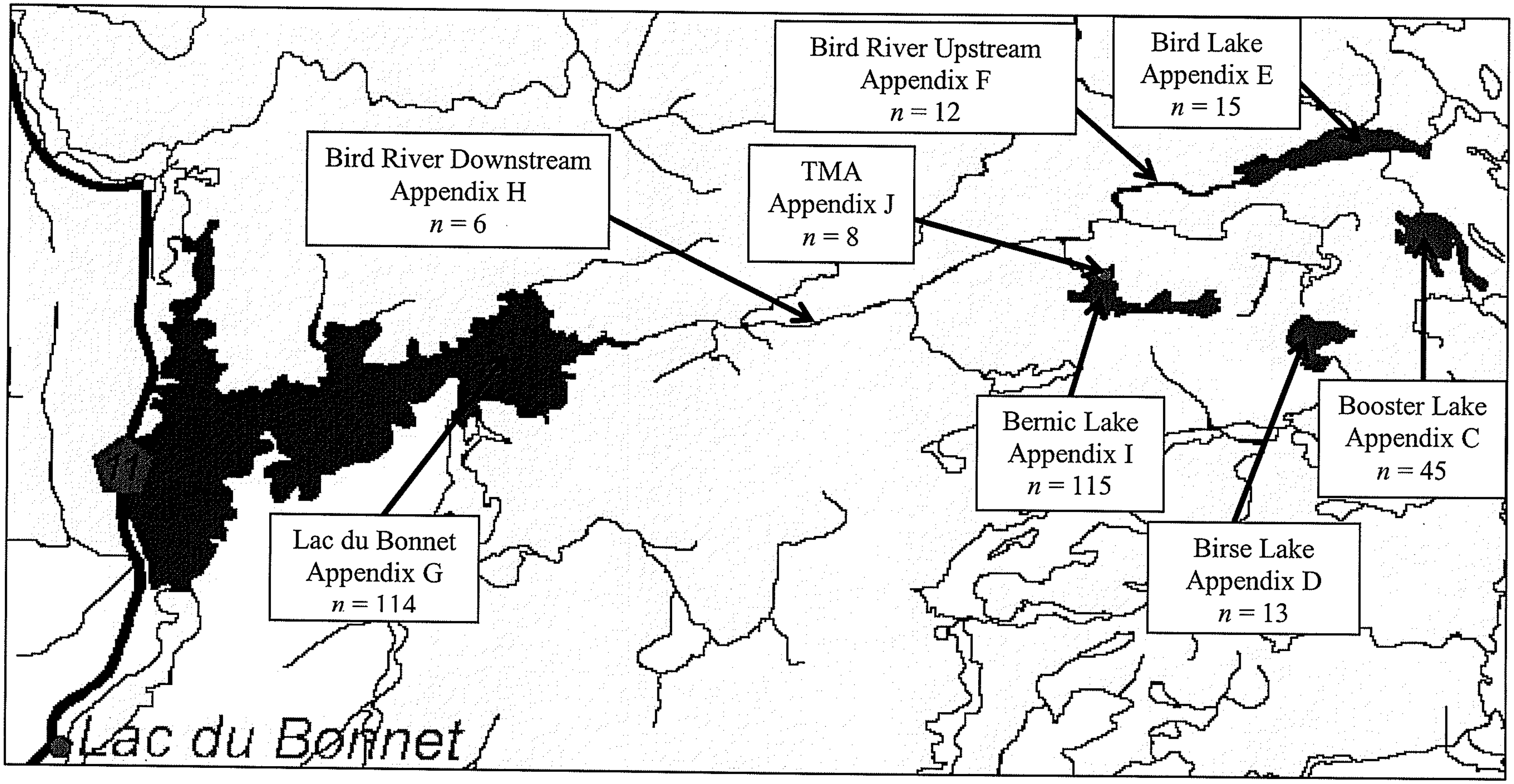
Lynn08_16


Mn Concentration (ppm)
60
40
20
0
0
250
500
750
1000
1250
1500
Zn Concentration (ppm)
160
120
80
40
0
0
250
500
750
1000
1250
1500
Sr Concentration (ppm)
600
500
400
300
200
100
0
0
250
500
750
1000
1250
1500
Ba Concentration (ppm)
30
24
18
12
6
0
0
250
500
750
1000
1250
1500
Distance from otolith core (μm)

Lynn08_16 *continued*



Appendices C-J: LA-ICP-MS data for Lac du Bonnet area otoliths



Appendix C LA-ICP-MS data for Booster Lake otoliths

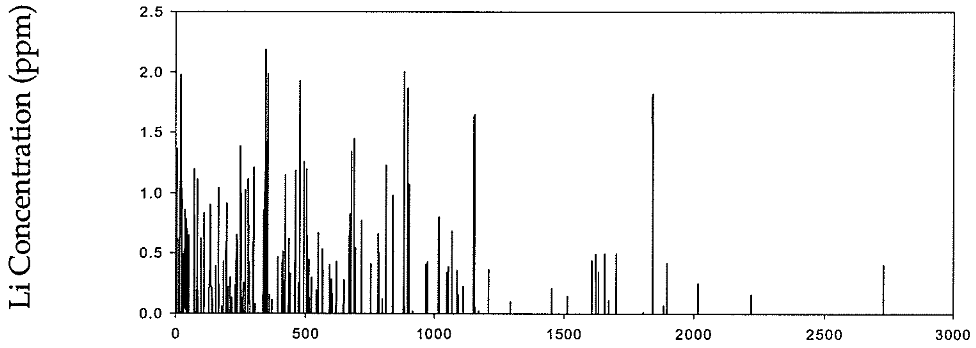
Species: Walleye (*Sander vitreus*), Northern Pike (*Esox lucius*), White Sucker (*Catostomus commersoni*), Small Mouth Bass (*Micropterus dolomieu*)

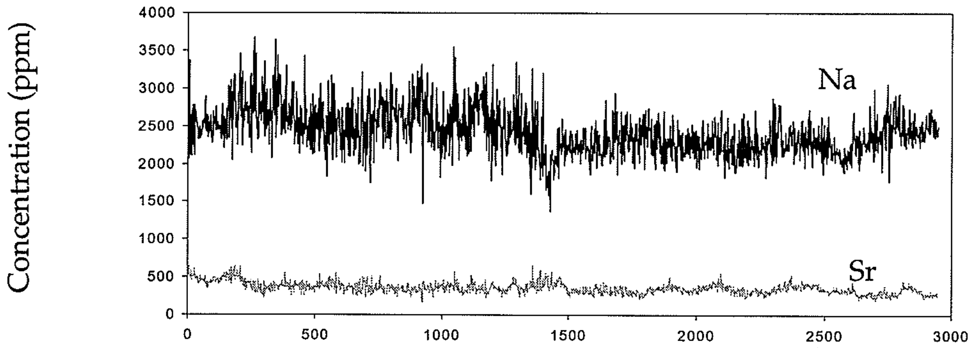
Captured: 2008

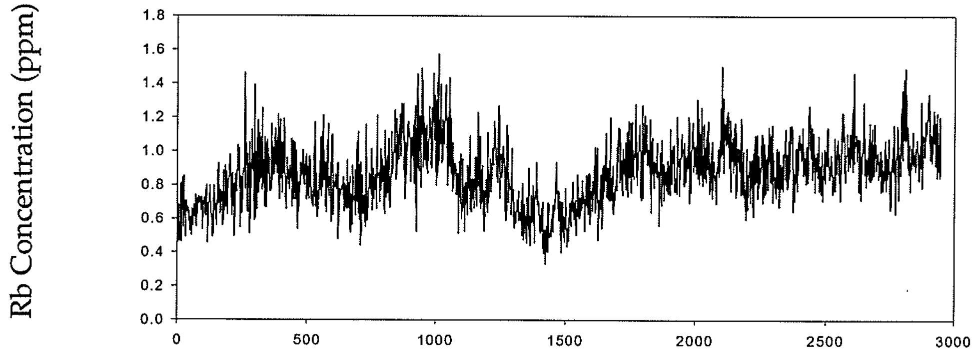
Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

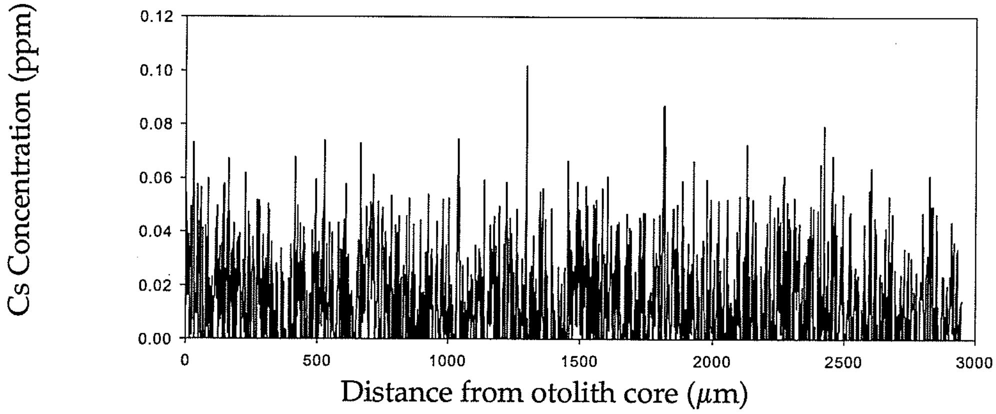
Sample Number	***Species***	***Age***
01	Northern Pike	13
02	Northern Pike	7
03	White Sucker	11
04	Small Mouth Bass	6
05	Small Mouth Bass	5
06	Small Mouth Bass	9
07	Walleye	18
08	Northern Pike	11
09	Northern Pike	6
10	Walleye	6
11	Walleye	6
12	Walleye	6
13	Walleye	7
14	Walleye	7
15	Walleye	7

BooL08_01

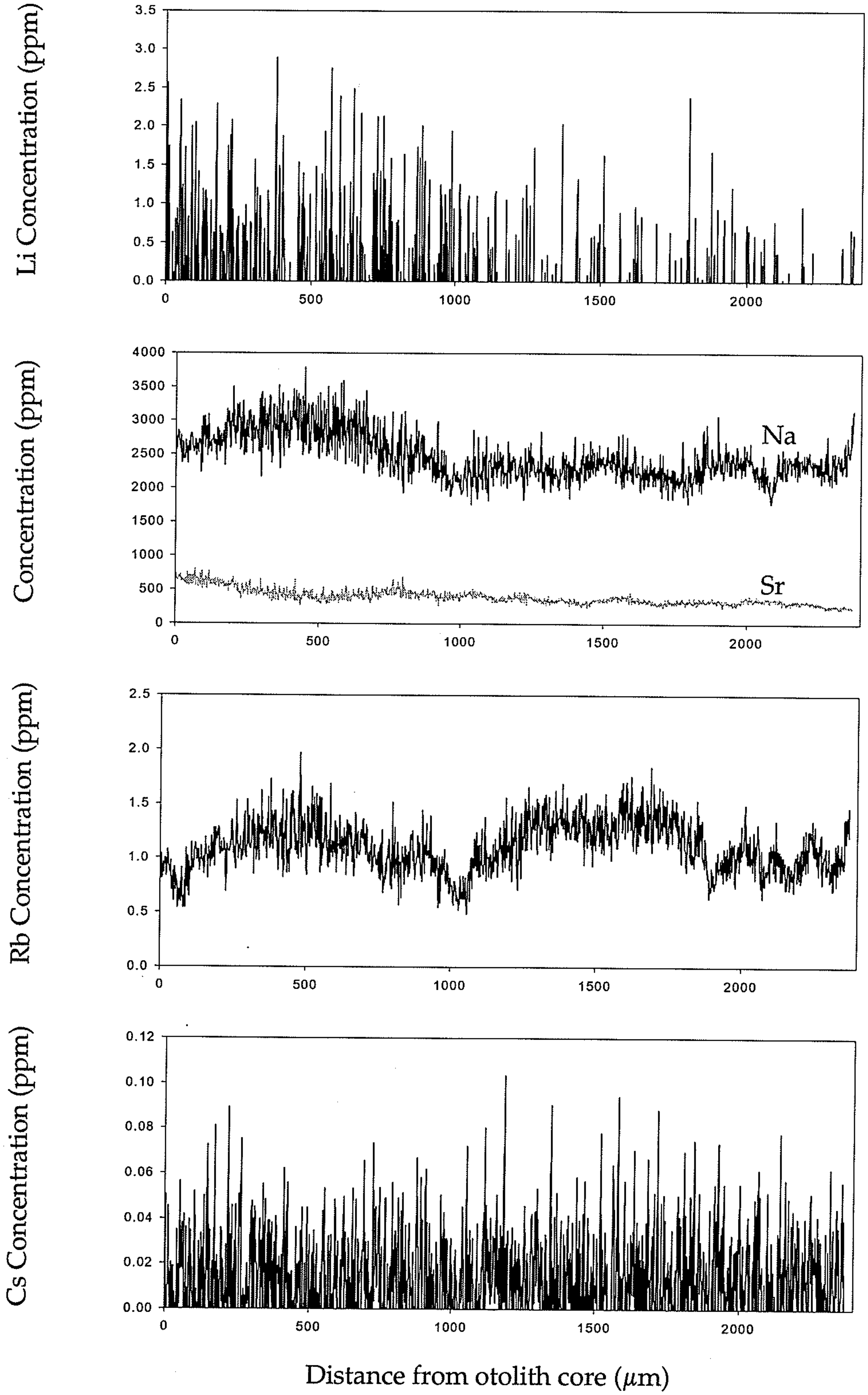

Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
2500
3000


Concentration (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
500
1000
1500
2000
2500
3000

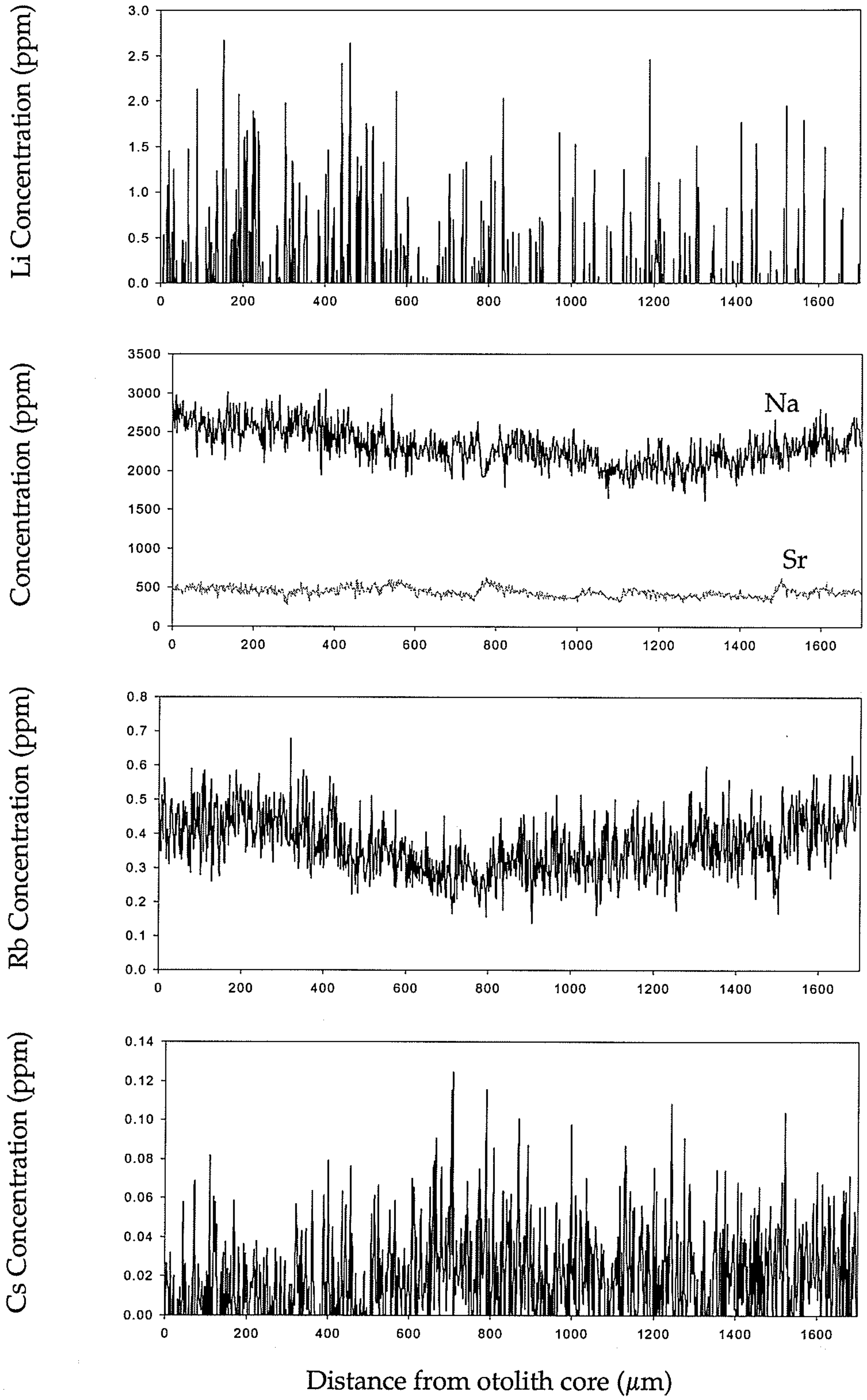

Rb Concentration (ppm)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500
2000
2500
3000


Cs Concentration (ppm)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
500
1000
1500
2000
2500
3000
Distance from otolith core (μm)

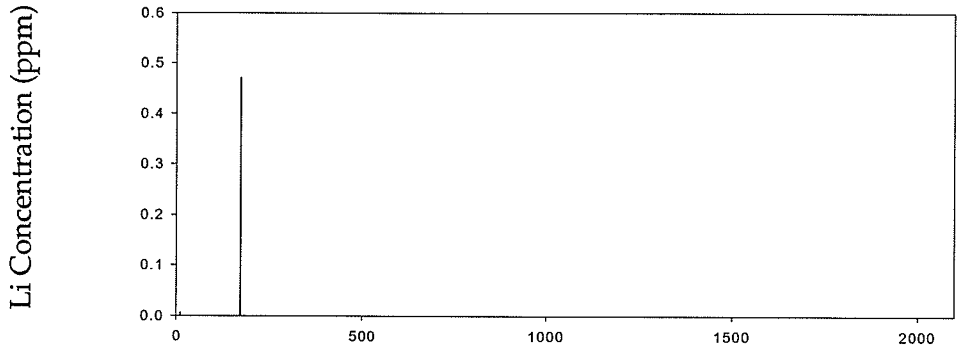
BooL08_02

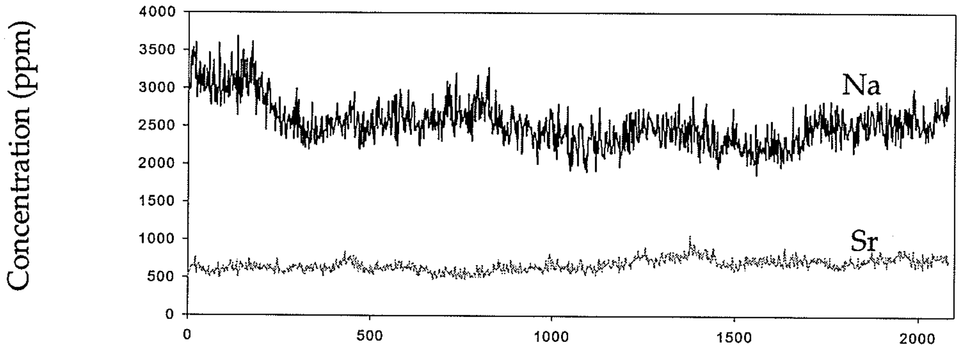

Li Concentration (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
Concentration (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
Cs Concentration (ppm)
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
500
1000
1500
2000
Distance from otolith core (μm)

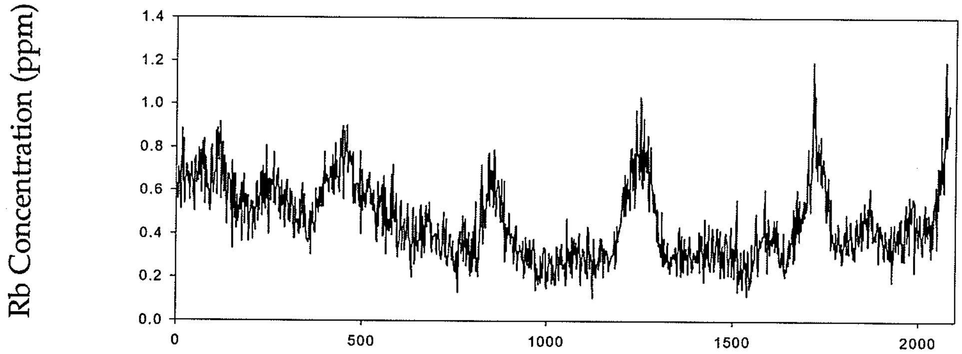
BooL08_03

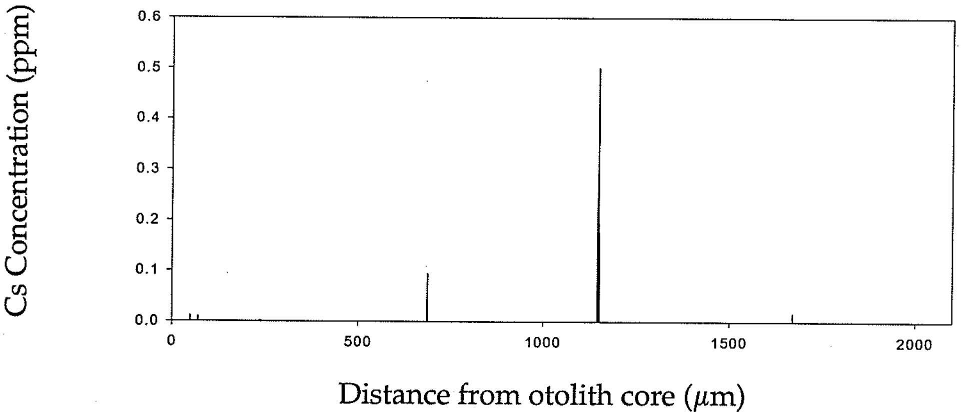

Li Concentration (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
Rb Concentration (ppm)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
1200
1400
1600
Cs Concentration (ppm)
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (µm)

BooL08_04

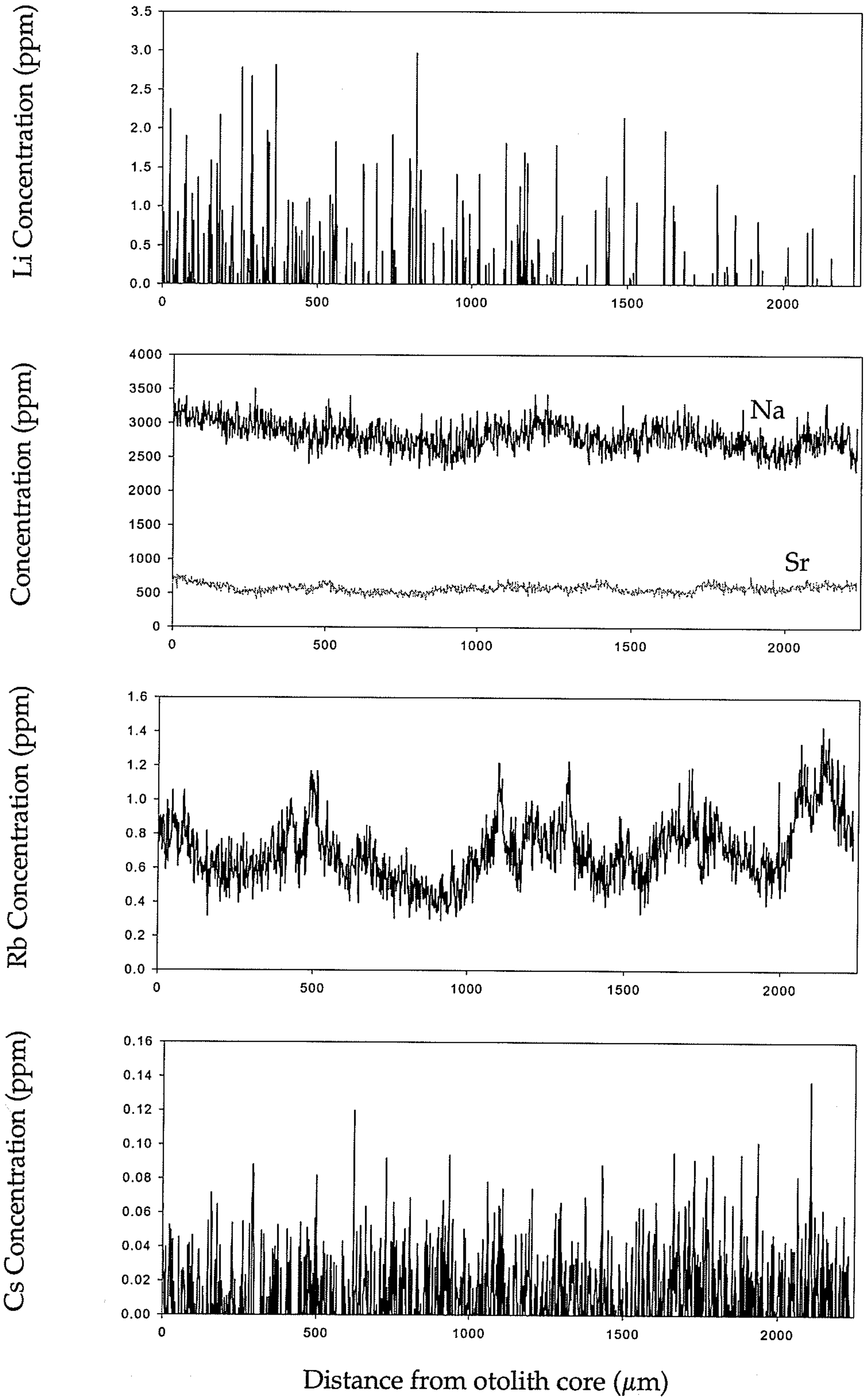

Li Concentration (ppm)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
500
1000
1500
2000


Concentration (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
500
1000
1500
2000

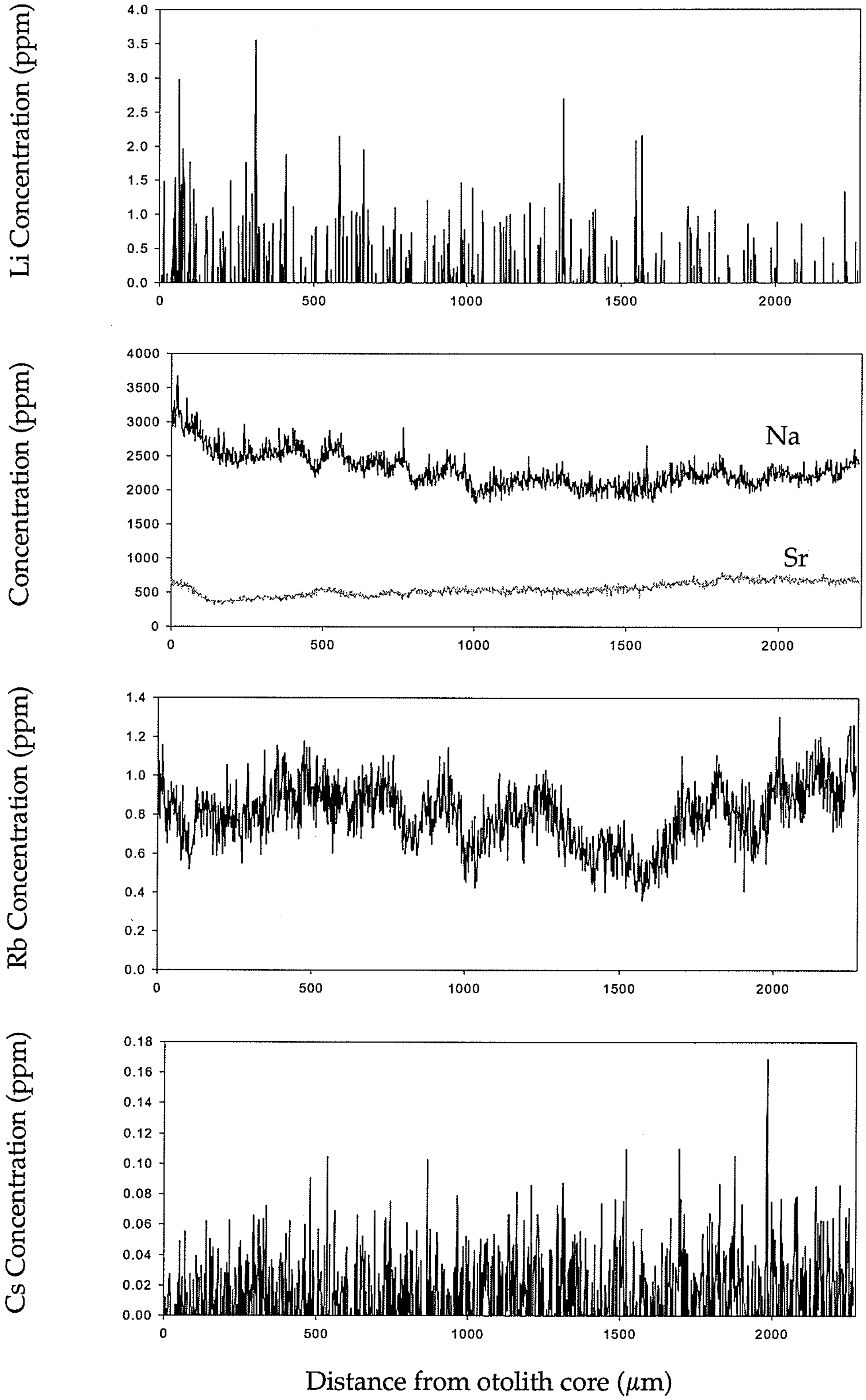

Rb Concentration (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500
2000


Cs Concentration (ppm)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
500
1000
1500
2000
Distance from otolith core (μm)

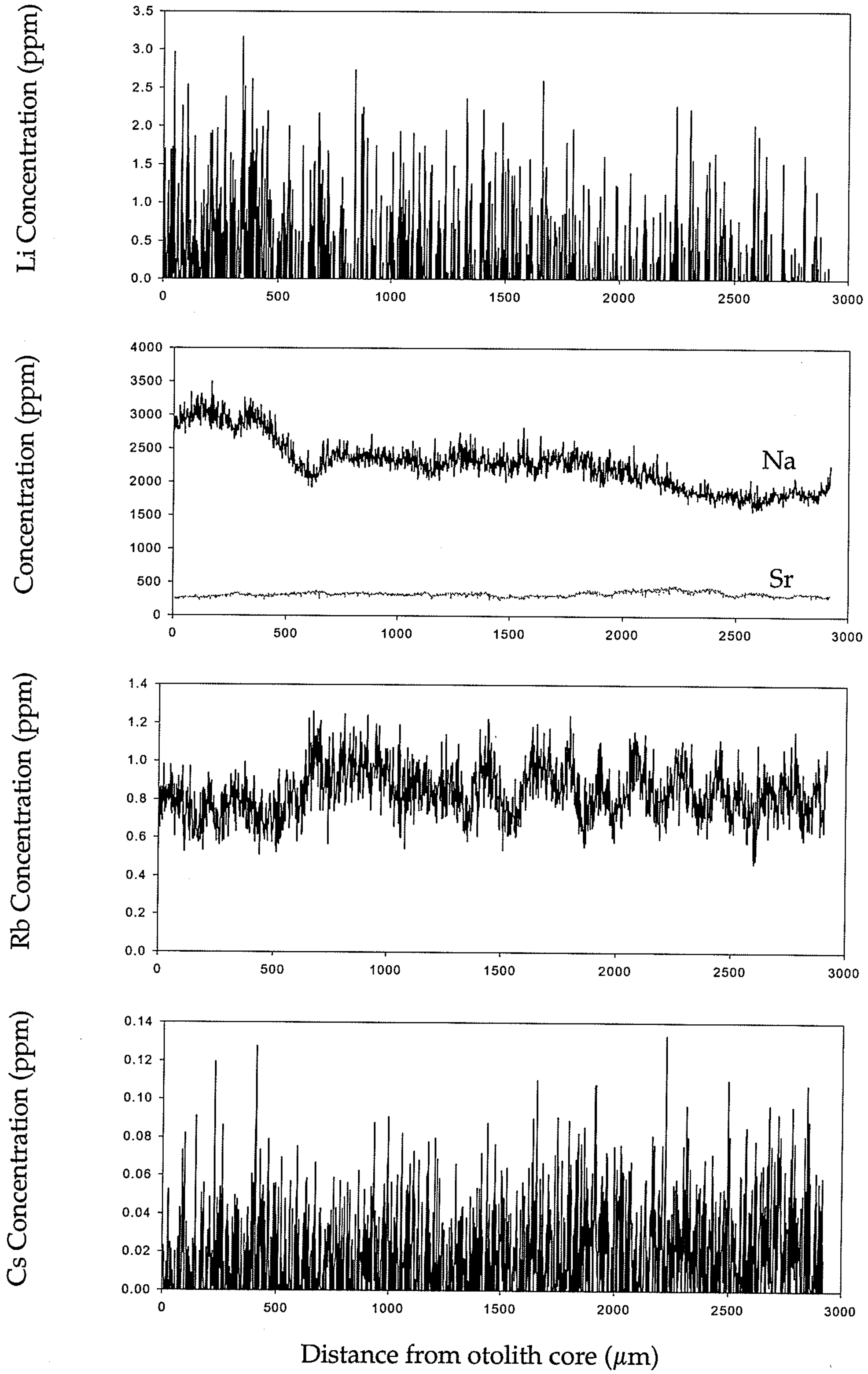
BooL08_05


Li Concentration (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
Concentration (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
Rb Concentration (ppm)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Cs Concentration (ppm)
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Distance from otolith core (μm)

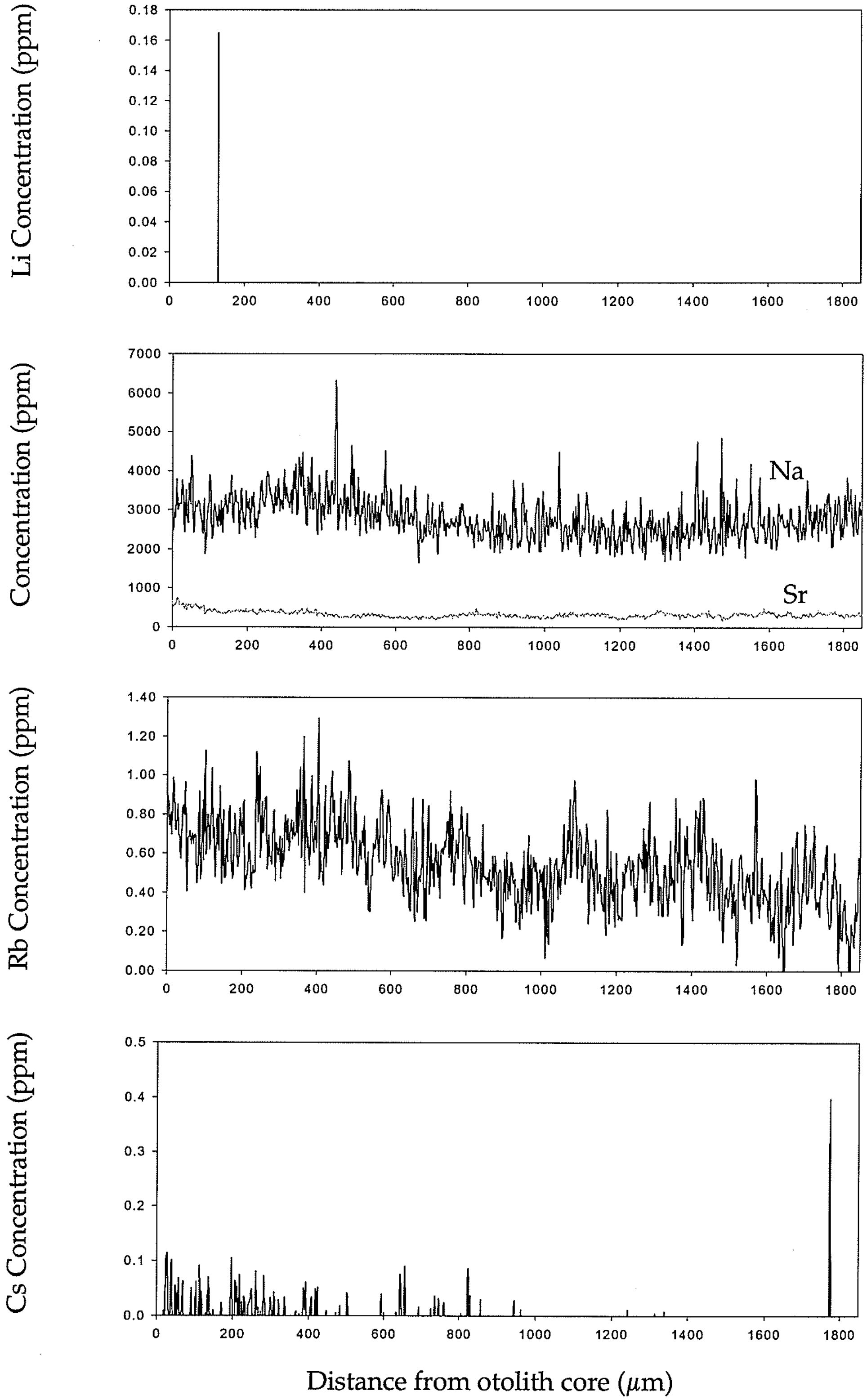
BooL08_06


Li Concentration (ppm)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
Concentration (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500
2000
Cs Concentration (ppm)
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
500
1000
1500
2000
Distance from otolith core (μm)

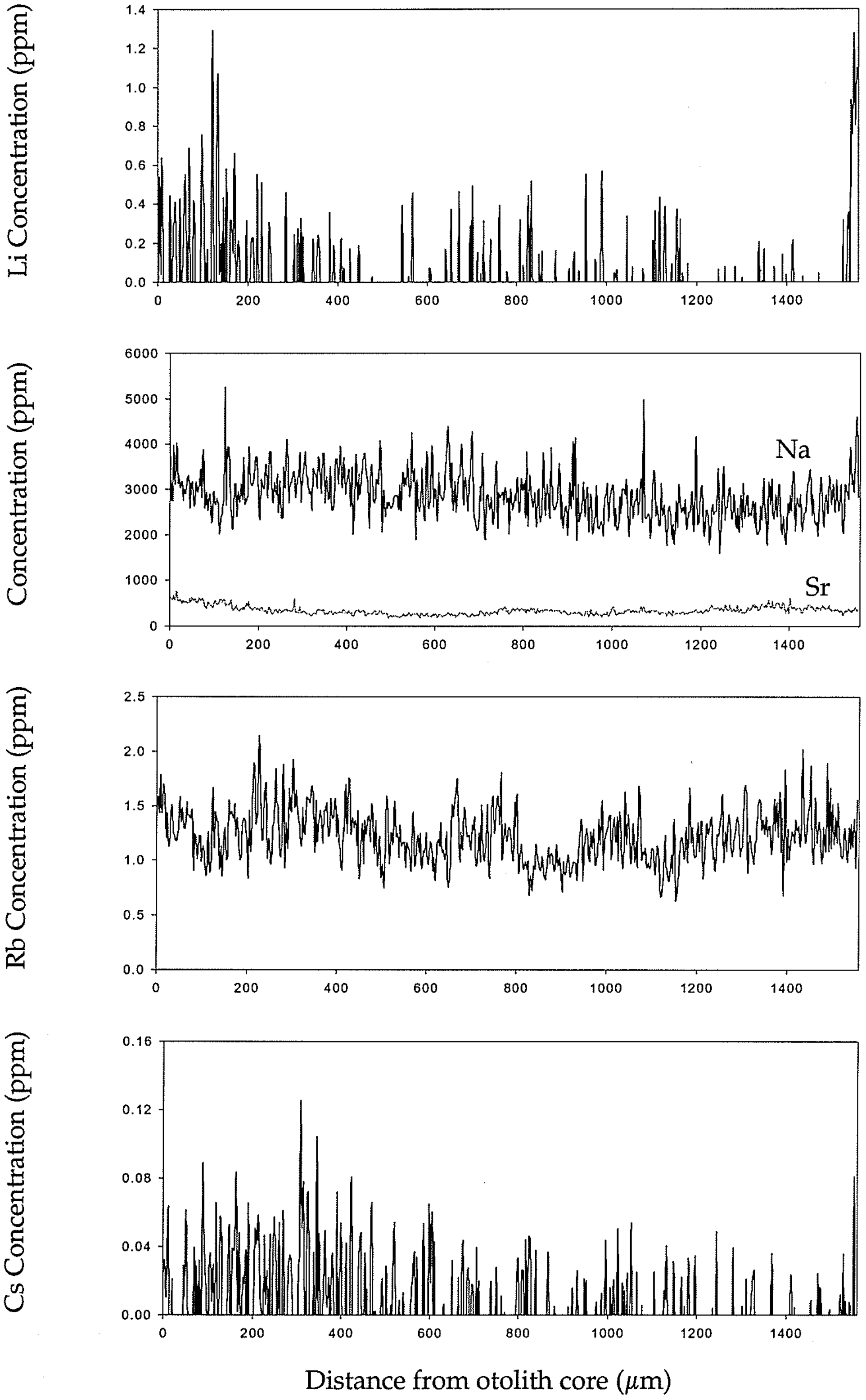
BooL08_07


Li Concentration (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
2500
3000
Concentration (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
500
1000
1500
2000
2500
3000
Rb Concentration (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500
2000
2500
3000
Cs Concentration (ppm)
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
500
1000
1500
2000
2500
3000
Distance from otolith core (μm)

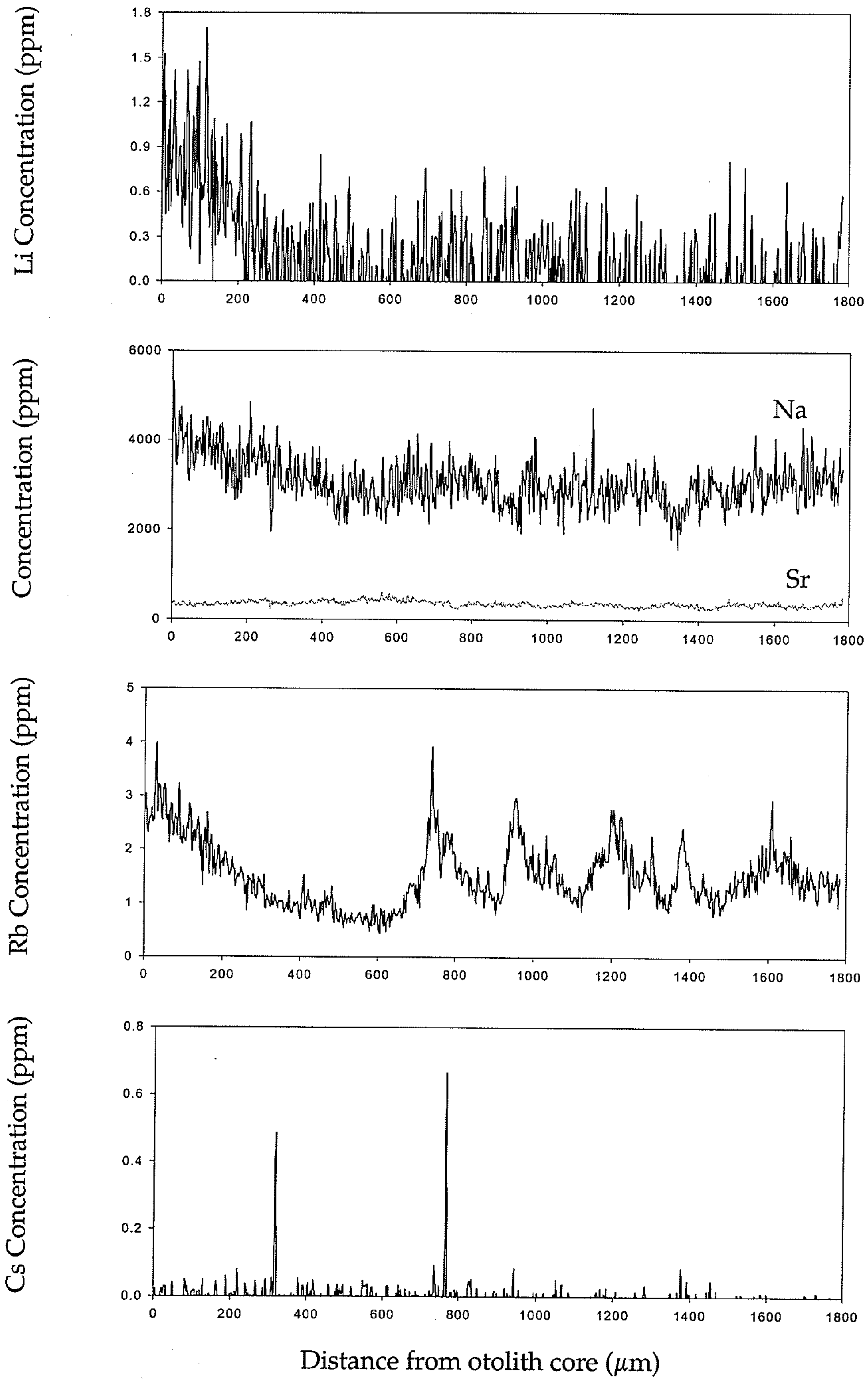
BooL08_08


Li Concentration (ppm)
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
200
400
600
800
1000
1200
1400
1600
1800
Concentration (ppm)
7000
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
1800
Rb Concentration (ppm)
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0
200
400
600
800
1000
1200
1400
1600
1800
Cs Concentration (ppm)
0.5
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
Distance from otolith core (μm)

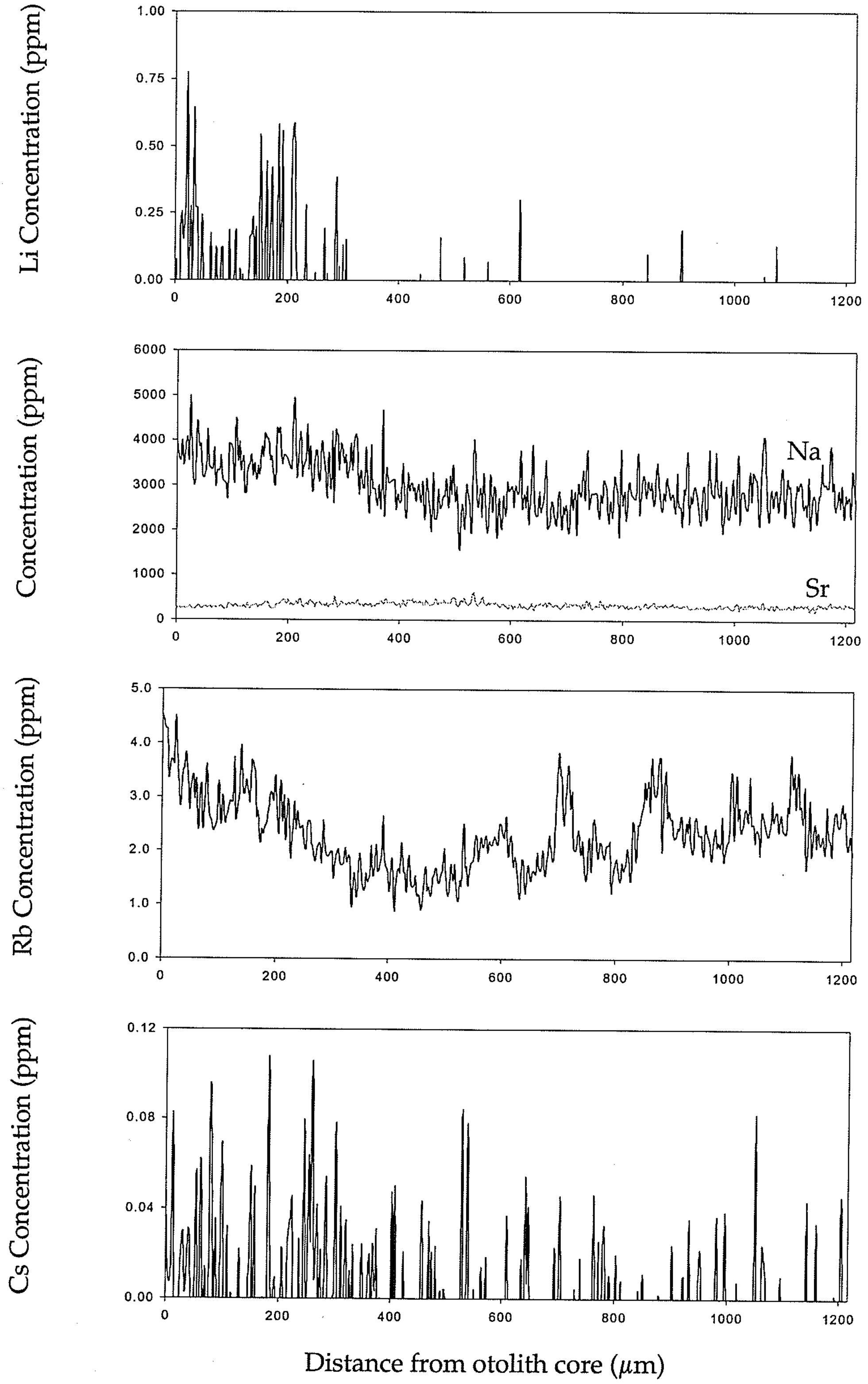
BooL08_09


Li Concentration (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
0.16
0.12
0.08
0.04
0.00
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

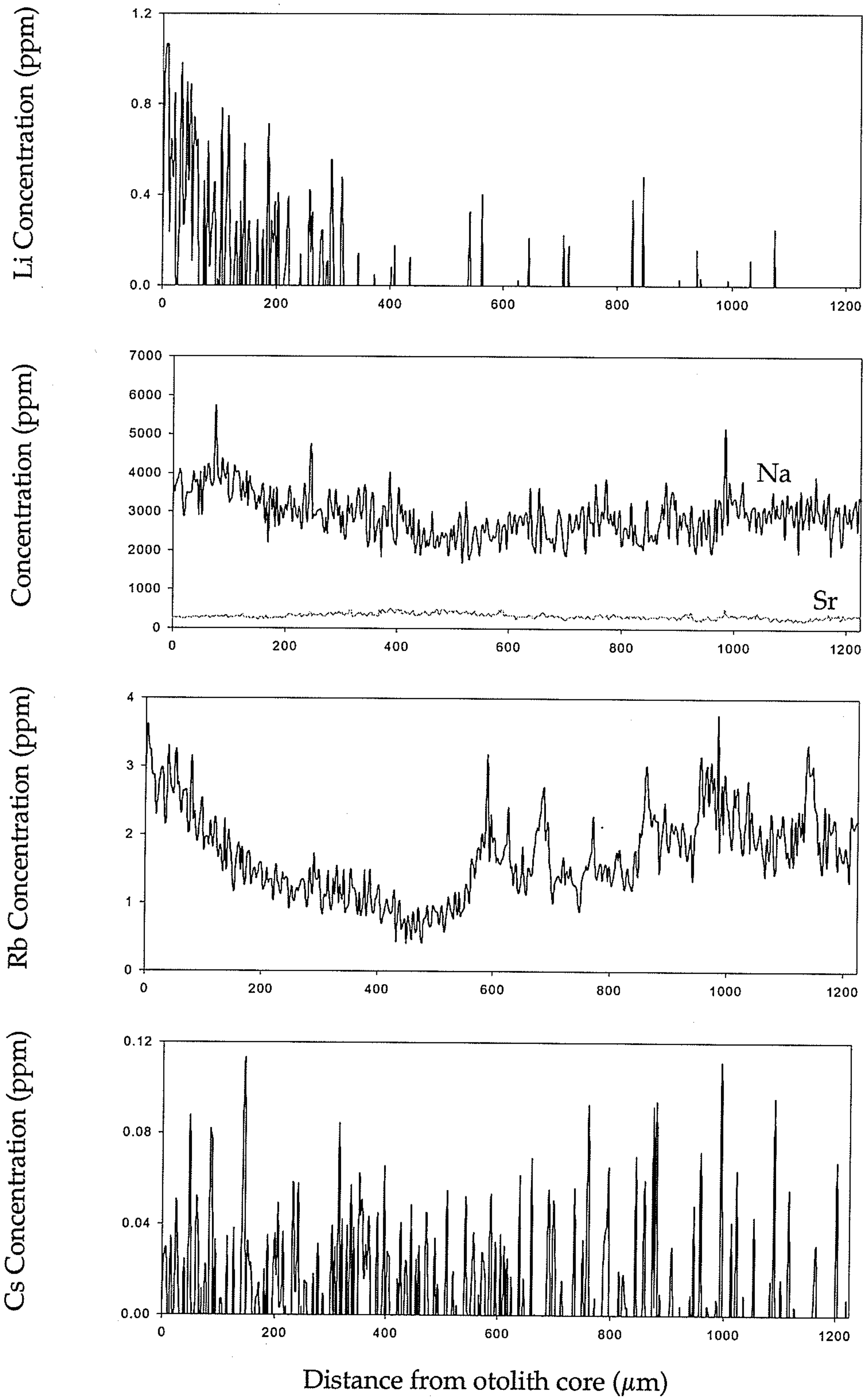
BooL08_10


Li Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
Concentration (ppm)
6000
4000
2000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
1800
Rb Concentration (ppm)
5
4
3
2
1
0
0
200
400
600
800
1000
1200
1400
1600
1800
Cs Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
Distance from otolith core (μm)

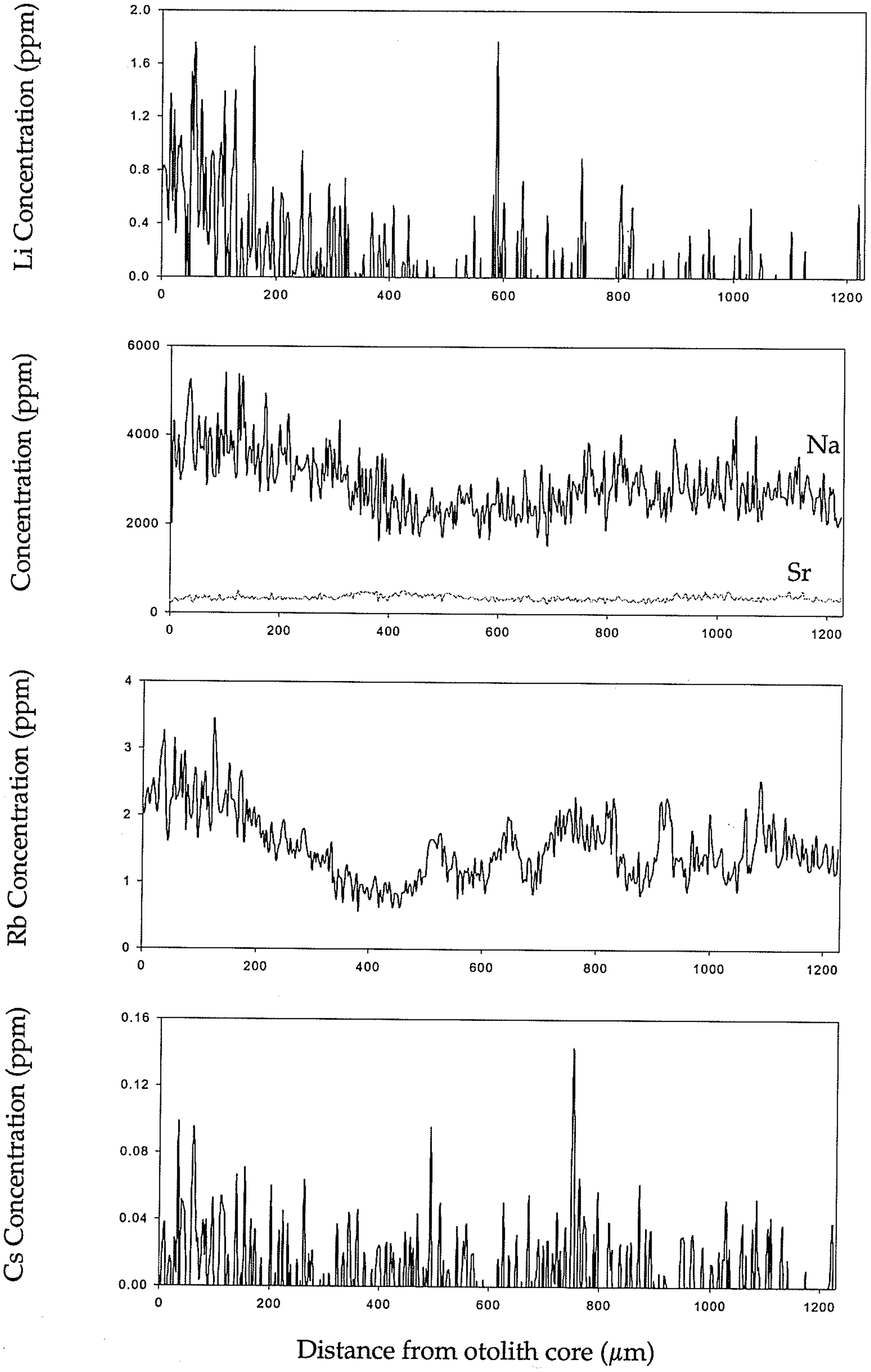
BooL08_11


Li Concentration (ppm)
1.00
0.75
0.50
0.25
0.00
Concentration (ppm)
6000
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
5.0
4.0
3.0
2.0
1.0
0.0
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

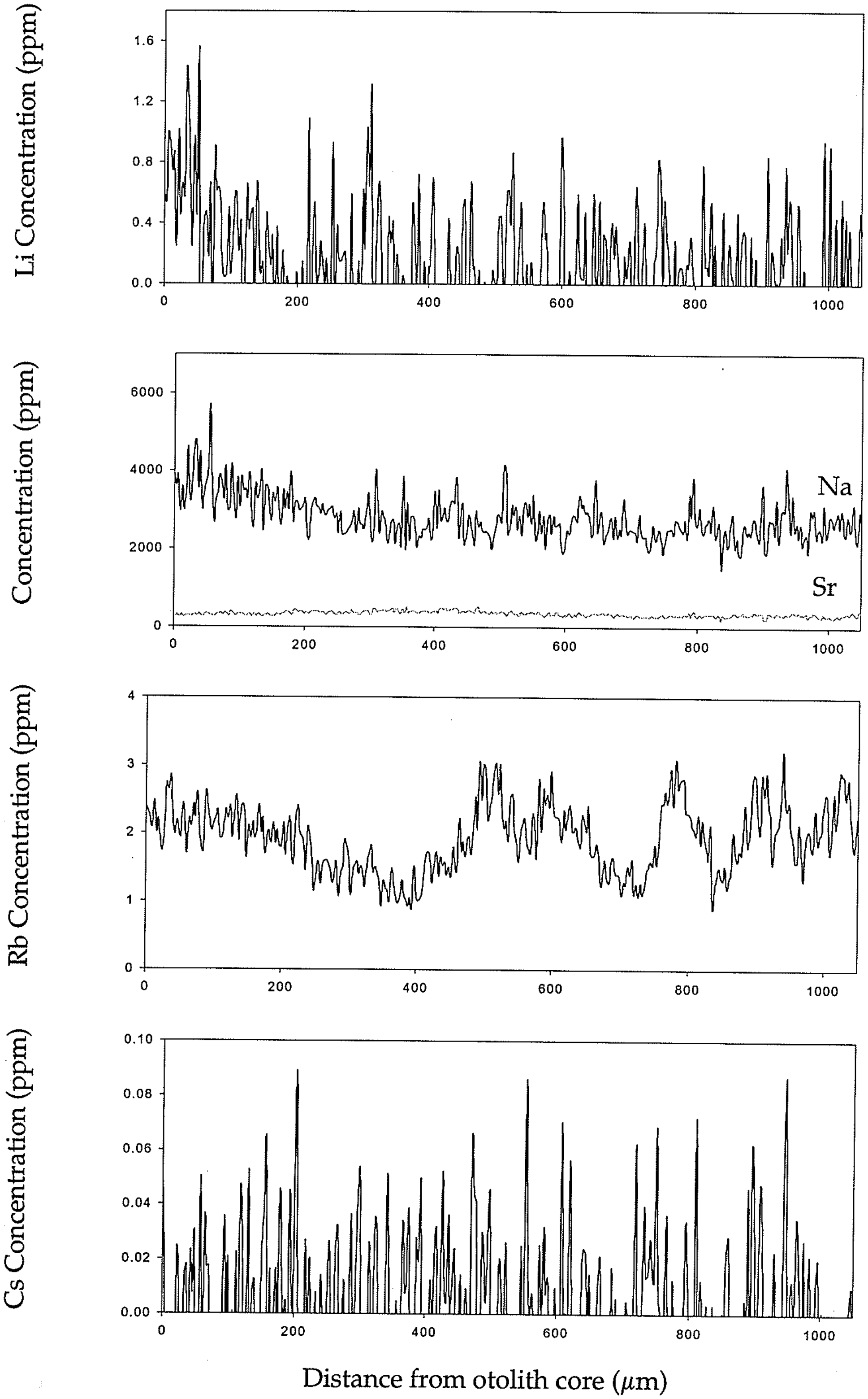
BooL08_12


Li Concentration (ppm)
1.2
0.8
0.4
0.0
Concentration (ppm)
7000
6000
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
4
3
2
1
0
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

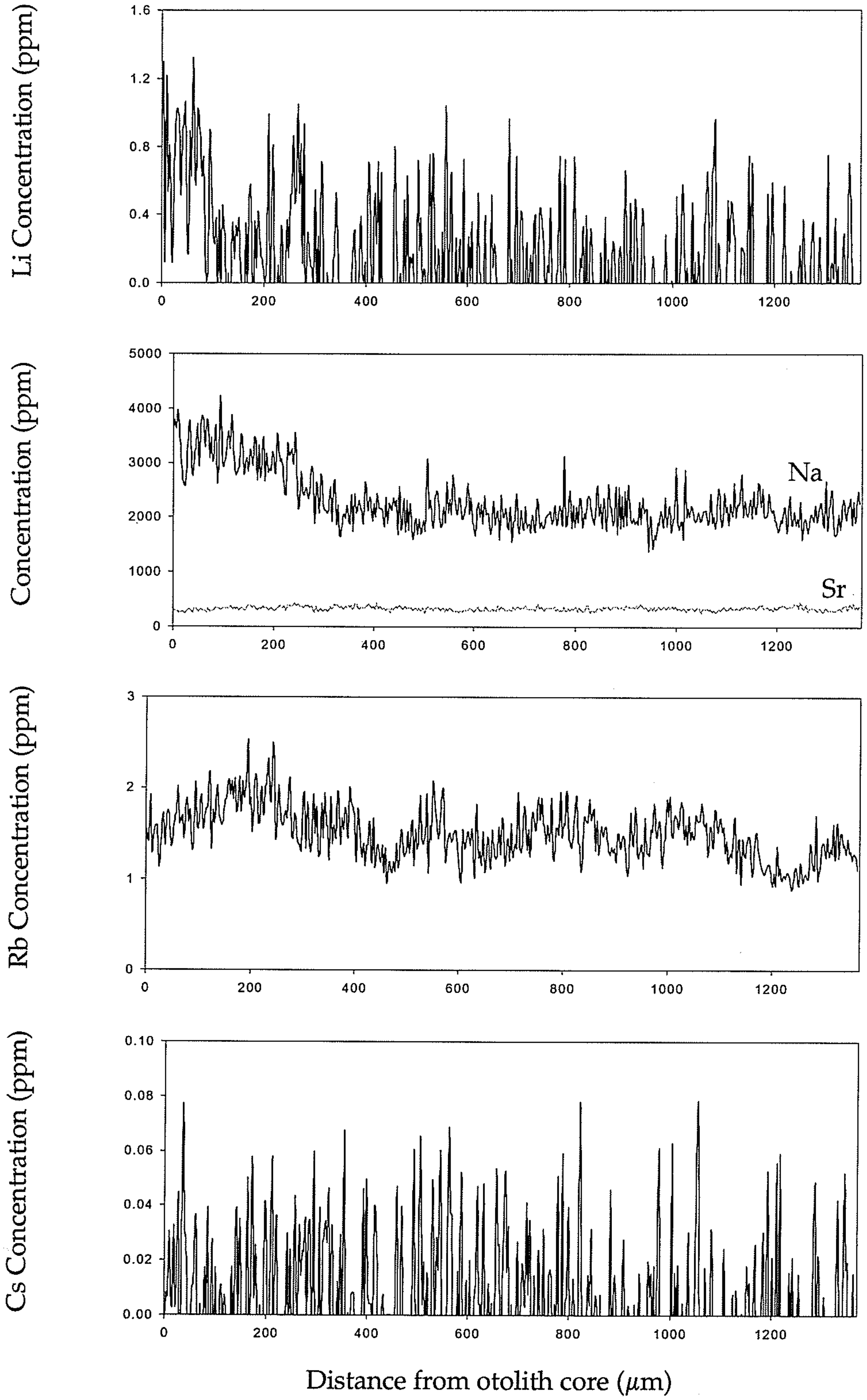
BooL08_13


Li Concentration (ppm)
2.0
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
6000
4000
2000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
4
3
2
1
0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.16
0.12
0.08
0.04
0.00
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

BooL08_14


Li Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
Concentration (ppm)
6000
4000
2000
0
Na
Sr
Rb Concentration (ppm)
4
3
2
1
0
Cs Concentration (ppm)
0.10
0.08
0.06
0.04
0.02
0.00
Distance from otolith core (μm)

BooL08_15



Li Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
3
2
1
0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.10
0.08
0.06
0.04
0.02
0.00
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

Appendix C LA-ICP-MS data for Booster Lake otoliths *continued*

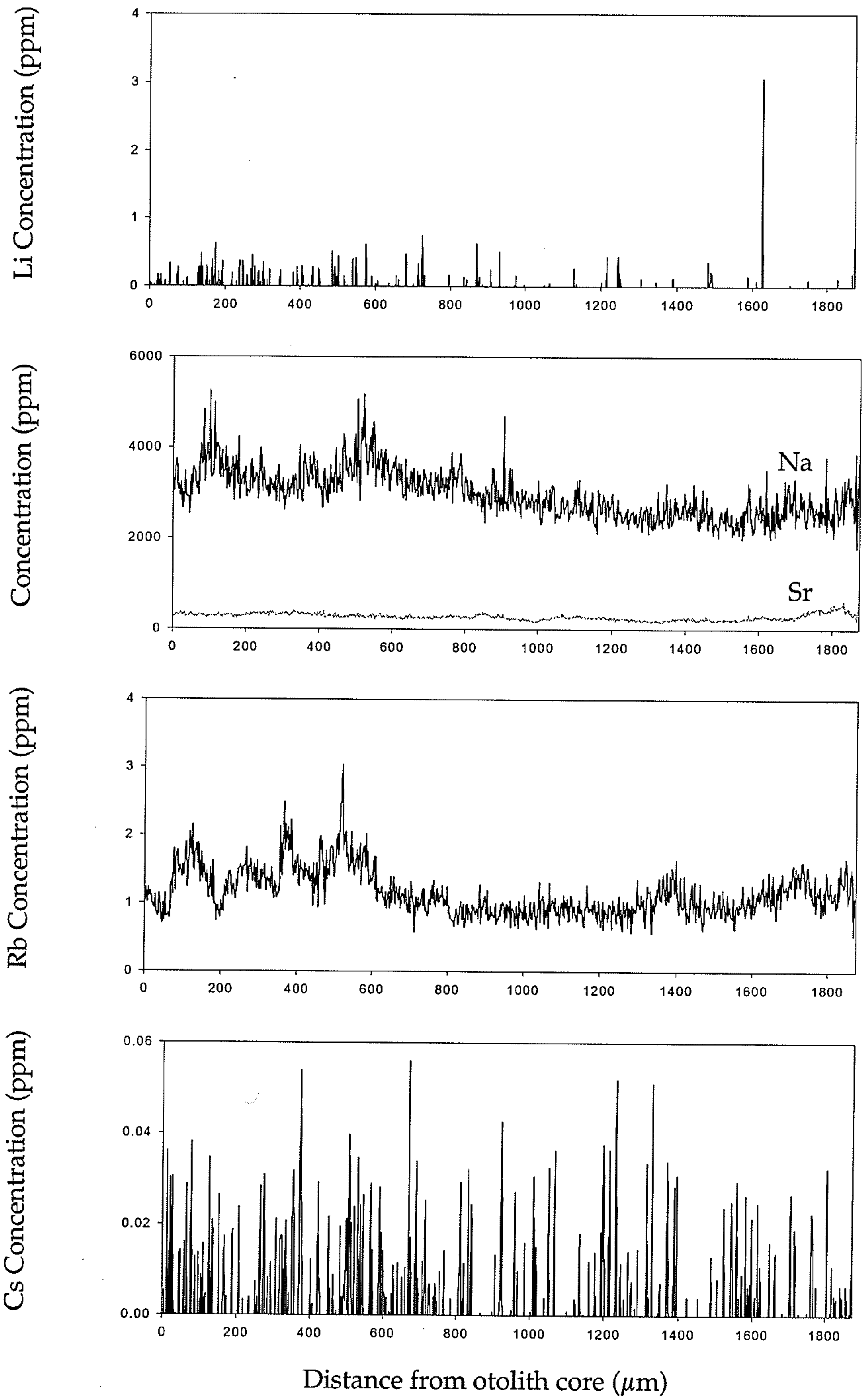
Species: Walleye (*Sander vitreus*), Northern Pike (*Esox lucius*), Small Mouth Bass (*Micropterus dolomieu*)

Captured: 2007

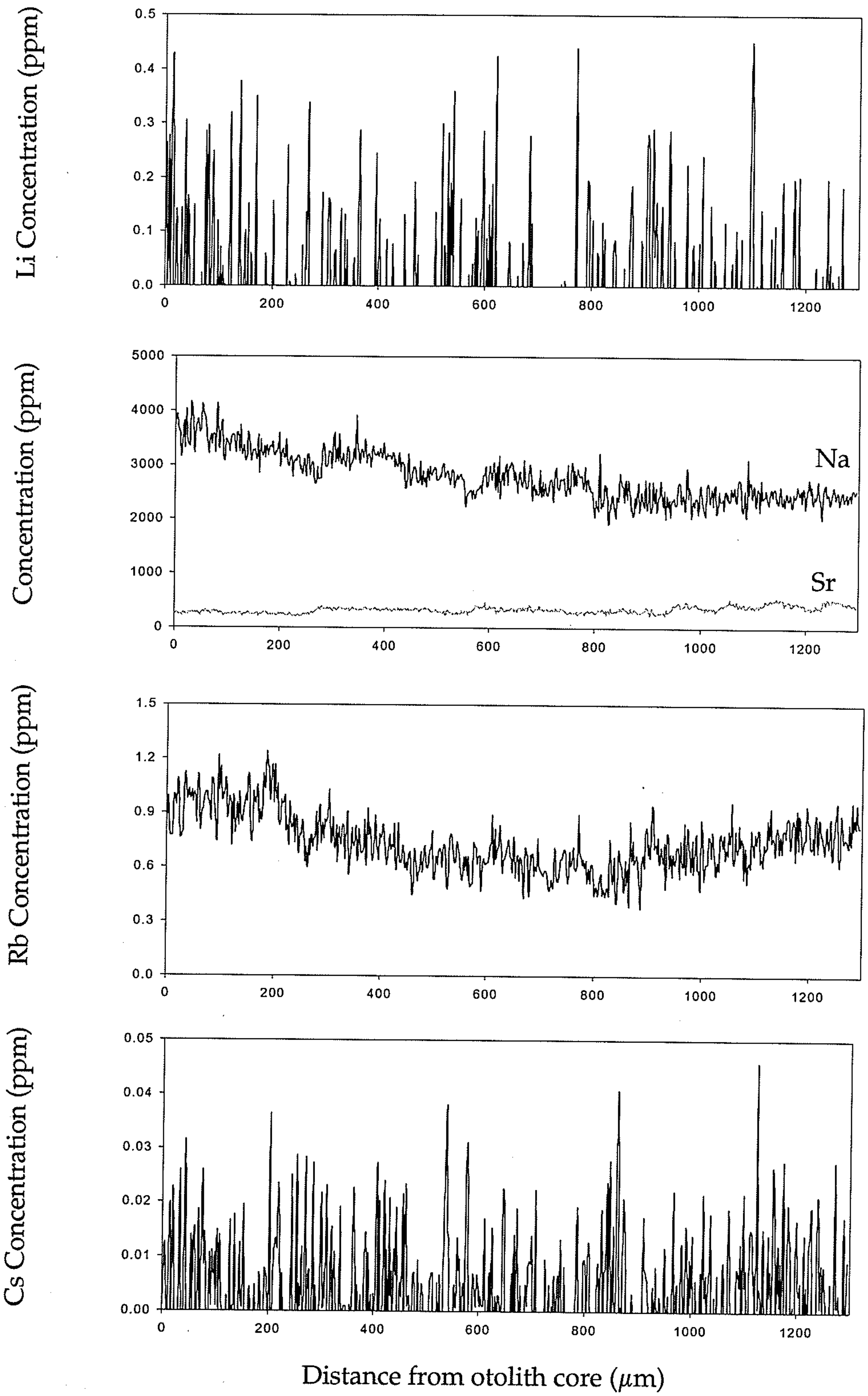
Isotopes: Li^{7}, Na^{23}, Rb^{85}, Sr^{88}, Cs^{133}

Sample Number	***Species***	***Age***
01	Northern Pike	8
02	Northern Pike	9
03	Northern Pike	7
04	Northern Pike	8
05	Northern Pike	8
06	Walleye	5
07	Walleye	5
08	Walleye	5
09	Walleye	7
10	Small Mouth Bass	3

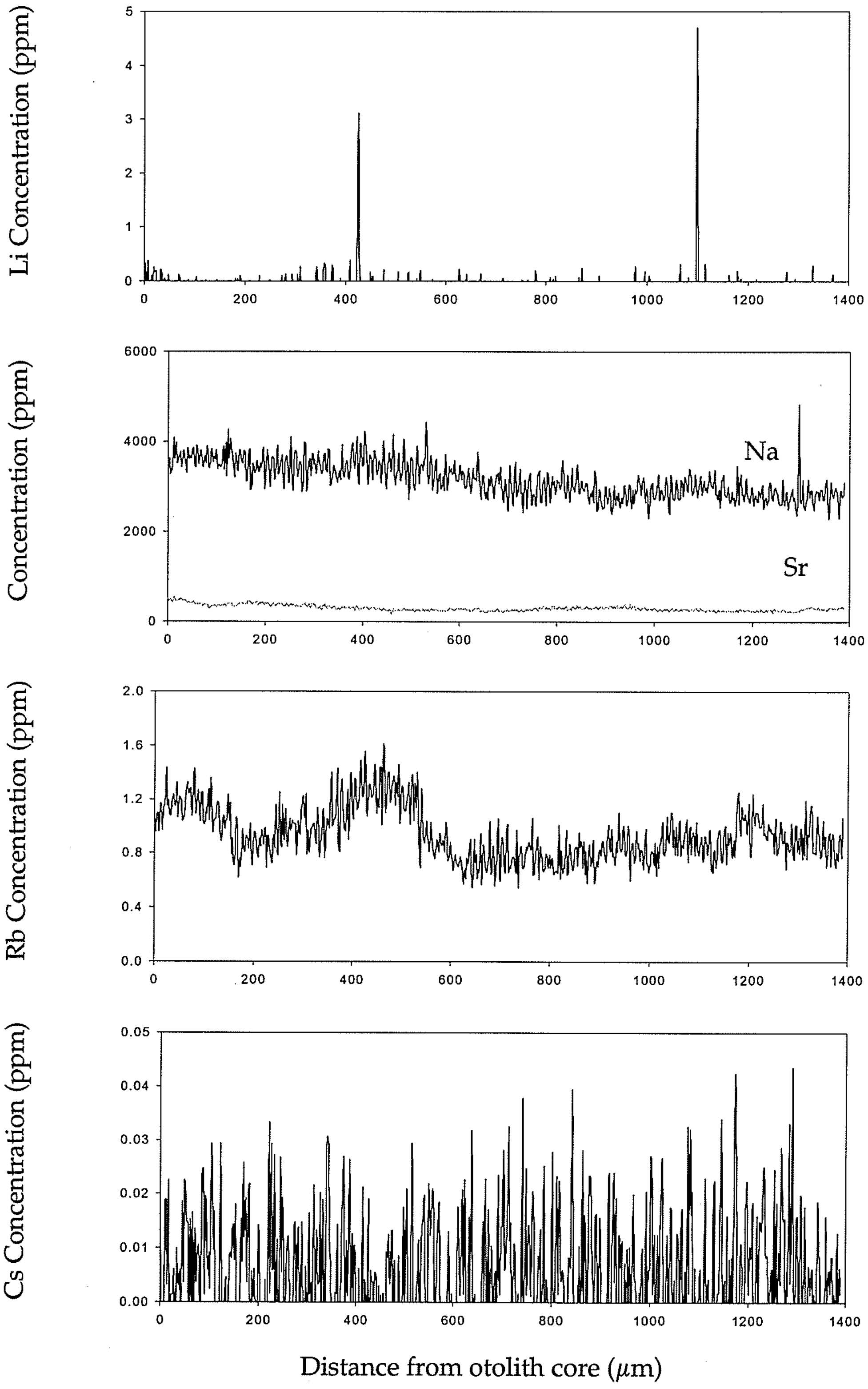
BooL07_01


Li Concentration (ppm)
0
1
2
3
4
Concentration (ppm)
0
2000
4000
6000
Na
Sr
Rb Concentration (ppm)
0
1
2
3
4
Cs Concentration (ppm)
0.00
0.02
0.04
0.06
0
200
400
600
800
1000
1200
1400
1600
1800
Distance from otolith core (μm)

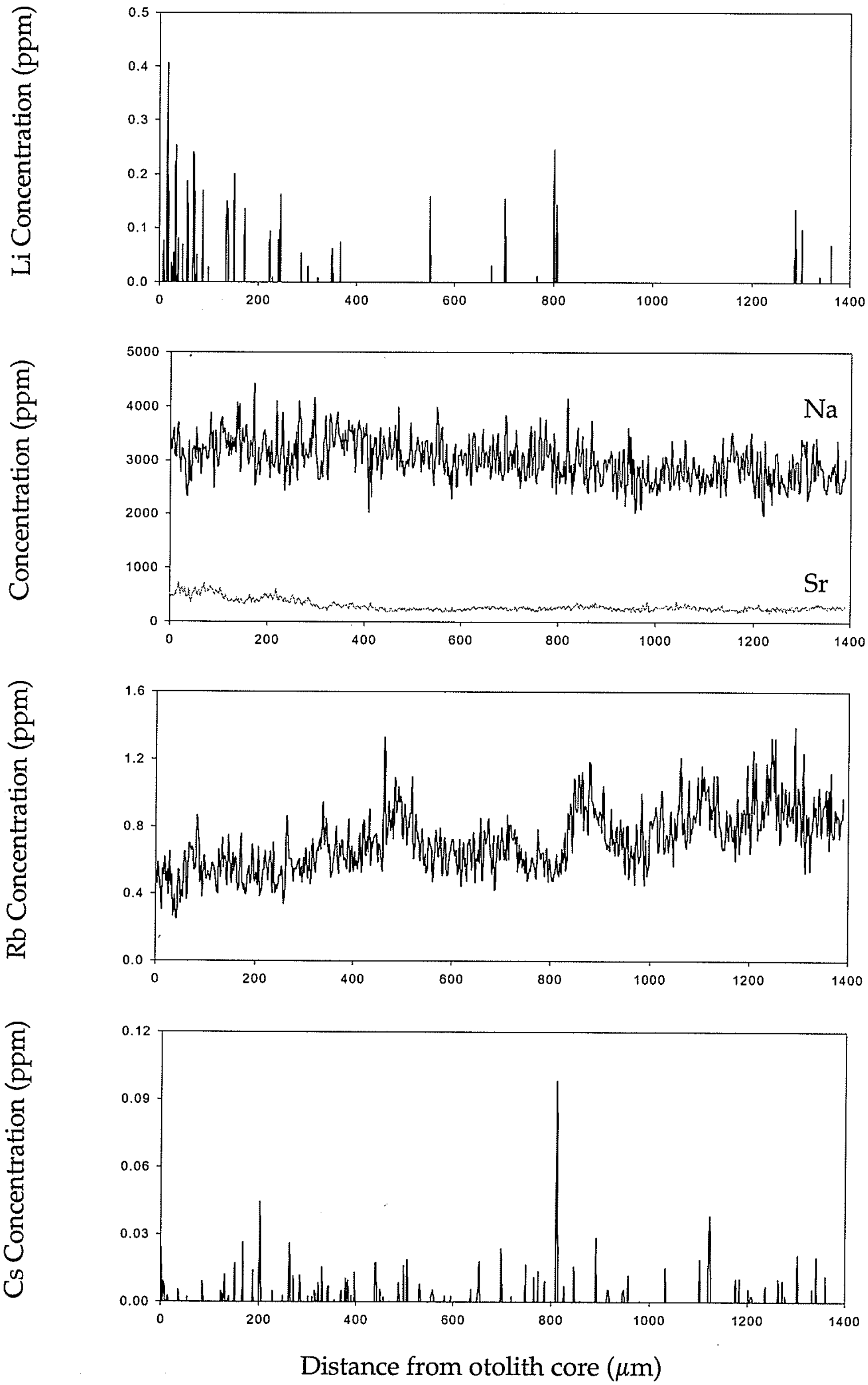
BooL07_02


Li Concentration (ppm)
0.5
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
1.5
1.2
0.9
0.6
0.3
0.0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.05
0.04
0.03
0.02
0.01
0.00
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

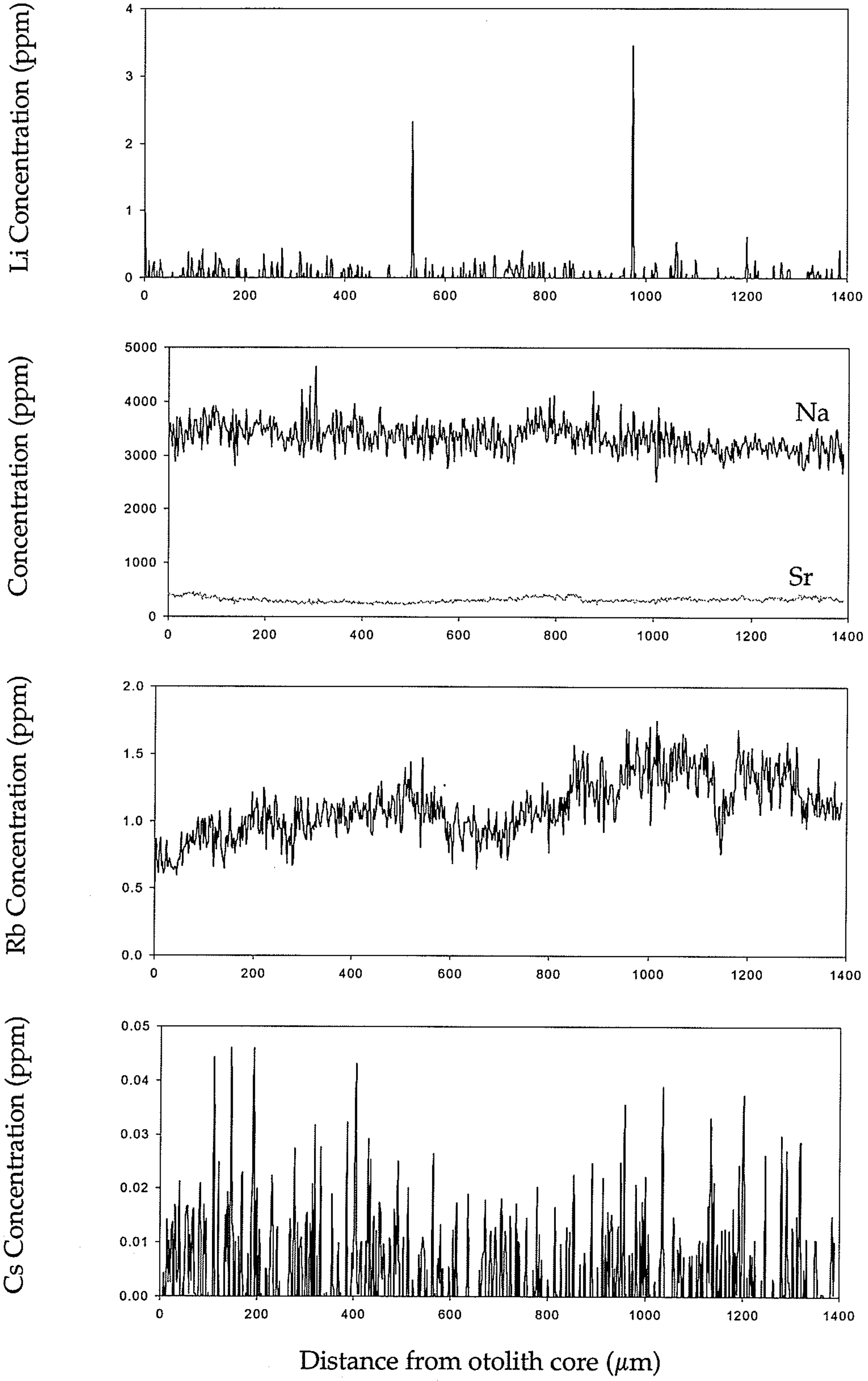
BooL07_03


Li Concentration (ppm)
5
4
3
2
1
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
6000
4000
2000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
2.0
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
0.05
0.04
0.03
0.02
0.01
0.00
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

BooL07_04

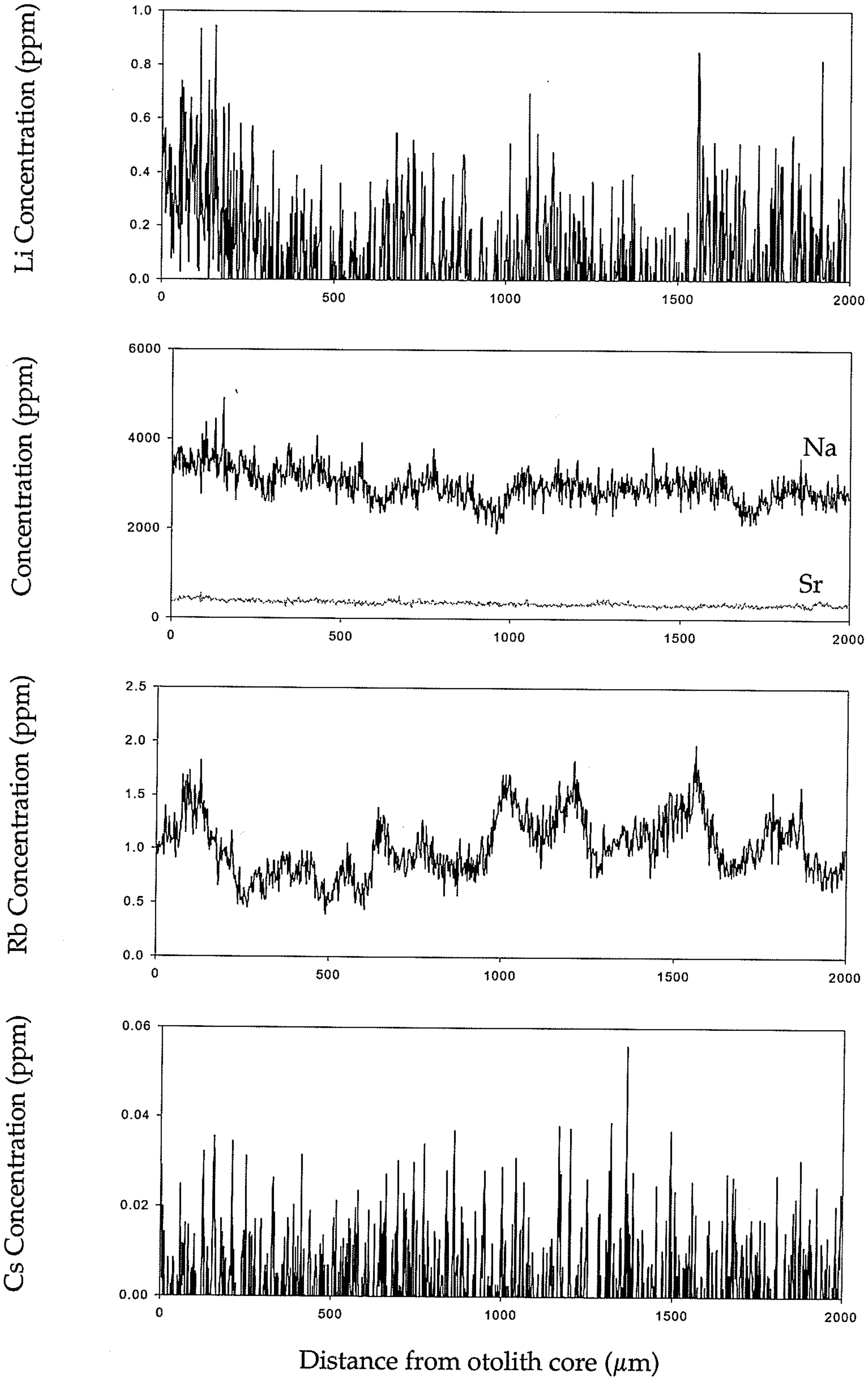

Li Concentration (ppm)
0.0
0.1
0.2
0.3
0.4
0.5
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
Rb Concentration (ppm)
0.0
0.4
0.8
1.2
1.6
Cs Concentration (ppm)
0.00
0.03
0.06
0.09
0.12
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

BooL07_05

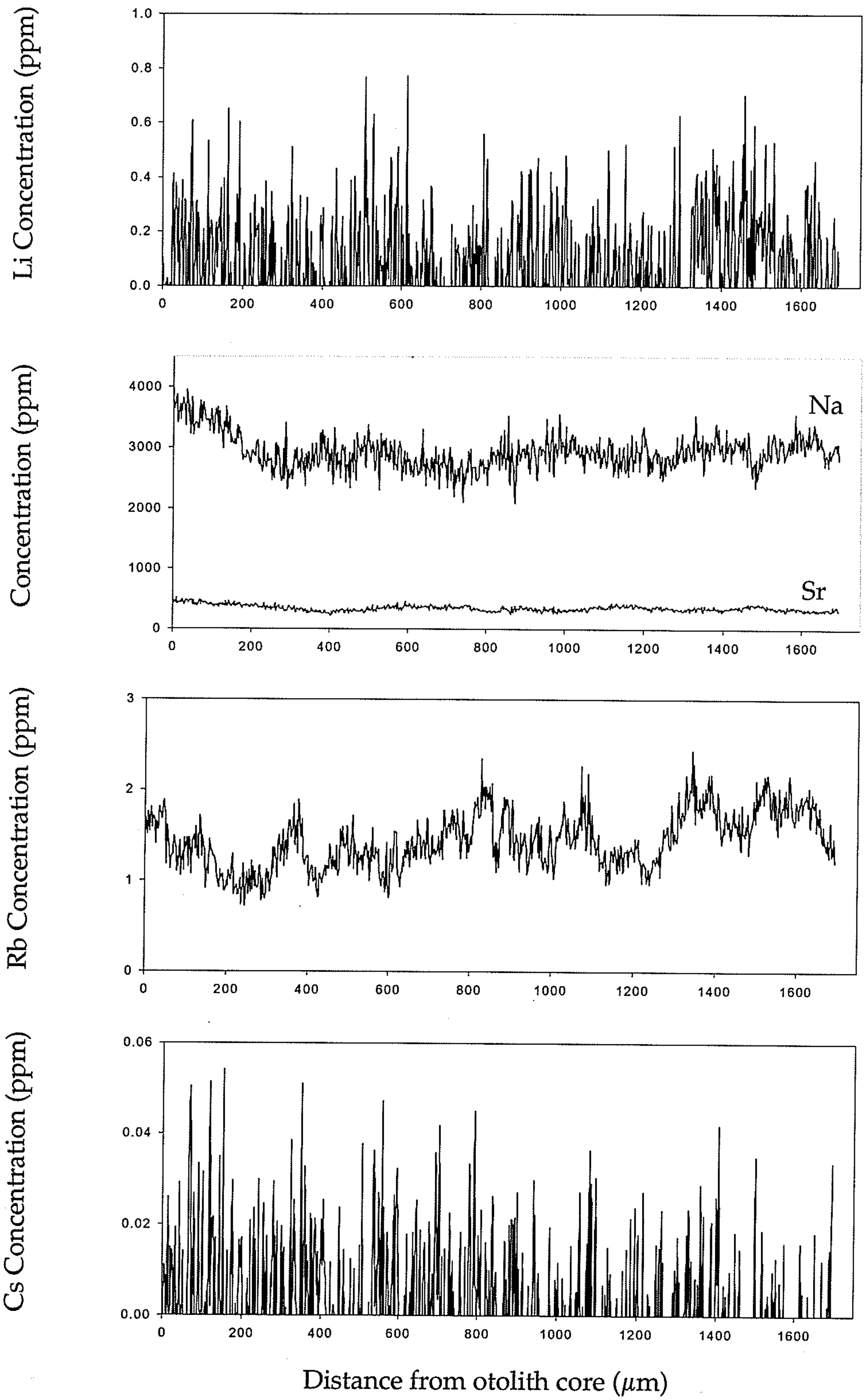


Li Concentration (ppm)
0
1
2
3
4
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
0.00
0.01
0.02
0.03
0.04
0.05
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

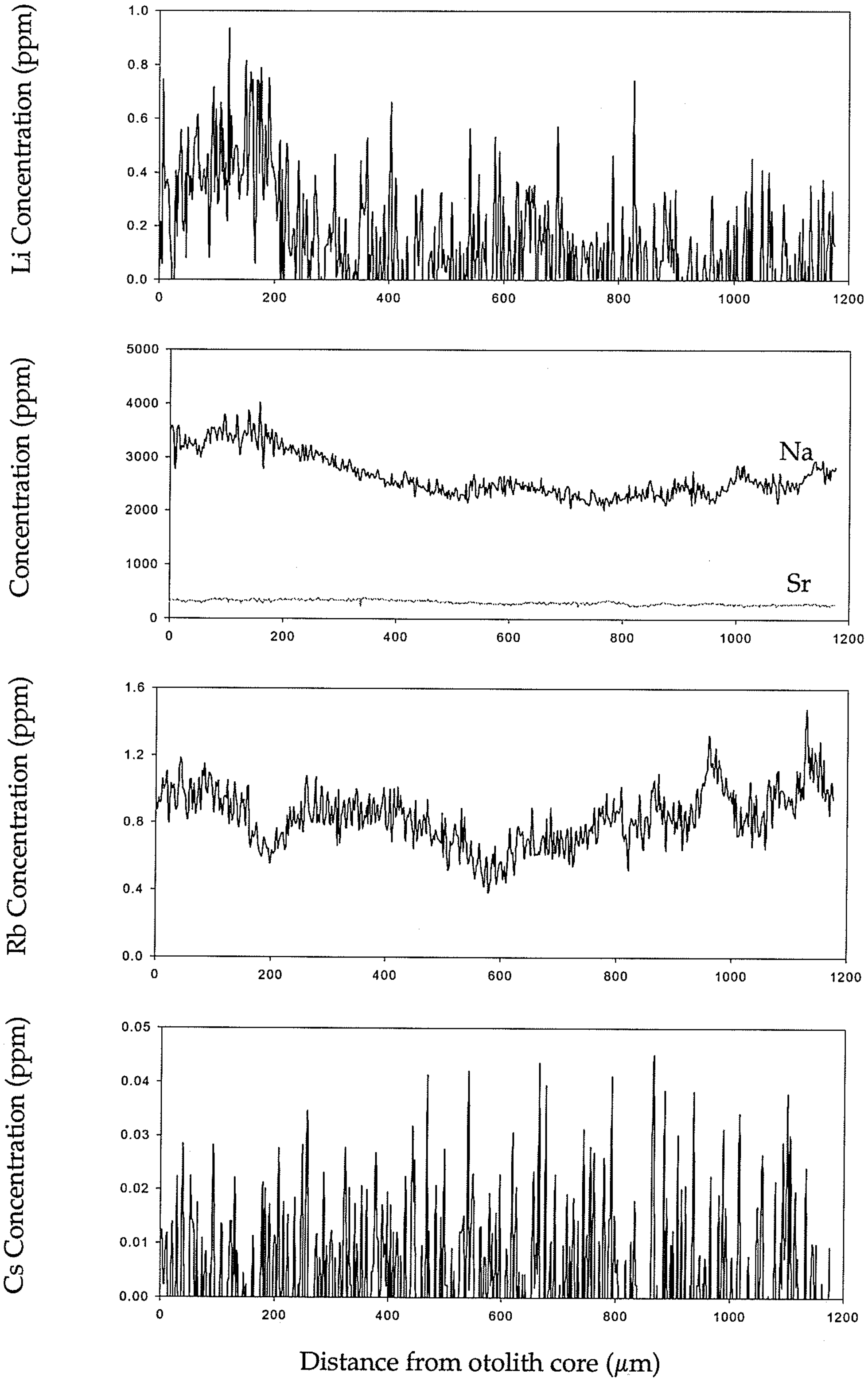
BooL07_06


Li Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500
2000
Concentration (ppm)
6000
4000
2000
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
Cs Concentration (ppm)
0.06
0.04
0.02
0.00
0
500
1000
1500
2000
Distance from otolith core (μm)

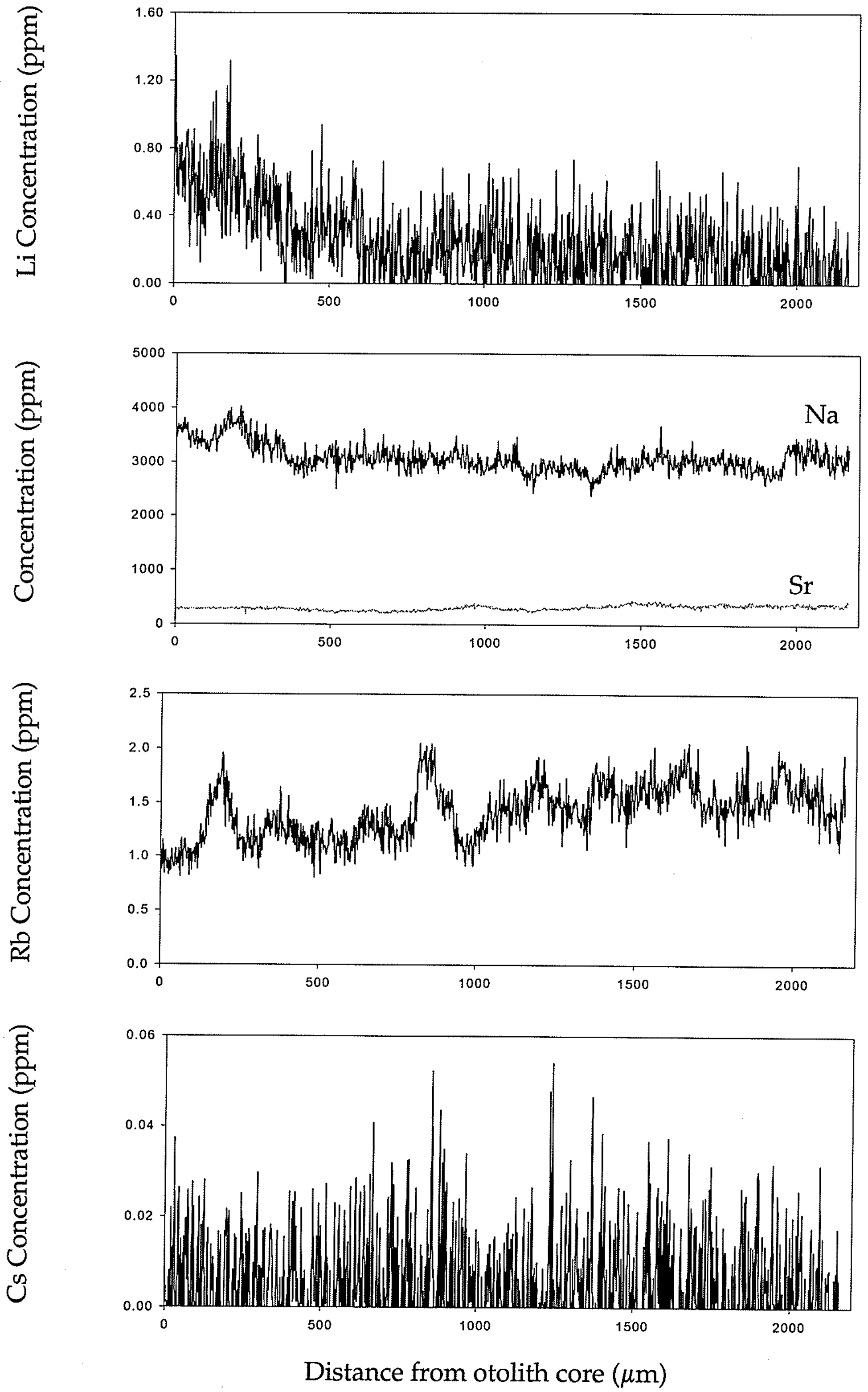
BooL07_07


Li Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
Rb Concentration (ppm)
3
2
1
0
0
200
400
600
800
1000
1200
1400
1600
Cs Concentration (ppm)
0.06
0.04
0.02
0.00
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

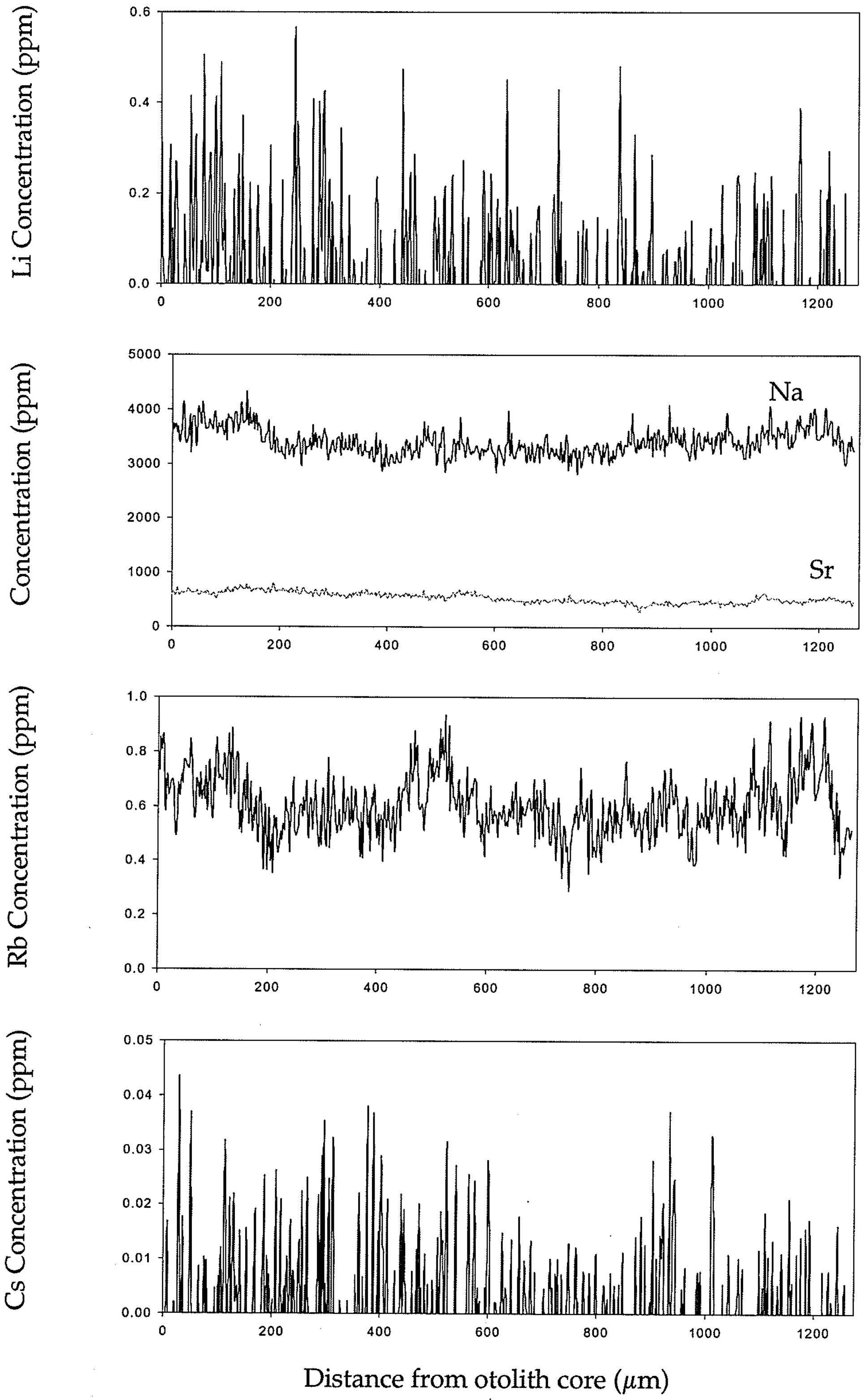
BooL07_08


Li Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.05
0.04
0.03
0.02
0.01
0.00
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

BooL07_09


Li Concentration (ppm)
1.60
1.20
0.80
0.40
0.00
0
500
1000
1500
2000
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
Cs Concentration (ppm)
0.06
0.04
0.02
0.00
0
500
1000
1500
2000
Distance from otolith core (μm)

BooL07_10


Li Concentration (ppm)
0.0
0.2
0.4
0.6
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
Rb Concentration (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
Cs Concentration (ppm)
0.00
0.01
0.02
0.03
0.04
0.05
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

Appendix C LA-ICP-MS data for Booster Lake otoliths *continued*

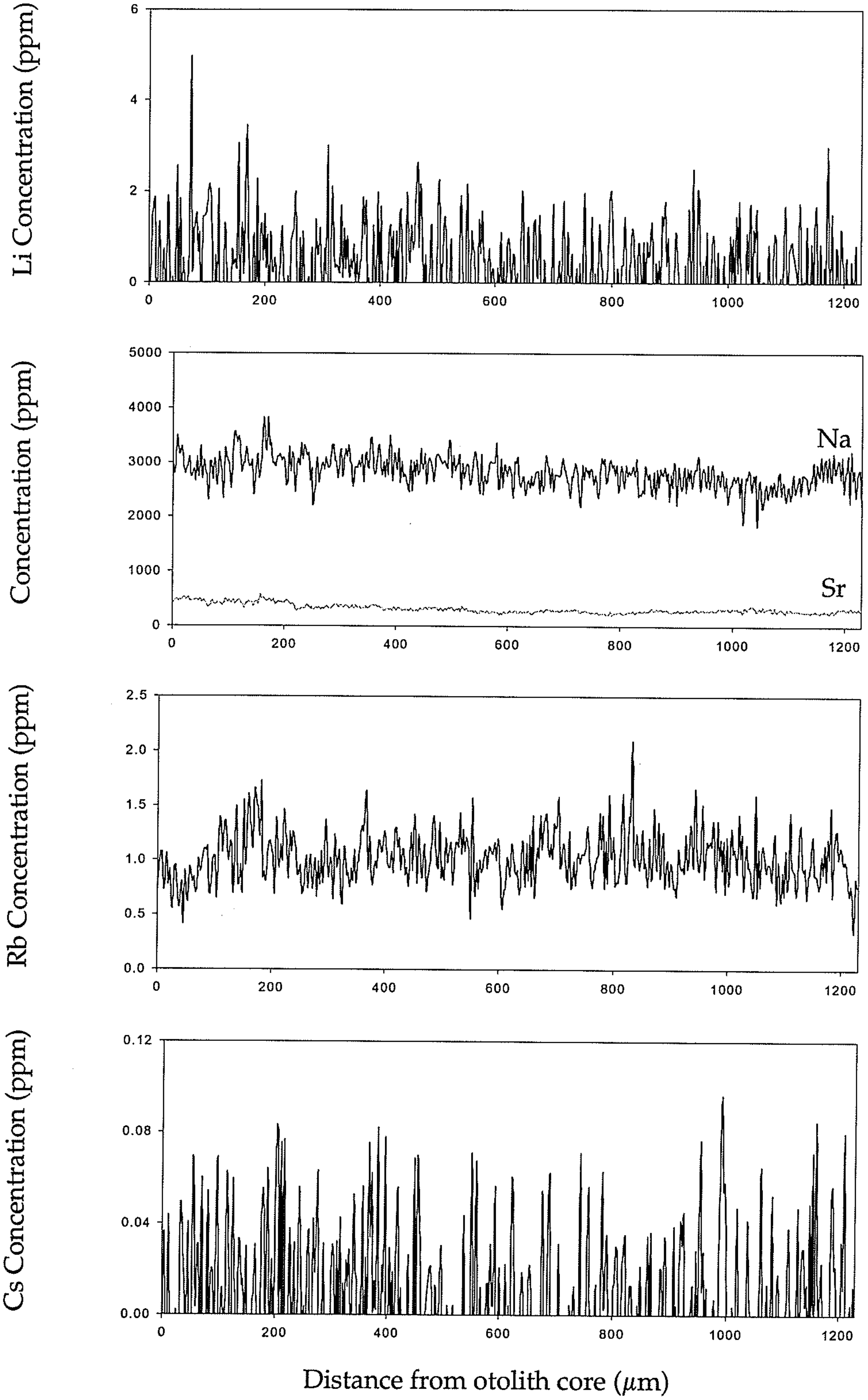
Species: Walleye (*Sander vitreus*), Northern Pike (*Esox lucius*), Small Mouth Bass (*Micropterus dolomieu*), Yellow Perch (*Perca flavescens*)

Captured: 2006

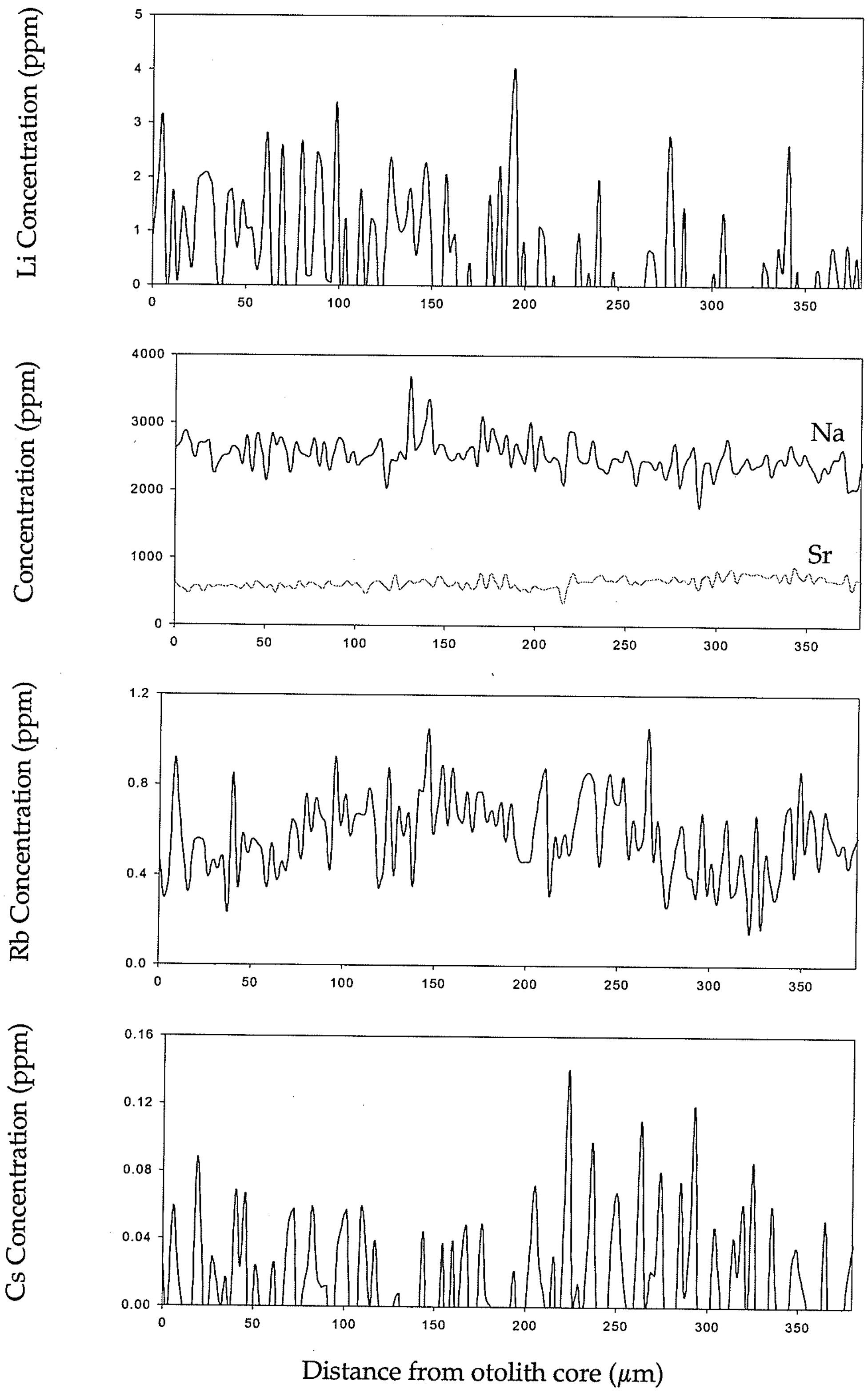
Isotopes: Li^{7}, Na^{23}, Rb^{85}, Sr^{88}, Cs^{133}

Sample Number	***Species***	***Age***
01	Northern Pike	8
03	Small Mouth Bass	4
04	Small Mouth Bass	6
05	Small Mouth Bass	6
06	Northern Pike	8
07	Walleye	6
08	Yellow Perch	5
09	Northern Pike	7
10	Small Mouth Bass	6

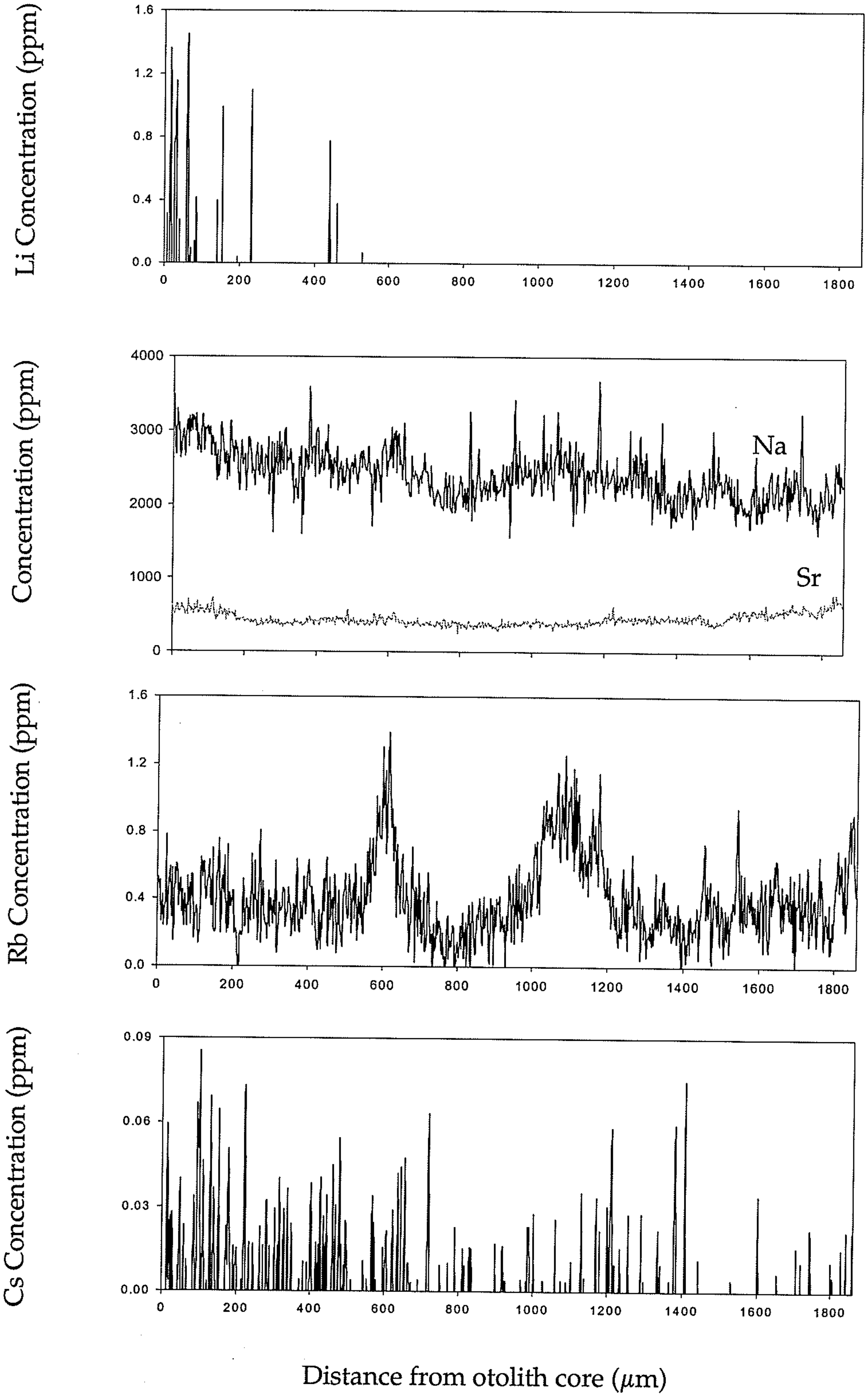
BooL06_01


Li Concentration (ppm)
6
4
2
0
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

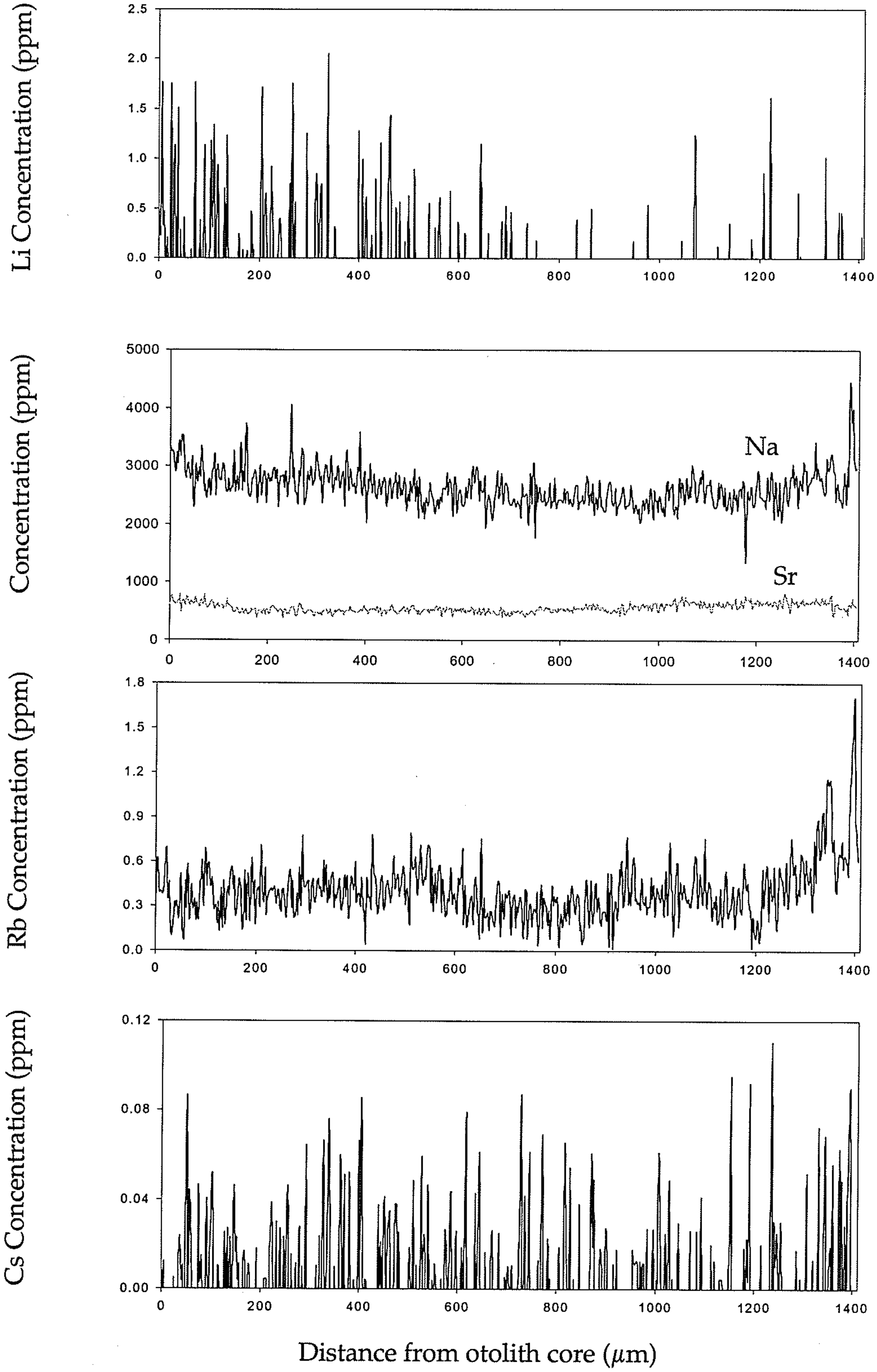
BooL06_03


Li Concentration (ppm)
0
1
2
3
4
5
Concentration (ppm)
0
1000
2000
3000
4000
Na
Sr
Rb Concentration (ppm)
0.0
0.4
0.8
1.2
Cs Concentration (ppm)
0.00
0.04
0.08
0.12
0.16
0
50
100
150
200
250
300
350
Distance from otolith core (μm)

BooL06_04

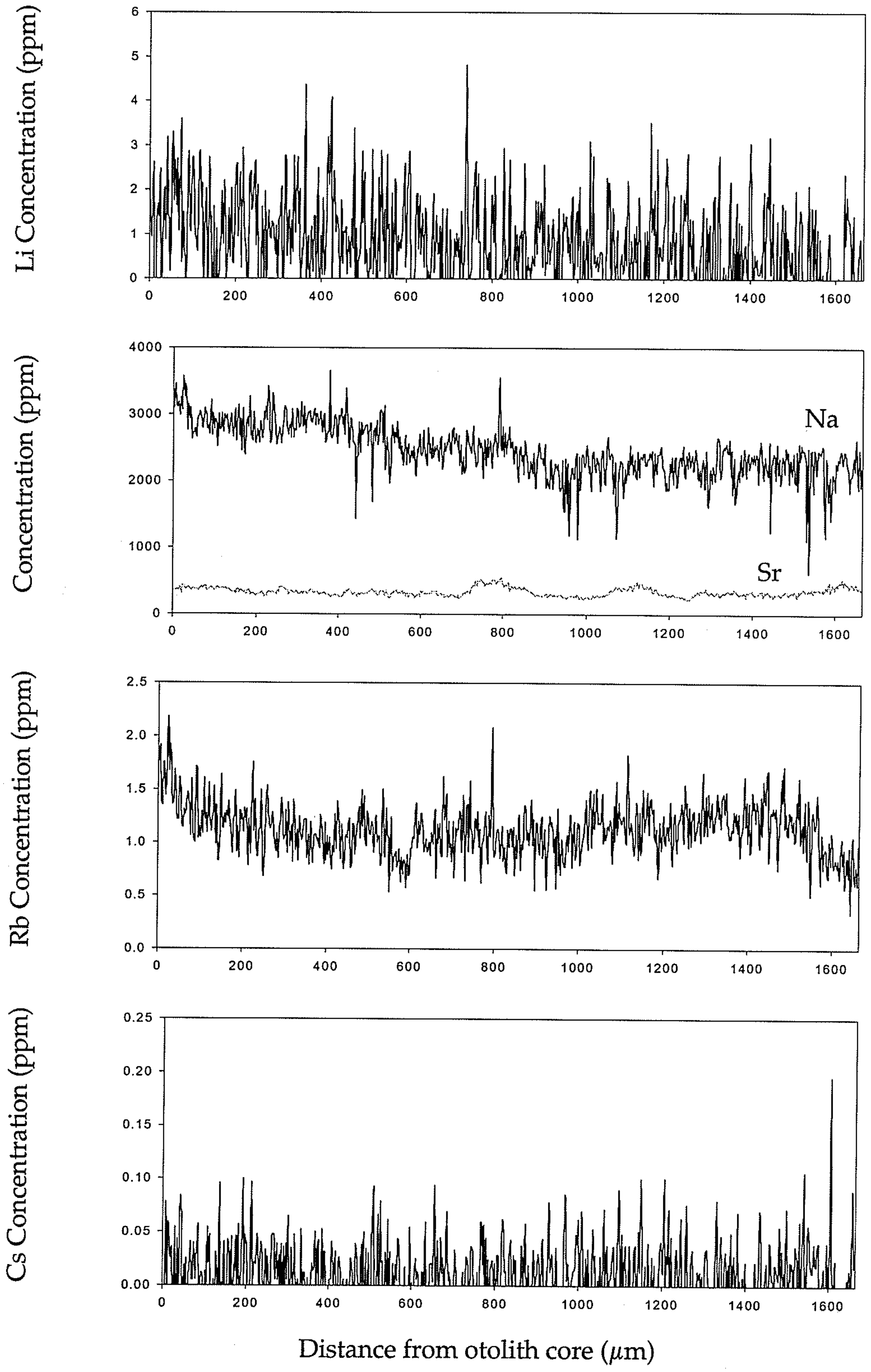

Li Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
Cs Concentration (ppm)
0.09
0.06
0.03
0.00
0
200
400
600
800
1000
1200
1400
1600
1800
Distance from otolith core (μm)

BooL06_05



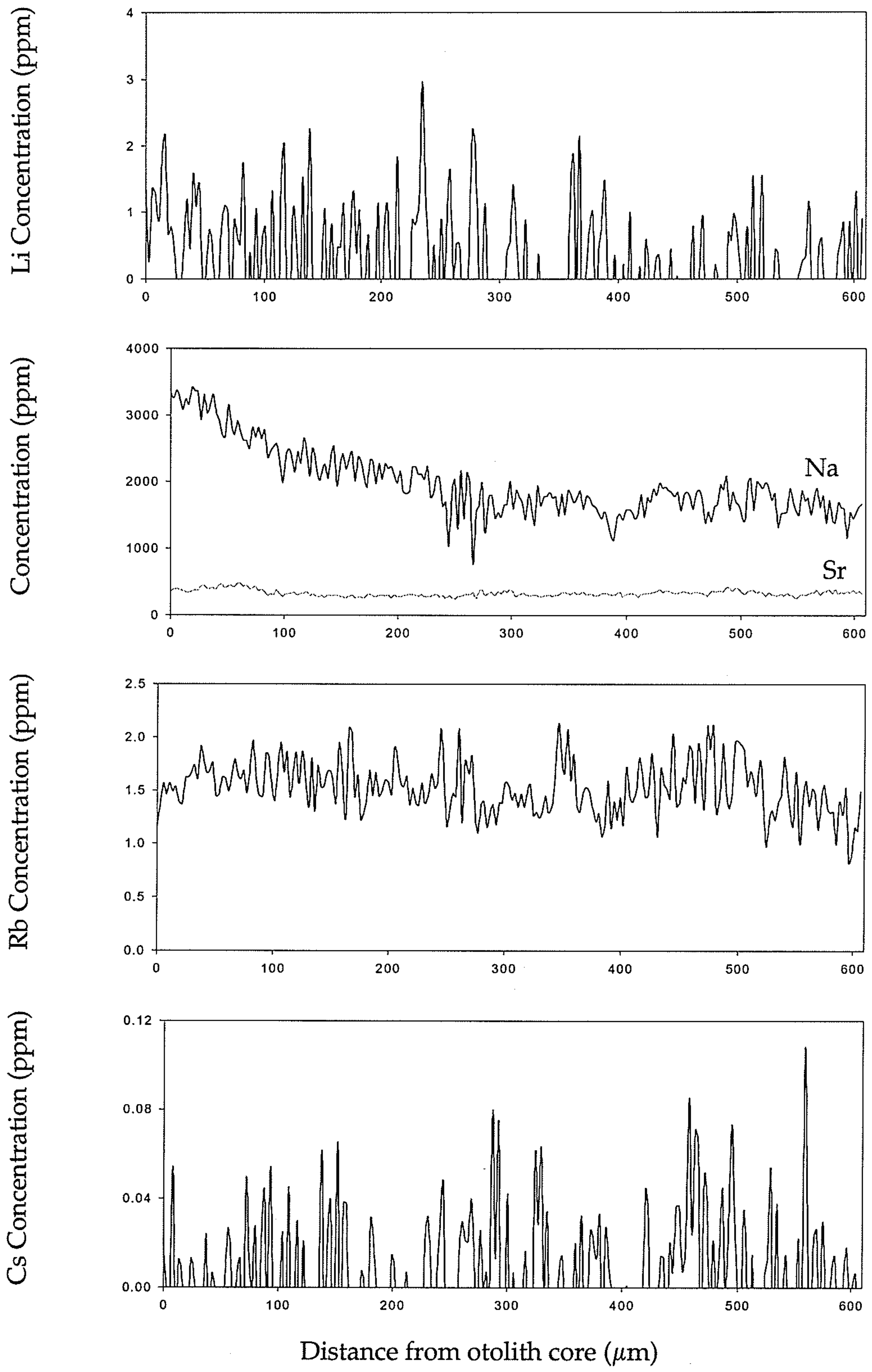
Li Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
Rb Concentration (ppm)
0.0
0.3
0.6
0.9
1.2
1.5
1.8
Cs Concentration (ppm)
0.00
0.04
0.08
0.12
0
200
400
600
800
1000
1200
1400
Distance from otolith core (µm)

BooL06_06



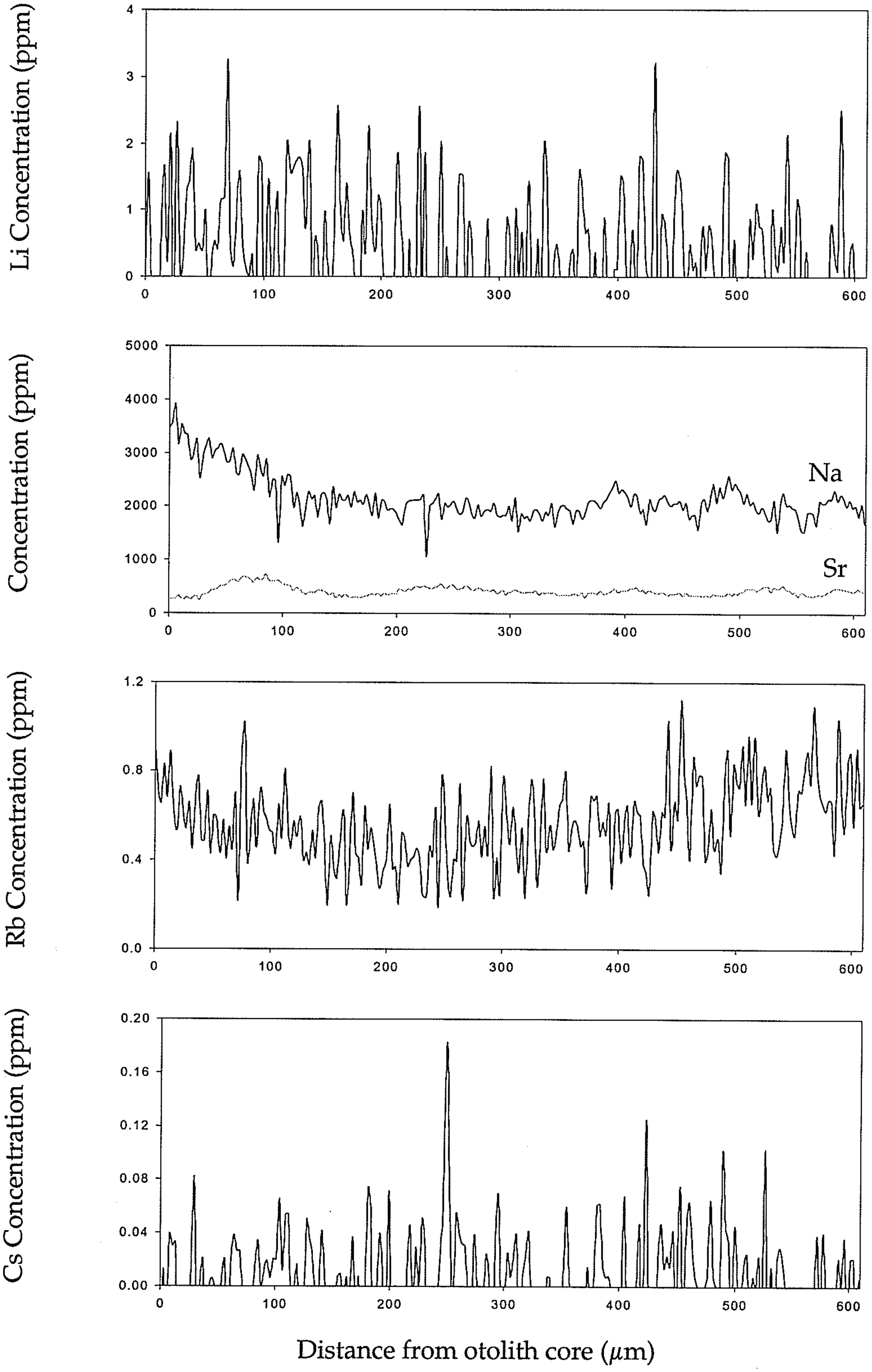
Li Concentration (ppm)
0
1
2
3
4
5
6
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
0
1000
2000
3000
4000
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
0
200
400
600
800
1000
1200
1400
1600
Cs Concentration (ppm)
0.00
0.05
0.10
0.15
0.20
0.25
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

BooL06_07

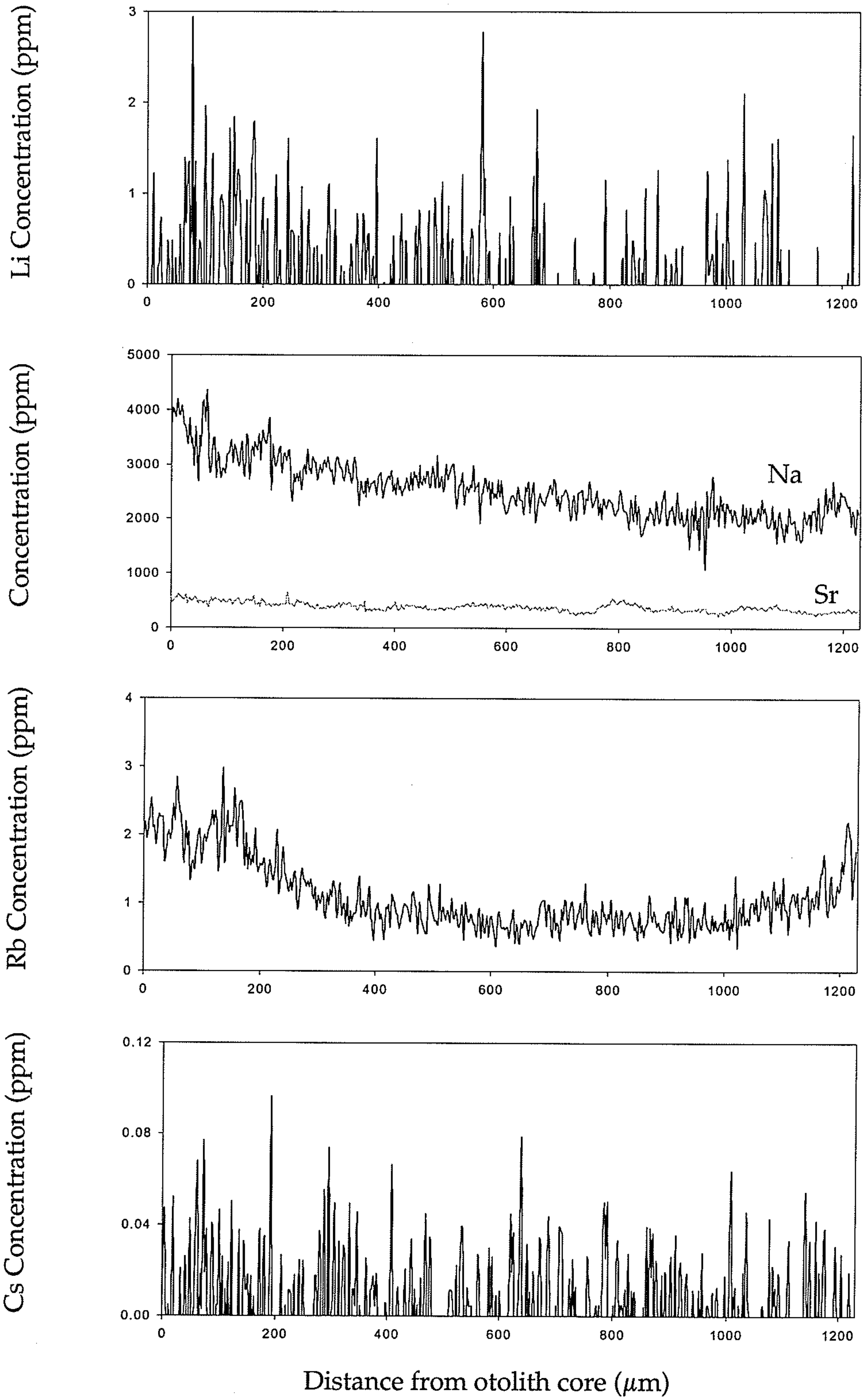


Li Concentration (ppm)
4
3
2
1
0
0
100
200
300
400
500
600
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
0
100
200
300
400
500
600
Distance from otolith core (μm)

BooL06_08

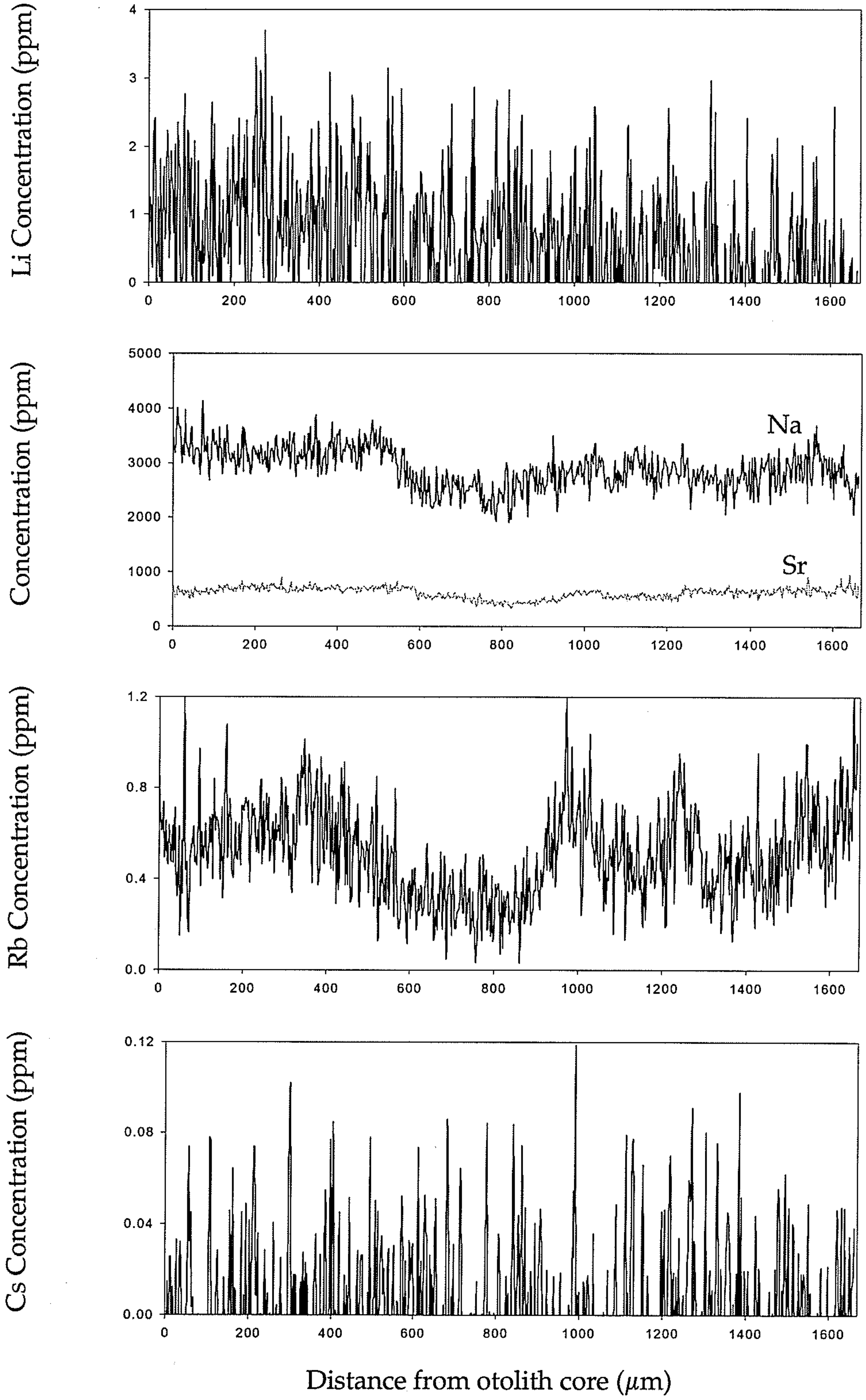

Li Concentration (ppm)
0
1
2
3
4
0
100
200
300
400
500
600
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
100
200
300
400
500
600
Rb Concentration (ppm)
0.0
0.4
0.8
1.2
0
100
200
300
400
500
600
Cs Concentration (ppm)
0.00
0.04
0.08
0.12
0.16
0.20
0
100
200
300
400
500
600
Distance from otolith core (μm)

BooL06_09



Li Concentration (ppm)
0
1
2
3
0
200
400
600
800
1000
1200
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
0
1
2
3
4
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.00
0.04
0.08
0.12
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

BooL06_10


Li Concentration (ppm)
0
1
2
3
4
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
Rb Concentration (ppm)
0.0
0.4
0.8
1.2
Cs Concentration (ppm)
0.00
0.04
0.08
0.12
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

Appendix C LA-ICP-MS data for Booster Lake otoliths *continued*

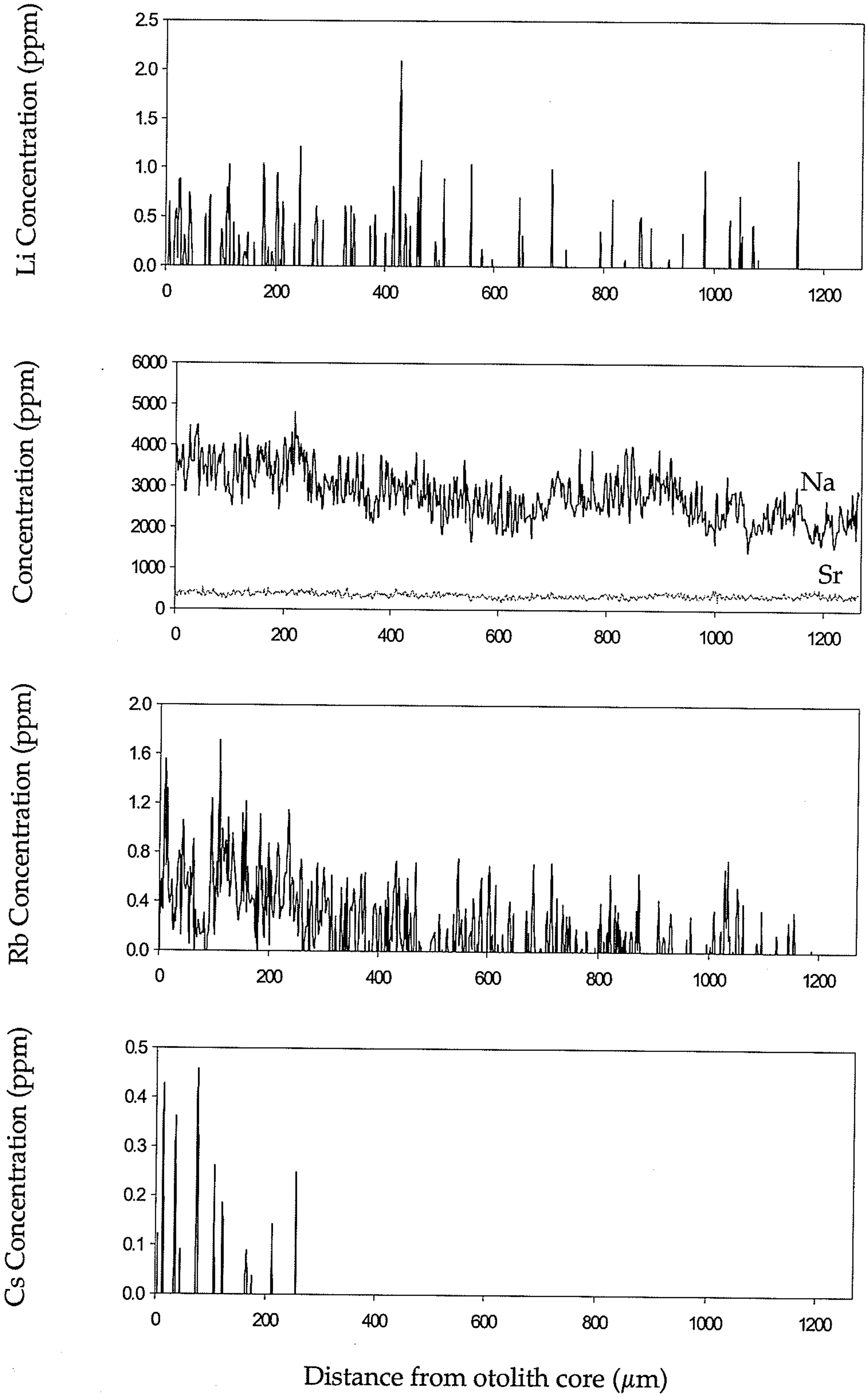
Species: Walleye (*Sander vitreus*)

Captured: 2004 (Manitoba Conservation Archives)

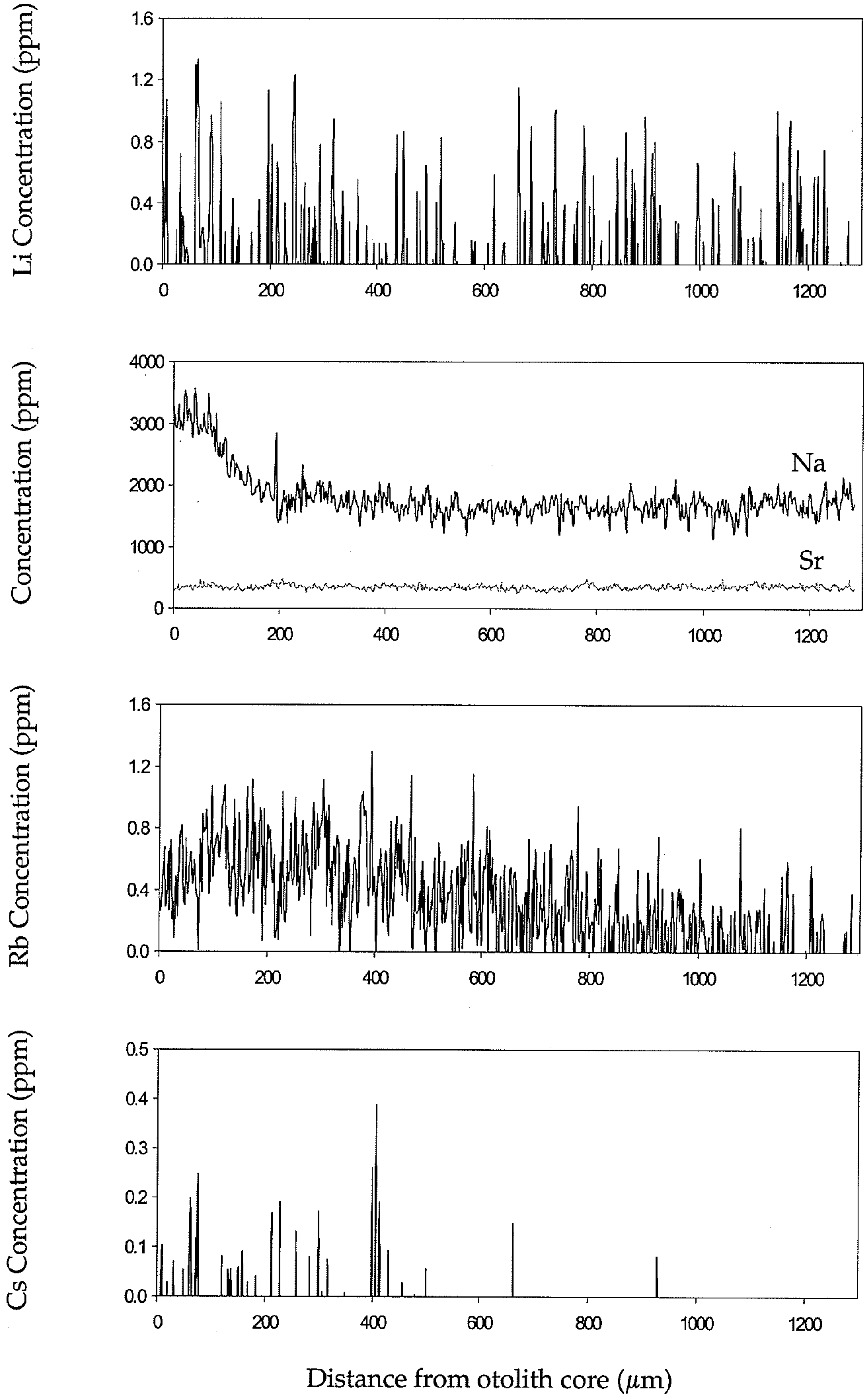
Isotopes: Li^{7}, Na^{23}, Rb^{85}, Sr^{88}, Cs^{133}

Sample Number	***Species***	***Age***
10	Walleye	8
14	Walleye	22
15	Walleye	7
16	Walleye	17
17	Walleye	10

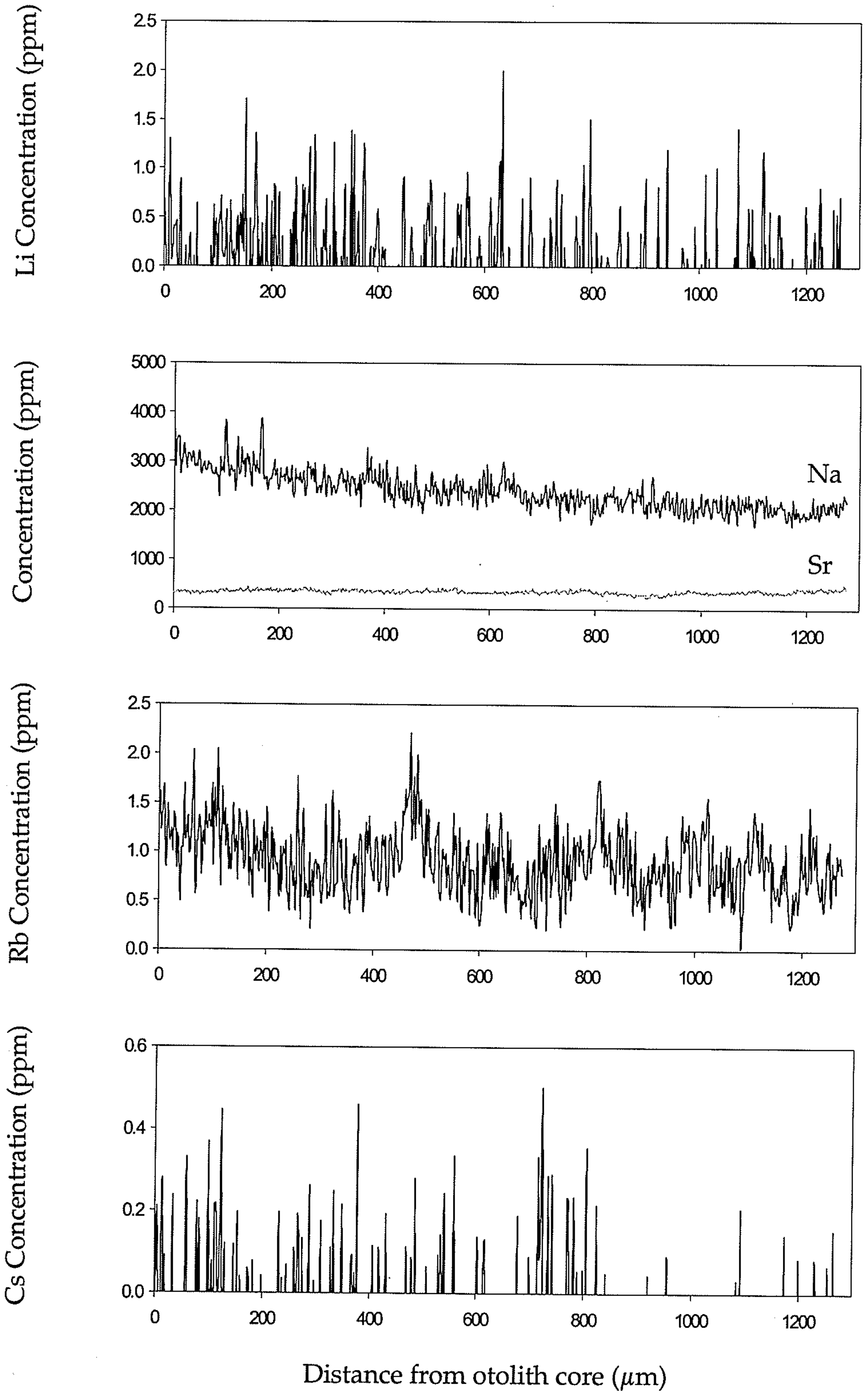
BooL04_10


Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
2.0
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.5
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

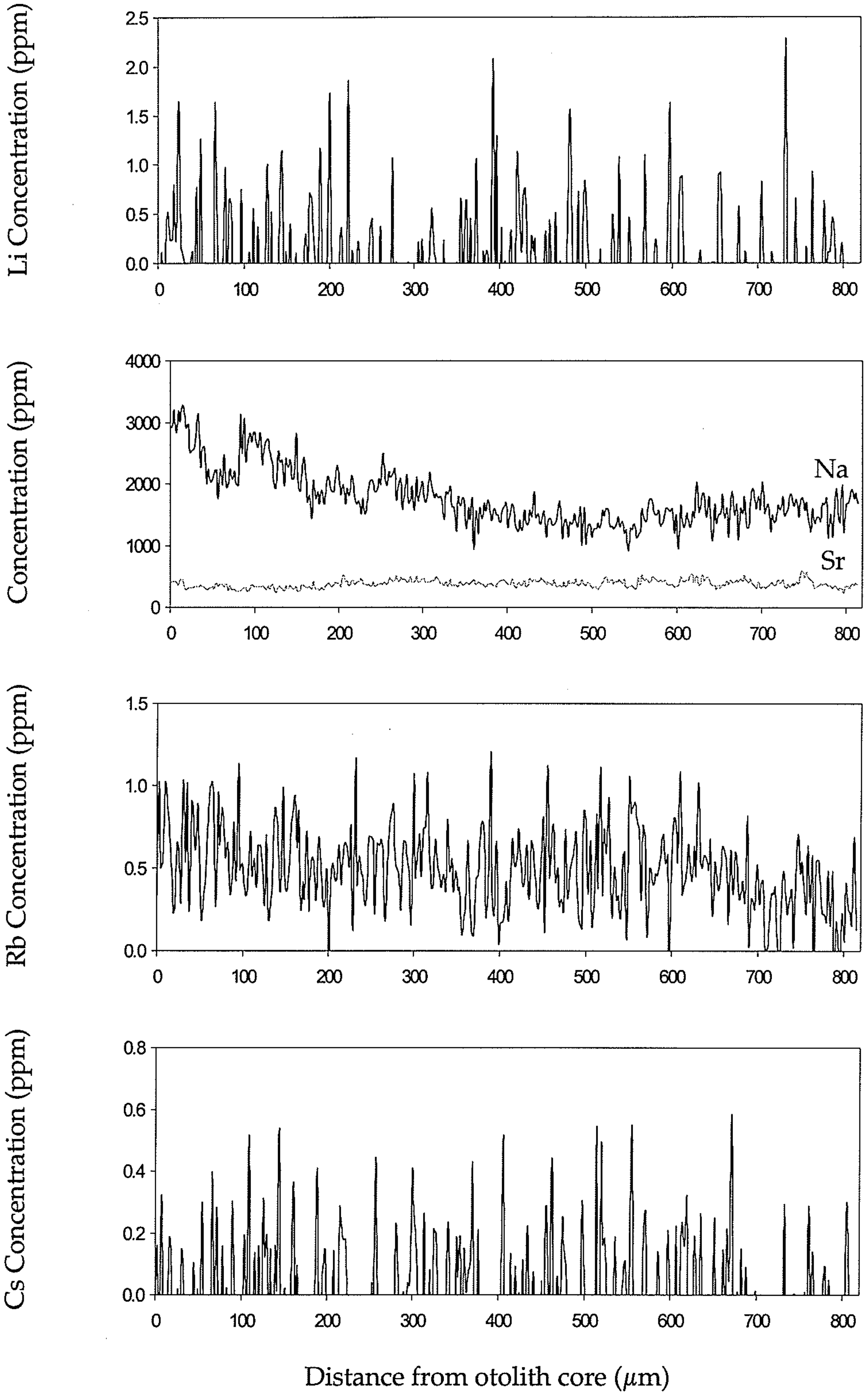
BooL04_14


Li Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
Cs Concentration (ppm)
0.5
0.4
0.3
0.2
0.1
0.0
Distance from otolith core (μm)

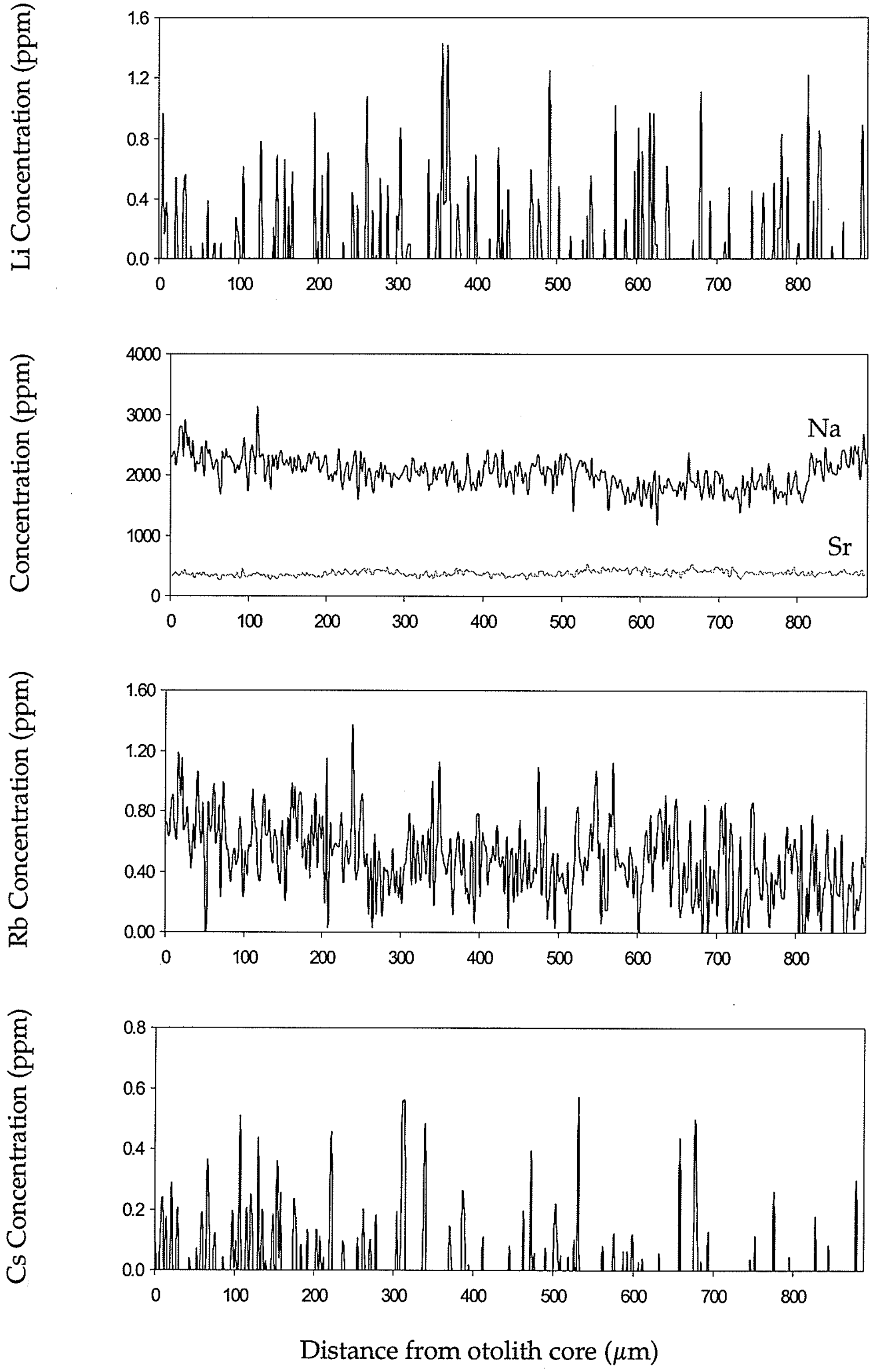
BooL04_15


Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

BooL04_16


Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
800
Rb Concentration (ppm)
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
Cs Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

BooL04_17


Li Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
800
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
800
Rb Concentration (ppm)
1.60
1.20
0.80
0.40
0.00
0
100
200
300
400
500
600
700
800
Cs Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

Appendix C LA-ICP-MS data for Booster Lake otoliths *continued*

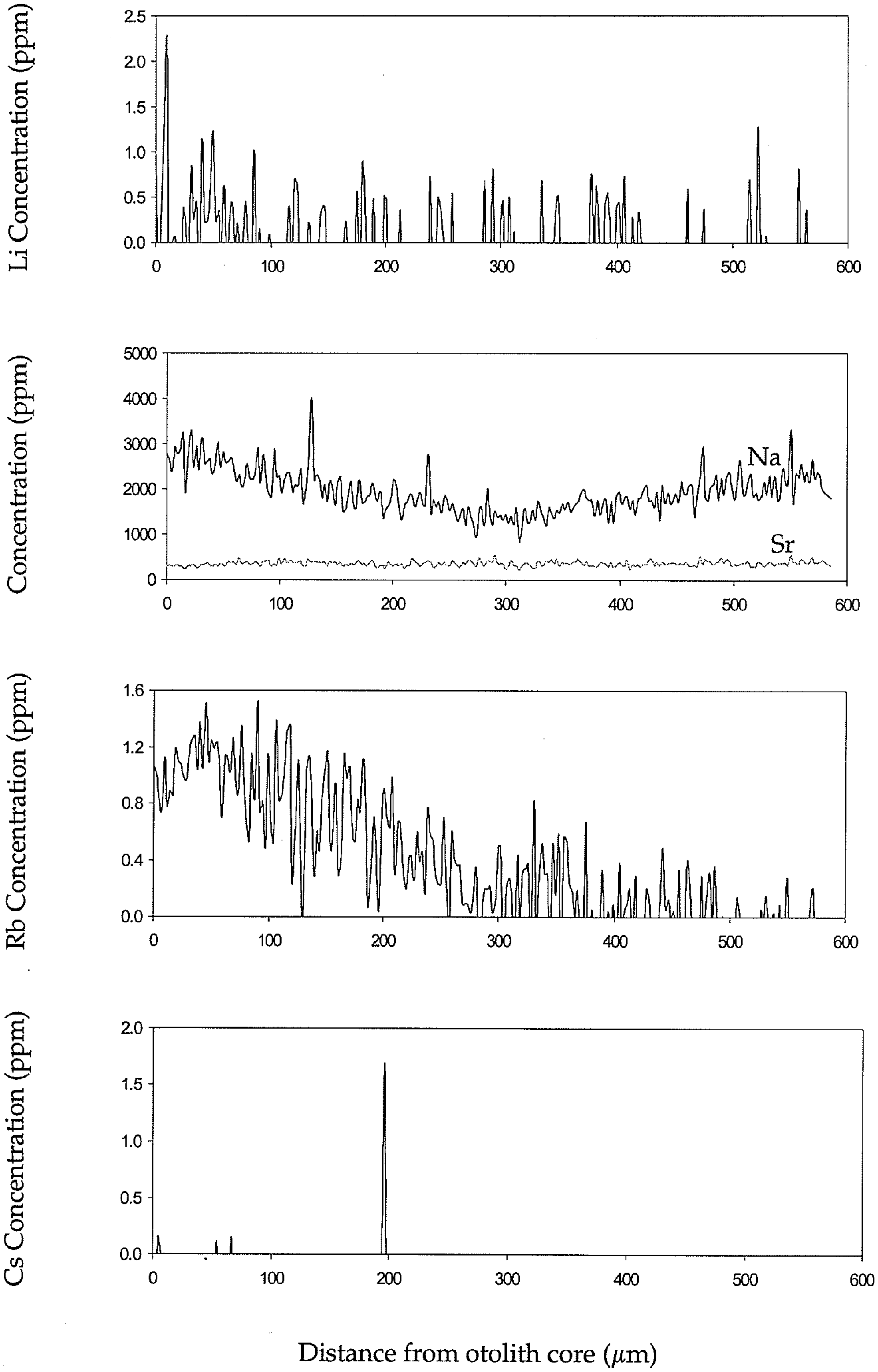
Species: Walleye (*Sander vitreus*)

Captured: 1995 (Manitoba Conservation Archives)

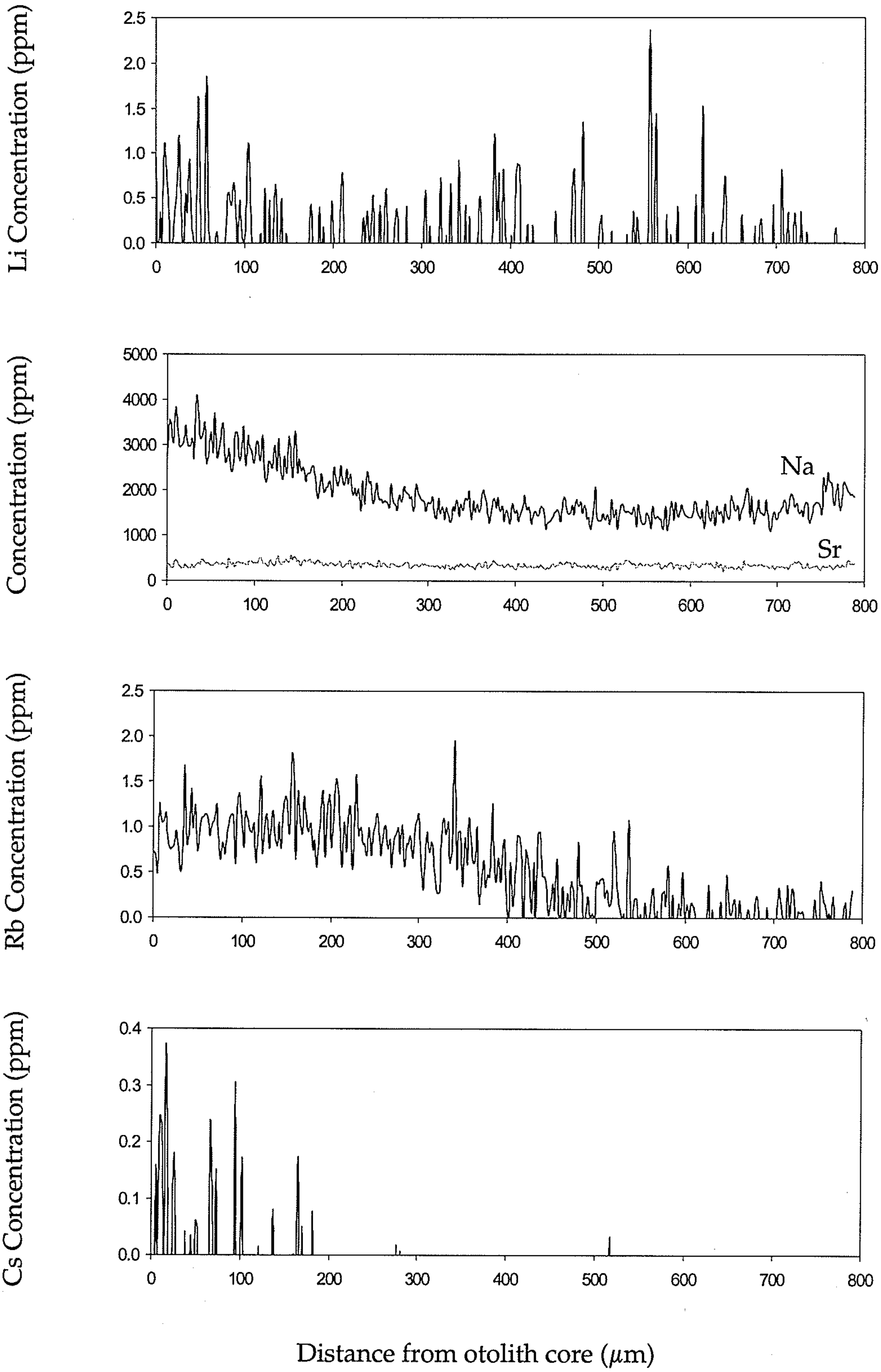
Isotopes: Li^{7}, Na^{23}, Rb^{85}, Sr^{88}, Cs^{133}

Sample Number	***Species***	***Age***
10	Walleye	6
11	Walleye	8
12	Walleye	5
38	Walleye	5
41	Walleye	6
42	Walleye	5

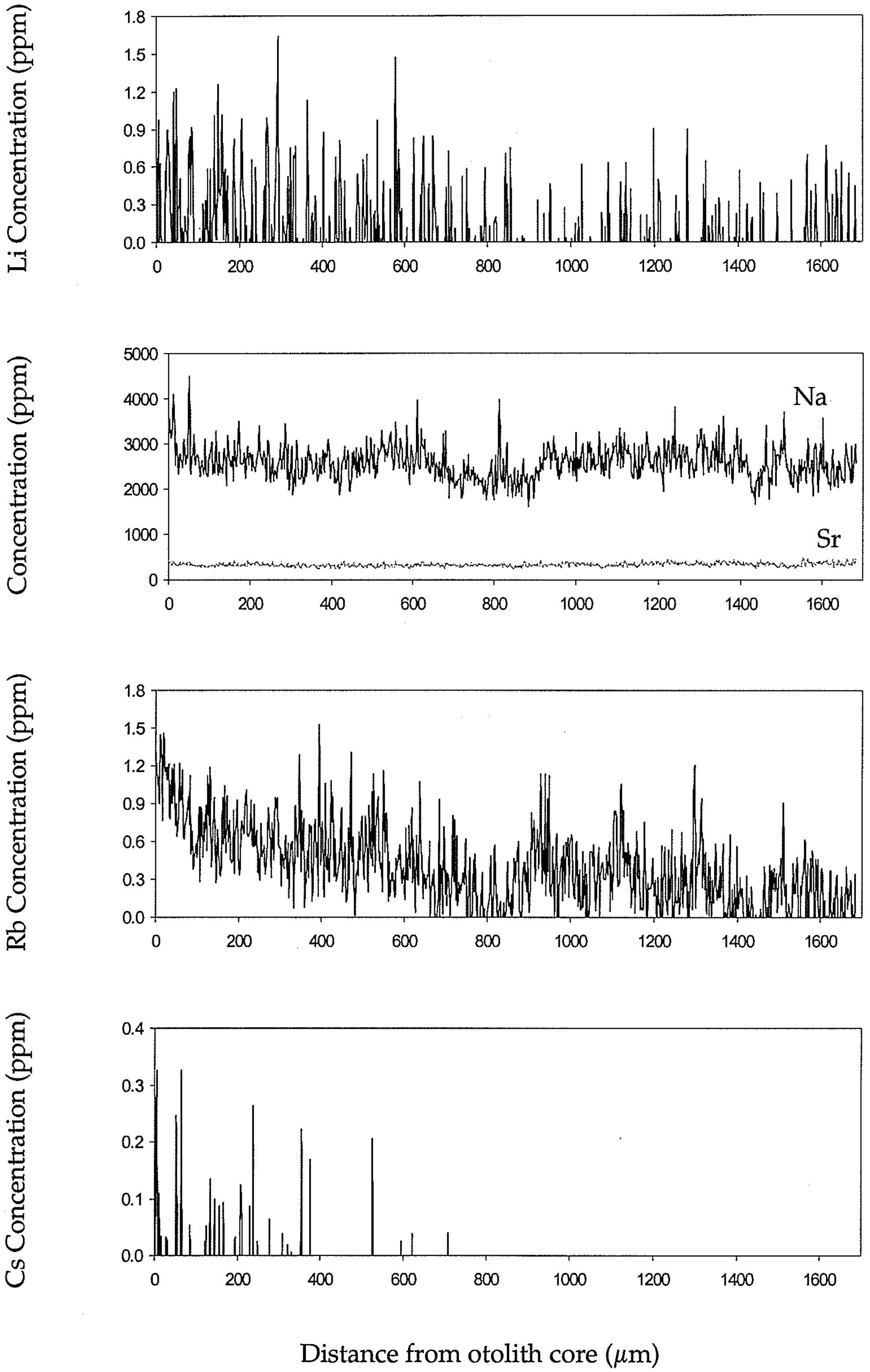
BooL95_10


Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
Cs Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
Distance from otolith core (μm)

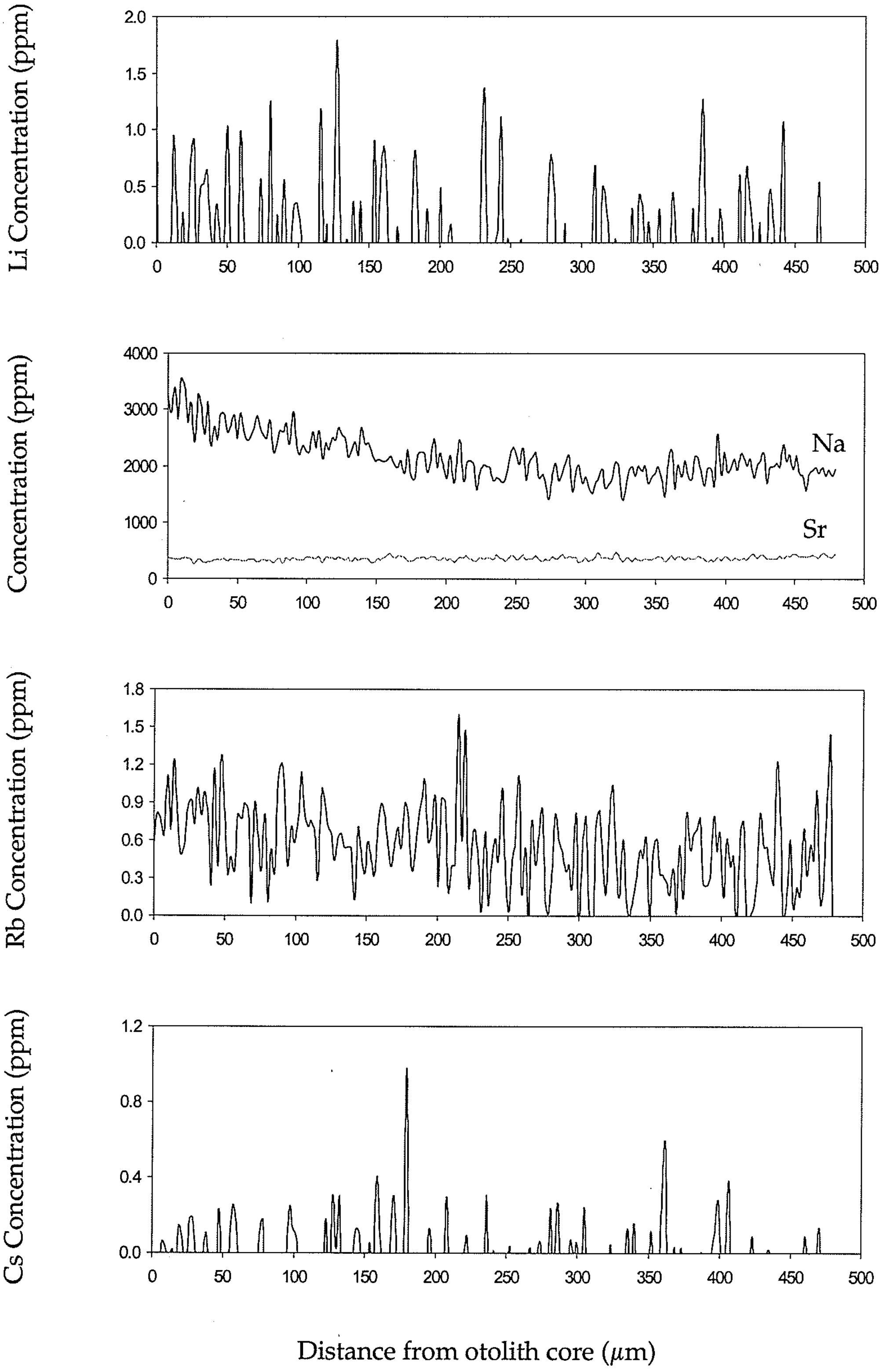
BooL95_11


Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
800
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
Cs Concentration (ppm)
0.4
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

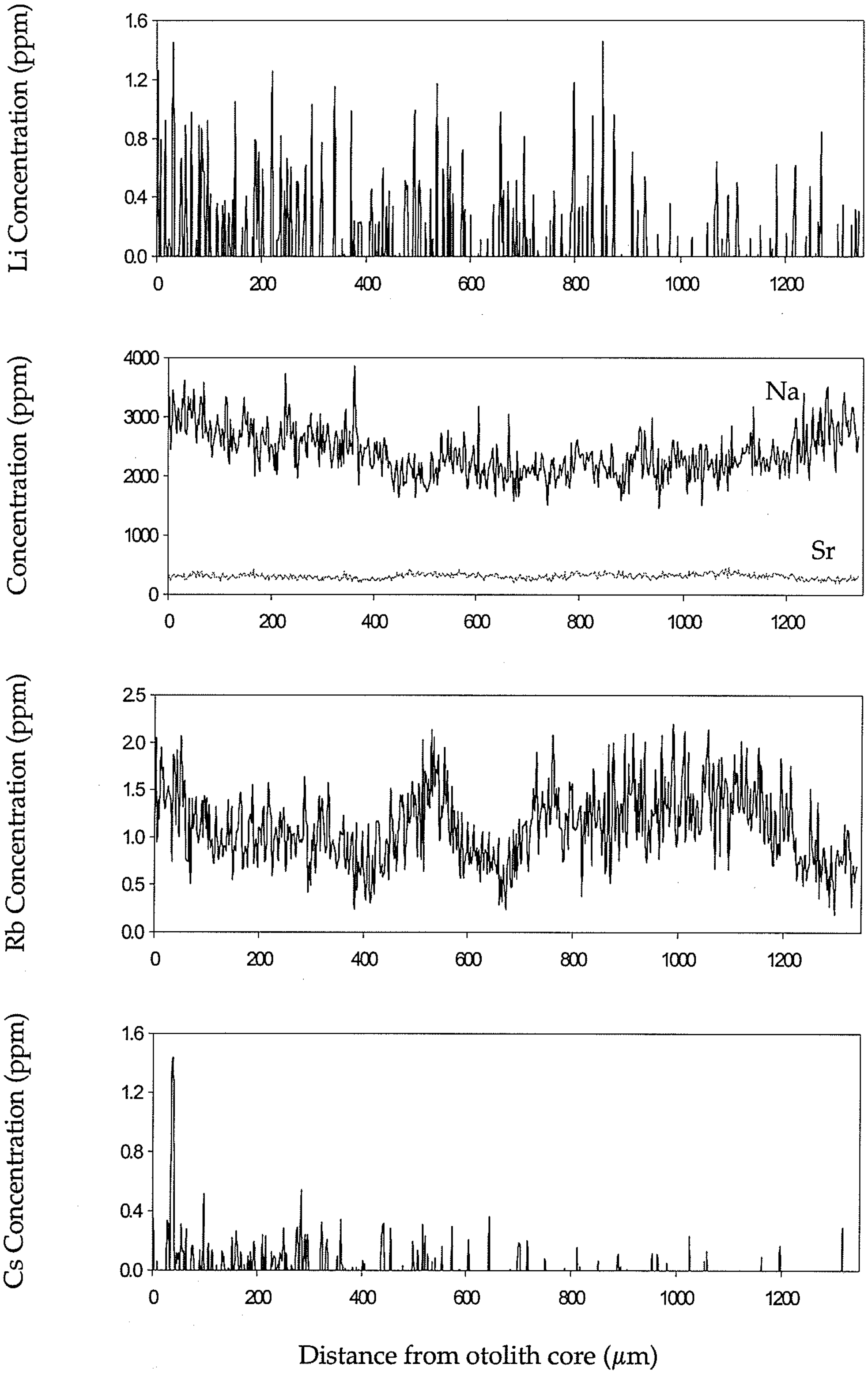
BooL95_12


Li Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
Cs Concentration (ppm)
0.4
0.3
0.2
0.1
0.0
Distance from otolith core (μm)

BooL95_38

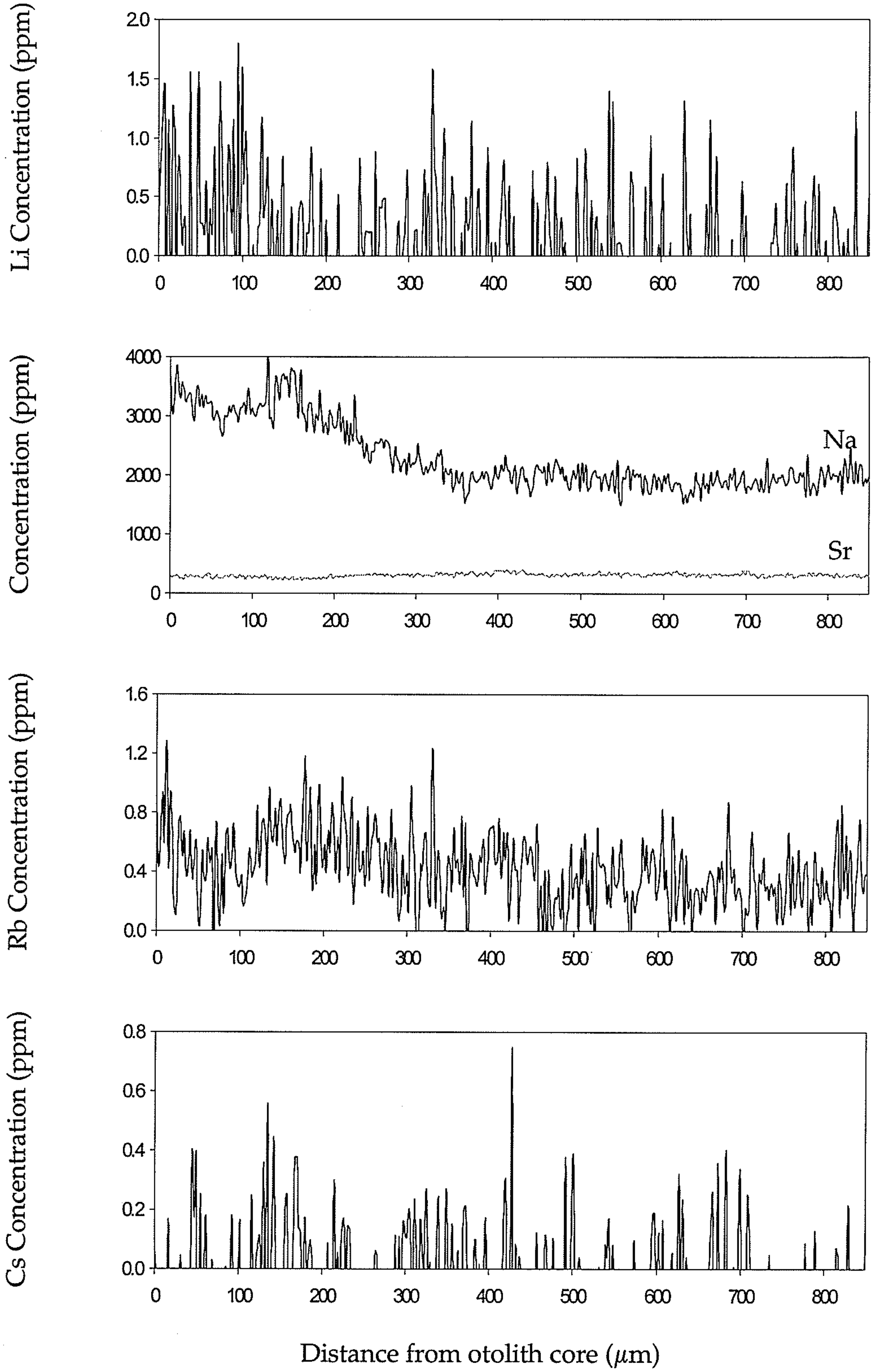

Li Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
50
100
150
200
250
300
350
400
450
500
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
Cs Concentration (ppm)
1.2
0.8
0.4
0.0
Distance from otolith core (μm)

BooL95_41



Li Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

BooL95_42


Li Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
800
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
800
Cs Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

Appendix D LA-ICP-MS data for Birse Lake otoliths

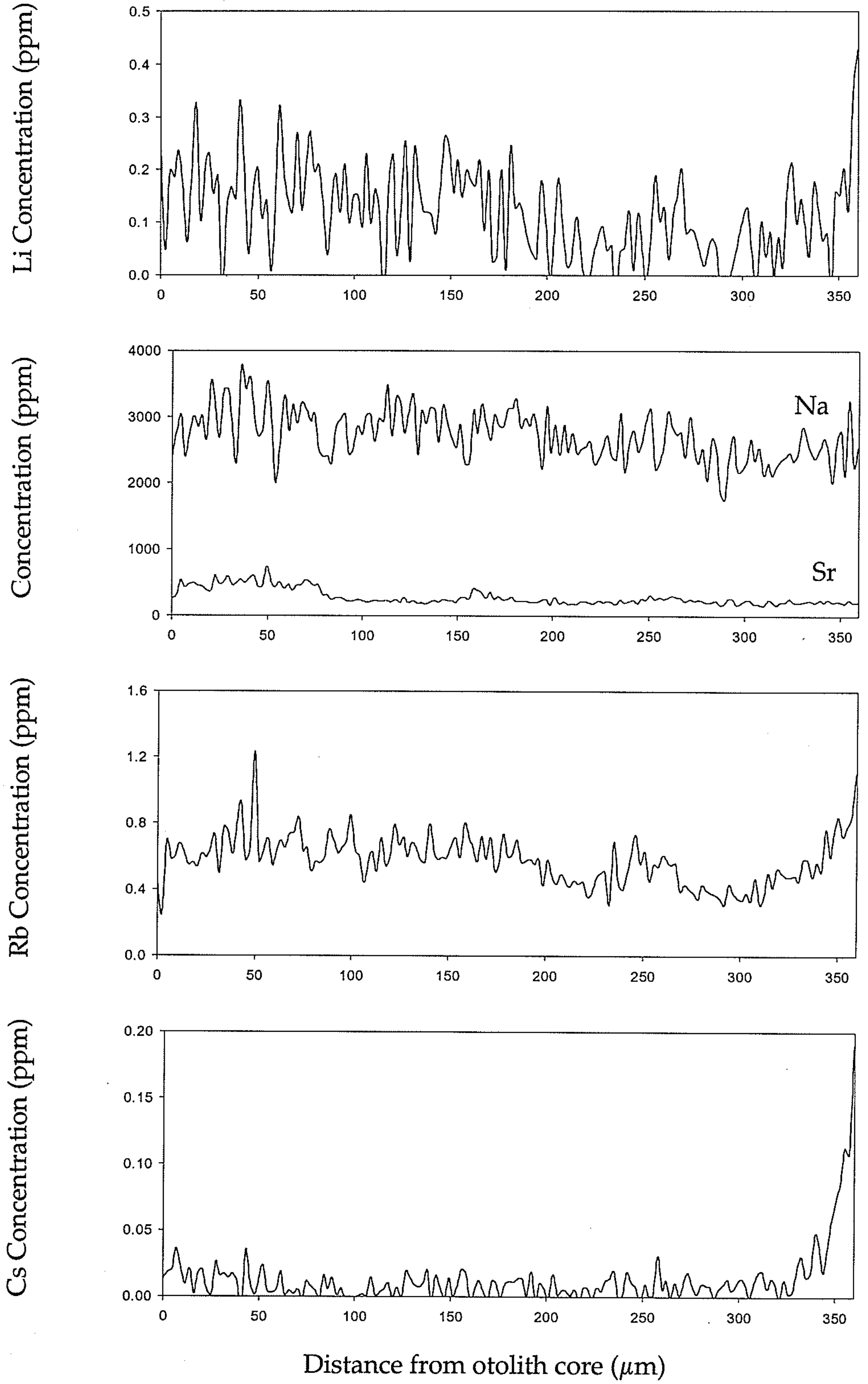
Species: Walleye (*Sander vitreus*), Northern Pike (*Esox lucius*), Silver Redhorse(*Moxostoma anisurum*)

Captured: 1998 (TetrES Consultants, Inc.)

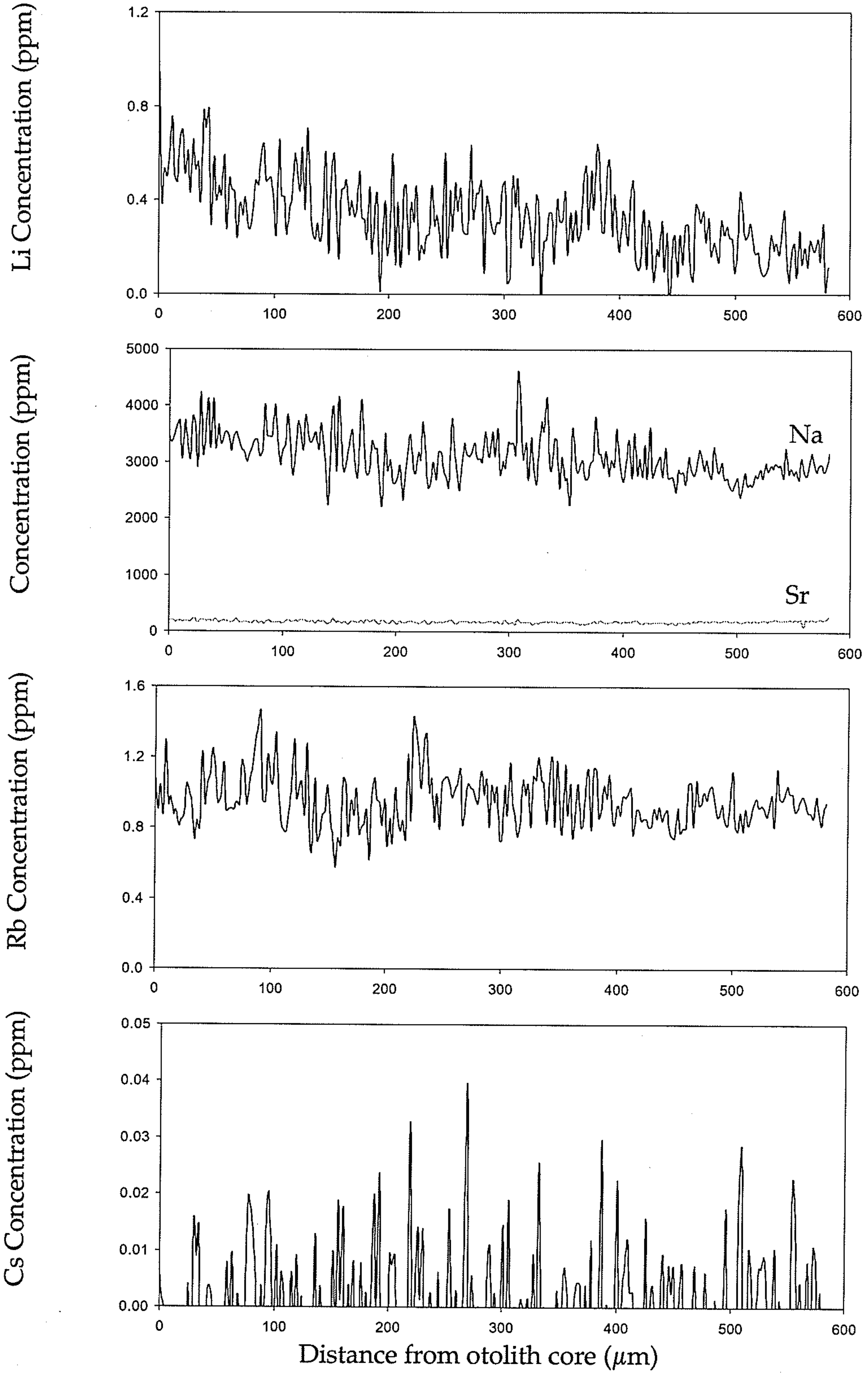
Isotopes	**Li^{7}**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
01	Northern Pike	13
03	Walleye	7
14	Northern Pike	11
16	Northern Pike	6
39	Northern Pike	5
41	Northern Pike	9
42	Northern Pike	18
44	Silver Redhorse	11
45	Walleye	6
65	Walleye	6
68	Walleye	6
70	Northern Pike	6
73	Northern Pike	7

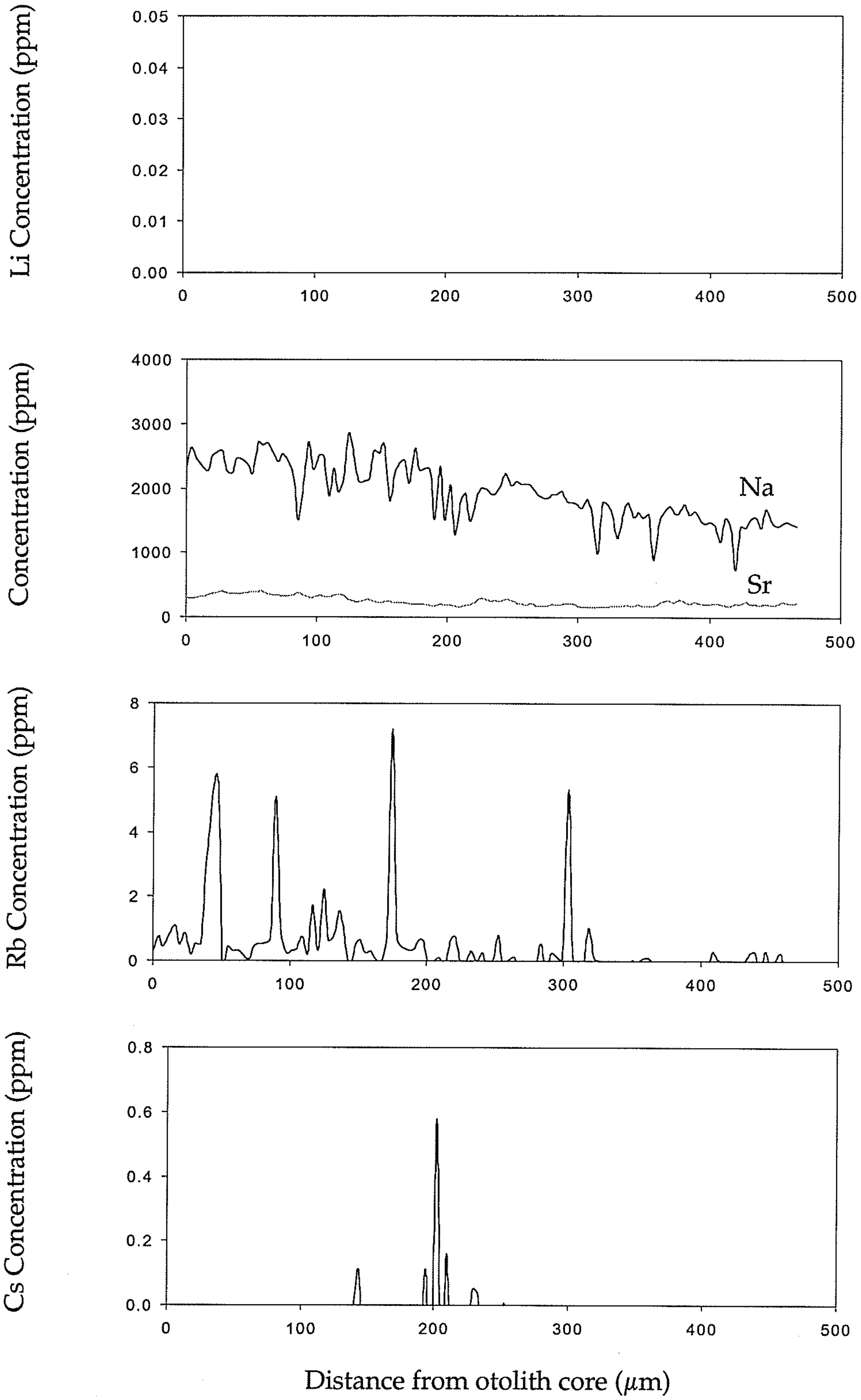
Birse98_01


Li Concentration (ppm)
0.5
0.4
0.3
0.2
0.1
0.0
0
50
100
150
200
250
300
350
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
Cs Concentration (ppm)
0.20
0.15
0.10
0.05
0.00
Distance from otolith core (µm)

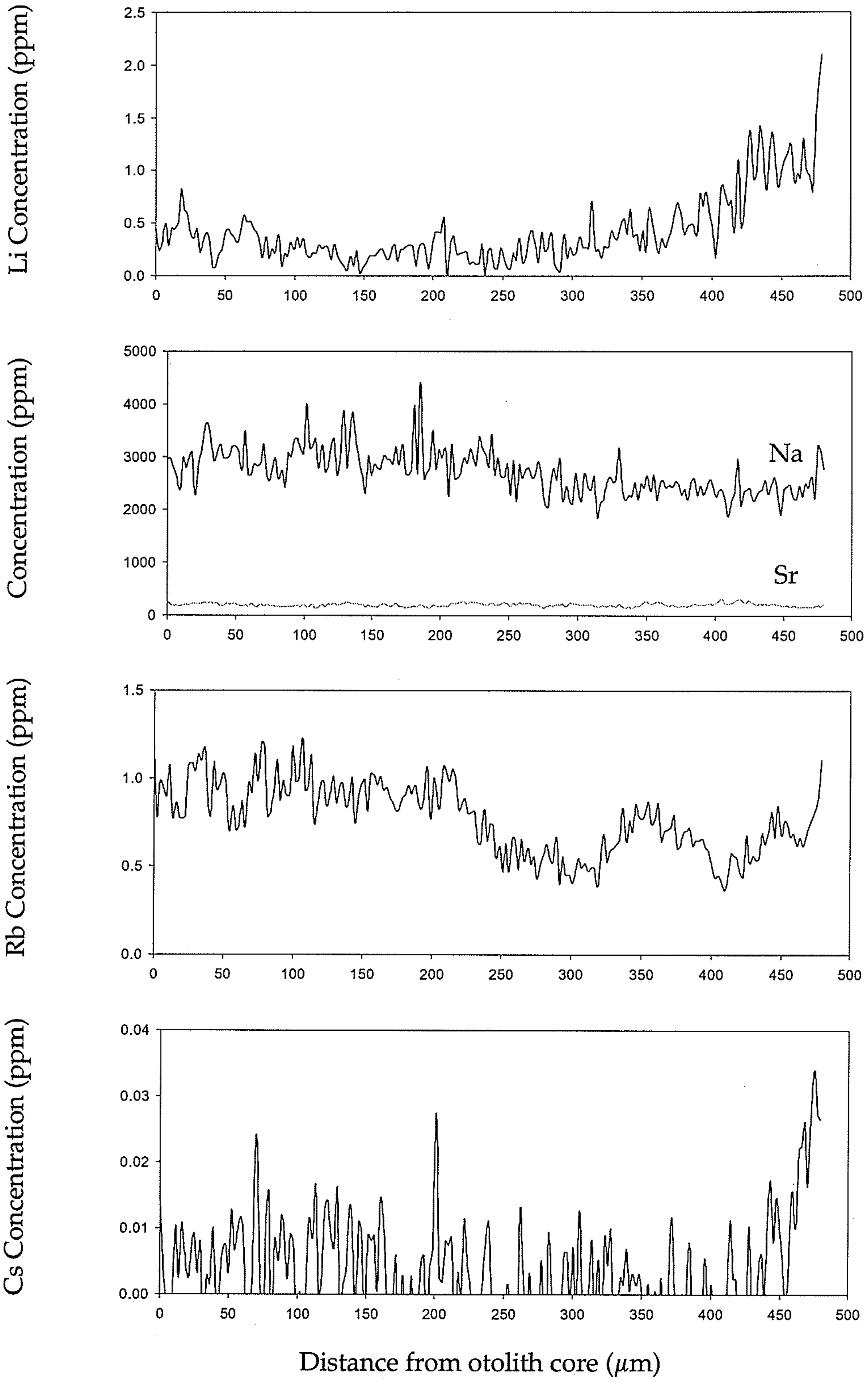
Birse98_03


Li Concentration (ppm)
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
Cs Concentration (ppm)
0.05
0.04
0.03
0.02
0.01
0.00
0
100
200
300
400
500
600
Distance from otolith core (μm)

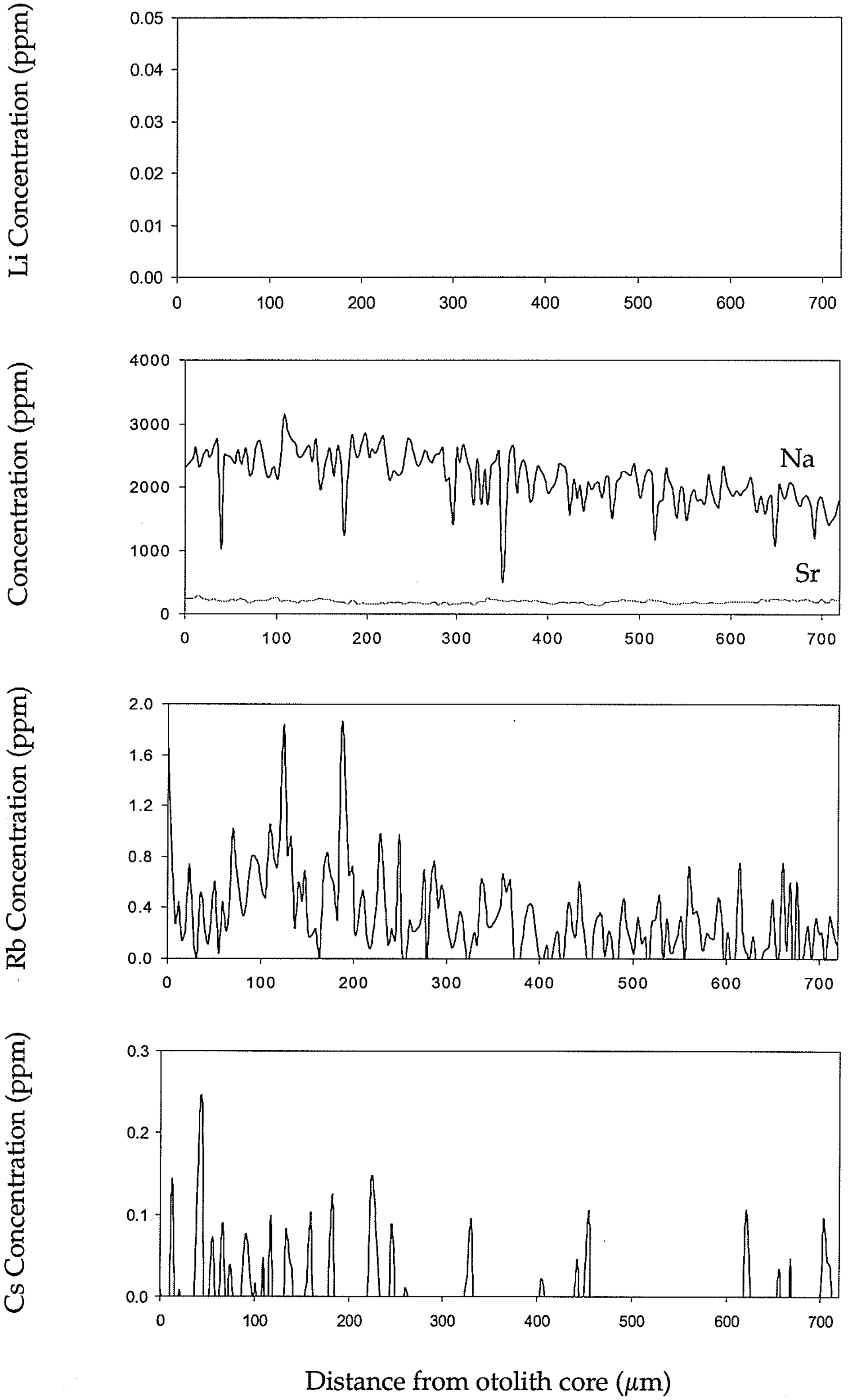
Birse98_14


Li Concentration (ppm)
0.05
0.04
0.03
0.02
0.01
0.00
0
100
200
300
400
500
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
8
6
4
2
Cs Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
Distance from otolith core (μm)

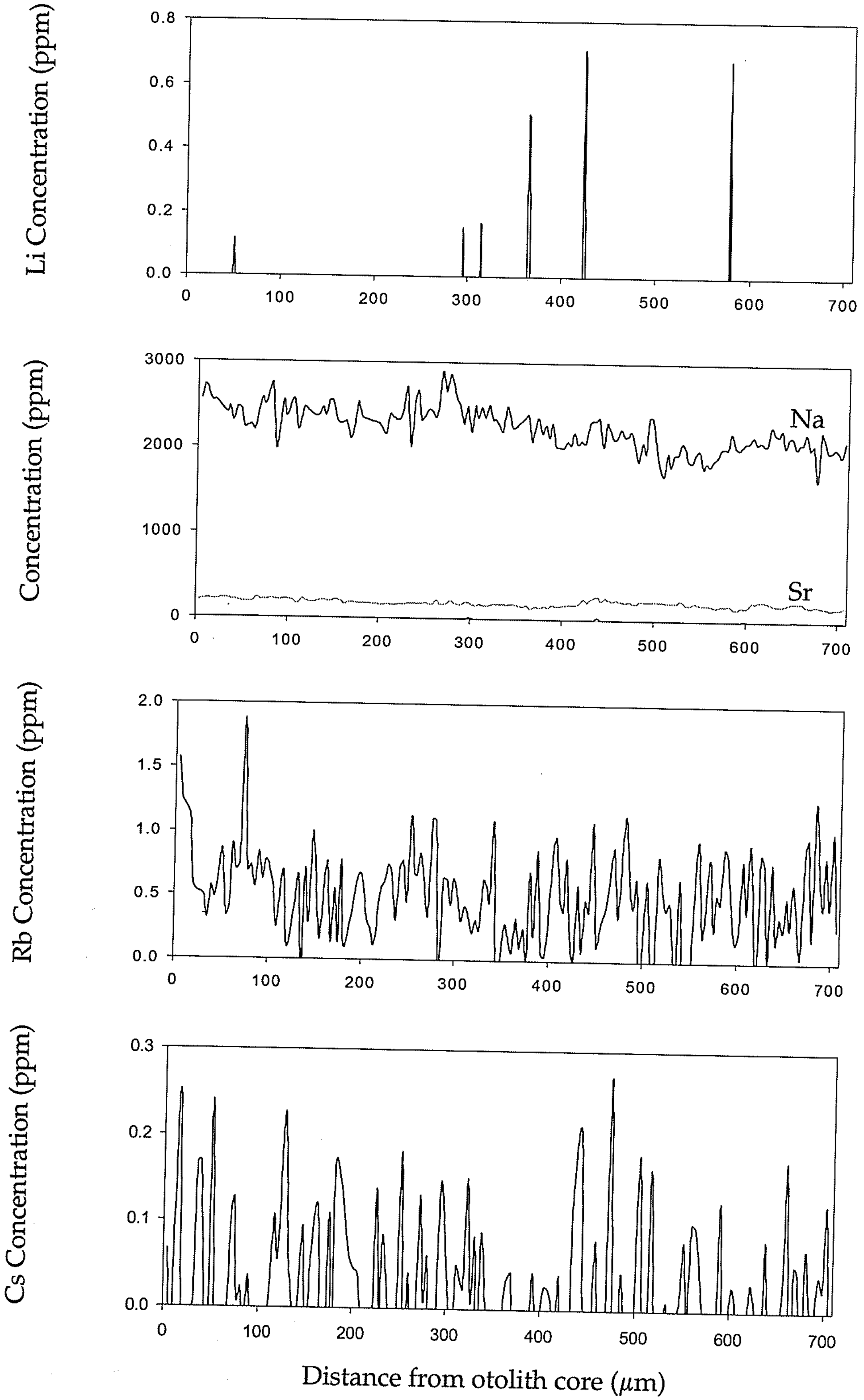
Birse98_16


Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
50
100
150
200
250
300
350
400
450
500
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
50
100
150
200
250
300
350
400
450
500
Rb Concentration (ppm)
1.5
1.0
0.5
0.0
0
50
100
150
200
250
300
350
400
450
500
Cs Concentration (ppm)
0.04
0.03
0.02
0.01
0.00
0
50
100
150
200
250
300
350
400
450
500
Distance from otolith core (μm)

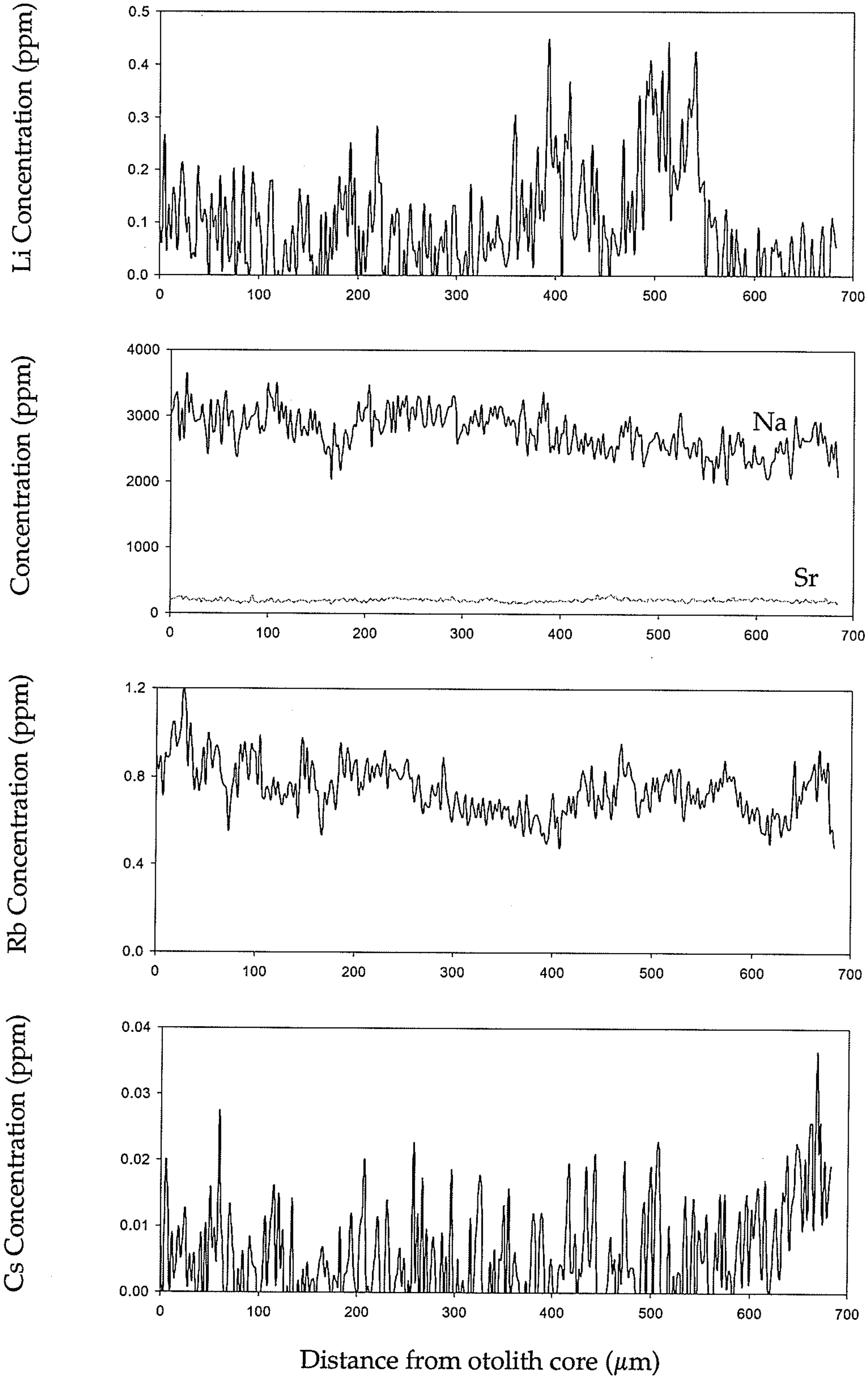
Birse98_39


Li Concentration (ppm)
0.05
0.04
0.03
0.02
0.01
0.00
0
100
200
300
400
500
600
700
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
Rb Concentration (ppm)
2.0
1.6
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
Cs Concentration (ppm)
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
Distance from otolith core (μm)

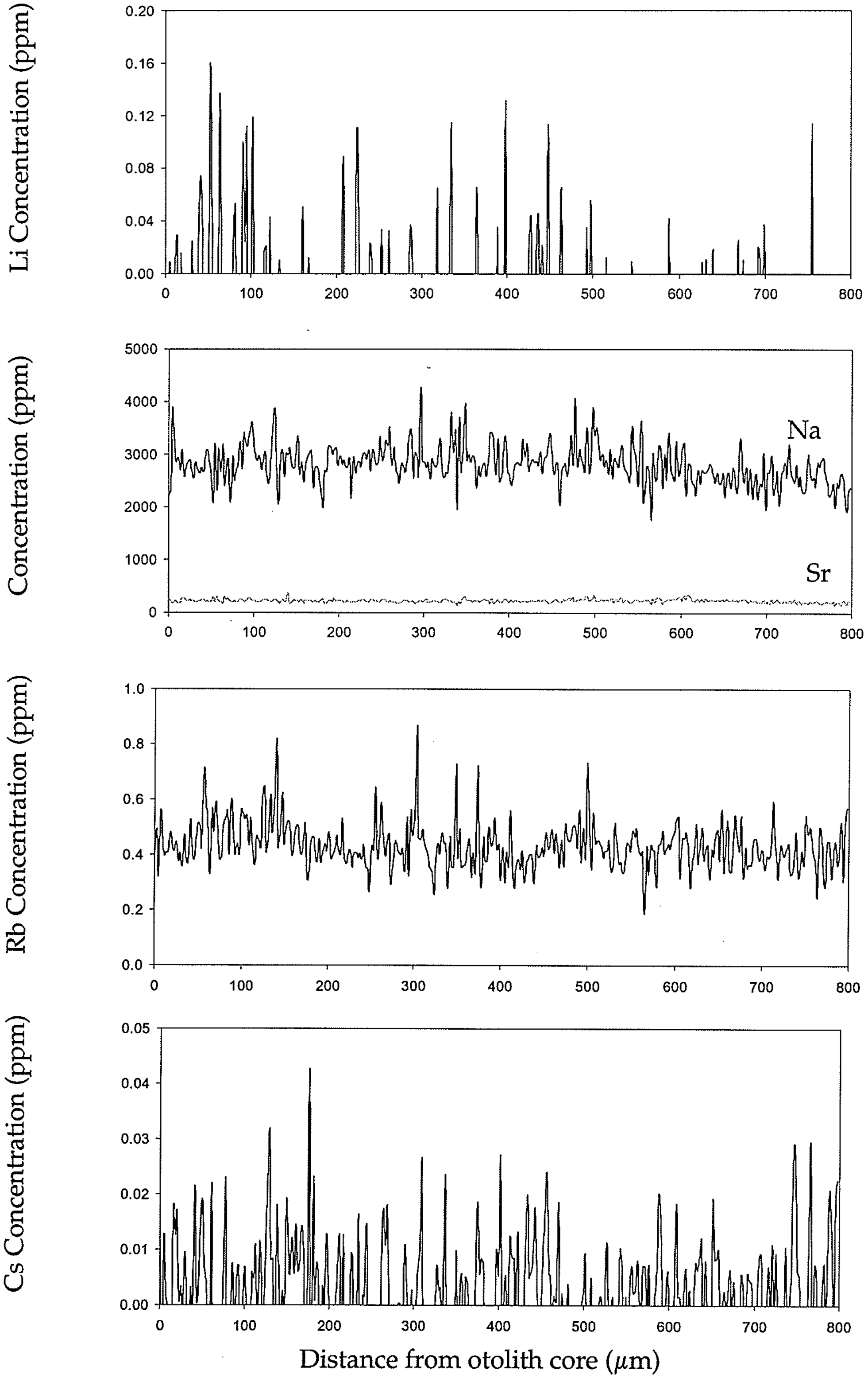
Birse98_41


Li Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
600
700
Concentration (ppm)
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
Rb Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
Cs Concentration (ppm)
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
Distance from otolith core (μm)

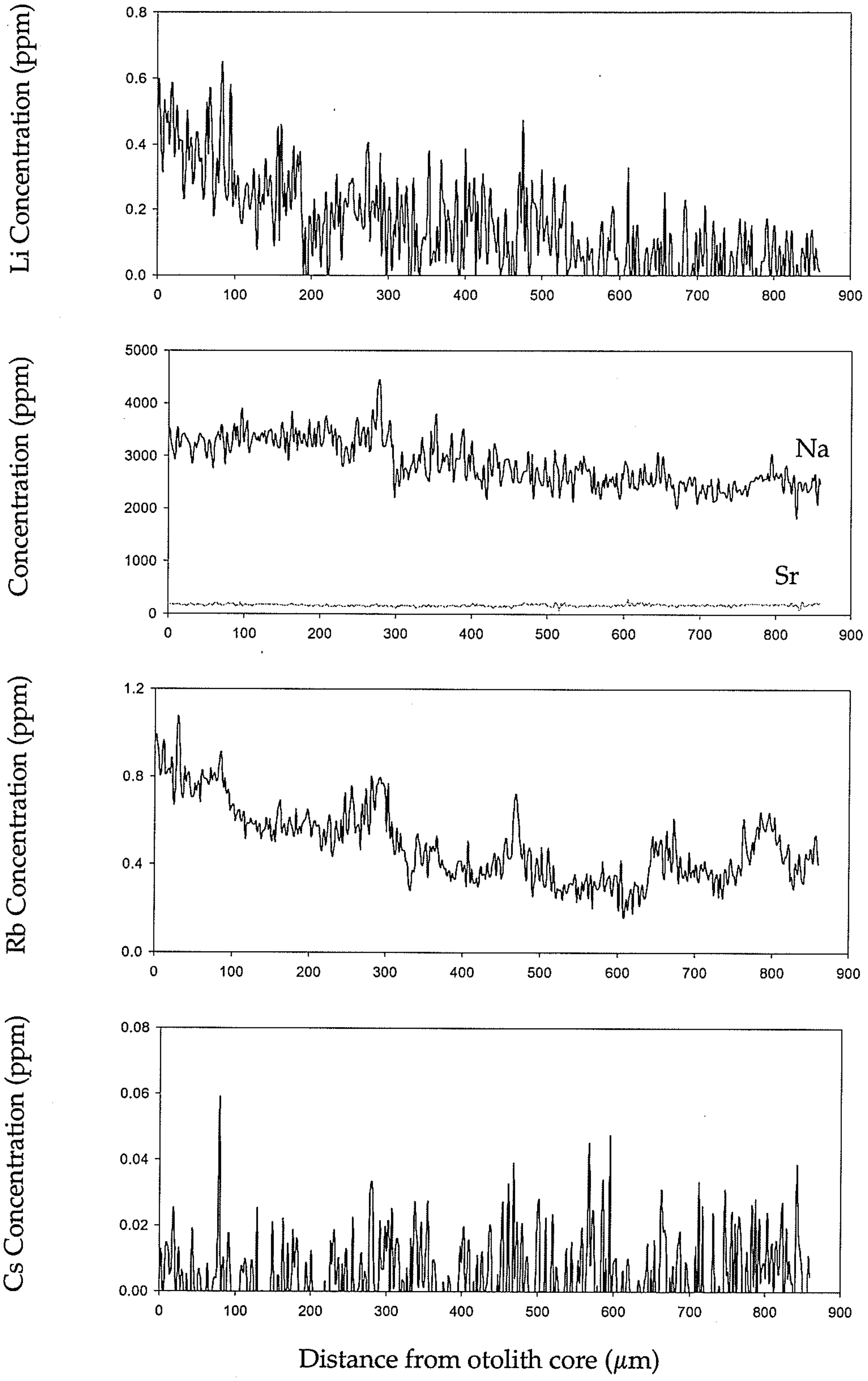
Birse98_42


Li Concentration (ppm)
0.5
0.4
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
Cs Concentration (ppm)
0.04
0.03
0.02
0.01
0.00
Distance from otolith core (μm)

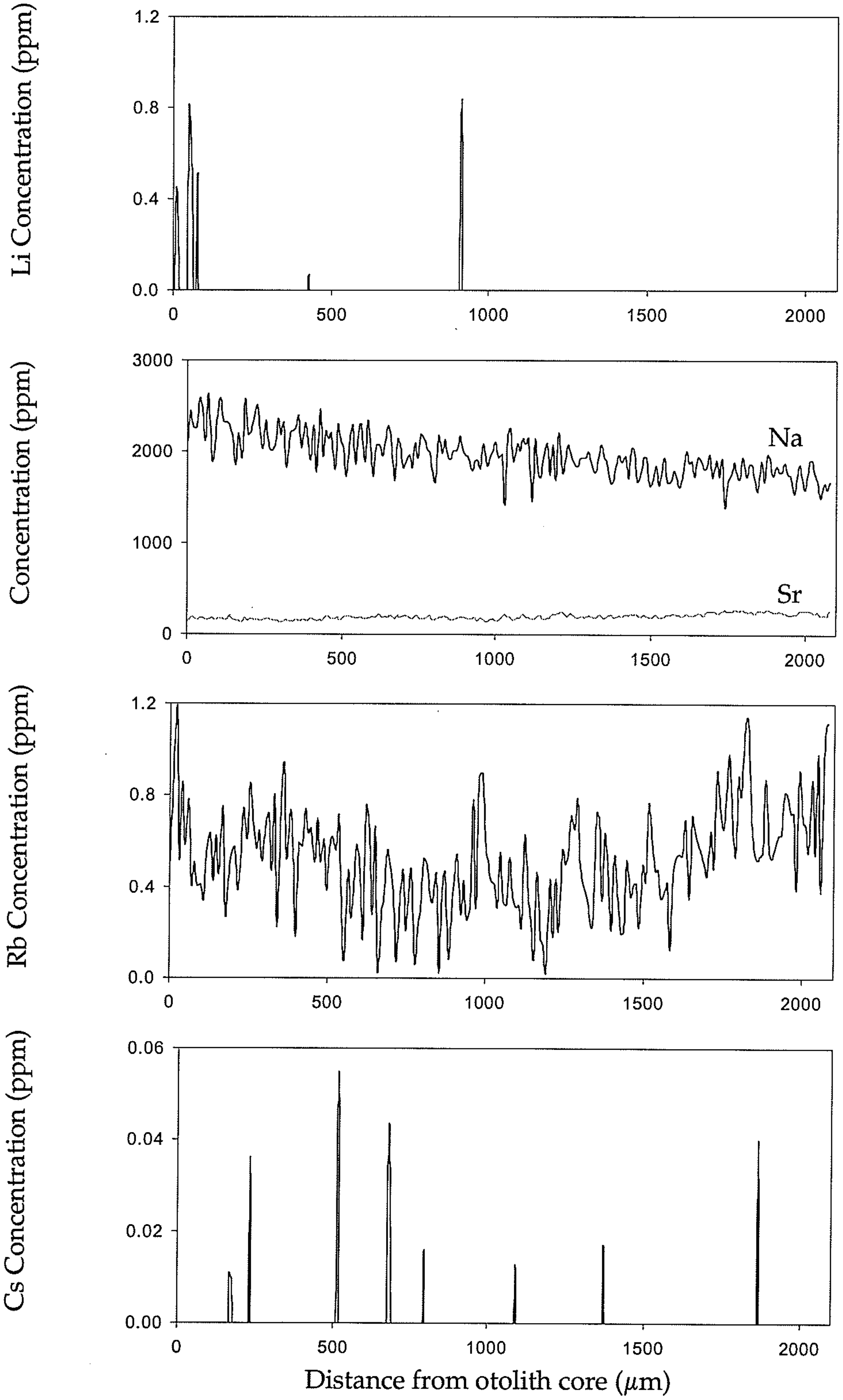
Birse98_44


Li Concentration (ppm)
0.20
0.16
0.12
0.08
0.04
0.00
0
100
200
300
400
500
600
700
800
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
800
Rb Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
600
700
800
Cs Concentration (ppm)
0.05
0.04
0.03
0.02
0.01
0.00
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

Birse98_45

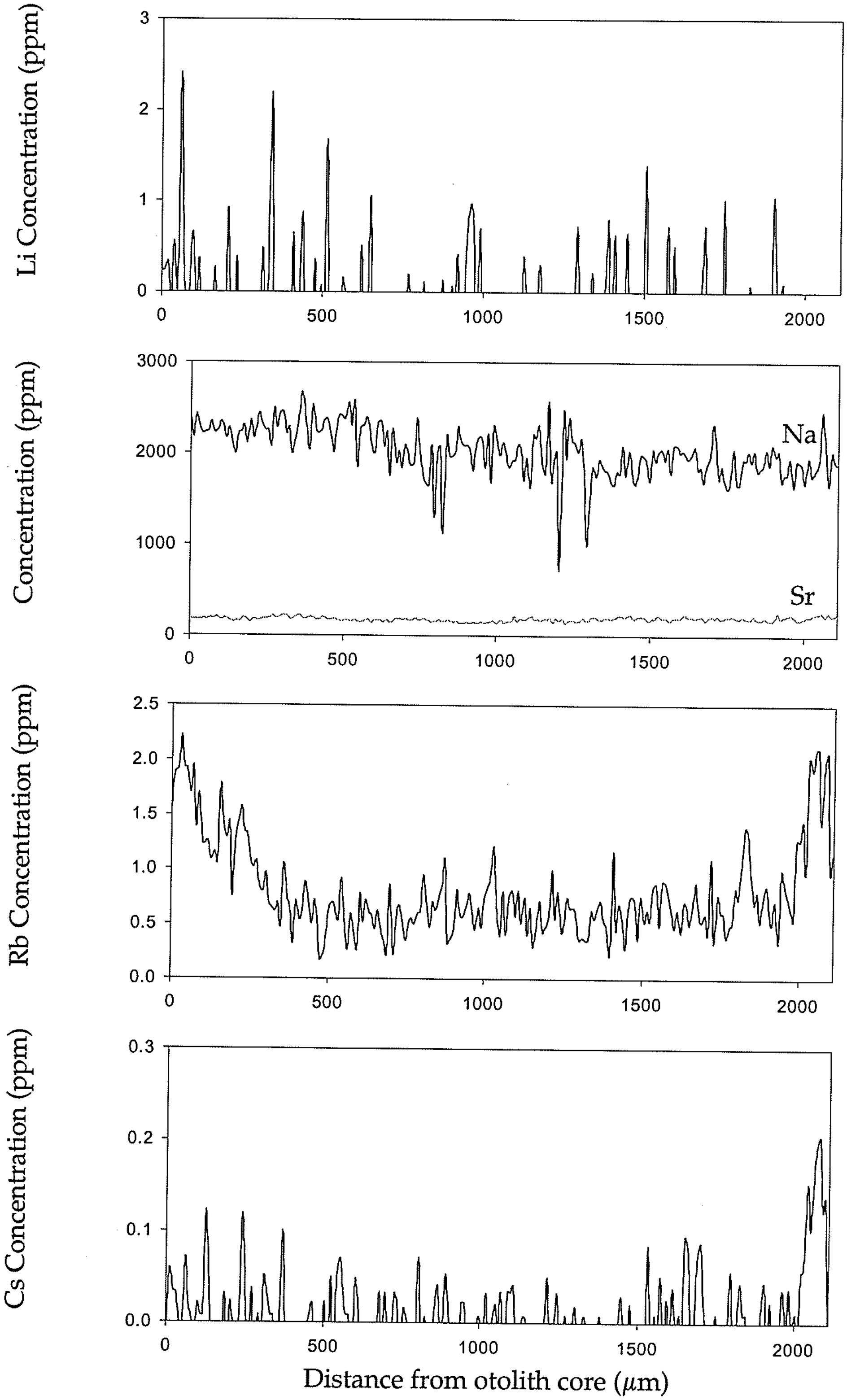

Li Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
600
700
800
900
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
800
900
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
800
900
Cs Concentration (ppm)
0.08
0.06
0.04
0.02
0.00
0
100
200
300
400
500
600
700
800
900
Distance from otolith core (μm)

Birse98_65



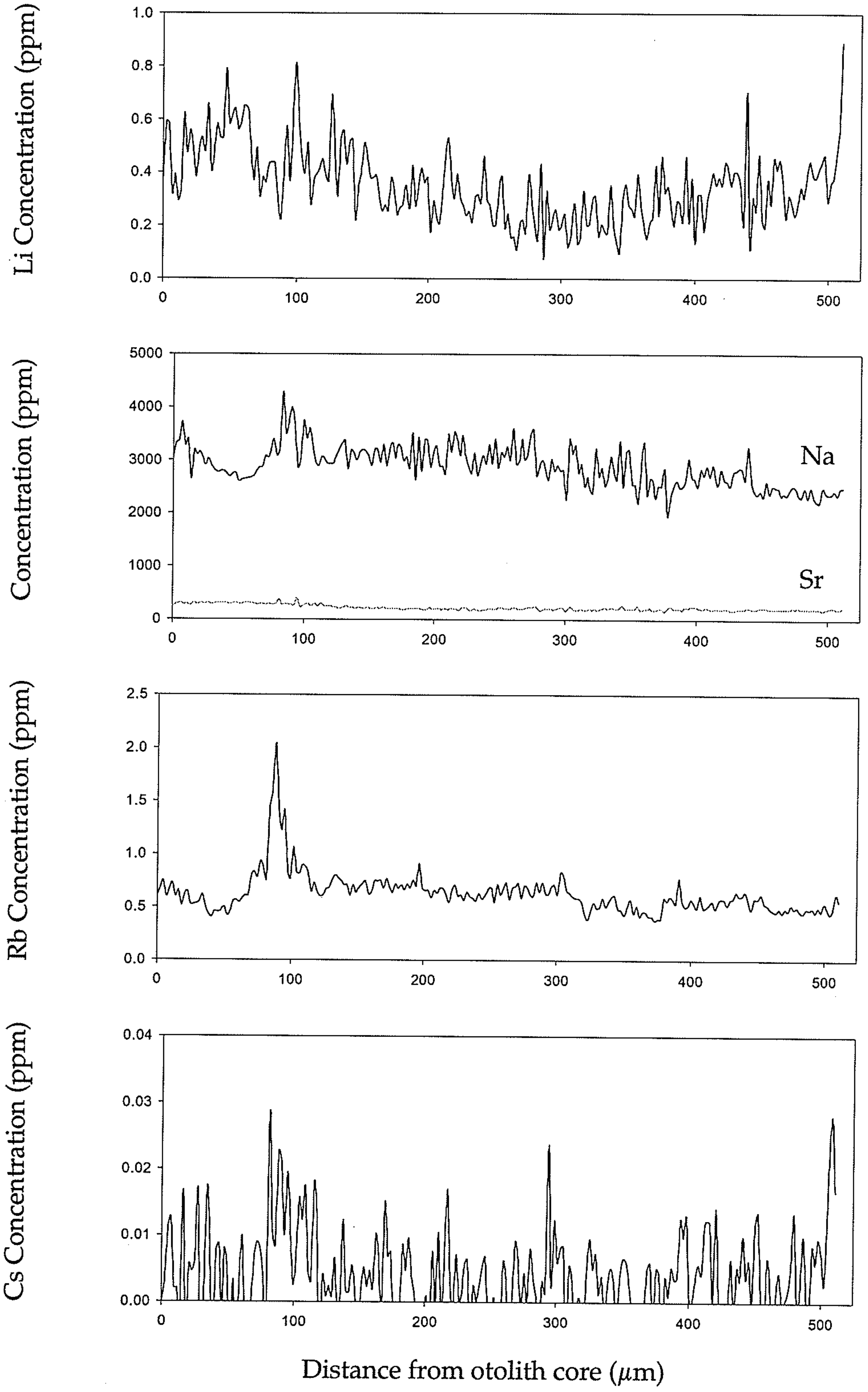
Li Concentration (ppm)
1.2
0.8
0.4
0.0
0
500
1000
1500
2000
Concentration (ppm)
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
500
1000
1500
2000
Cs Concentration (ppm)
0.06
0.04
0.02
0.00
0
500
1000
1500
2000
Distance from otolith core (μm)

Birse98_68

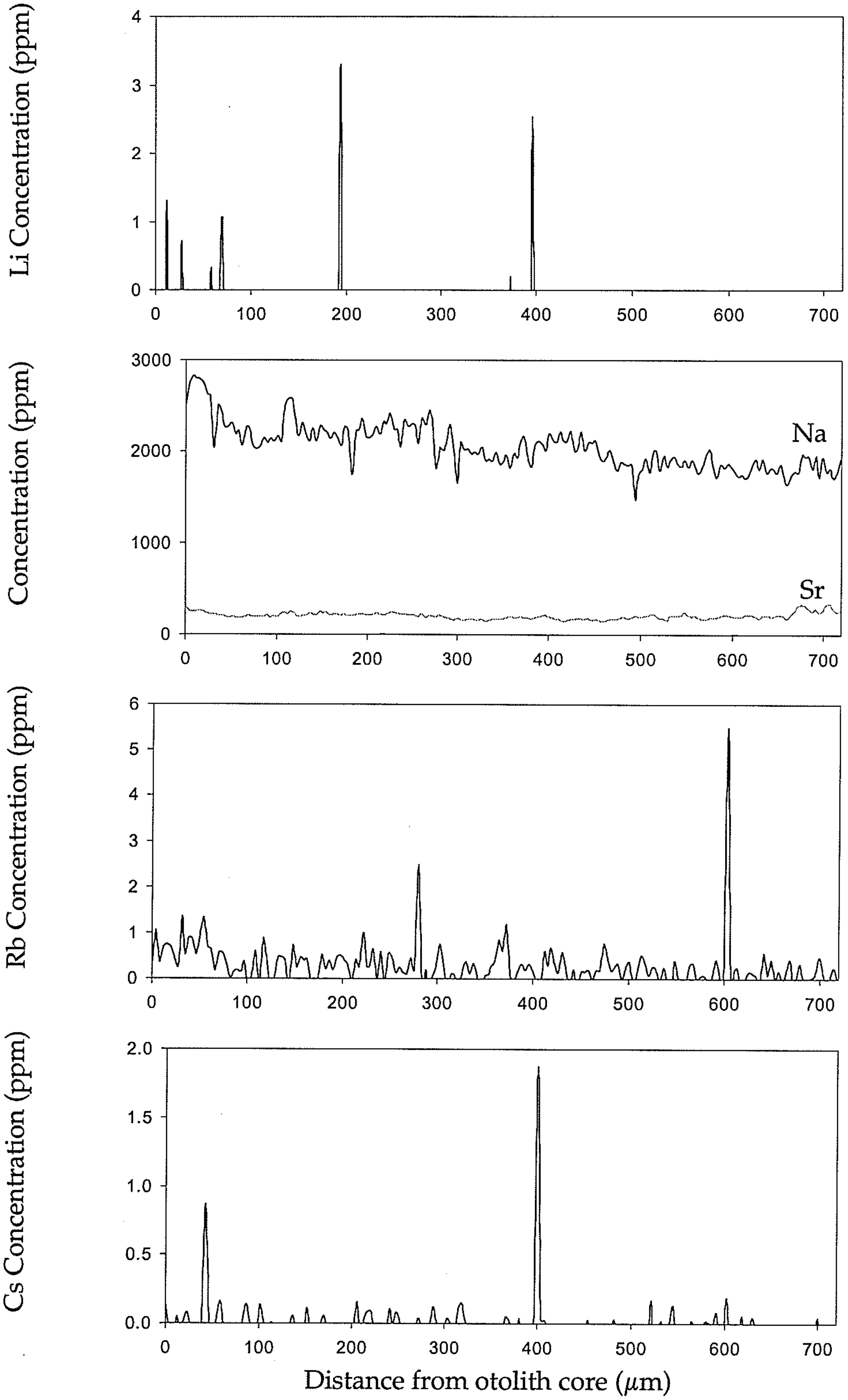


Li Concentration (ppm)
3
2
1
0
0
500
1000
1500
2000
Concentration (ppm)
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
Cs Concentration (ppm)
0.3
0.2
0.1
0.0
0
500
1000
1500
2000
Distance from otolith core (μm)

Birse98_70


Li Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
Cs Concentration (ppm)
0.04
0.03
0.02
0.01
0.00
0
100
200
300
400
500
Distance from otolith core (μm)

Birse98_73



Li Concentration (ppm)
0
1
2
3
4
0
100
200
300
400
500
600
700
Concentration (ppm)
0
1000
2000
3000
Na
Sr
0
100
200
300
400
500
600
700
Rb Concentration (ppm)
0
1
2
3
4
5
6
0
100
200
300
400
500
600
700
Cs Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
0
100
200
300
400
500
600
700
Distance from otolith core (μm)

Appendix E LA-ICP-MS data for Bird Lake otoliths

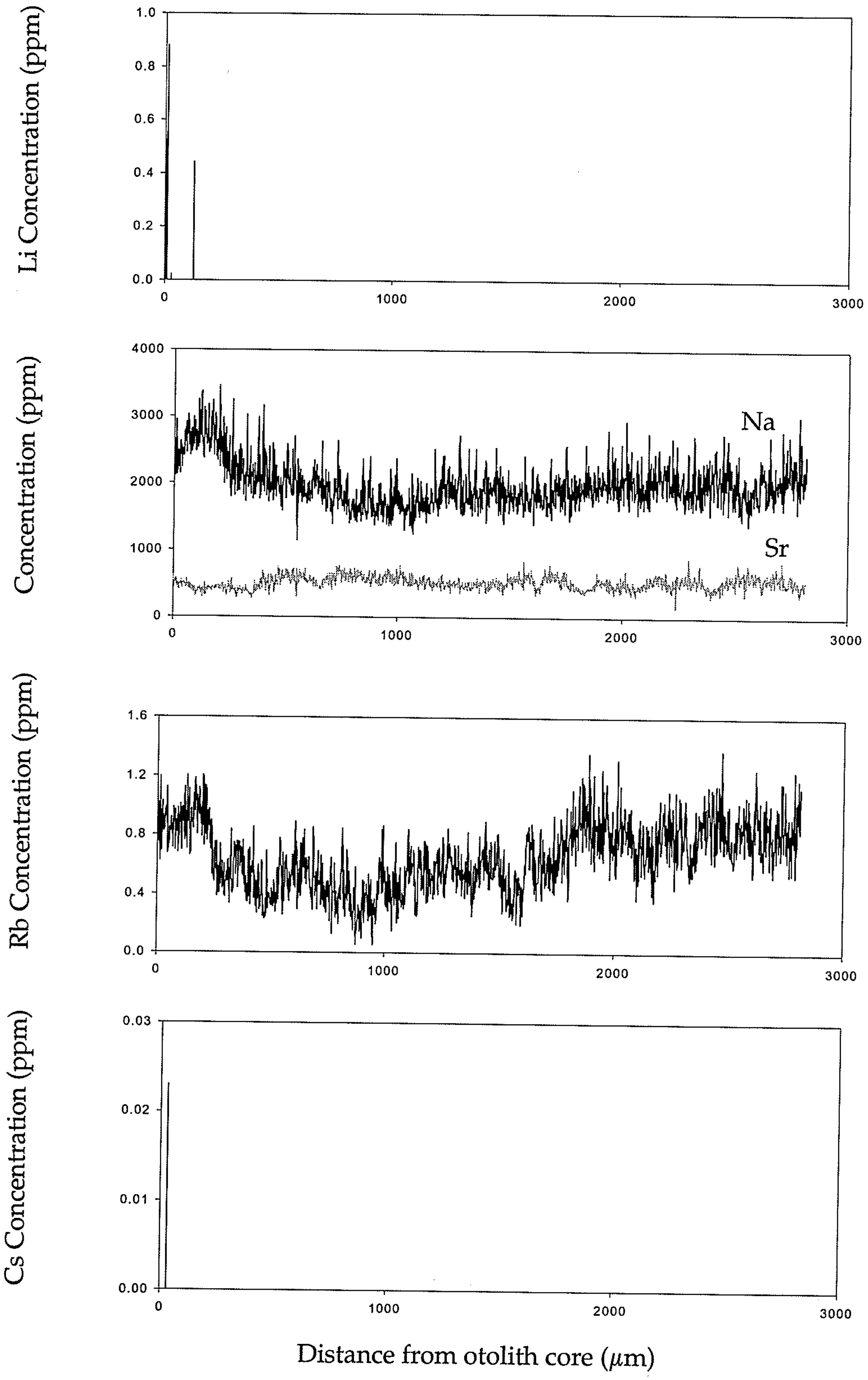
Species: Walleye (*Sander vitreus*), Northern Pike (*Esox lucius*), Silver Redhorse (*Moxostoma anisurum*), White Sucker (*Catostomus commersoni*)

Captured: 2008

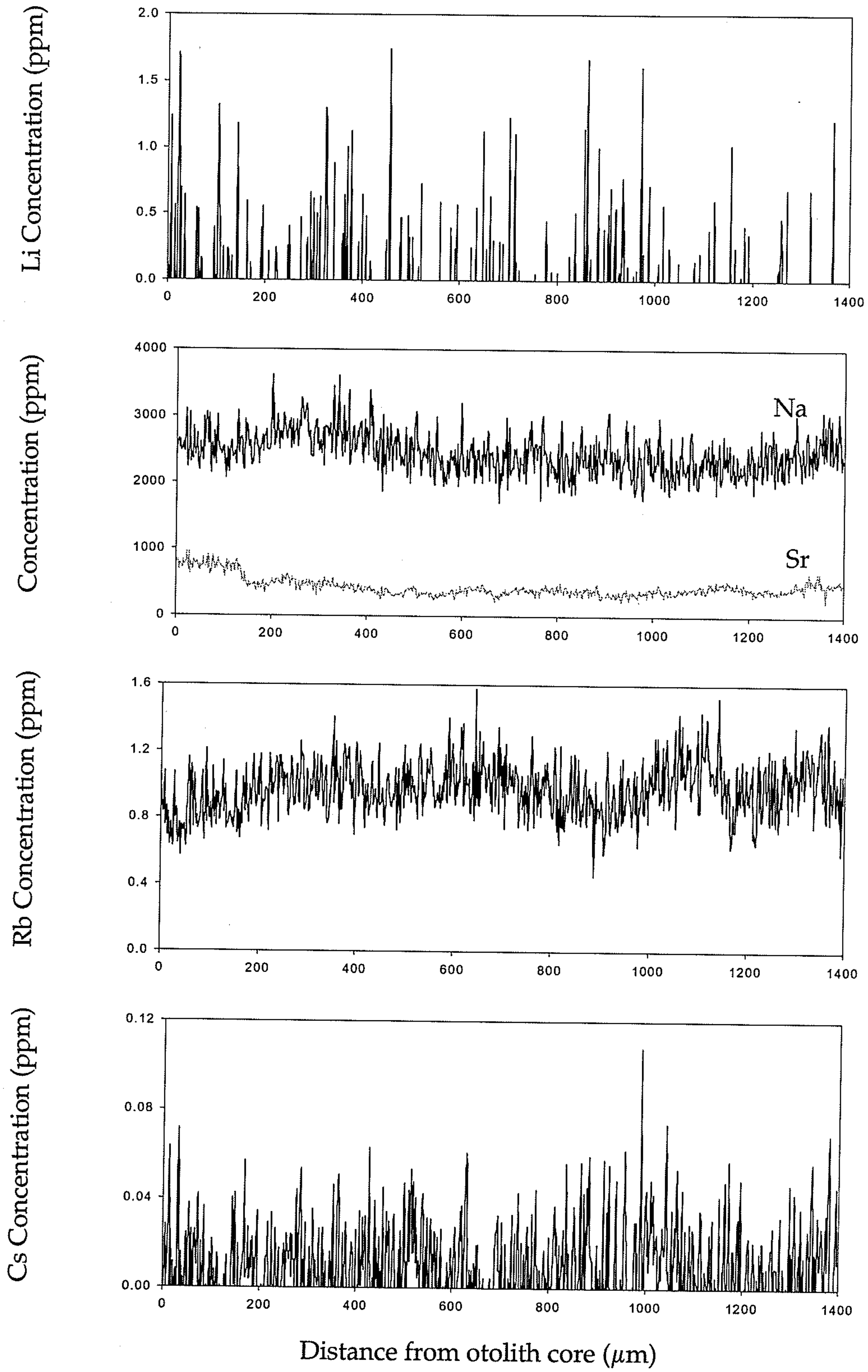
Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
TF01	Northern Pike	10
01	Northern Pike	5
02	Northern Pike	4
03	Northern Pike	4
04	Northern Pike	5
05	Walleye	4
06	Northern Pike	11
07	Silver Redhorse	7
08	White Sucker	7
09	White Sucker	6

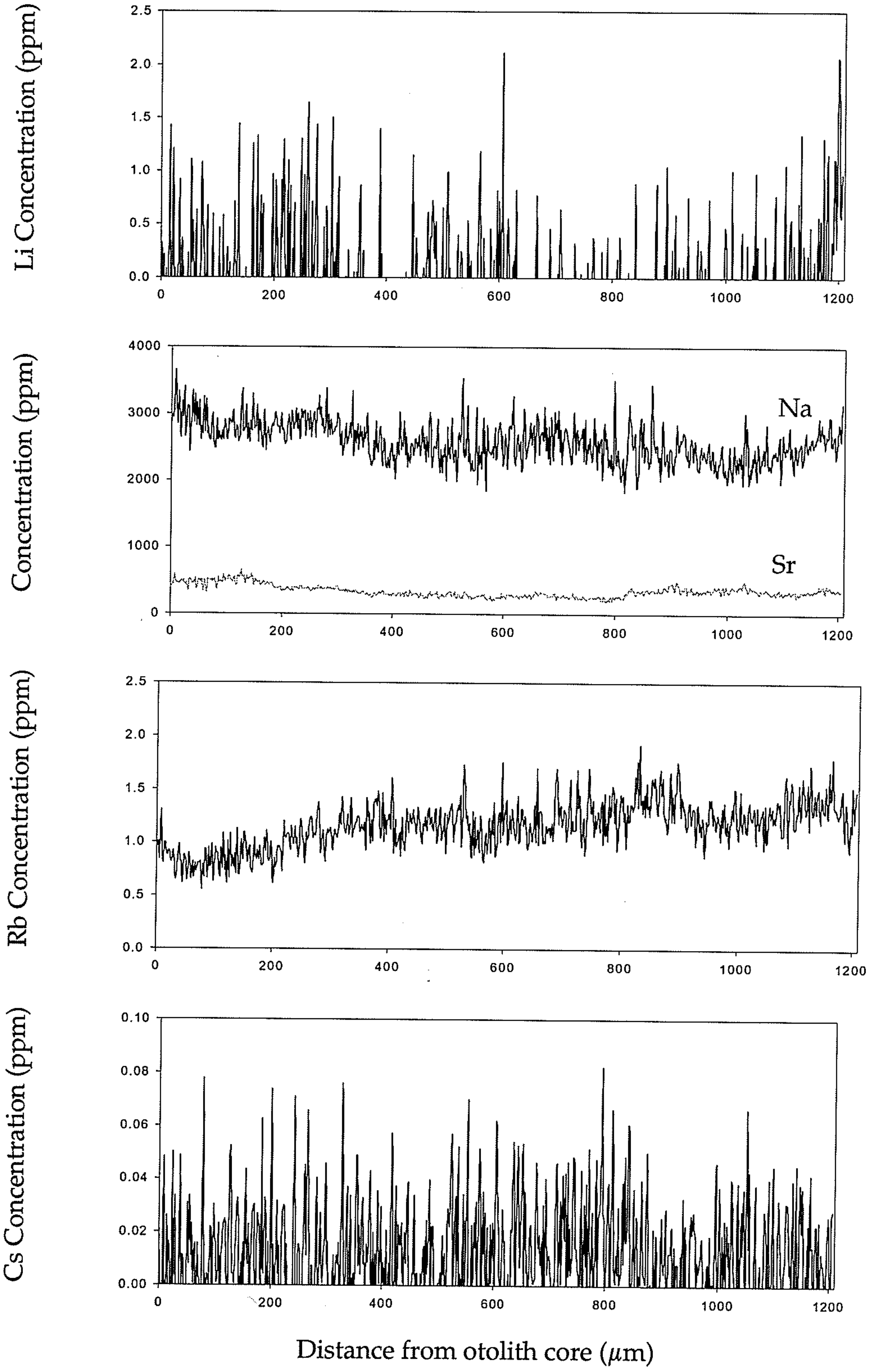
Bird08_TF01


Li Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
1000
2000
3000
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
1000
2000
3000
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
1000
2000
3000
Cs Concentration (ppm)
0.03
0.02
0.01
0.00
0
1000
2000
3000
Distance from otolith core (μm)

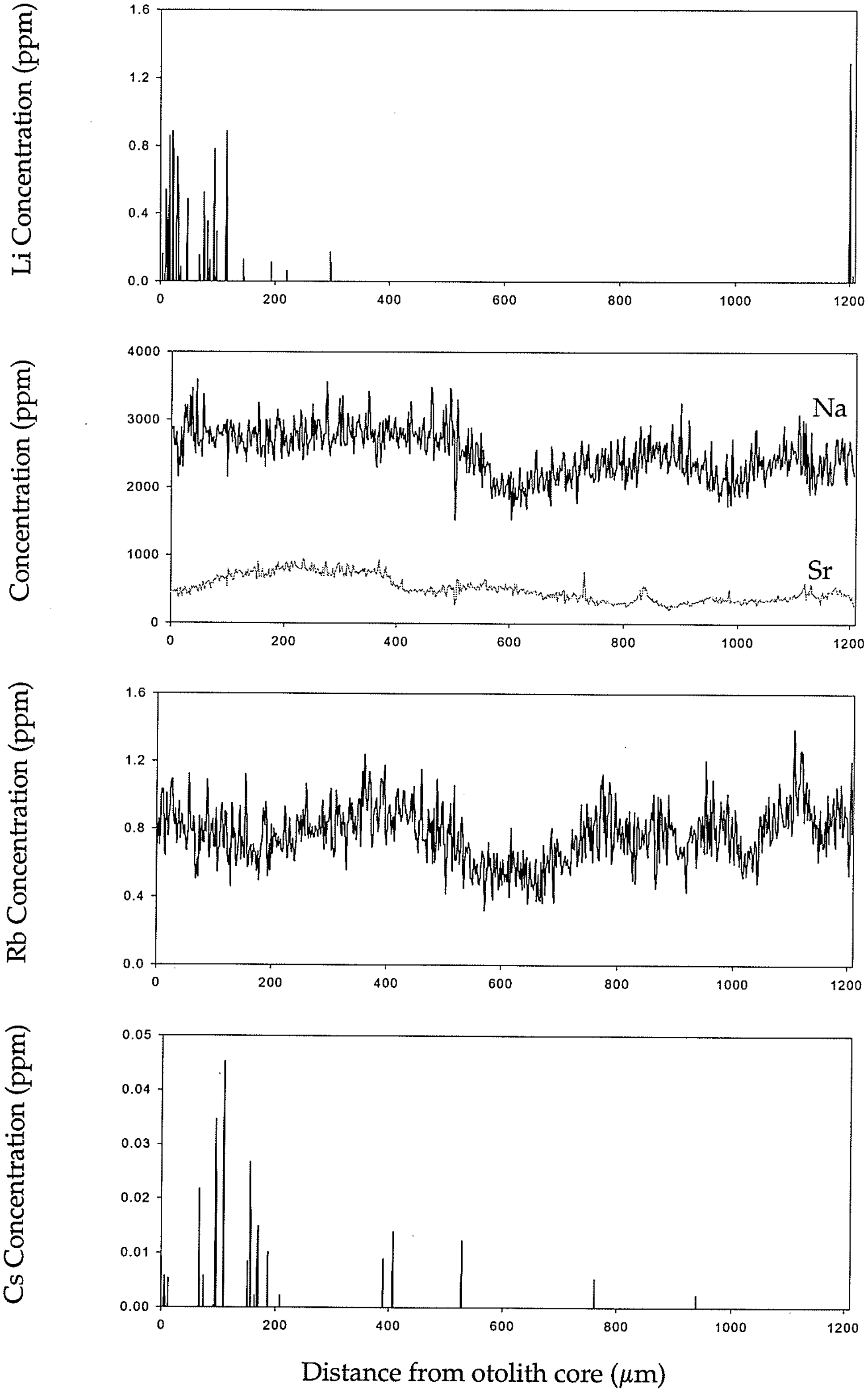
Bird08_01


Li Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

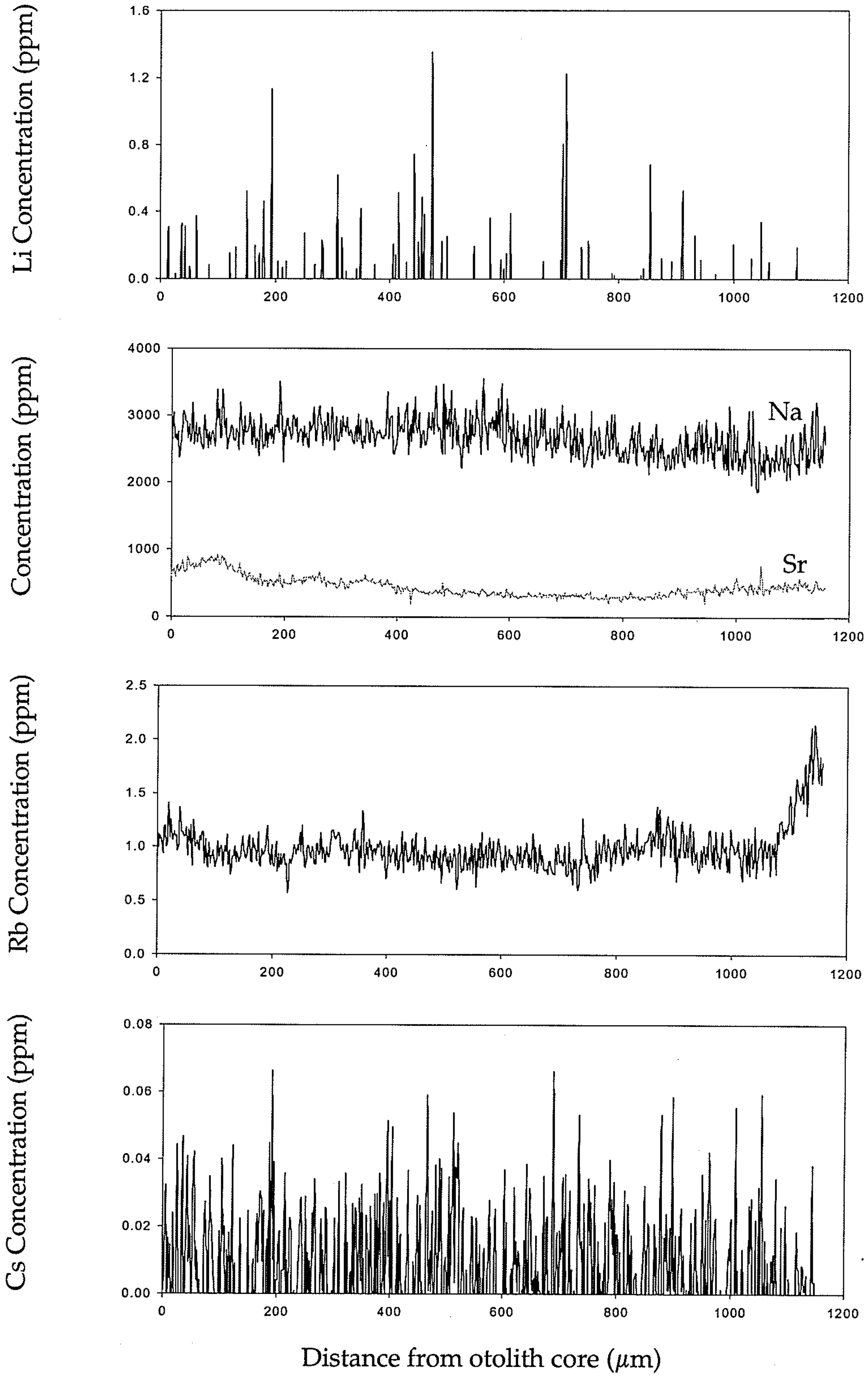
Bird08_02


Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.10
0.08
0.06
0.04
0.02
0.00
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

Bird08_03

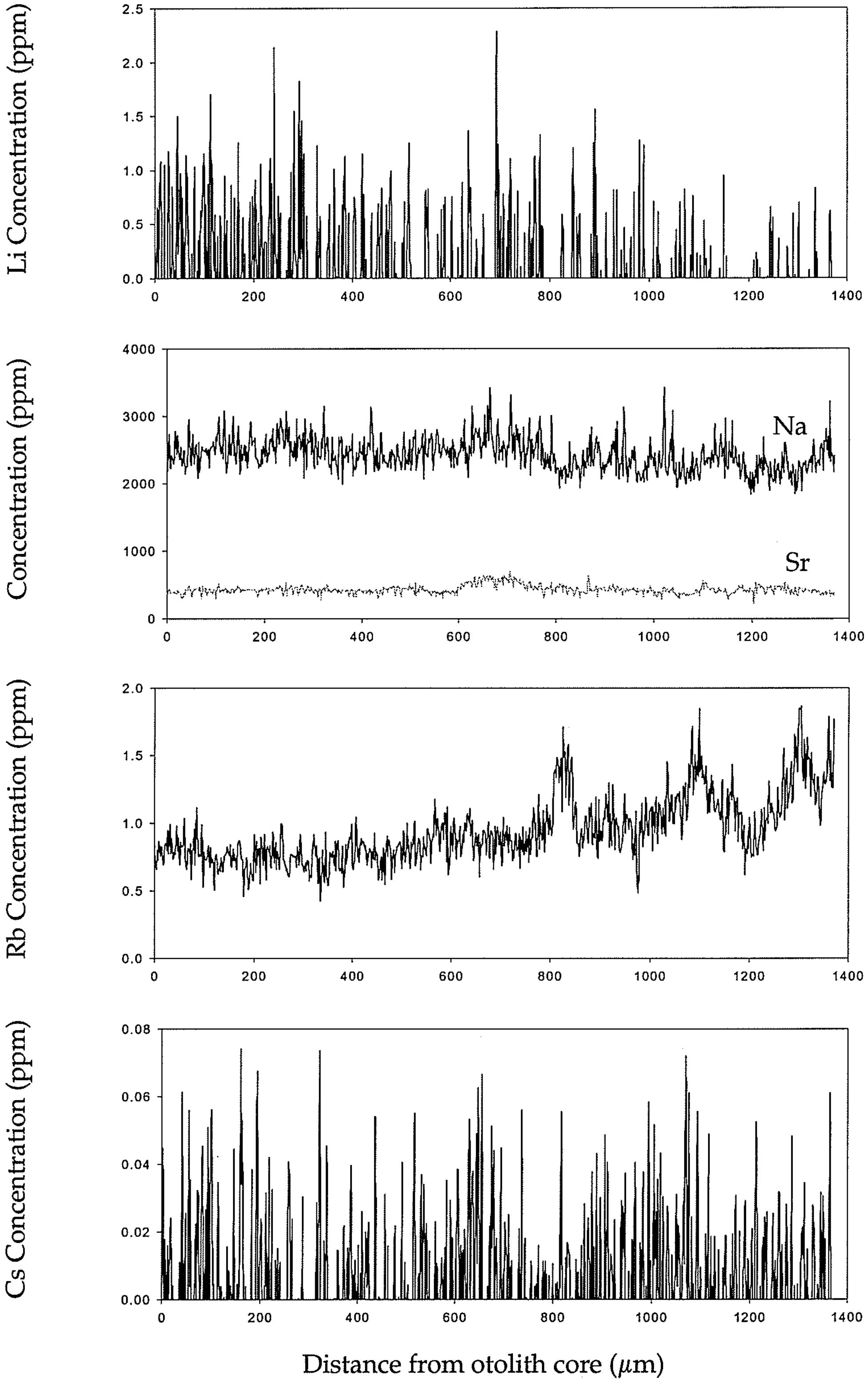

Li Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.05
0.04
0.03
0.02
0.01
0.00
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

Bird08_04

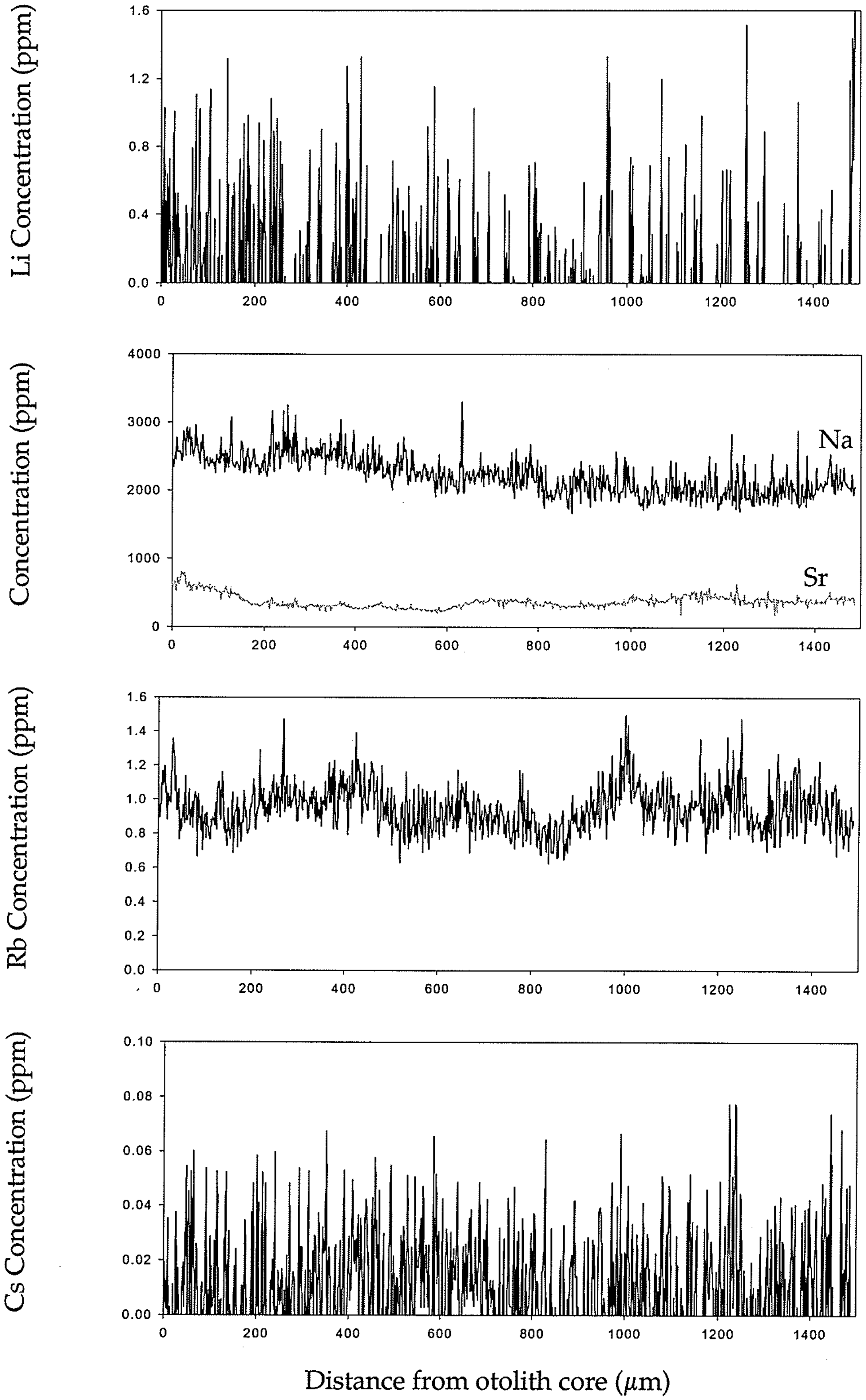


Li Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
Cs Concentration (ppm)
0.08
0.06
0.04
0.02
0.00
Distance from otolith core (μm)

Bird08_05

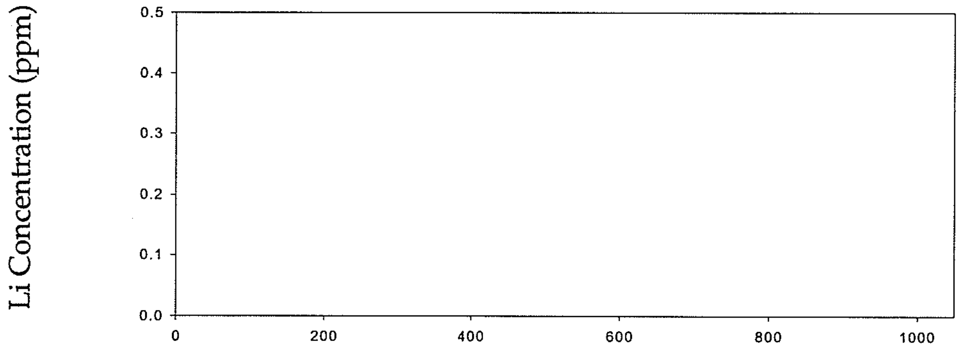

Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
Cs Concentration (ppm)
0.08
0.06
0.04
0.02
0.00
Distance from otolith core (μm)

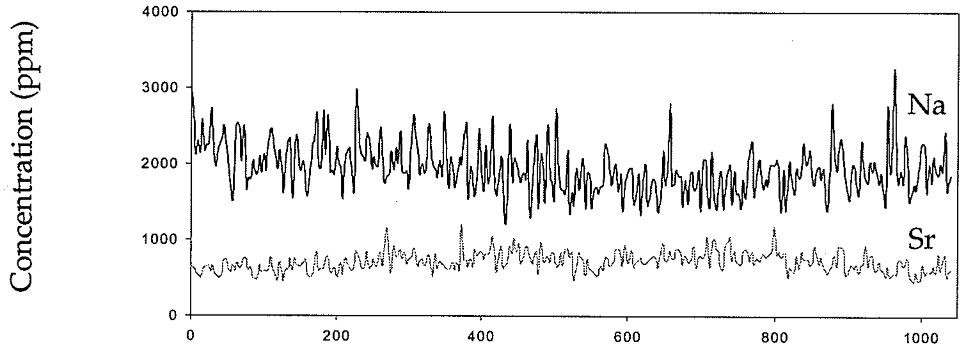
Bird08_06

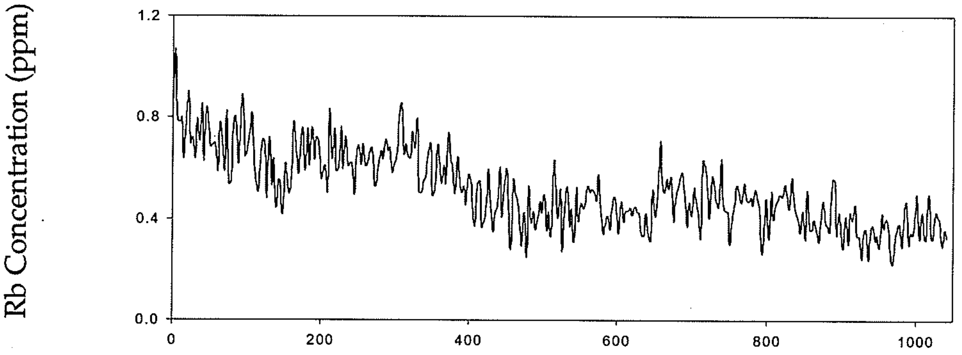


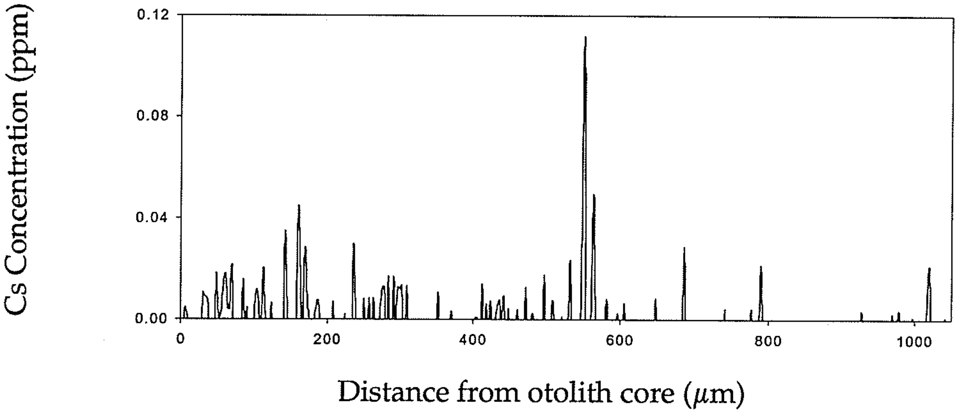
Li Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Cs Concentration (ppm)
0.10
0.08
0.06
0.04
0.02
0.00
Distance from otolith core (μm)

Bird08_07

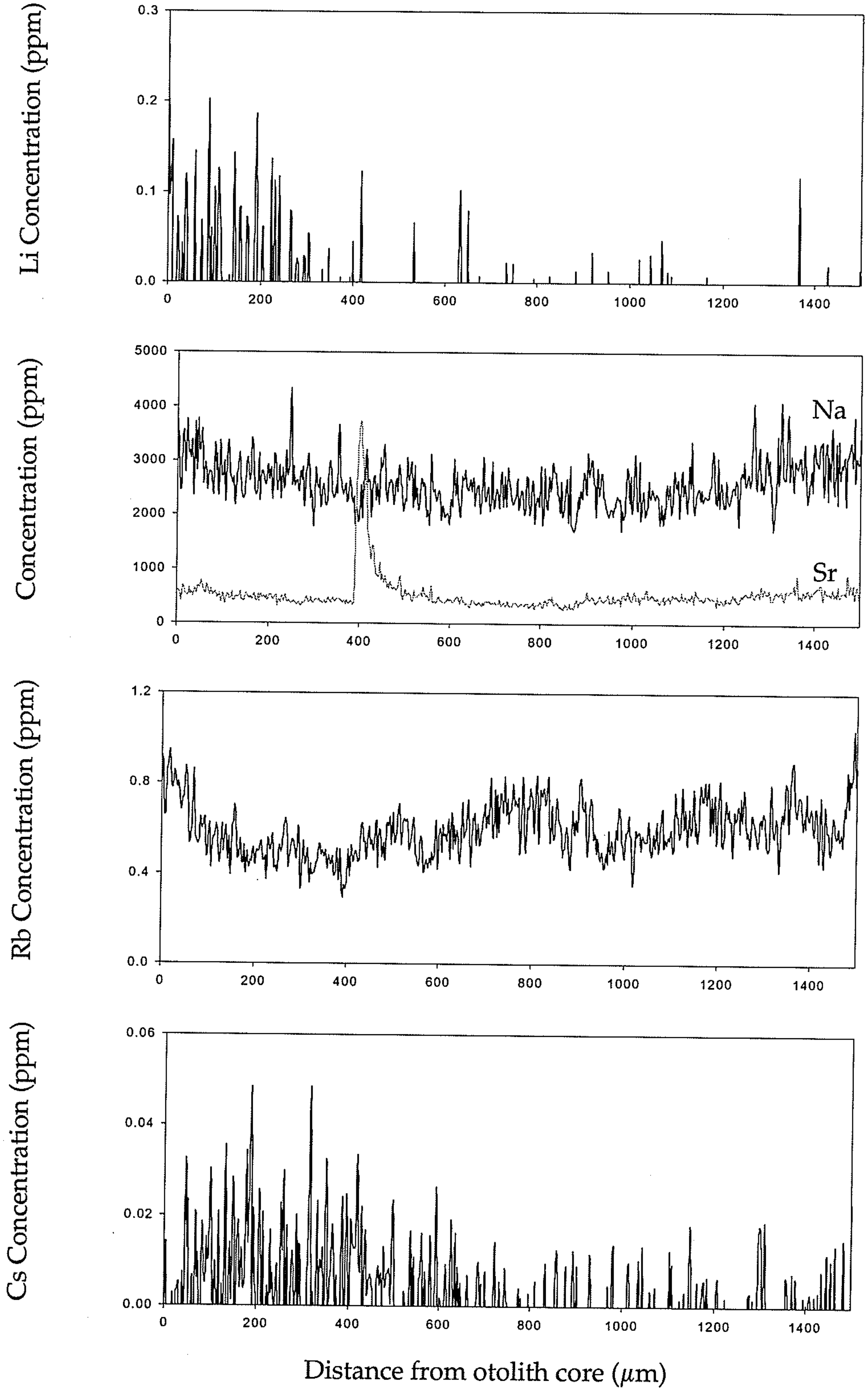

Li Concentration (ppm)
0.5
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000


Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000

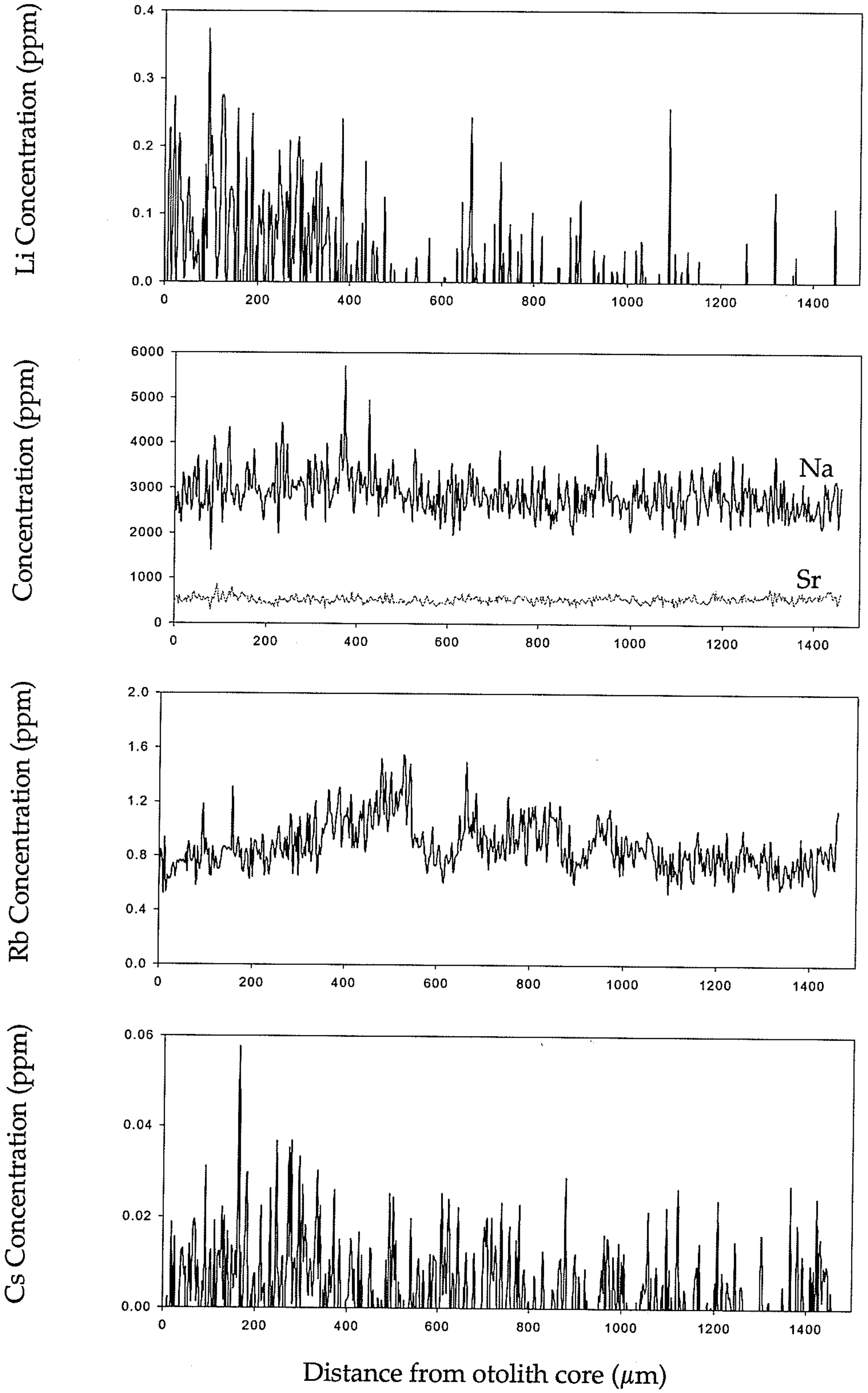

Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
200
400
600
800
1000


Cs Concentration (ppm)
0.12
0.08
0.04
0.00
0
200
400
600
800
1000
Distance from otolith core (μm)

Bird08_08


Li Concentration (ppm)
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
Cs Concentration (ppm)
0.06
0.04
0.02
0.00
Distance from otolith core (μm)

Bird08_09


Li Concentration (ppm)
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
6000
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
2.0
1.6
1.2
0.8
0.4
0.0
Cs Concentration (ppm)
0.06
0.04
0.02
0.00
Distance from otolith core (μm)

Appendix E LA-ICP-MS data for Bird Lake otoliths *continued*

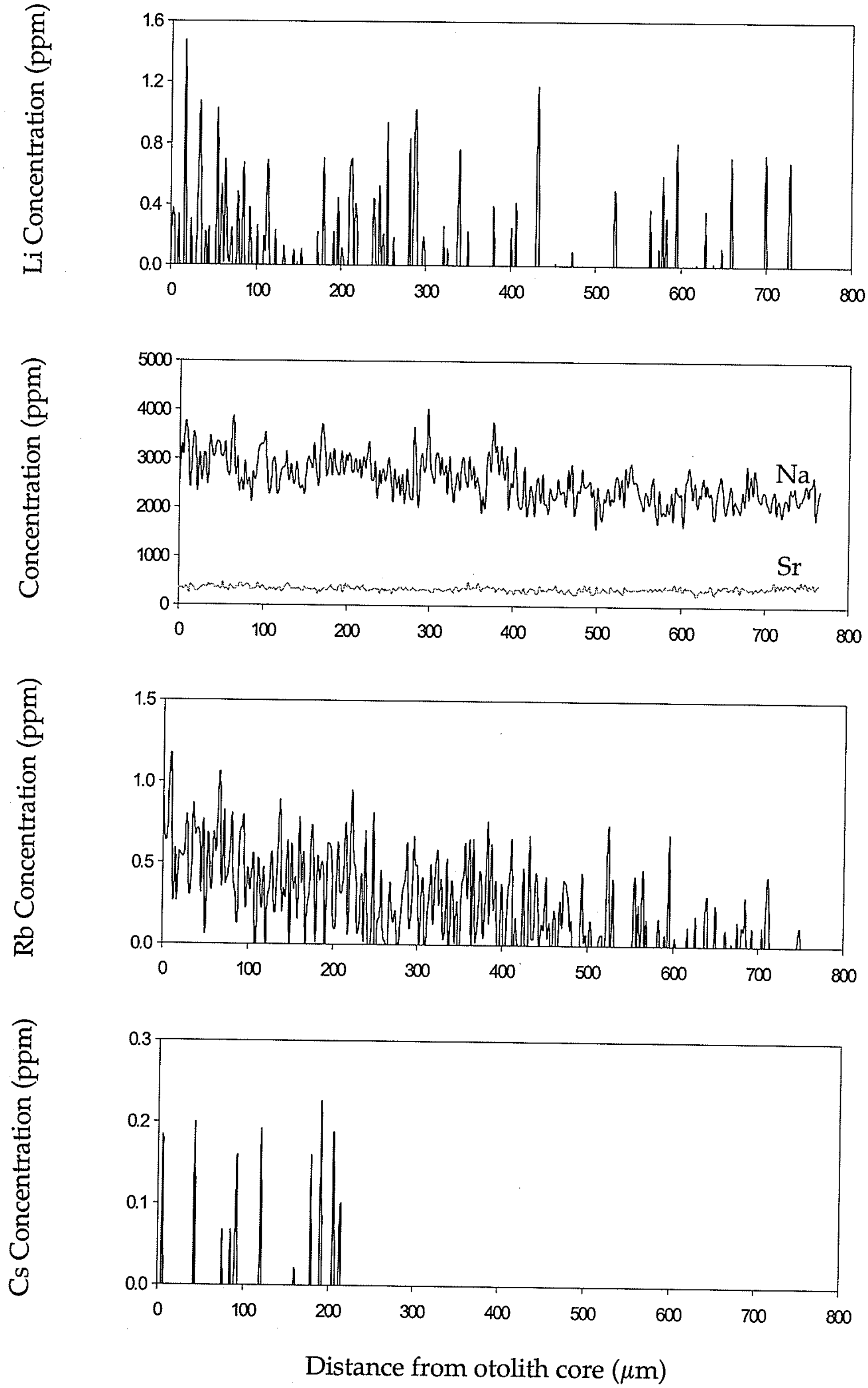
Species: Walleye (*Sander vitreus*), Small Mouth Bass (*Micropterus dolomieu*)

Captured: 2003 (Manitoba Conservation Archives)

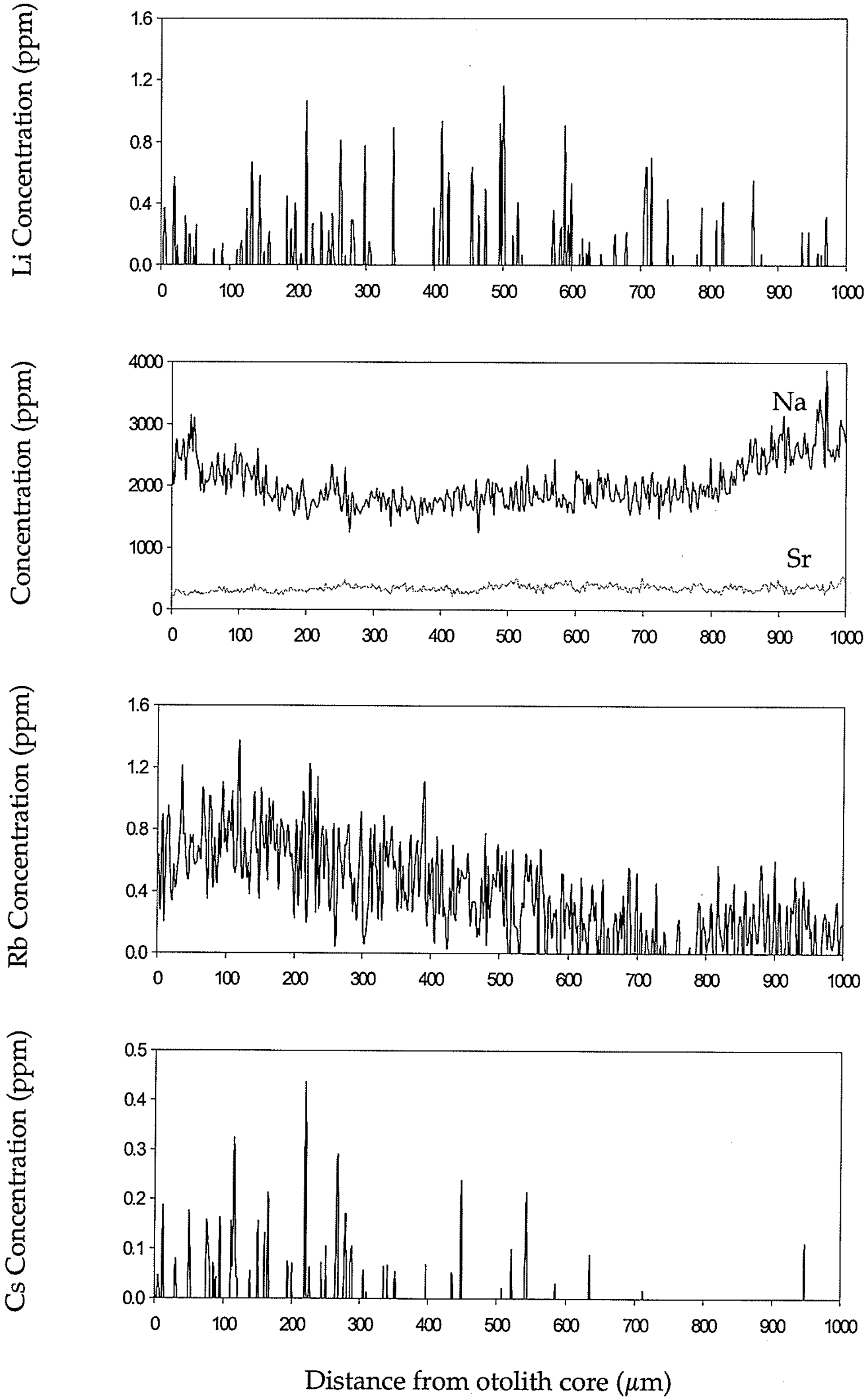
Isotopes	**Li^{7}**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
10	Walleye	9
11	Walleye	12
18	Walleye	9
45	Walleye	13
86	Small Mouth Bass	9

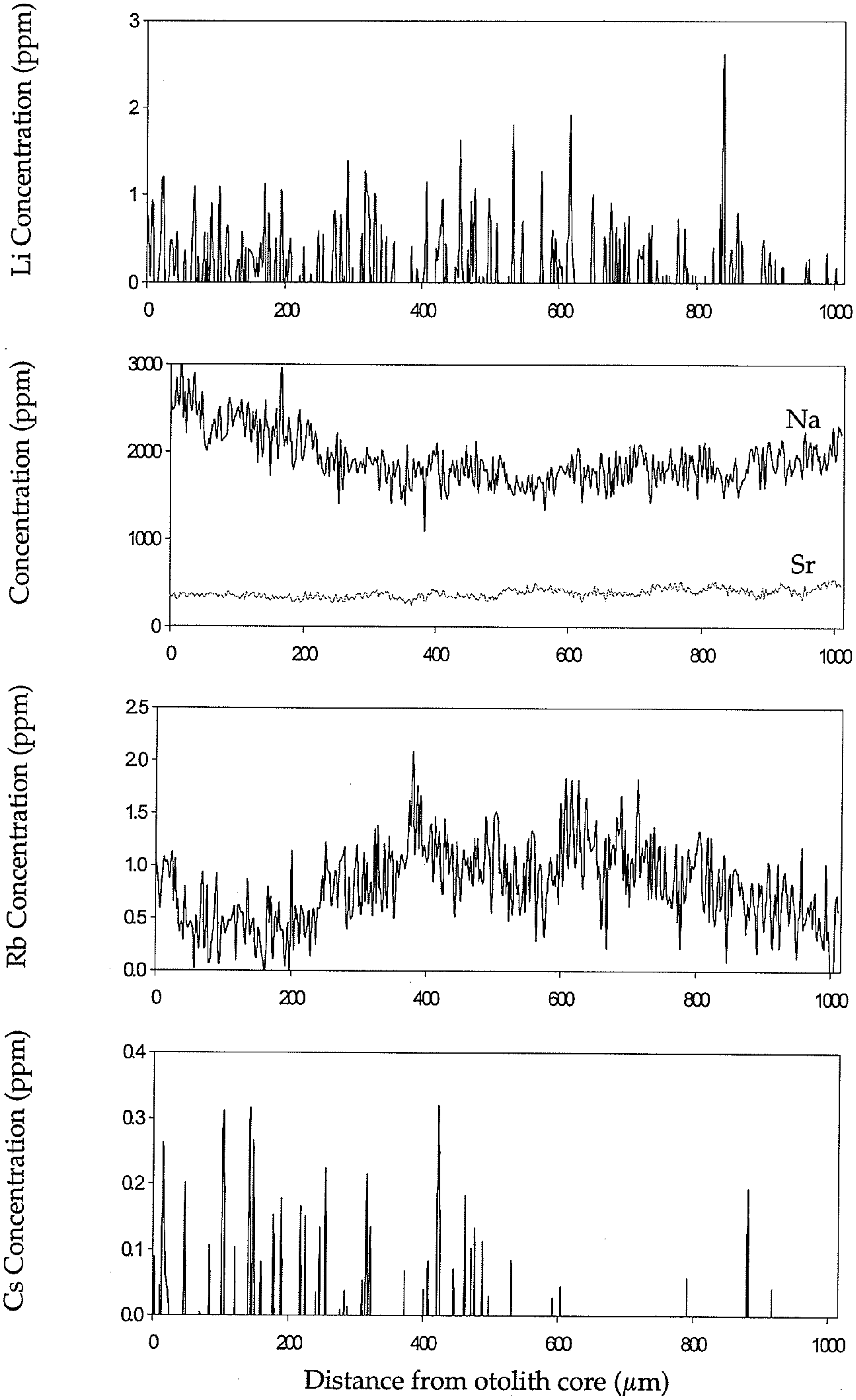
Bird03_10


Li Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.5
1.0
0.5
0.0
Cs Concentration (ppm)
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

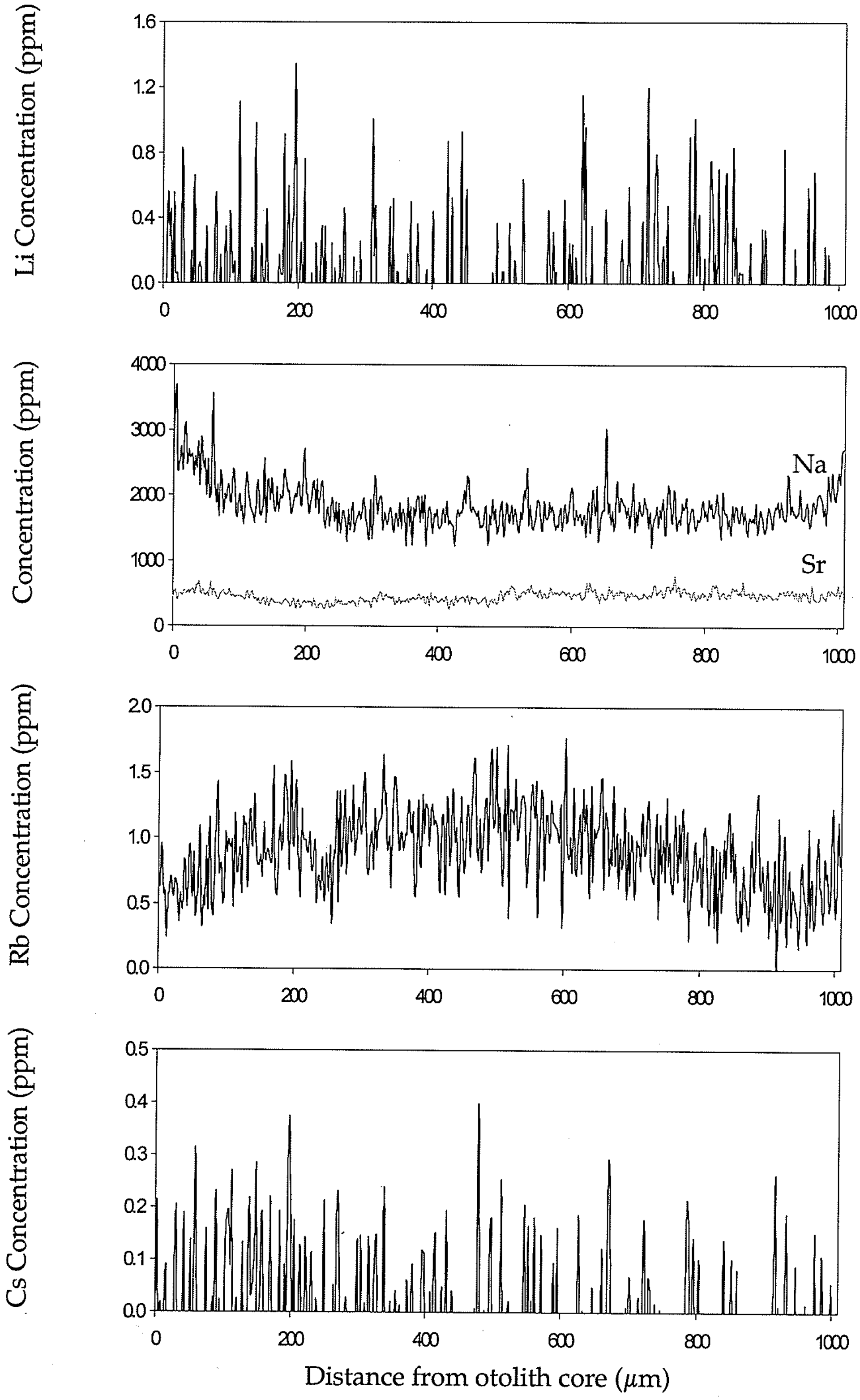
Bird03_11


Li Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
800
900
1000
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
800
900
1000
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
800
900
1000
Cs Concentration (ppm)
0.5
0.4
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
800
900
1000
Distance from otolith core (μm)

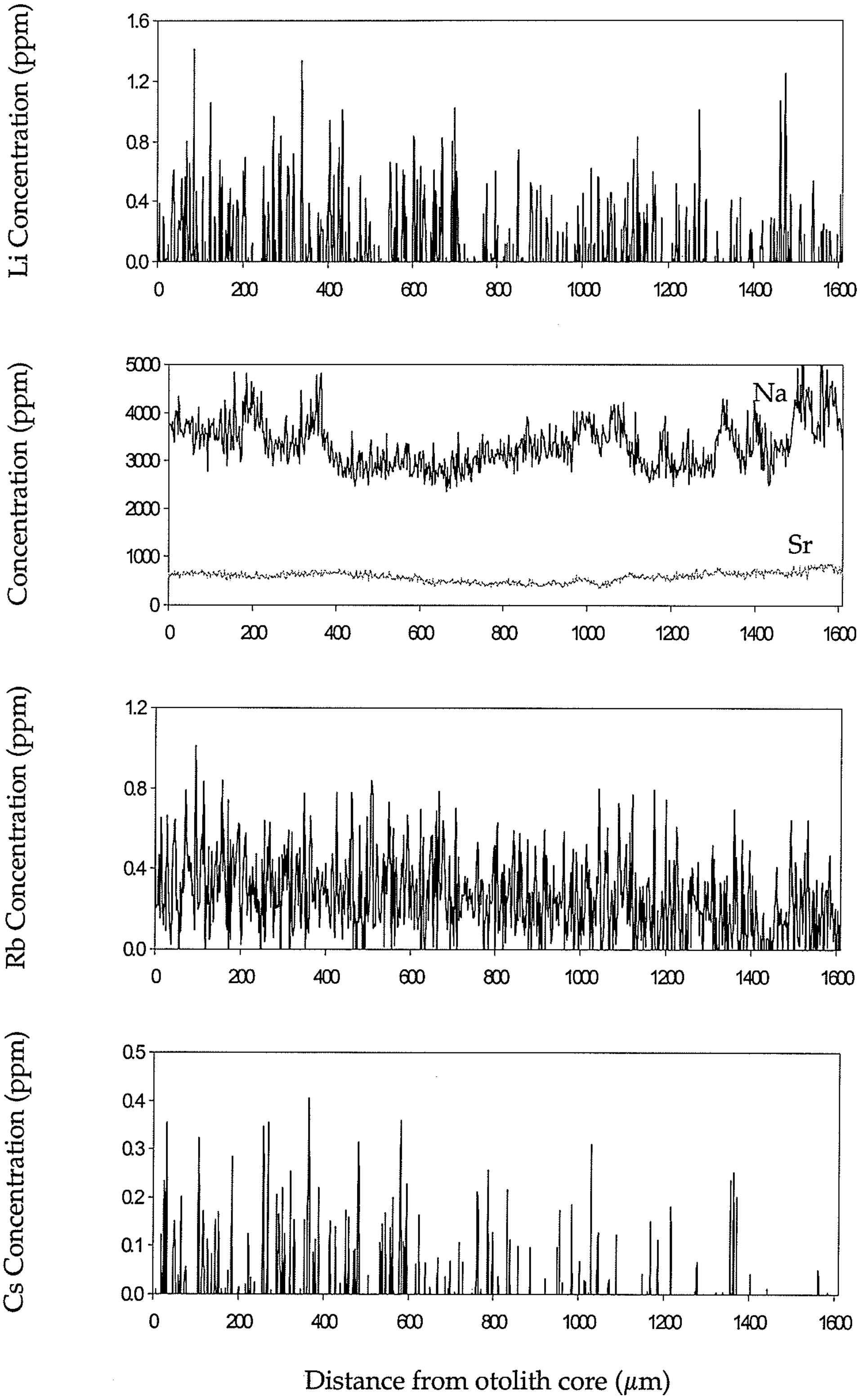
Bird03_18


Li Concentration (ppm)
3
2
1
0
0
200
400
600
800
1000
Concentration (ppm)
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Cs Concentration (ppm)
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

Bird03_45


Li Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Cs Concentration (ppm)
0.5
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

Bird03_86


Li Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
Cs Concentration (ppm)
0.5
0.4
0.3
0.2
0.1
0.0
Distance from otolith core (μm)

Appendix F LA-ICP-MS data for Bird River Upstream otoliths

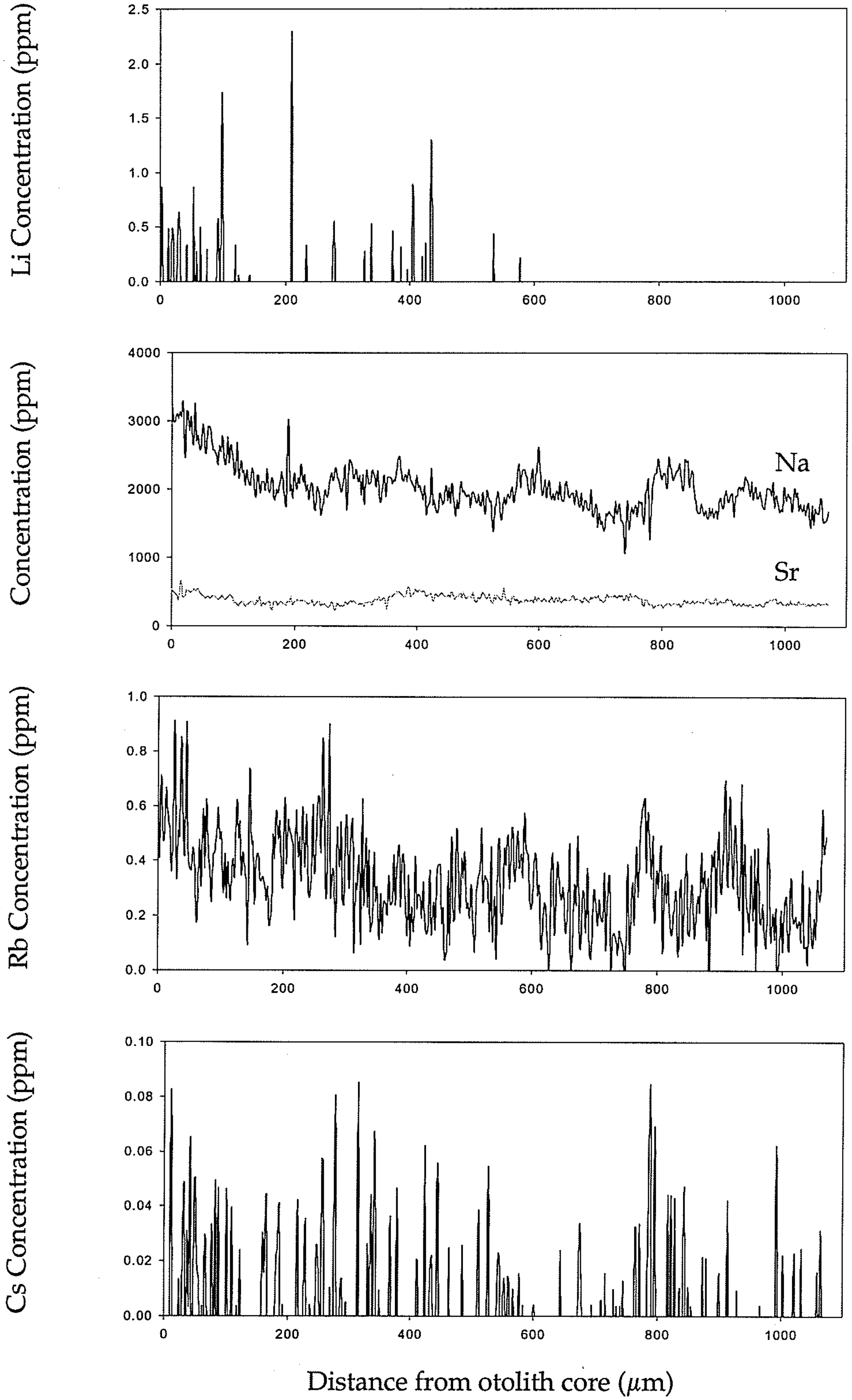
Species: Northern Pike (*Esox lucius*), Yellow Perch (*Perca flavescens*)

Captured: 2006

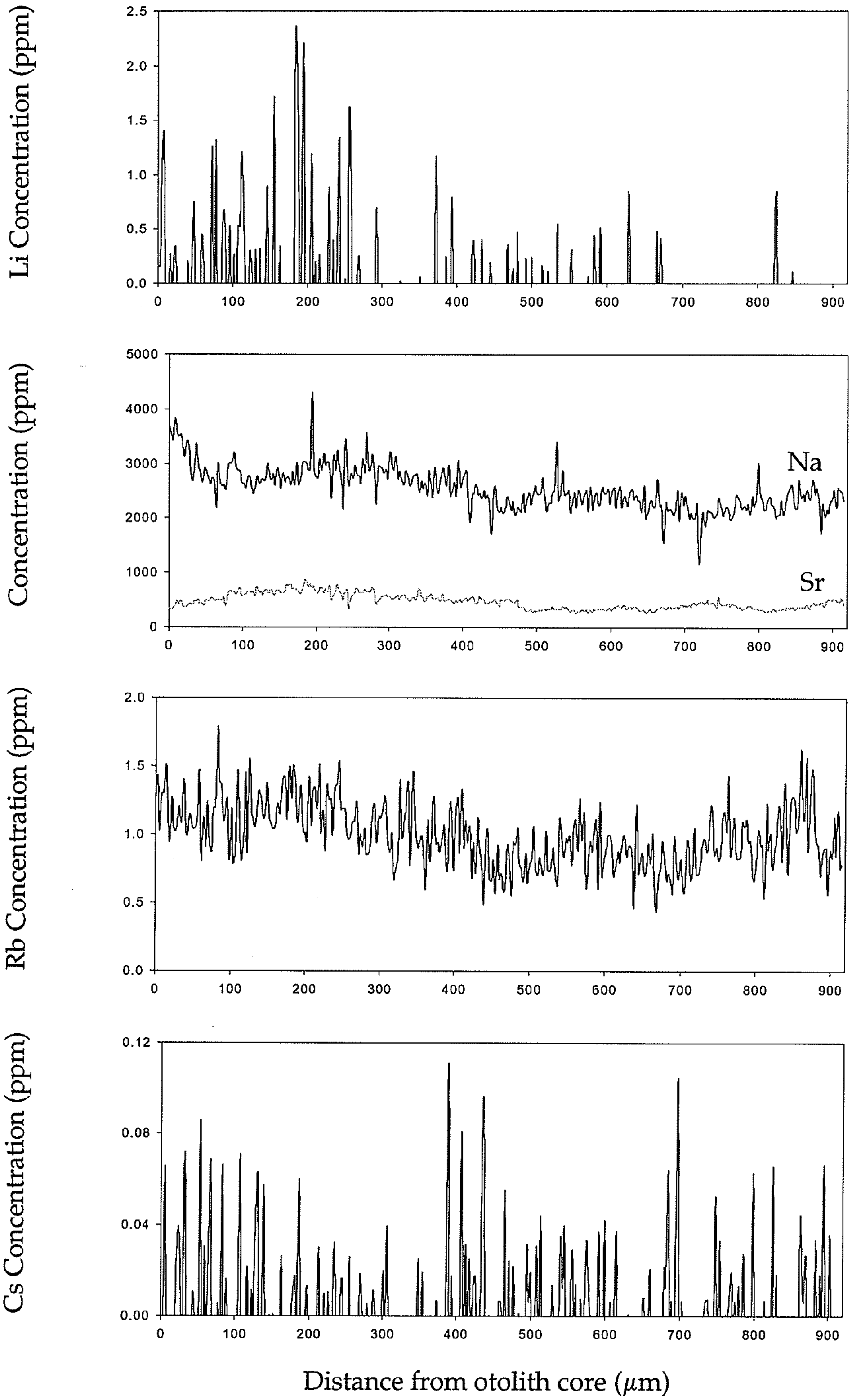
Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
01	Yellow Perch	6
02	Northern Pike	6
03	Northern Pike	8
04	Northern Pike	7
05	Northern Pike	6

BRUp06_01

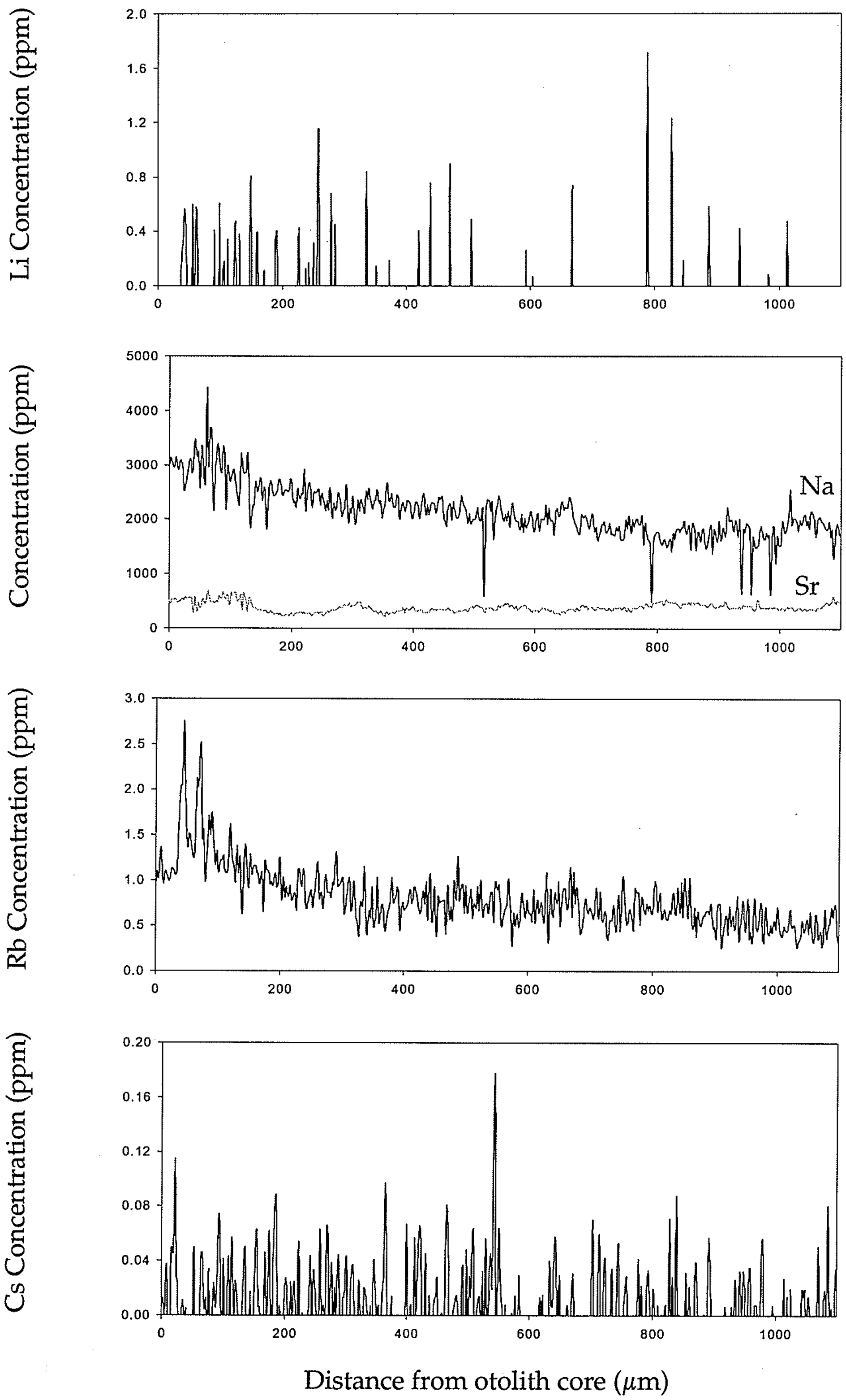

Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
Cs Concentration (ppm)
0.10
0.08
0.06
0.04
0.02
0.00
0
200
400
600
800
1000
Distance from otolith core (μm)

BRUp06_02

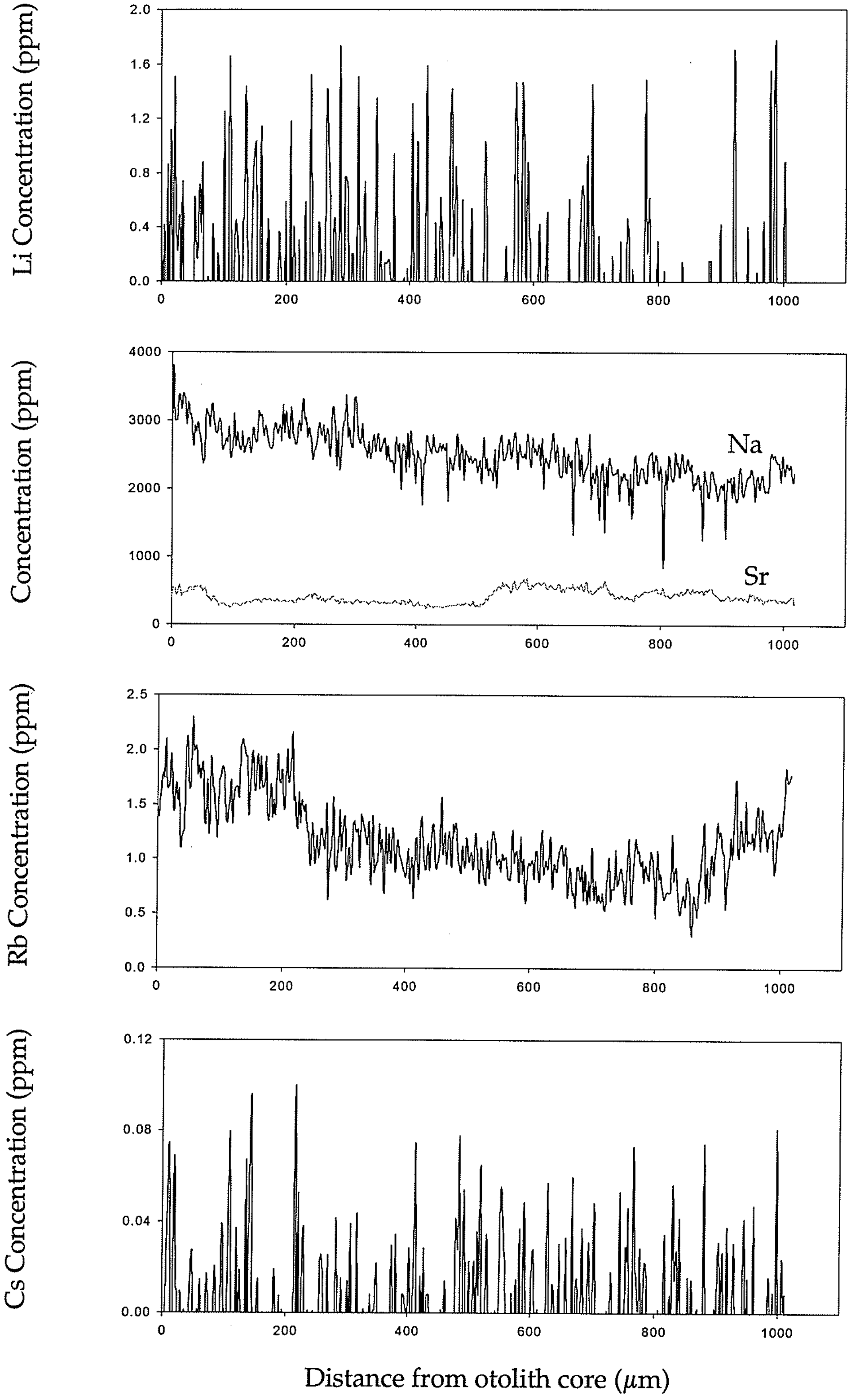


Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
900
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
Distance from otolith core (μm)

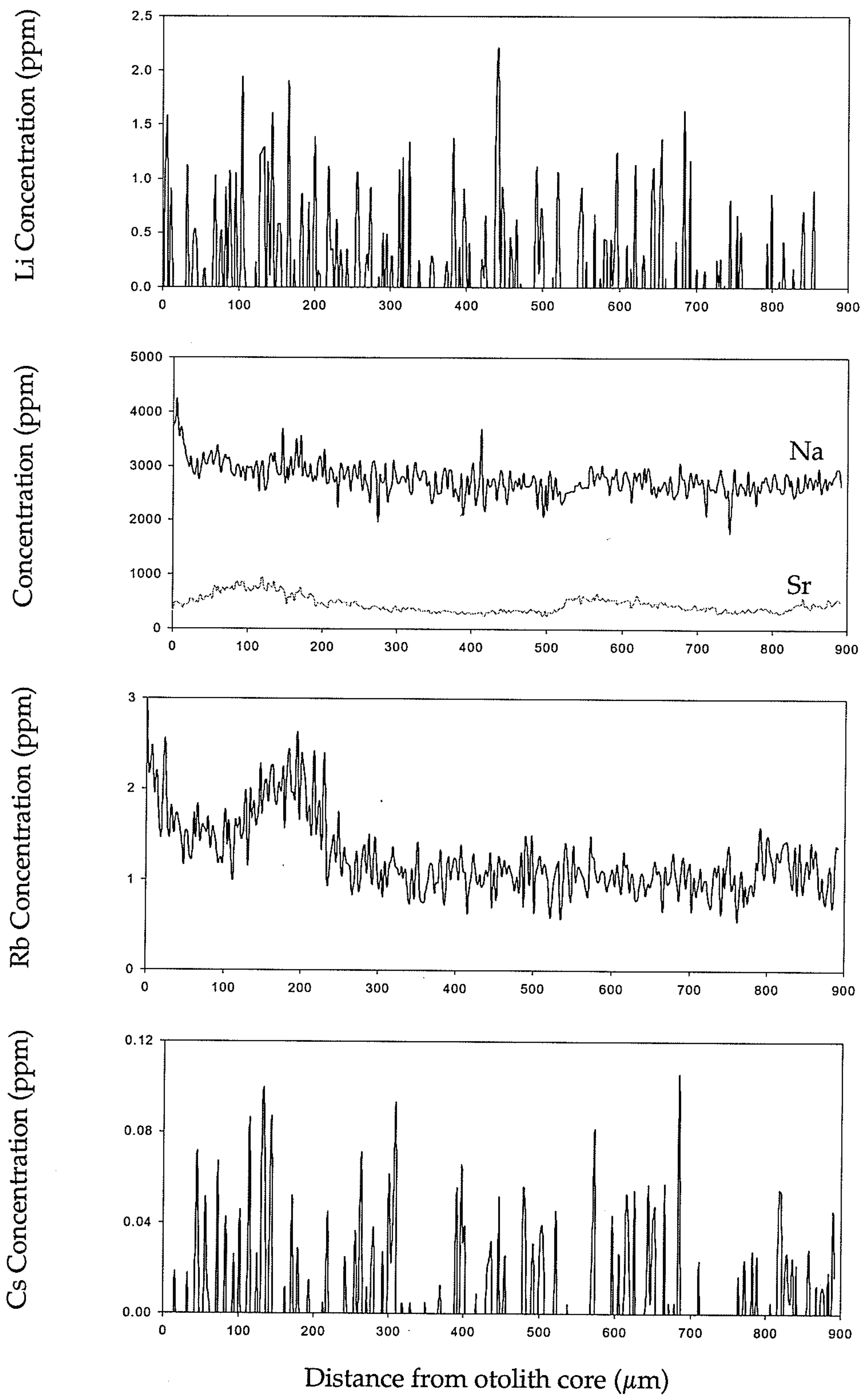
BRUp06_03


Li Concentration (ppm)
2.0
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Cs Concentration (ppm)
0.20
0.16
0.12
0.08
0.04
0.00
0
200
400
600
800
1000
Distance from otolith core (μm)

BRUp06_04


Li Concentration (ppm)
2.0
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
0
200
400
600
800
1000
Distance from otolith core (μm)

BRUp06_05


Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
900
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
3
2
1
0
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
Distance from otolith core (μm)

Appendix F LA-ICP-MS data for Bird River Upstream otoliths *continued*

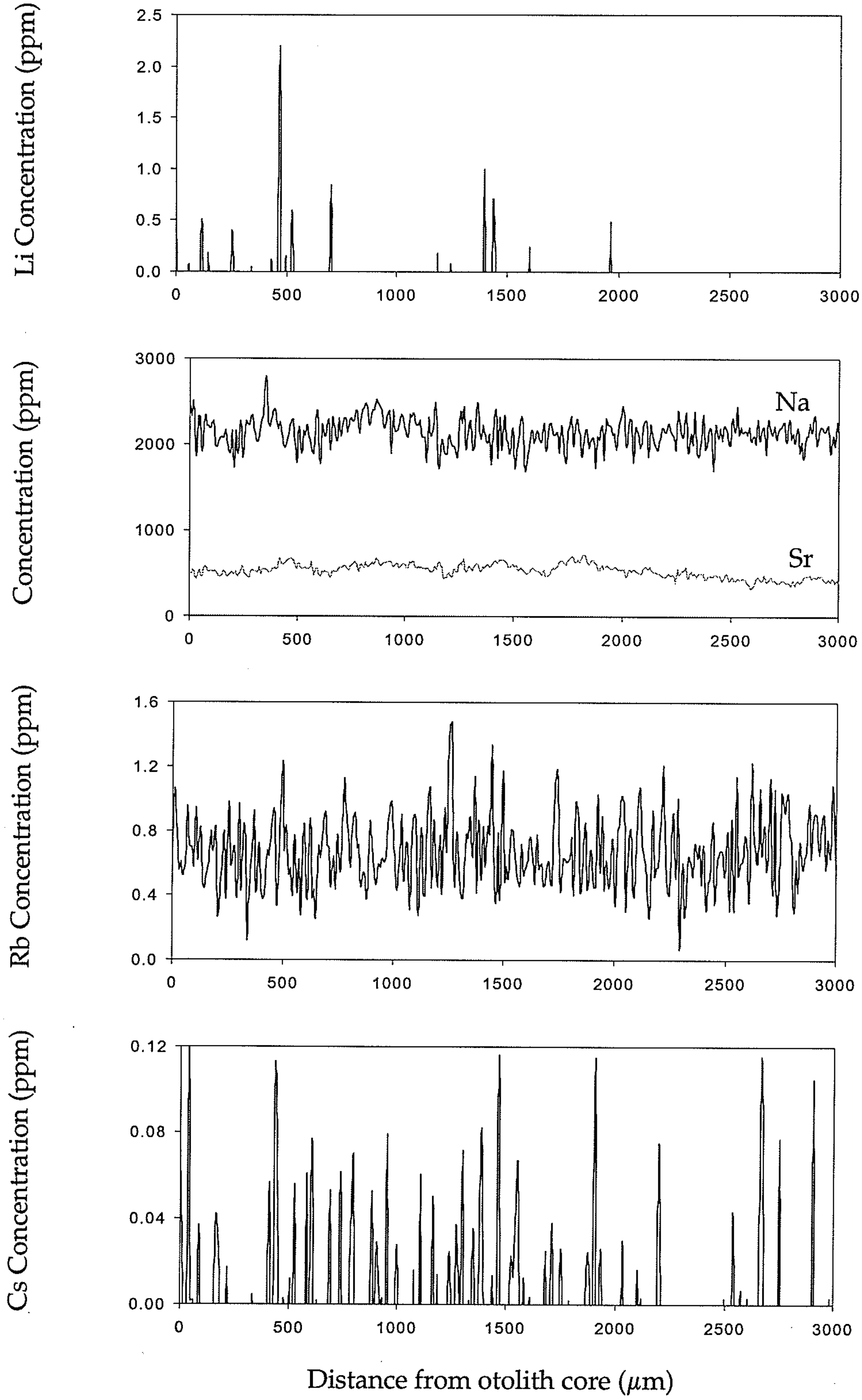
Species: Northern Pike (*Esox lucius*), Silver Redhorse (*Moxostoma anisurum*), White Sucker (*Catostomus commersoni*)

Captured: 1998 (TetrES Consultants, Inc.)

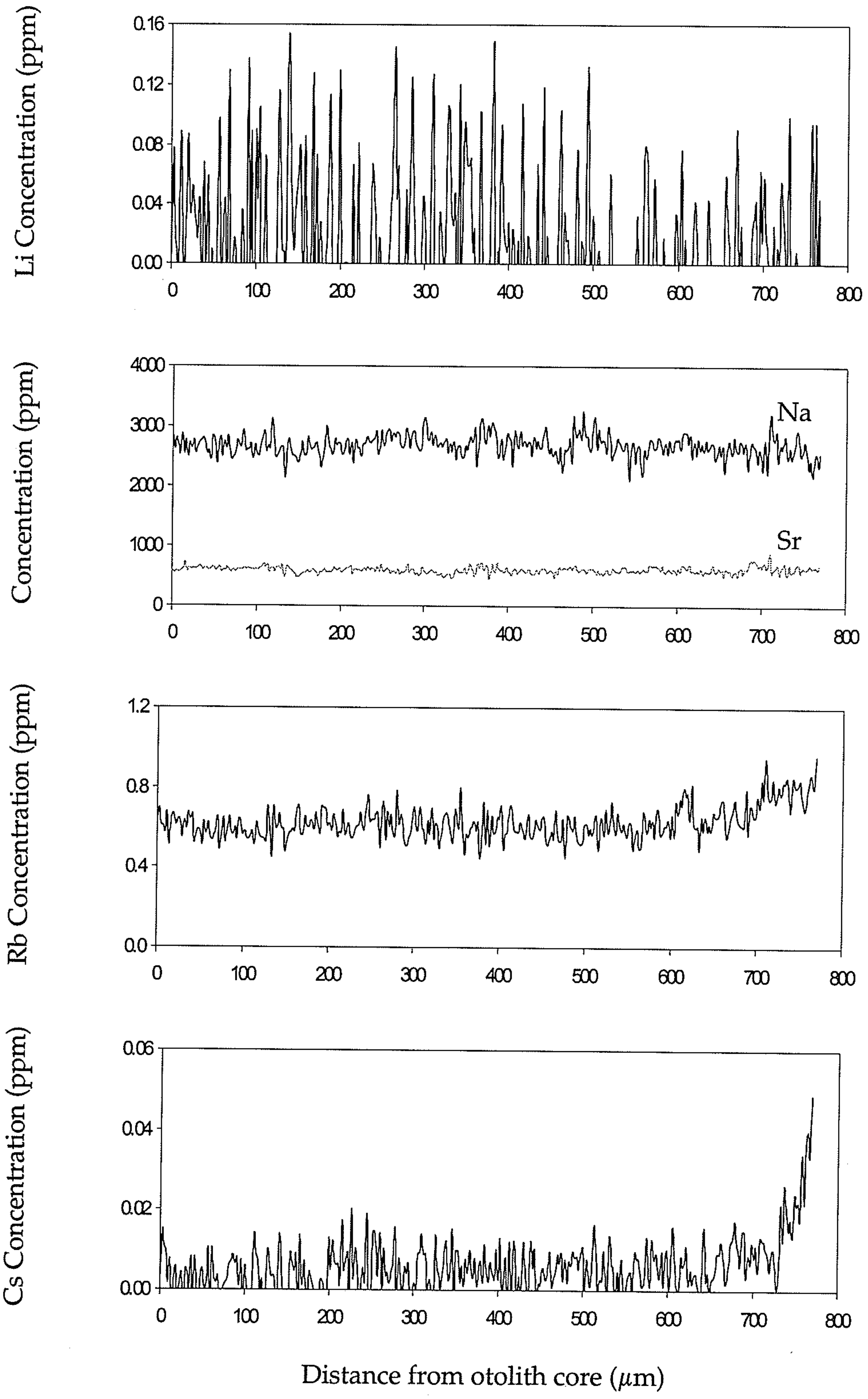
Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
20	White Sucker	12
21	White Sucker	5
22	Silver Redhorse	6
23	White Sucker	14
25	Northern Pike	7
26	Northern Pike	9
27	Northern Pike	6

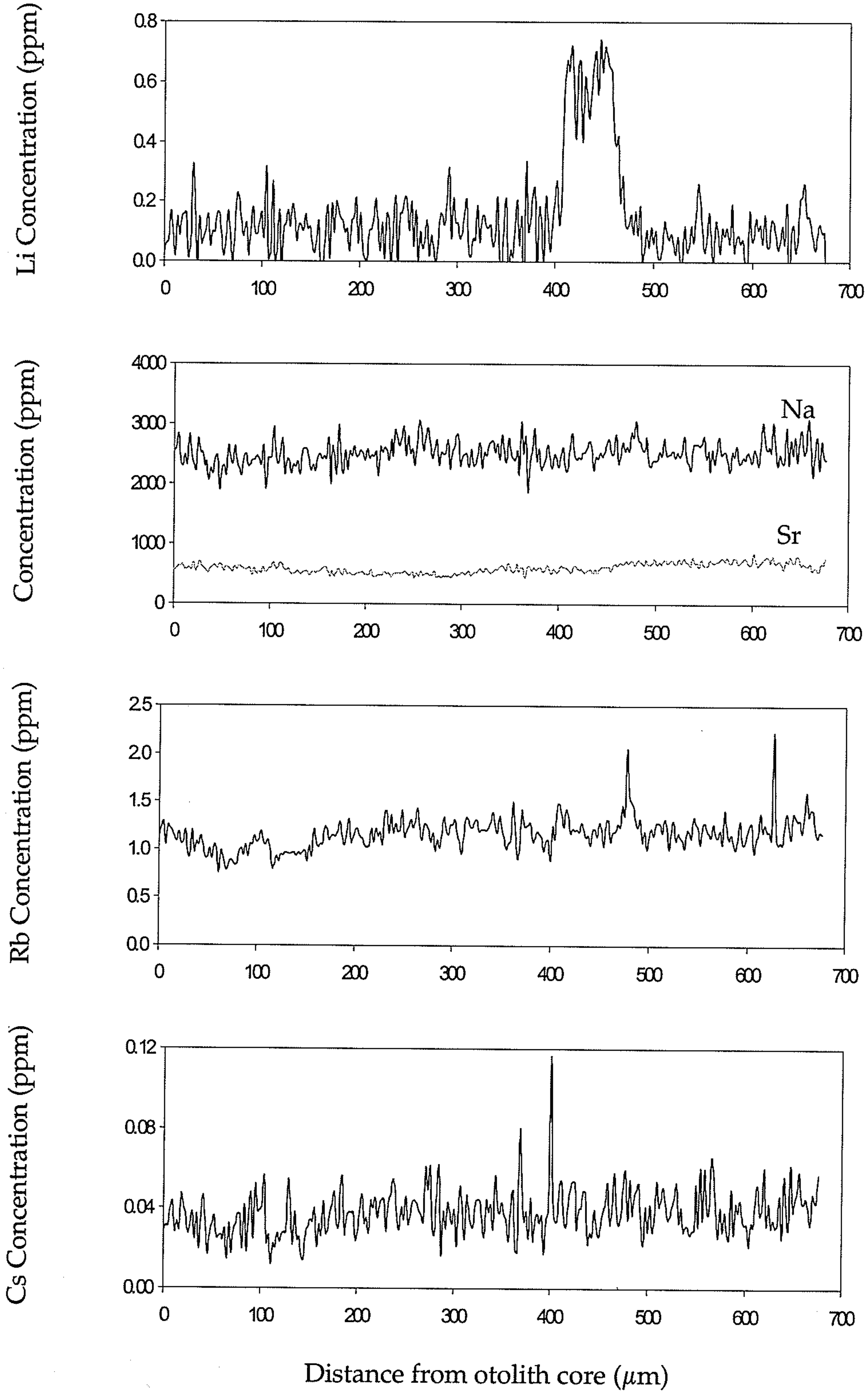
BRUp98_20


Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
2500
3000
Concentration (ppm)
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
2500
3000
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
500
1000
1500
2000
2500
3000
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
0
500
1000
1500
2000
2500
3000
Distance from otolith core (μm)

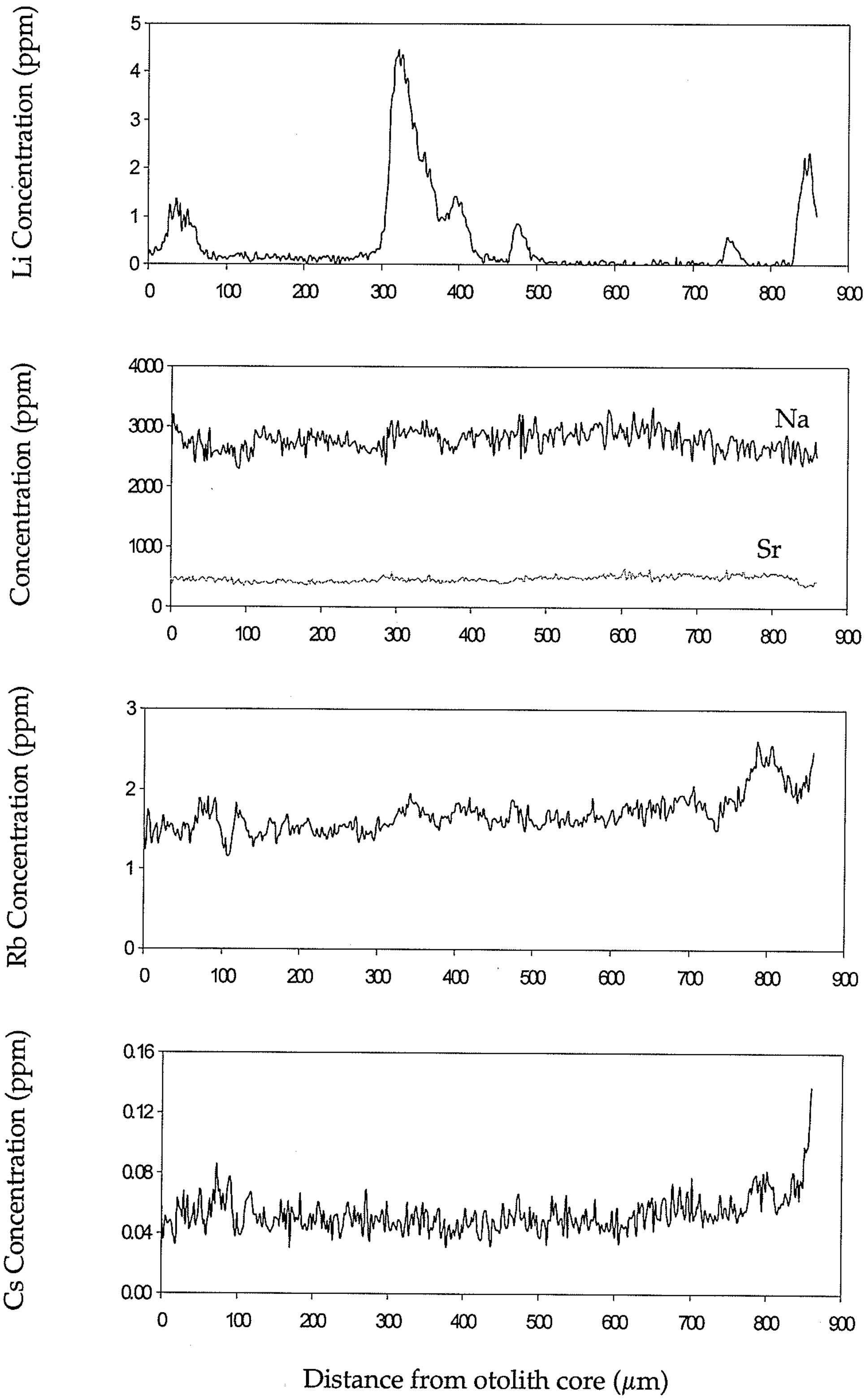
BRUp98_21


Li Concentration (ppm)
0.16
0.12
0.08
0.04
0.00
0
100
200
300
400
500
600
700
800
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
800
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
800
Cs Concentration (ppm)
0.06
0.04
0.02
0.00
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

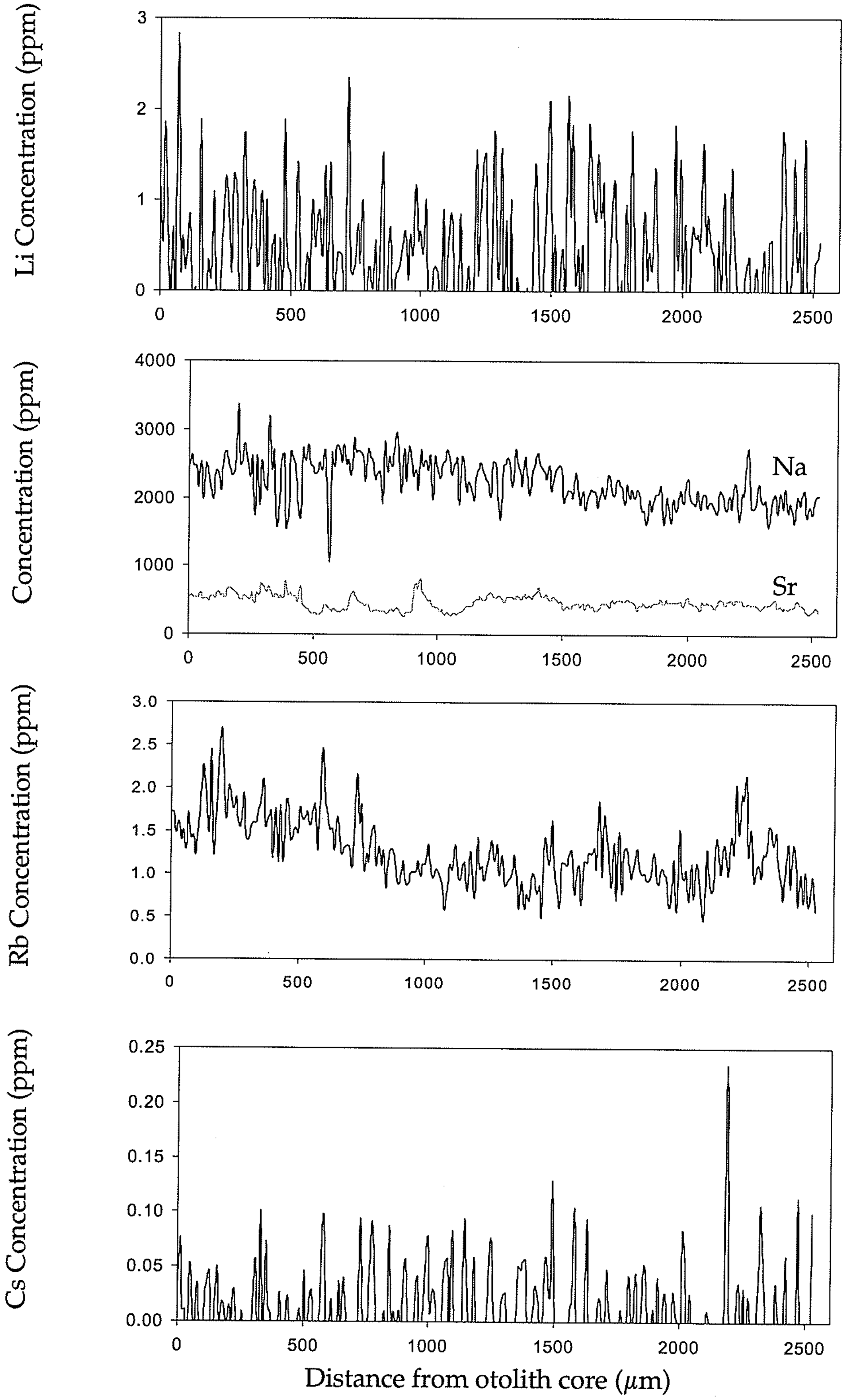
BRUp98_22


Li Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
600
700
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
Distance from otolith core (μm)

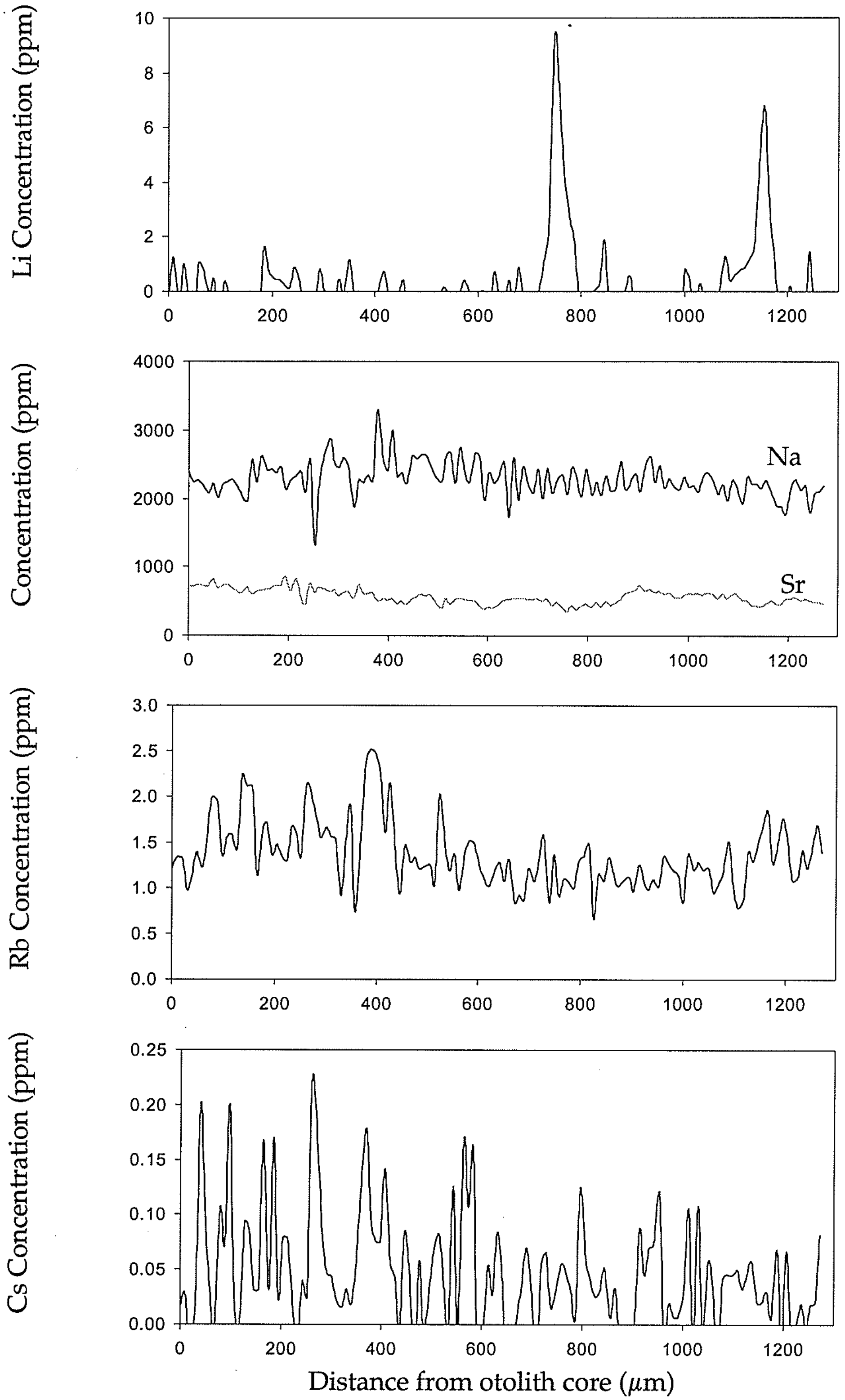
BRUp98_23


Li Concentration (ppm)
5
4
3
2
1
0
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
3
2
1
0
Cs Concentration (ppm)
0.16
0.12
0.08
0.04
0.00
0
100
200
300
400
500
600
700
800
900
Distance from otolith core (μm)

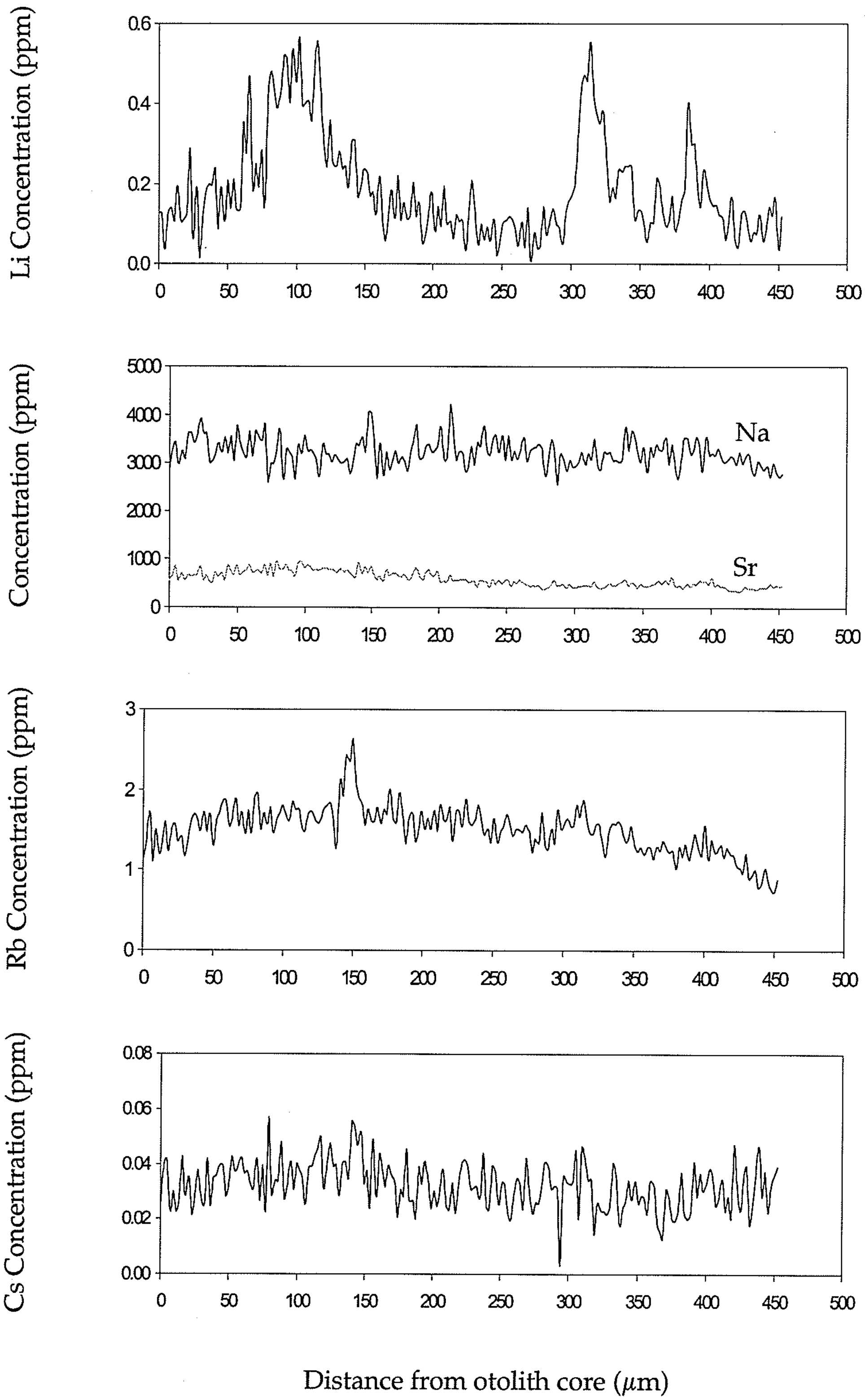
BRUp98_25


Li Concentration (ppm)
3
2
1
0
0
500
1000
1500
2000
2500
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
2500
Rb Concentration (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
2500
Cs Concentration (ppm)
0.25
0.20
0.15
0.10
0.05
0.00
0
500
1000
1500
2000
2500
Distance from otolith core (μm)

BRUp98_26


Li Concentration (ppm)
10
8
6
4
2
0
0
200
400
600
800
1000
1200
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.25
0.20
0.15
0.10
0.05
0.00
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

BRUp98_27


Li Concentration (ppm)
0.6
0.4
0.2
0.0
0
50
100
150
200
250
300
350
400
450
500
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
3
2
1
0
Cs Concentration (ppm)
0.08
0.06
0.04
0.02
0.00
Distance from otolith core (μm)

Appendix G LA-ICP-MS data for Lac du Bonnet otoliths

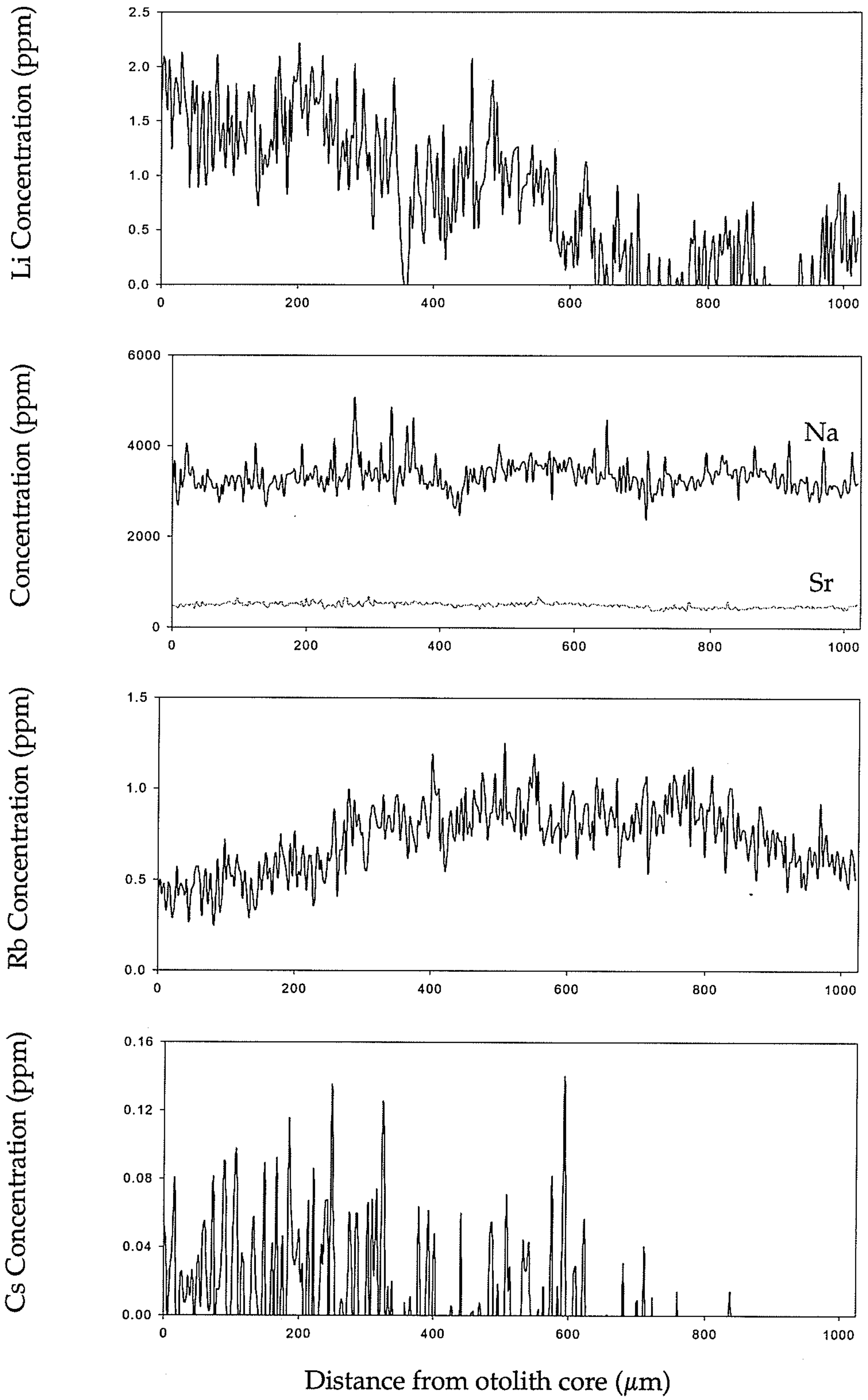
Species: Walleye (*Sander vitreous*), Sauger (*Stizostedion canadense*), Northern Pike (*Esox lucius*), Whitefish (*Coregonus clupeaformis*), Cisco (*Coregonus artedii*), Yellow Perch (*Perca flavescens*), Rock Bass (*Ambloplites rupestris*), Silver Redhorse (*Moxostoma anisurum*), White Sucker (*Catostomus commersoni*)

Captured: 2008

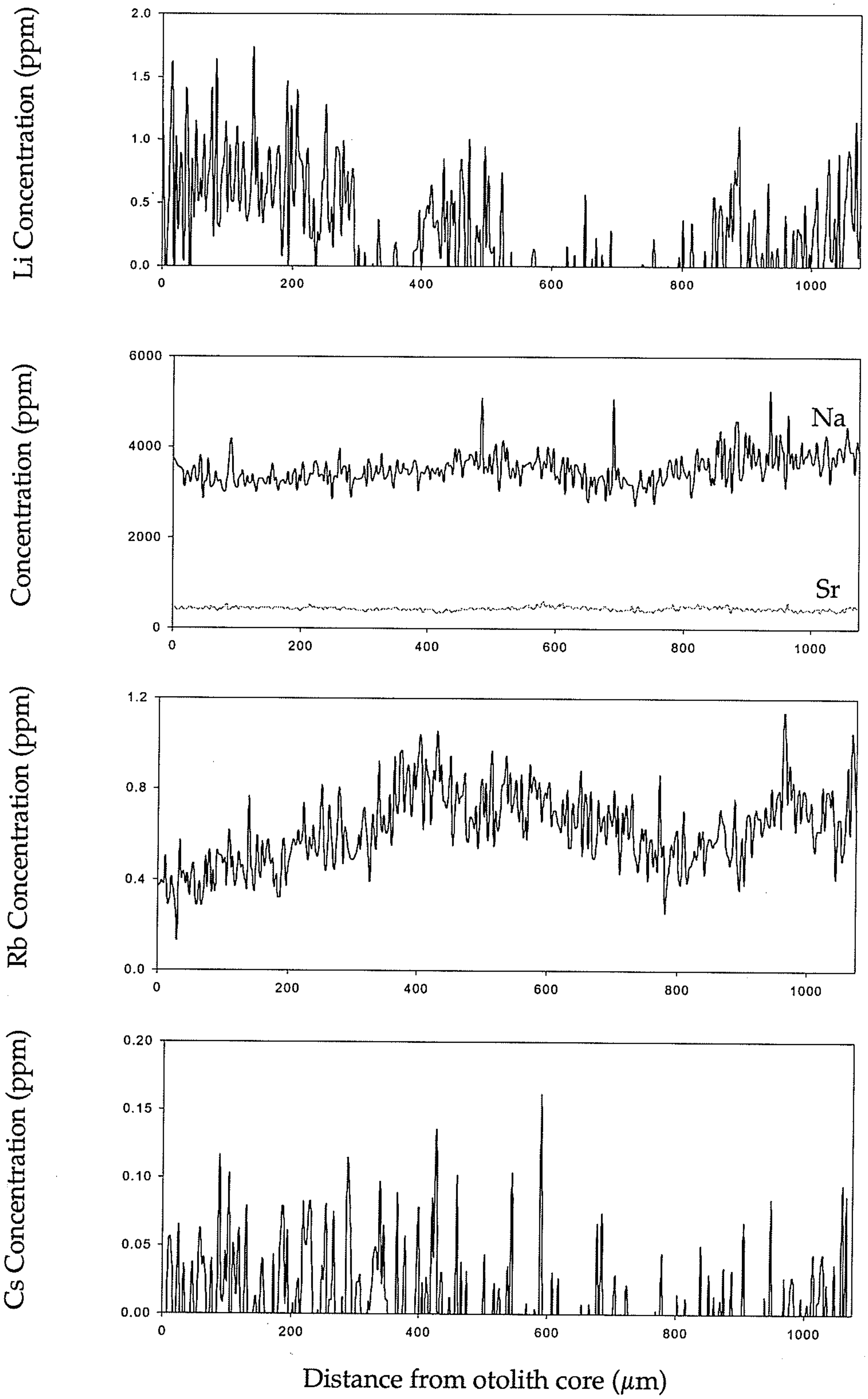
Isotopes	**Li^{7}**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
01	Cisco	5
02	Cisco	5
03	Cisco	4
04	Cisco	4
05	Yellow Perch	4
06	Rock Bass	7
07	Rock Bass	9
08	Silver Redhorse	13
09	White Sucker	9
10	White Sucker	6
11	White Sucker	14
12	White Sucker	7
13	White Sucker	6
14	White Sucker	10
15	White Sucker	11
16	White Sucker	6
17	White Sucker	12
18	White Sucker	8
22	Sauger	4
23	Whitefish	6
24	Northern Pike	14
25	Northern Pike	14
26	Walleye	4

LDB08_01

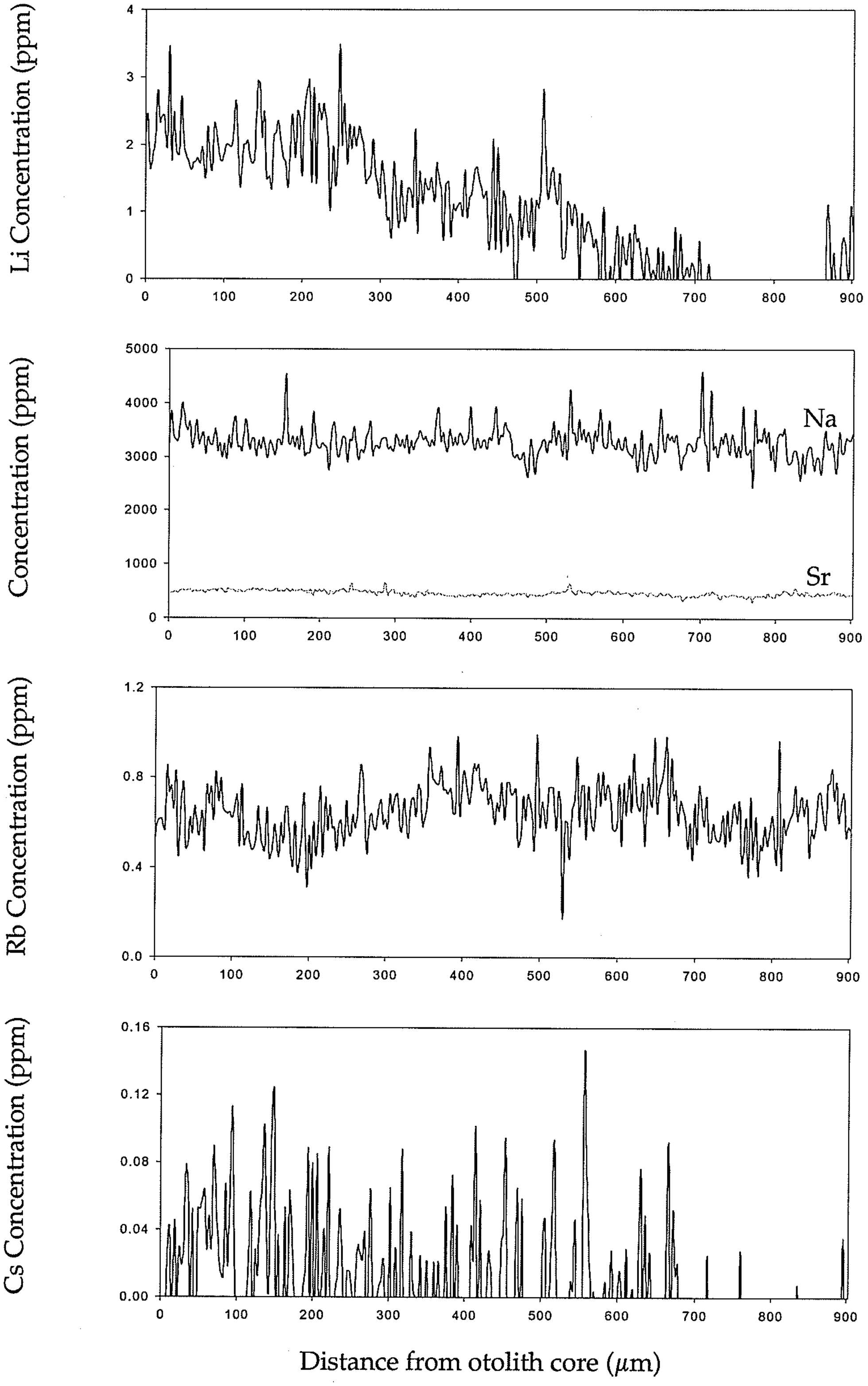

Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Concentration (ppm)
6000
4000
2000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Cs Concentration (ppm)
0.16
0.12
0.08
0.04
0.00
0
200
400
600
800
1000
Distance from otolith core (μm)

LDB08_02

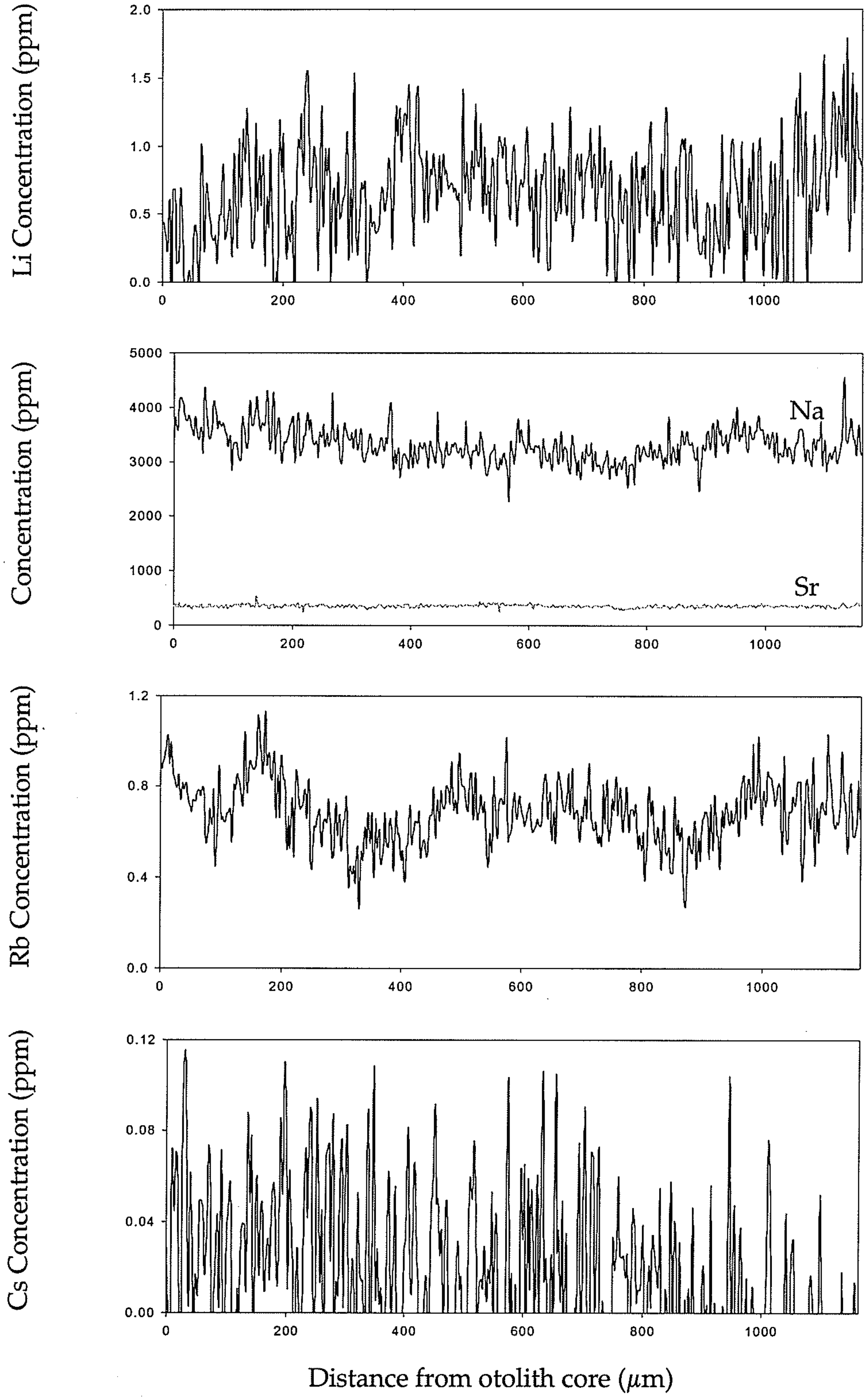


Li Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Concentration (ppm)
6000
4000
2000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
Cs Concentration (ppm)
0.20
0.15
0.10
0.05
0.00
0
200
400
600
800
1000
Distance from otolith core (μm)

LDB08_03

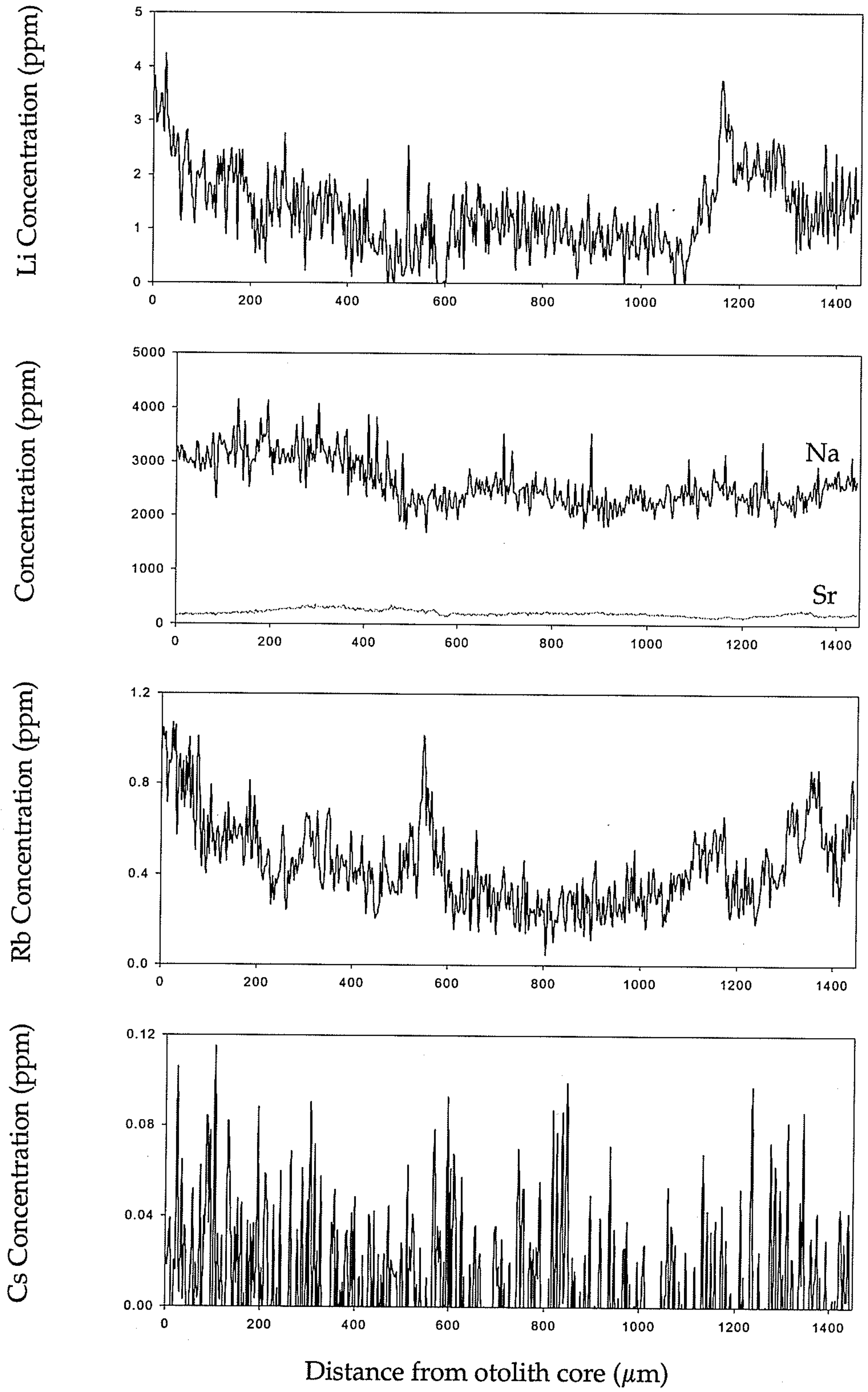

Li Concentration (ppm)
0
1
2
3
4
0
100
200
300
400
500
600
700
800
900
Concentration (ppm)
Na
Sr
0
1000
2000
3000
4000
5000
0
100
200
300
400
500
600
700
800
900
Rb Concentration (ppm)
0.0
0.4
0.8
1.2
0
100
200
300
400
500
600
700
800
900
Cs Concentration (ppm)
0.00
0.04
0.08
0.12
0.16
0
100
200
300
400
500
600
700
800
900
Distance from otolith core (μm)

LDB08_04

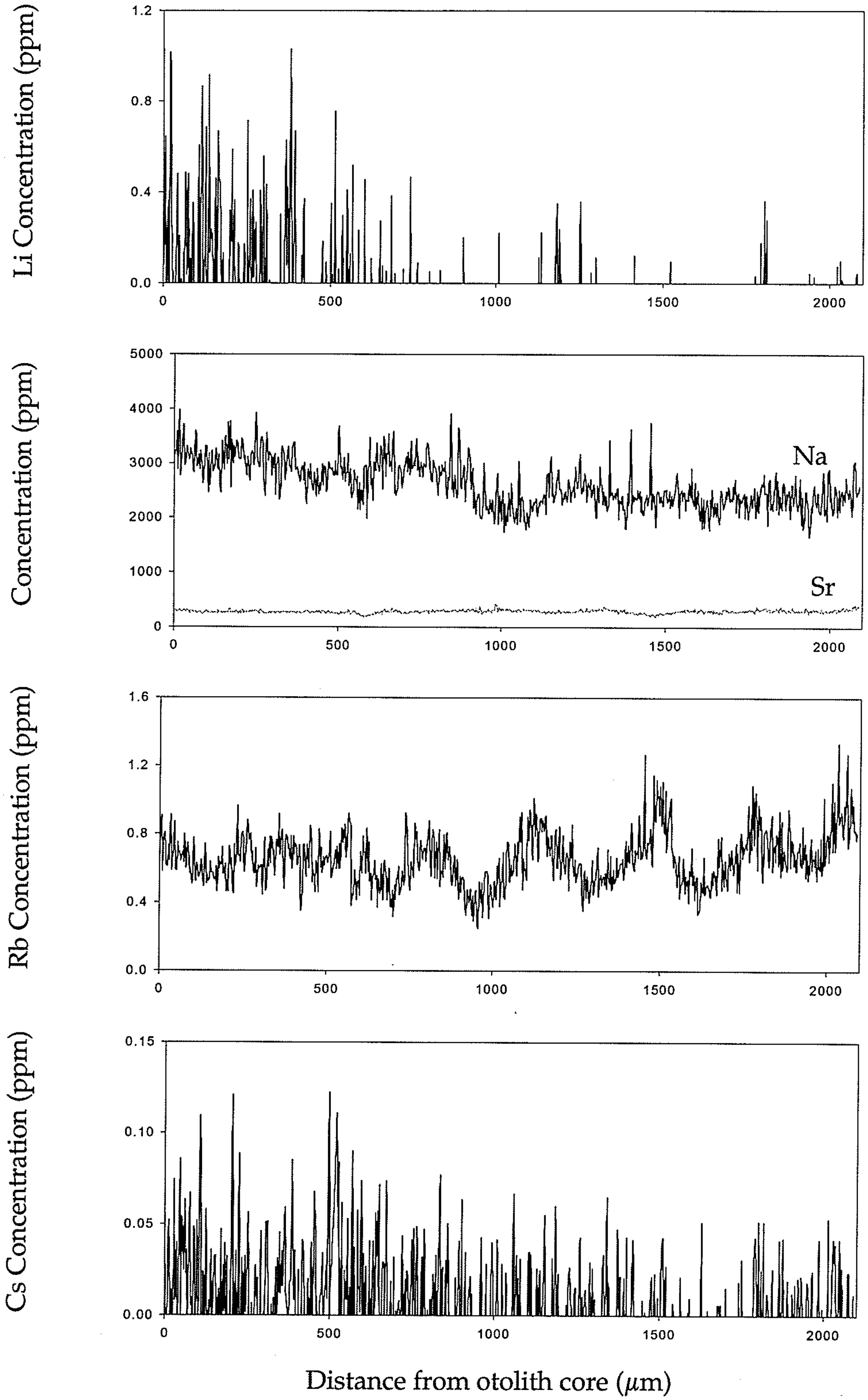


Li Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
0
200
400
600
800
1000
Distance from otolith core (μm)

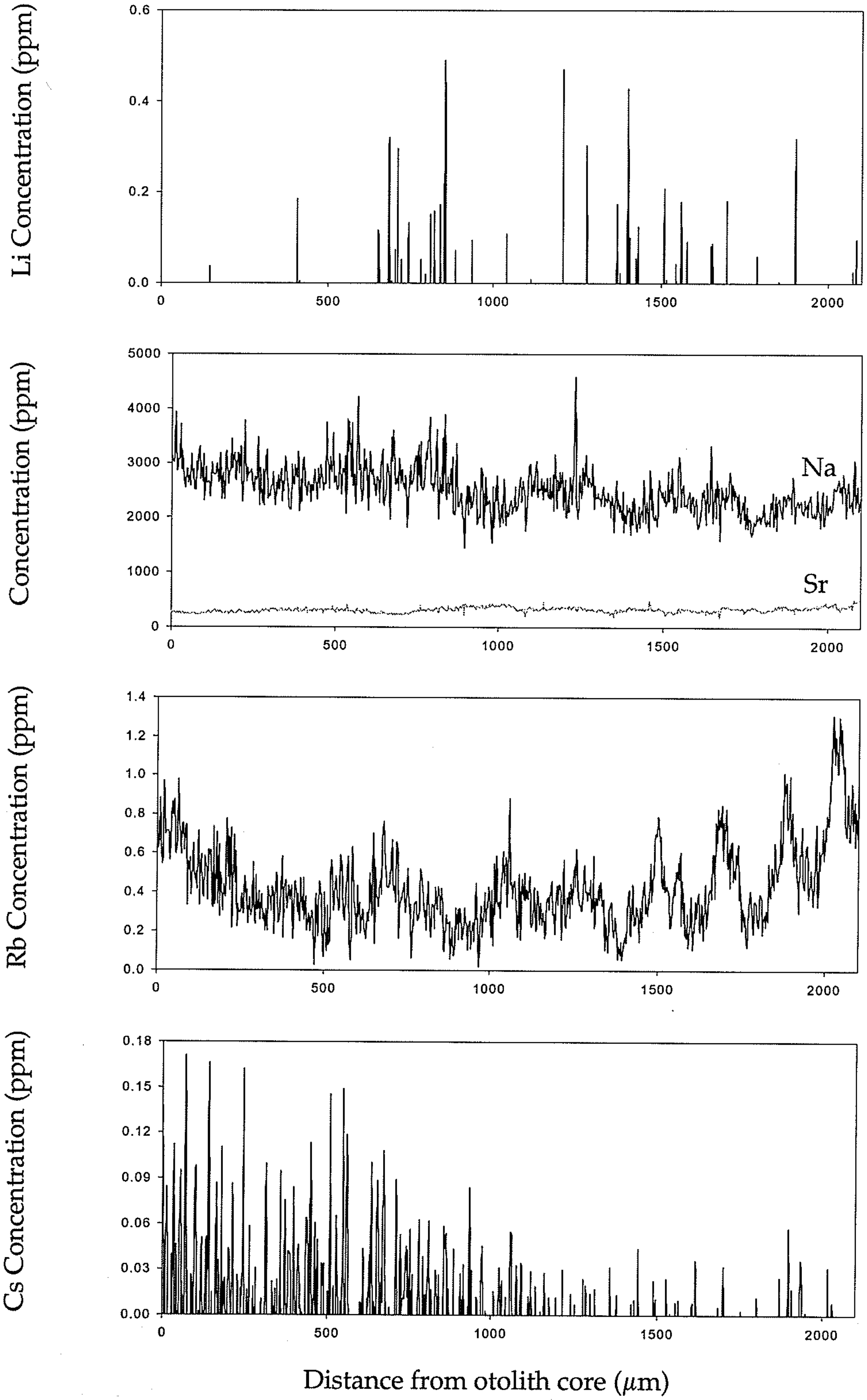
LDB08_05


Li Concentration (ppm)
5
4
3
2
1
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

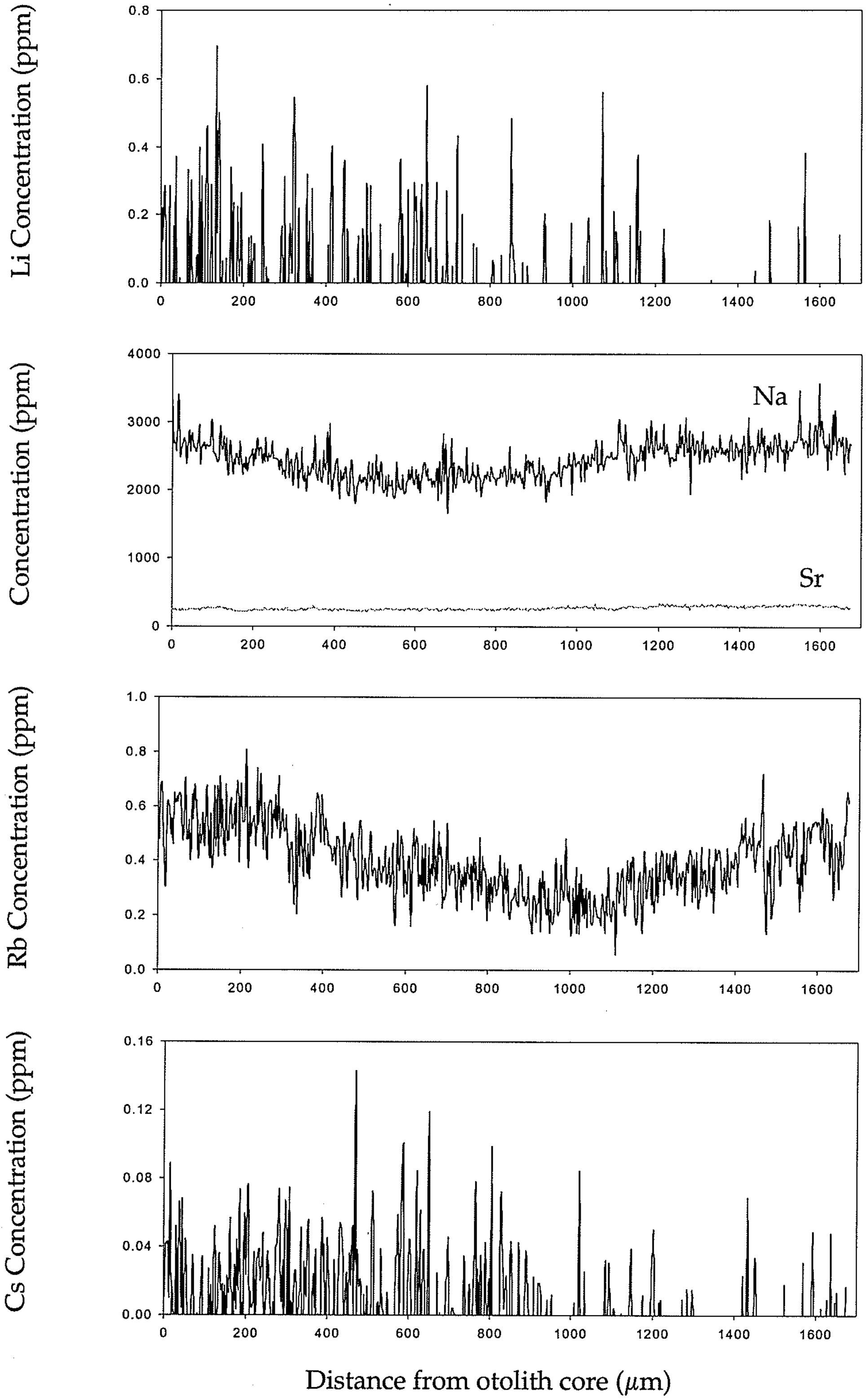
LDB08_06


Li Concentration (ppm)
1.2
0.8
0.4
0.0
0
500
1000
1500
2000
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
500
1000
1500
2000
Cs Concentration (ppm)
0.15
0.10
0.05
0.00
0
500
1000
1500
2000
Distance from otolith core (μm)

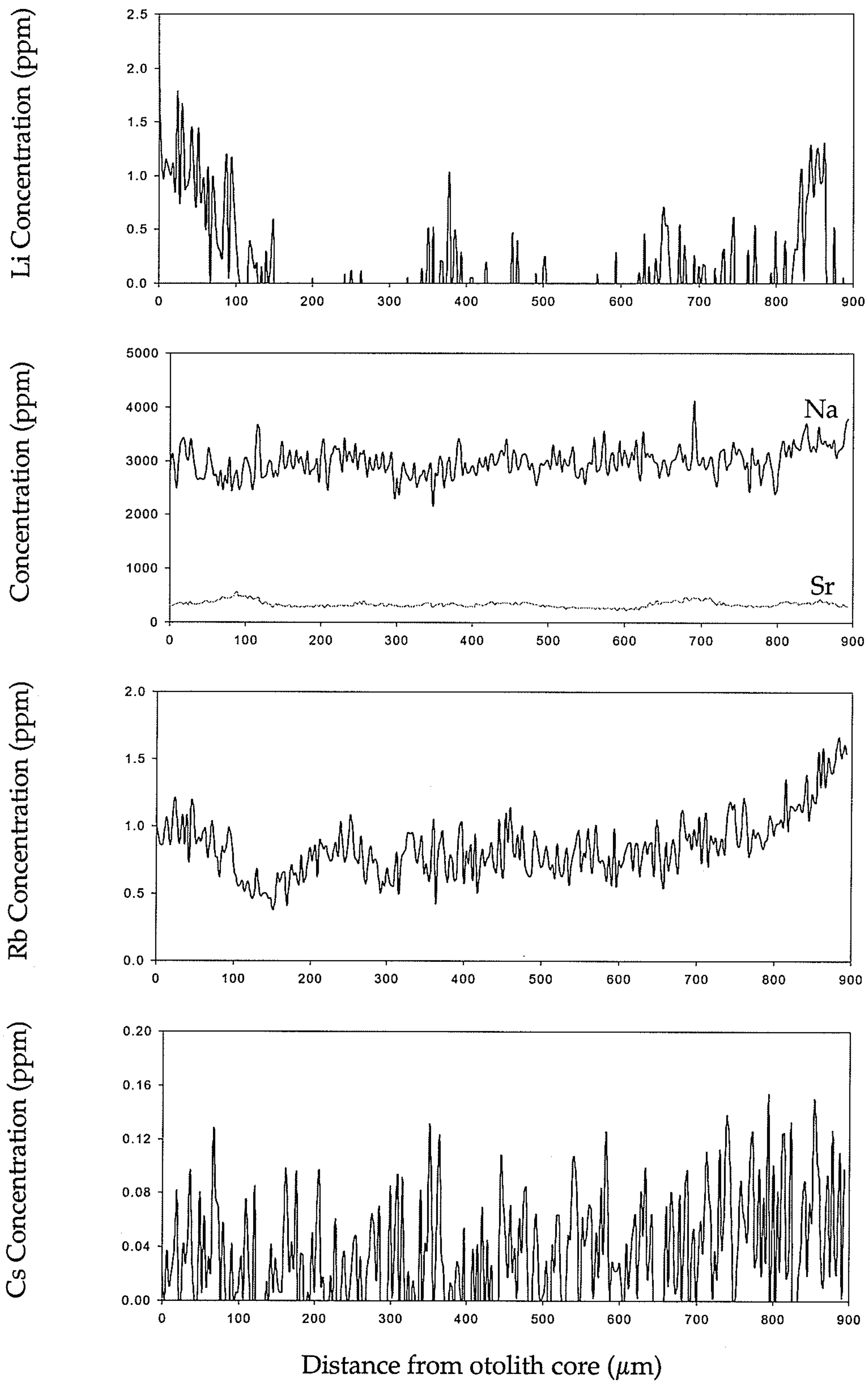
LDB08_07


Li Concentration (ppm)
0.6
0.4
0.2
0.0
0
500
1000
1500
2000
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500
2000
Cs Concentration (ppm)
0.18
0.15
0.12
0.09
0.06
0.03
0.00
0
500
1000
1500
2000
Distance from otolith core (μm)

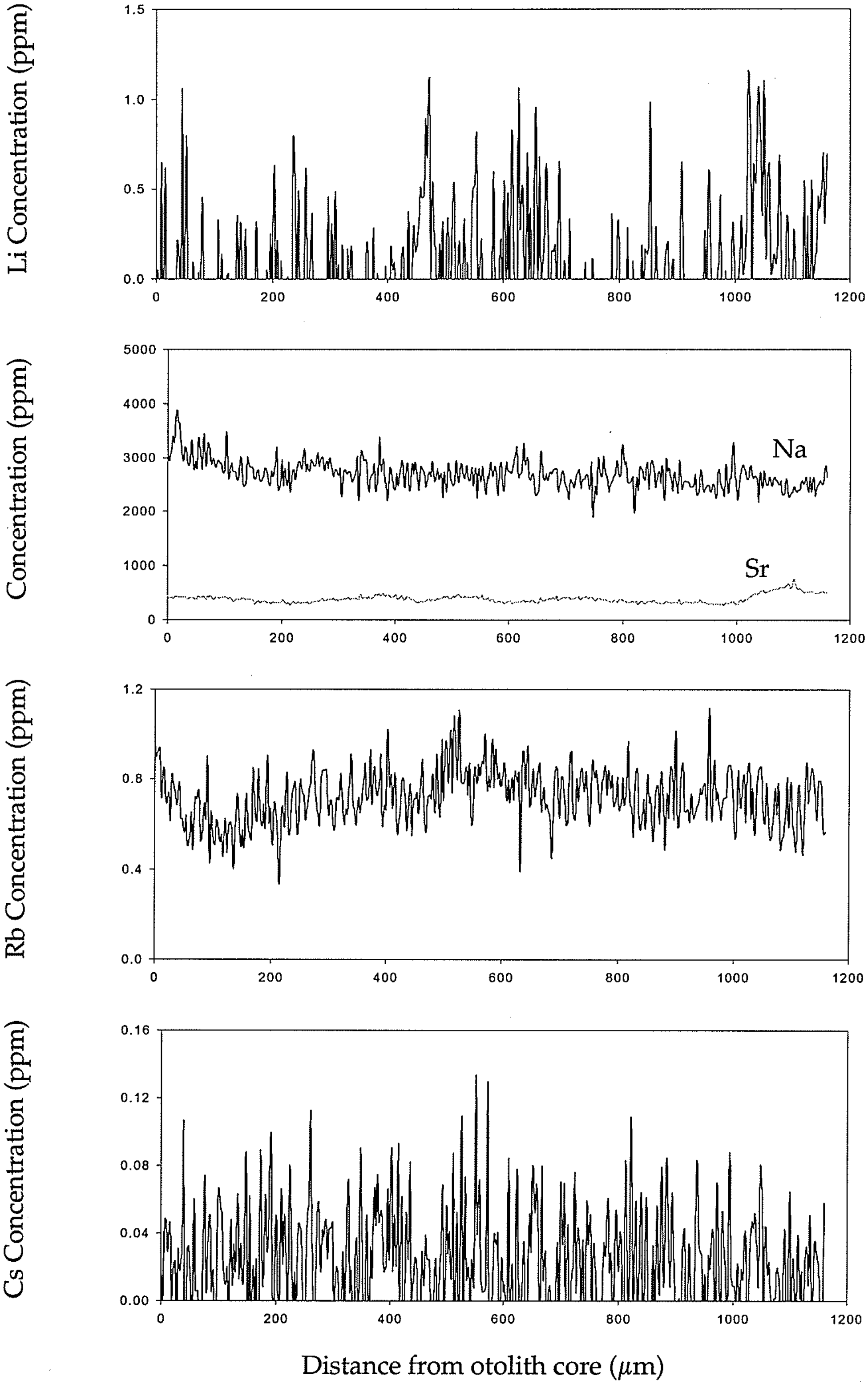
LDB08_08


Li Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
Rb Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
1600
Cs Concentration (ppm)
0.16
0.12
0.08
0.04
0.00
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

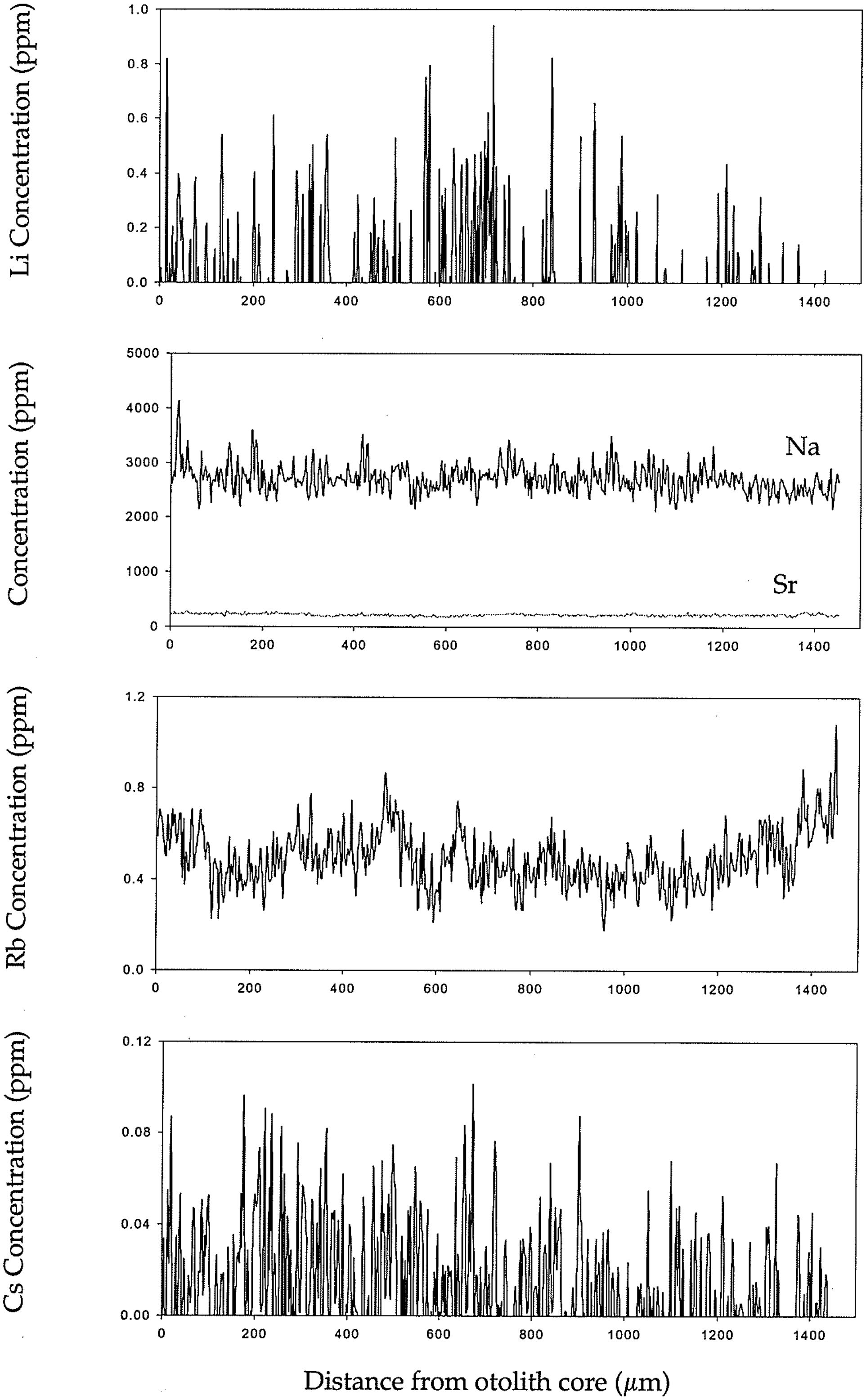
LDB08_09


Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
900
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
Cs Concentration (ppm)
0.20
0.16
0.12
0.08
0.04
0.00
Distance from otolith core (μm)

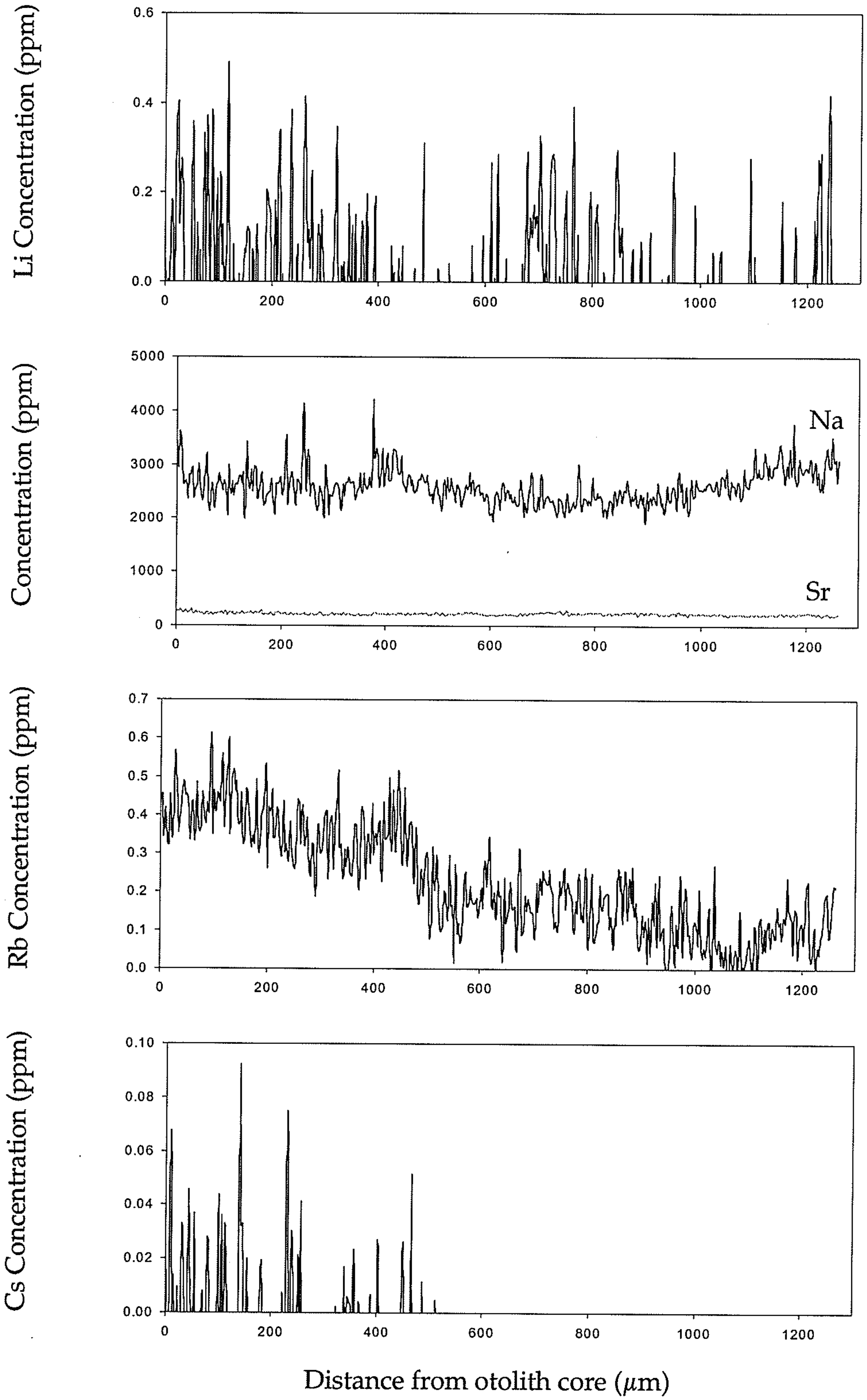
LDB08_10


Li Concentration (ppm)
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
Cs Concentration (ppm)
0.16
0.12
0.08
0.04
0.00
Distance from otolith core (μm)

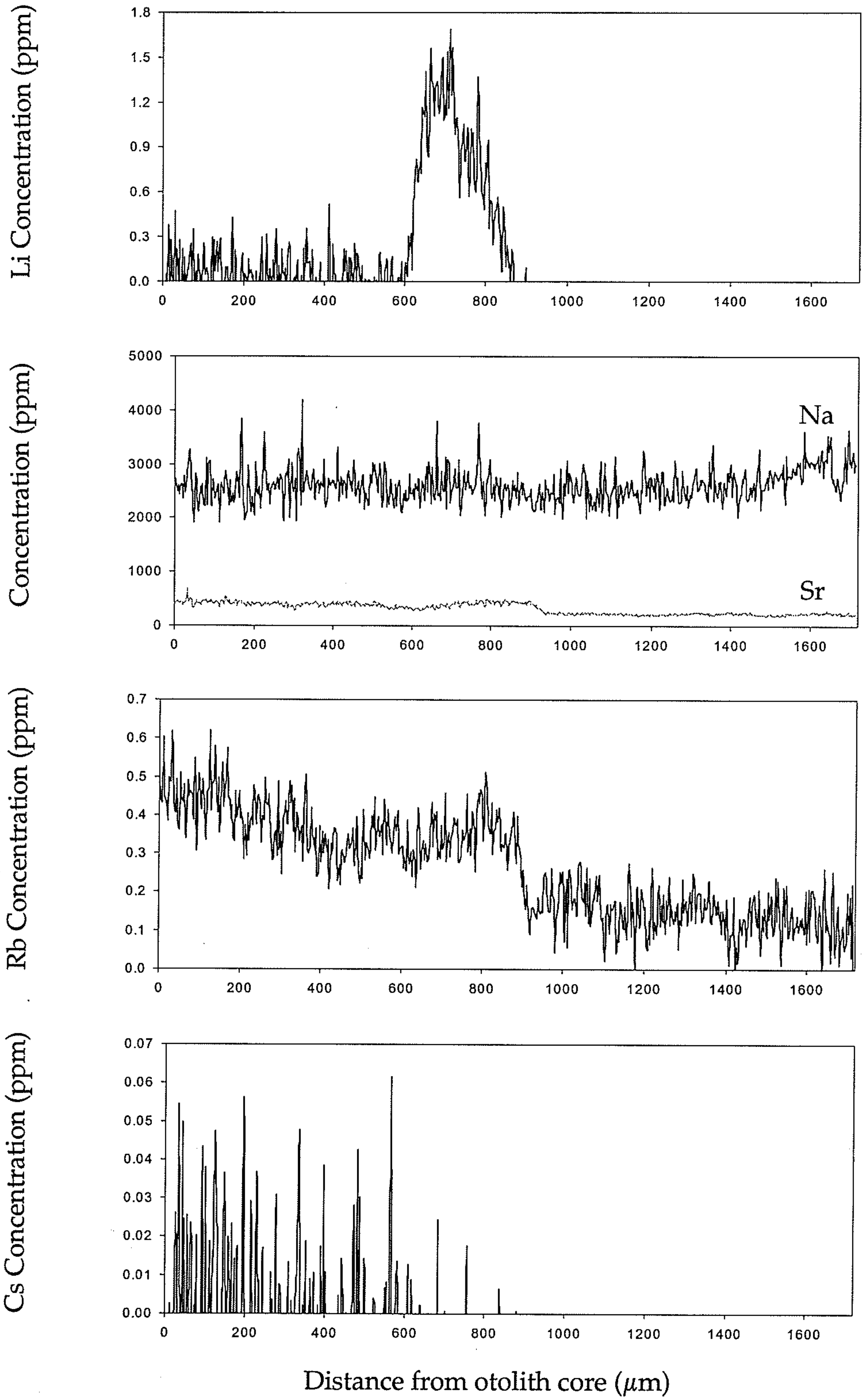
LDB08_11


Li Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

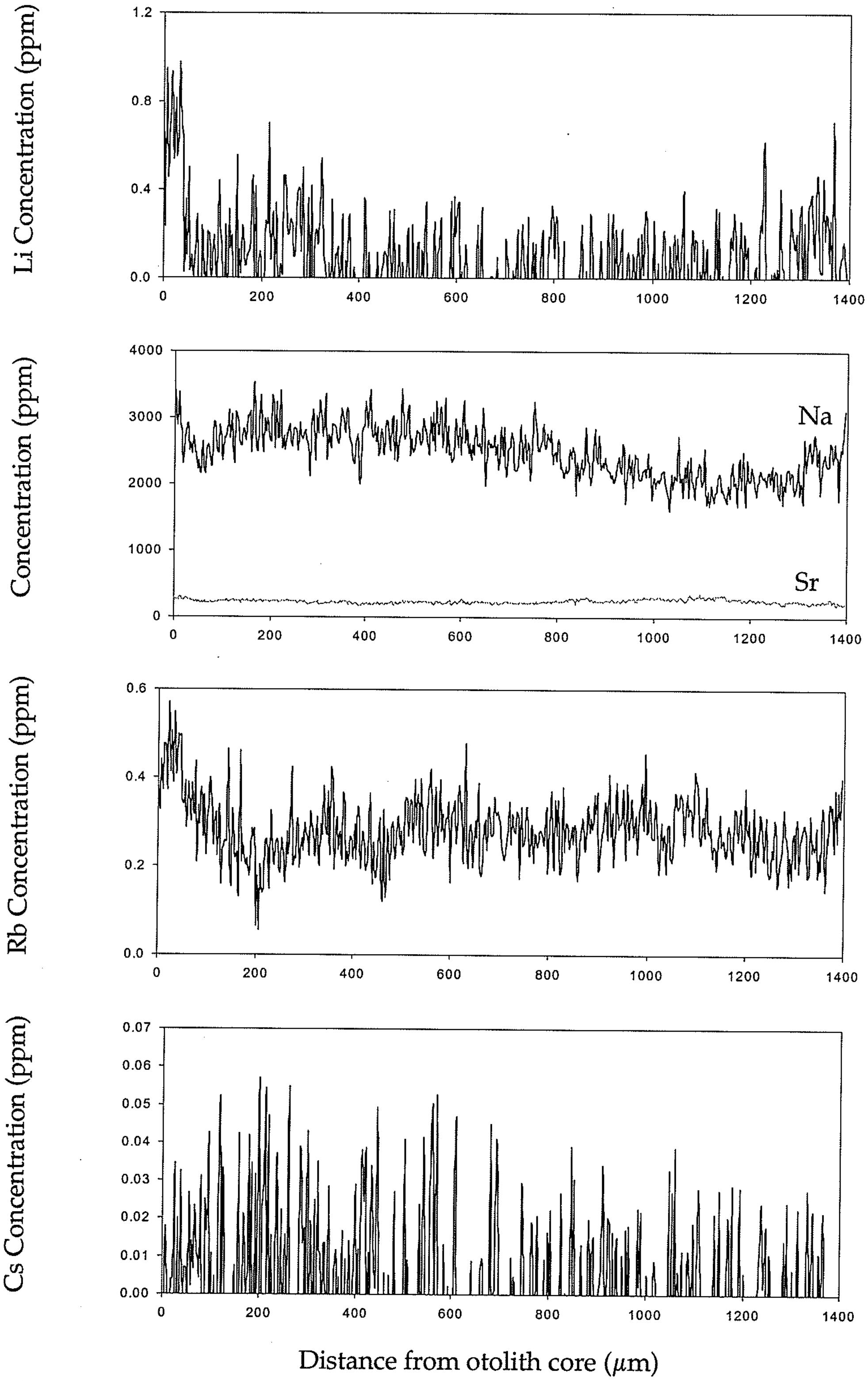
LDB08_12


Li Concentration (ppm)
0.0
0.2
0.4
0.6
0
200
400
600
800
1000
1200
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.00
0.02
0.04
0.06
0.08
0.10
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

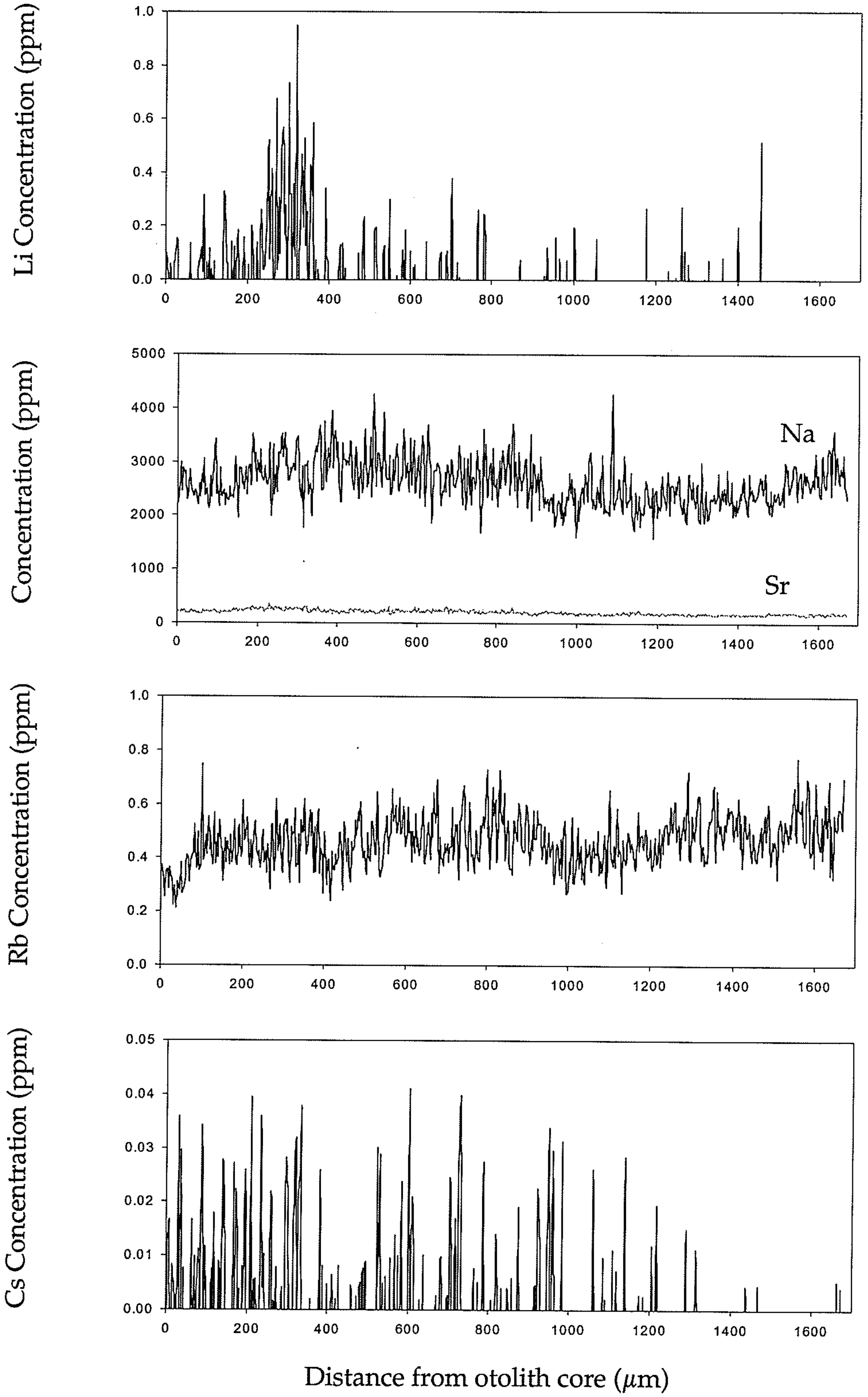
LDB08_13


Li Concentration (ppm)
0.0
0.3
0.6
0.9
1.2
1.5
1.8
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
Rb Concentration (ppm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
200
400
600
800
1000
1200
1400
1600
Cs Concentration (ppm)
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (µm)

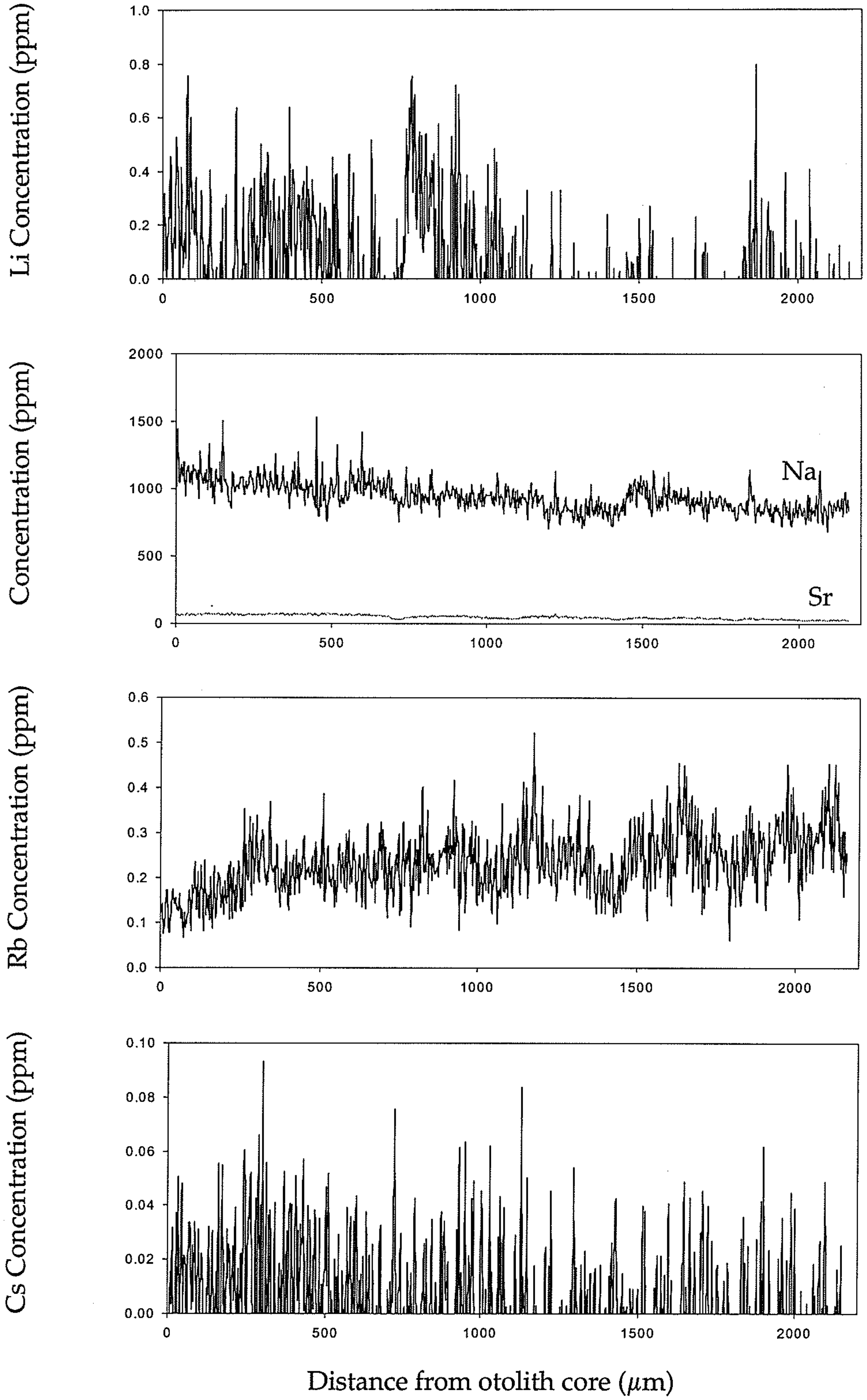
LDB08_14


Li Concentration (ppm)
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
0.6
0.4
0.2
0.0
Cs Concentration (ppm)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Distance from otolith core (μm)

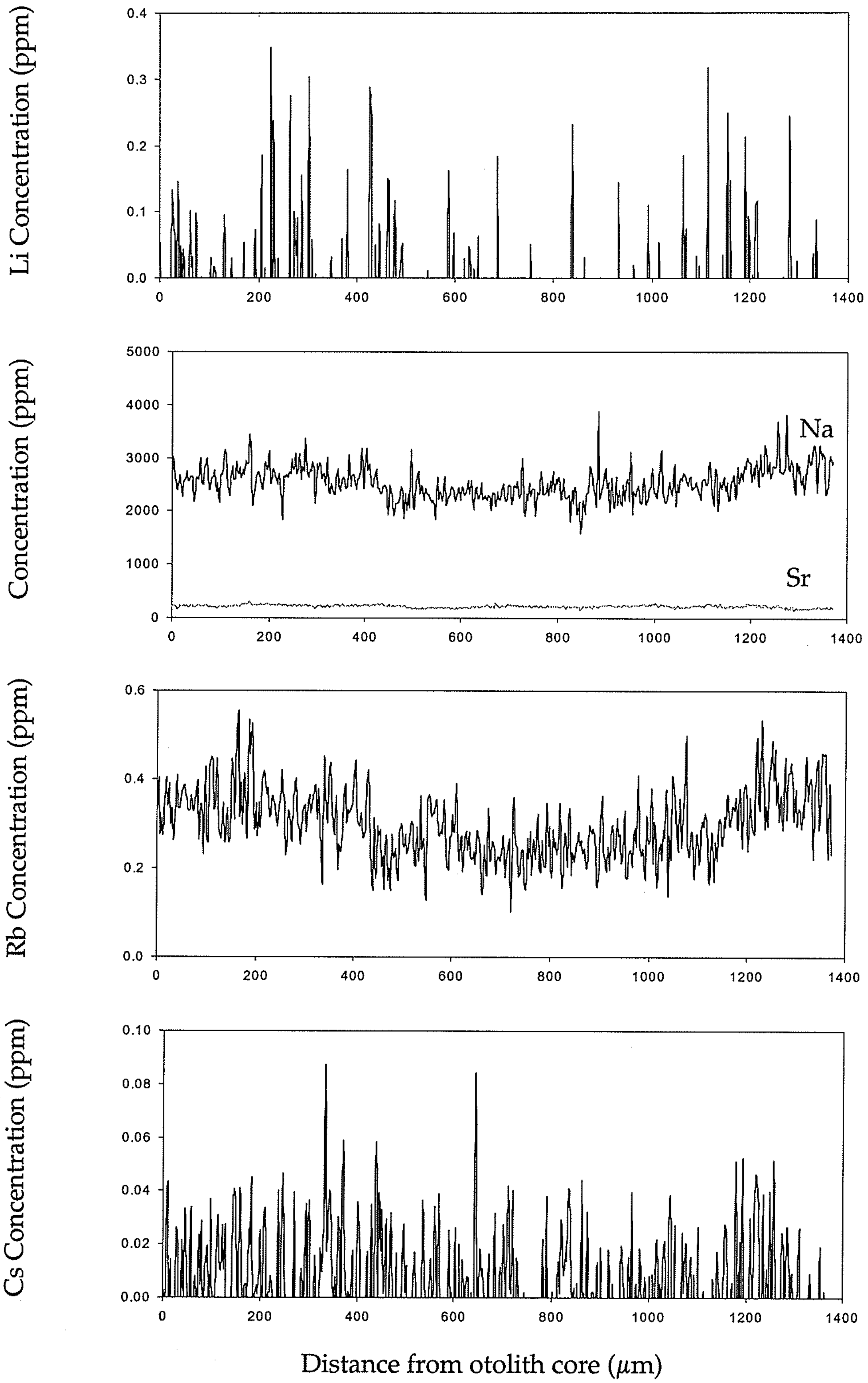
LDB08_15


Li Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
Rb Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
1600
Cs Concentration (ppm)
0.05
0.04
0.03
0.02
0.01
0.00
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

LDB08_16

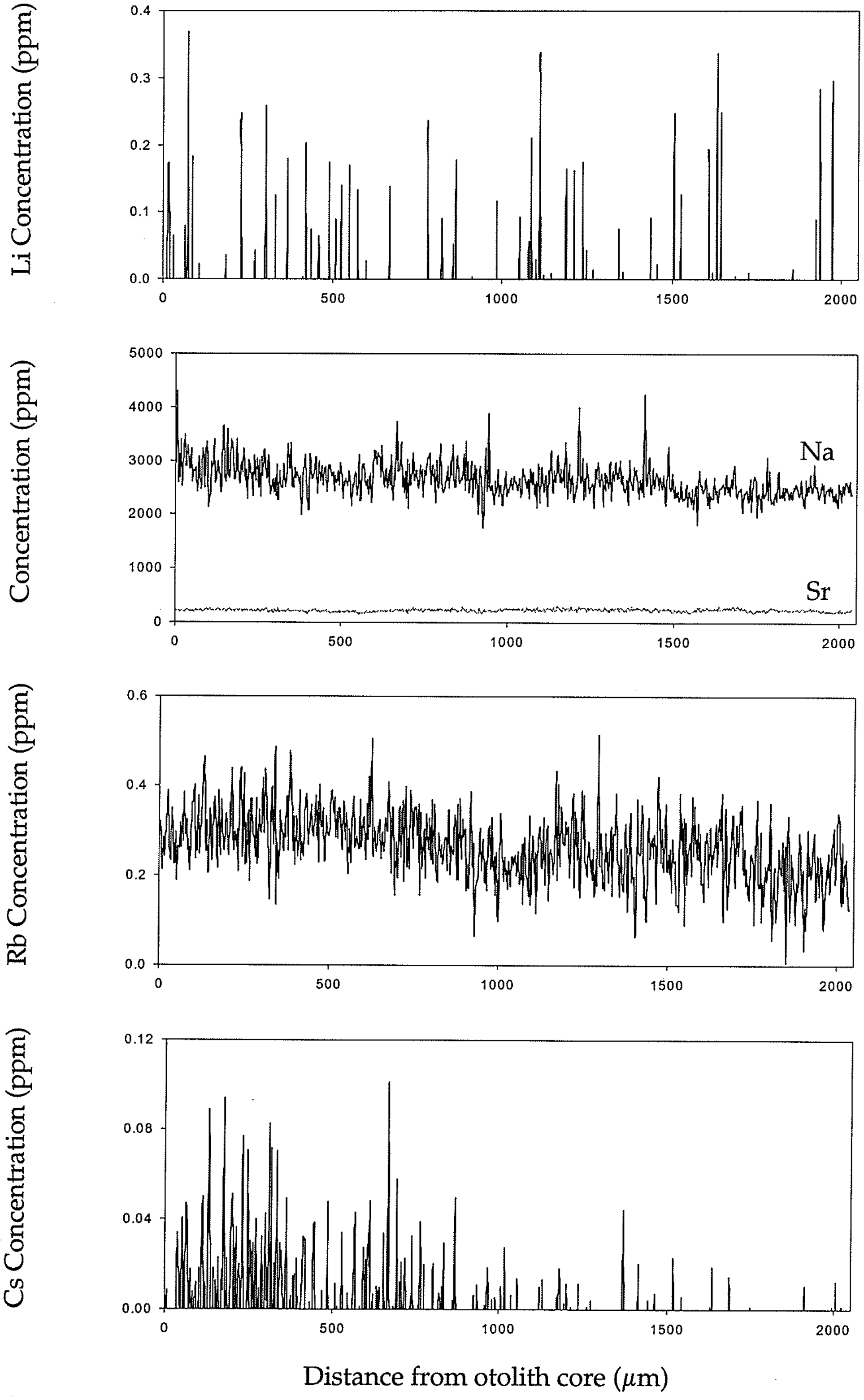

Li Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500
2000
Concentration (ppm)
2000
1500
1000
500
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
500
1000
1500
2000
Cs Concentration (ppm)
0.10
0.08
0.06
0.04
0.02
0.00
0
500
1000
1500
2000
Distance from otolith core (μm)

LDB08_17

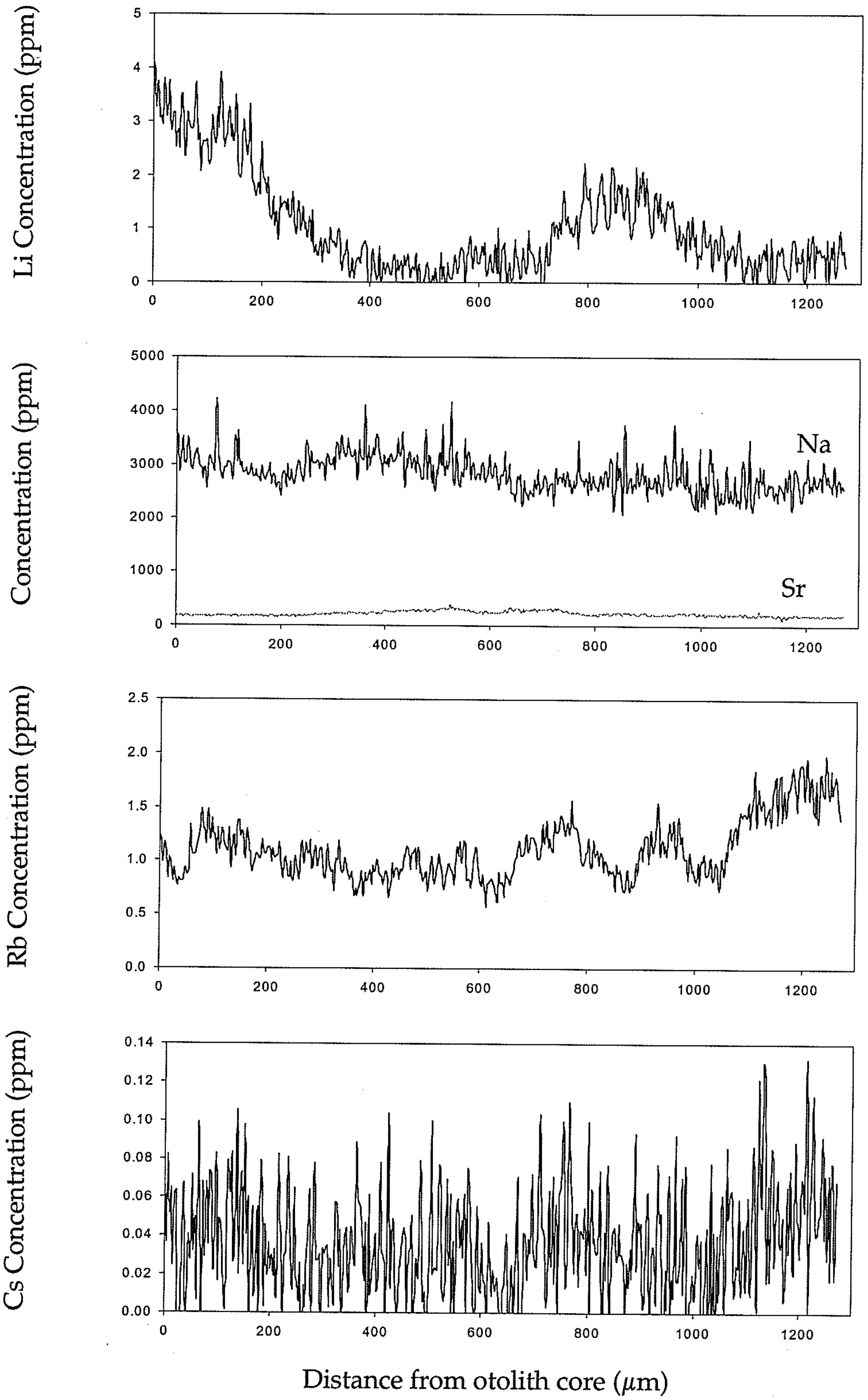


Li Concentration (ppm)
0.0
0.1
0.2
0.3
0.4
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
0.0
0.2
0.4
0.6
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
0.00
0.02
0.04
0.06
0.08
0.10
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

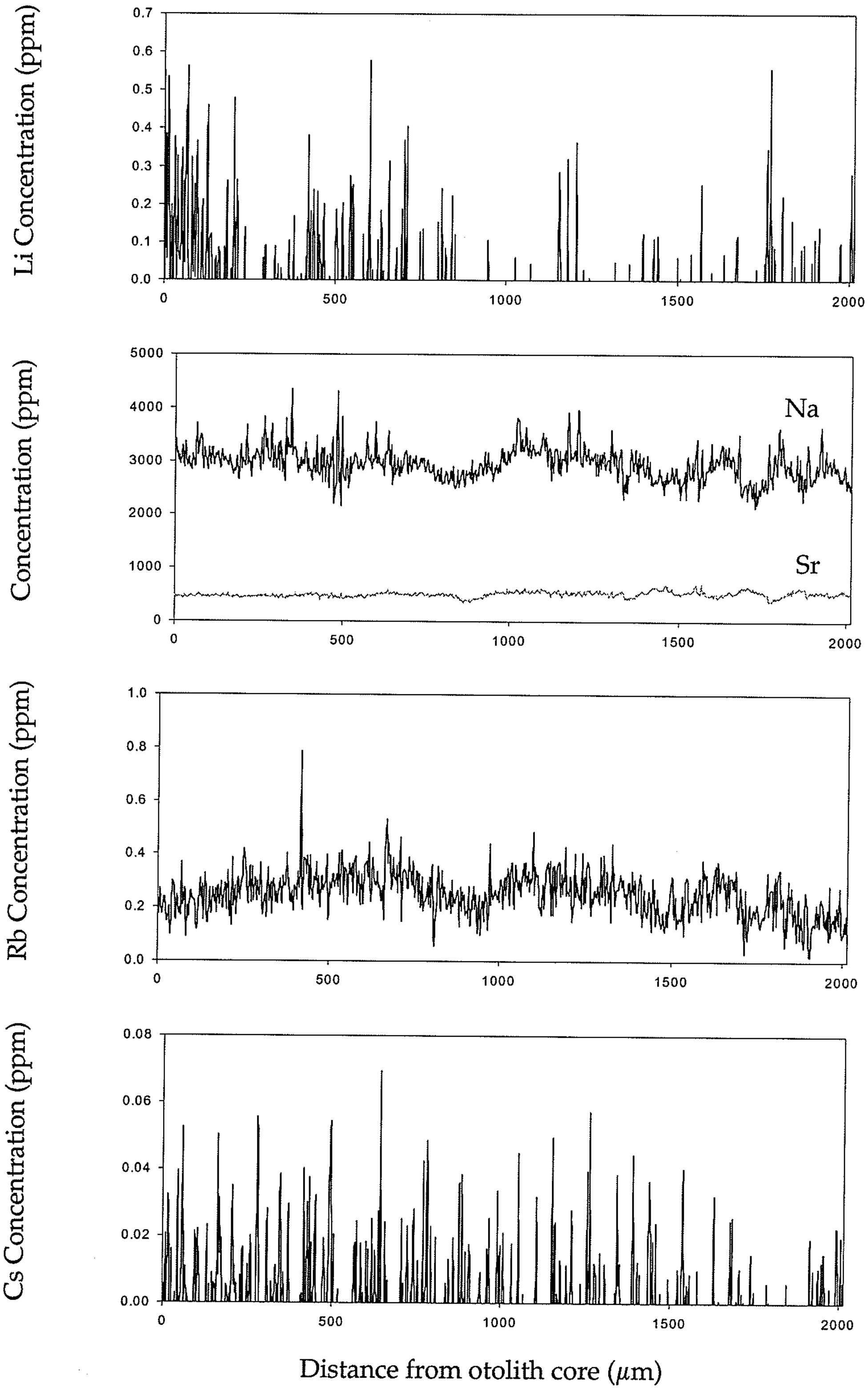
LDB08_18


Li Concentration (ppm)
0.4
0.3
0.2
0.1
0.0
0
500
1000
1500
2000
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
0.6
0.4
0.2
0.0
0
500
1000
1500
2000
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
0
500
1000
1500
2000
Distance from otolith core (μm)

LDB08_22

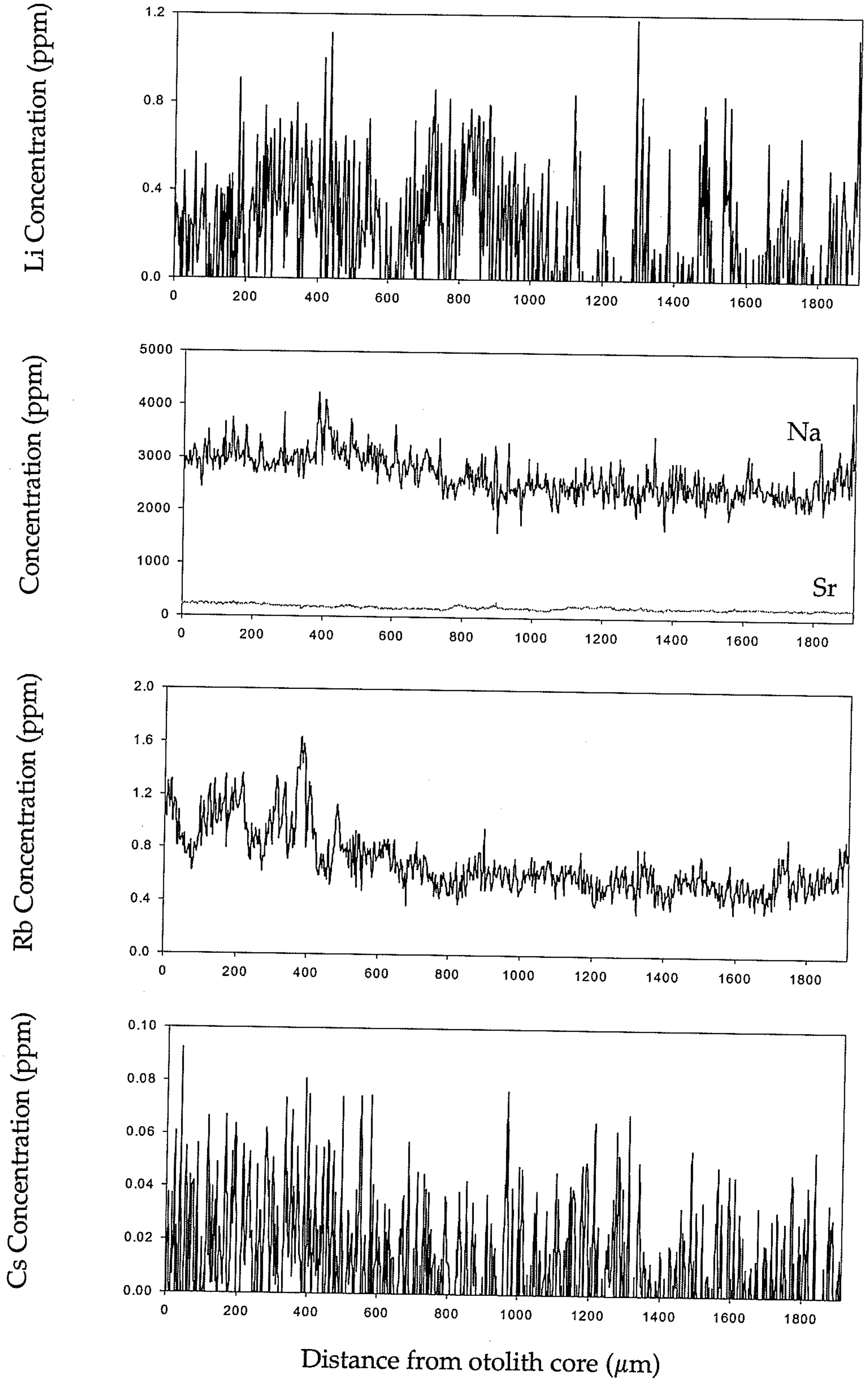

Li Concentration (ppm)
0
1
2
3
4
5
0
200
400
600
800
1000
1200
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

LDB08_23

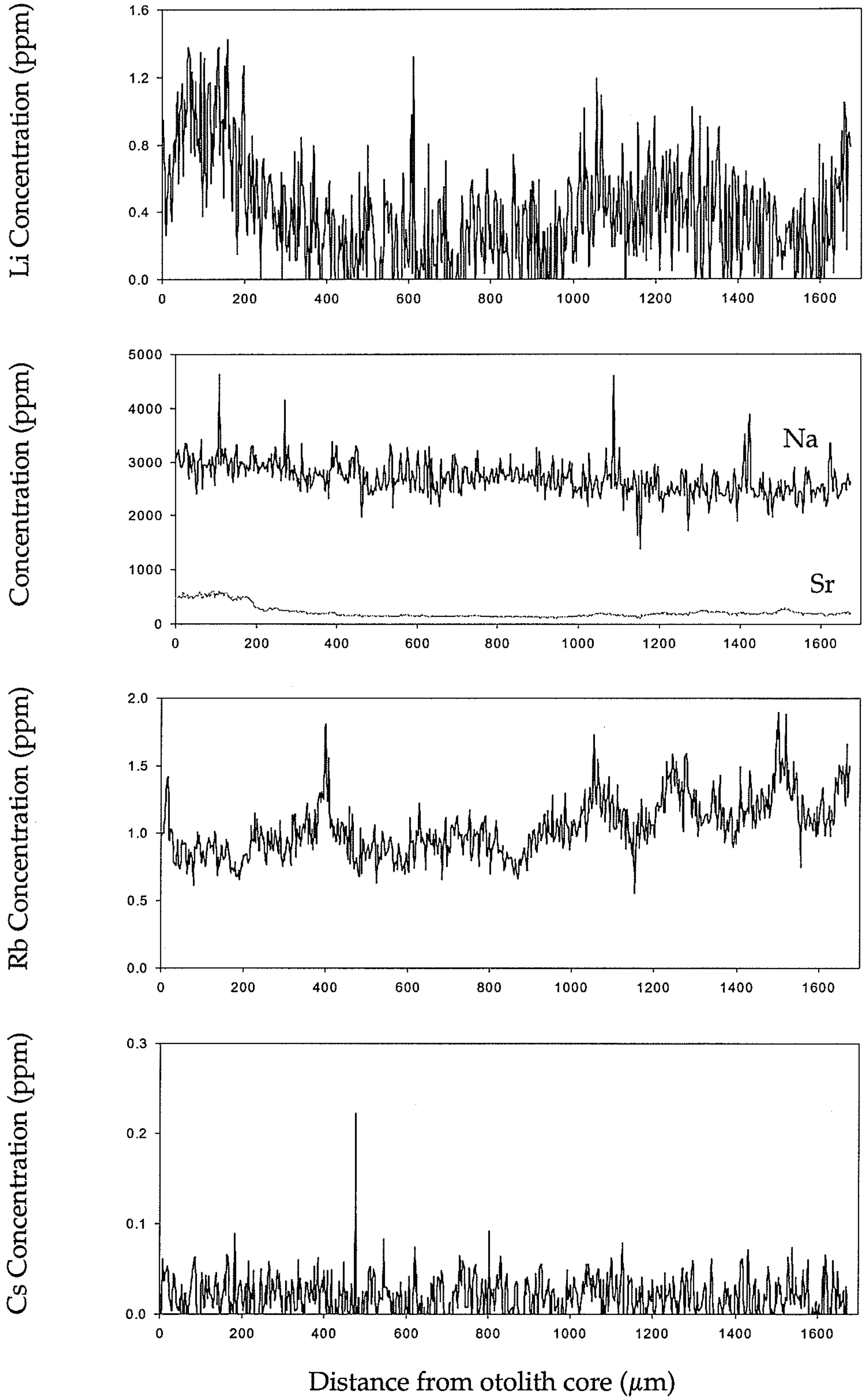


Li Concentration (ppm)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
500
1000
1500
2000
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500
2000
Cs Concentration (ppm)
0.08
0.06
0.04
0.02
0.00
0
500
1000
1500
2000
Distance from otolith core (μm)

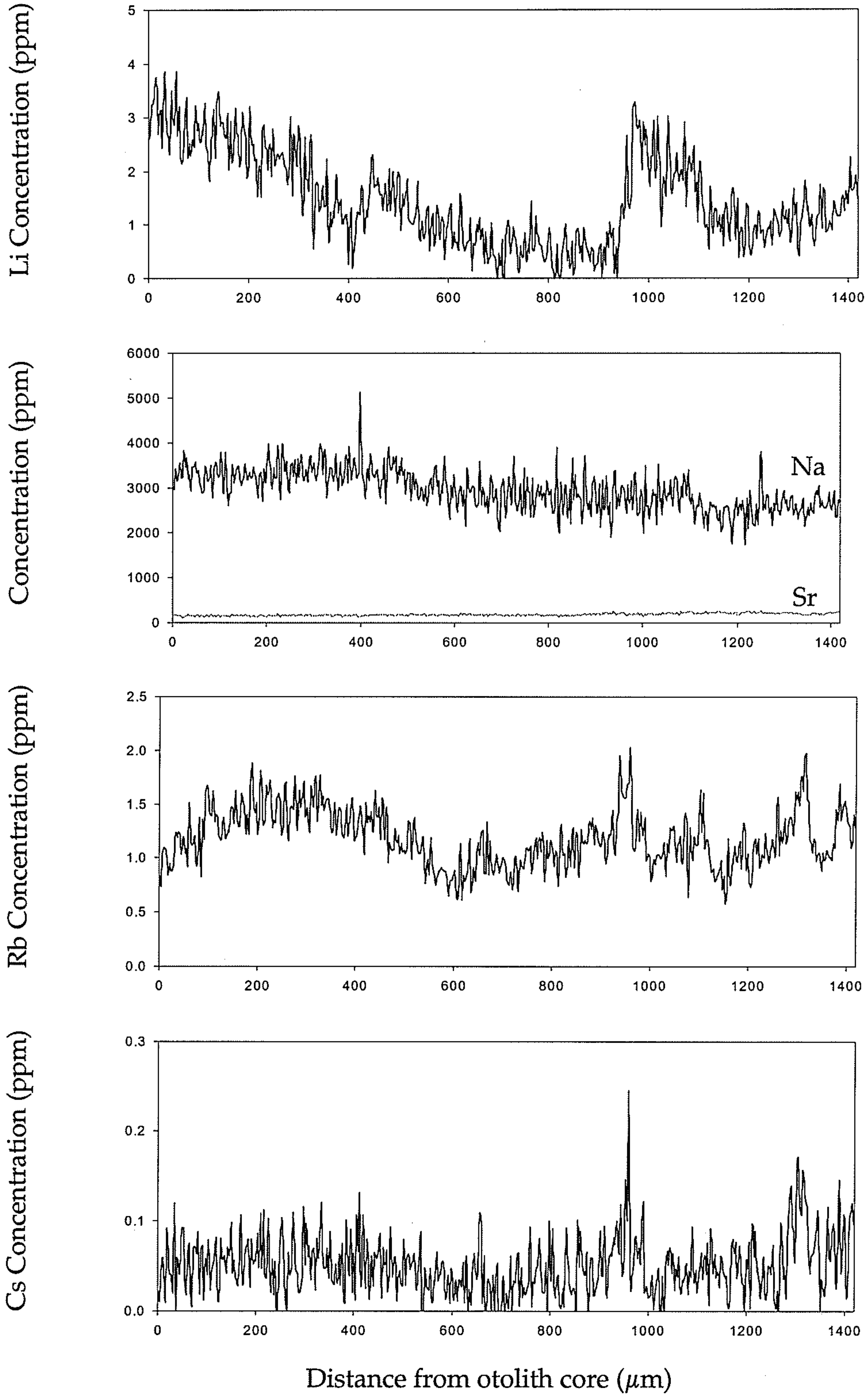
LDB08_24


Li Concentration (ppm)
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
1800
Rb Concentration (ppm)
2.0
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
Cs Concentration (ppm)
0.10
0.08
0.06
0.04
0.02
0.00
0
200
400
600
800
1000
1200
1400
1600
1800
Distance from otolith core (μm)

LDB08_25


Li Concentration (ppm)
0.0
0.4
0.8
1.2
1.6
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
Cs Concentration (ppm)
0.0
0.1
0.2
0.3
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

LDB08_26


Li Concentration (ppm)
5
4
3
2
1
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

Appendix G LA-ICP-MS data for Lac du Bonnet otoliths *continued*

Species: Walleye (*Sander vitreous*), Sauger (*Stizostedion canadense*), Northern Pike (*Esox lucius*), Whitefish (*Coregonus clupeaformis*), Cisco (*Coregonus artedii*), Yellow Perch (*Perca flavescens*), Black Crappie (*Pomoxis nigromaculatus*)

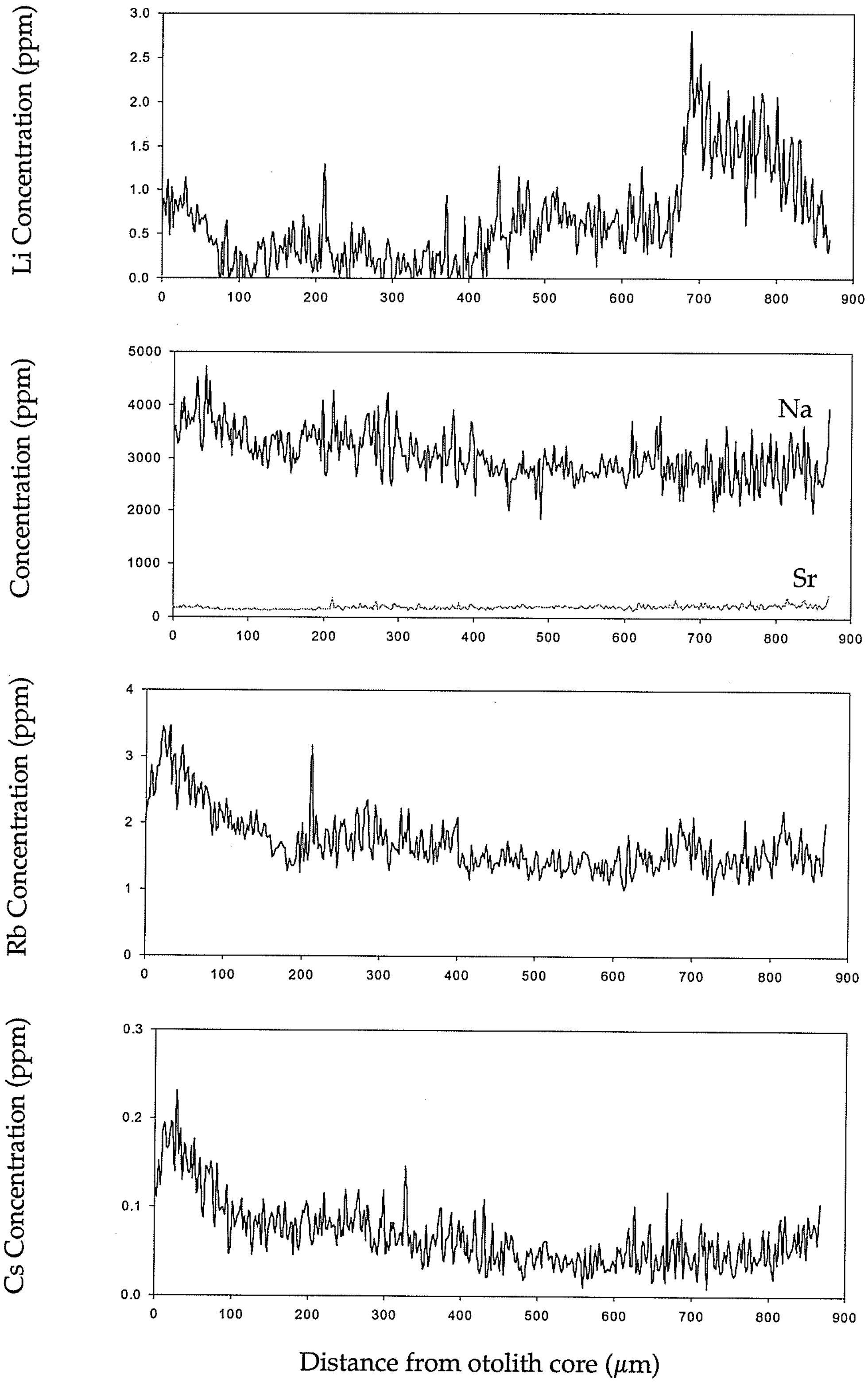
Captured: 2007

Isotopes	**Li^{7}**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

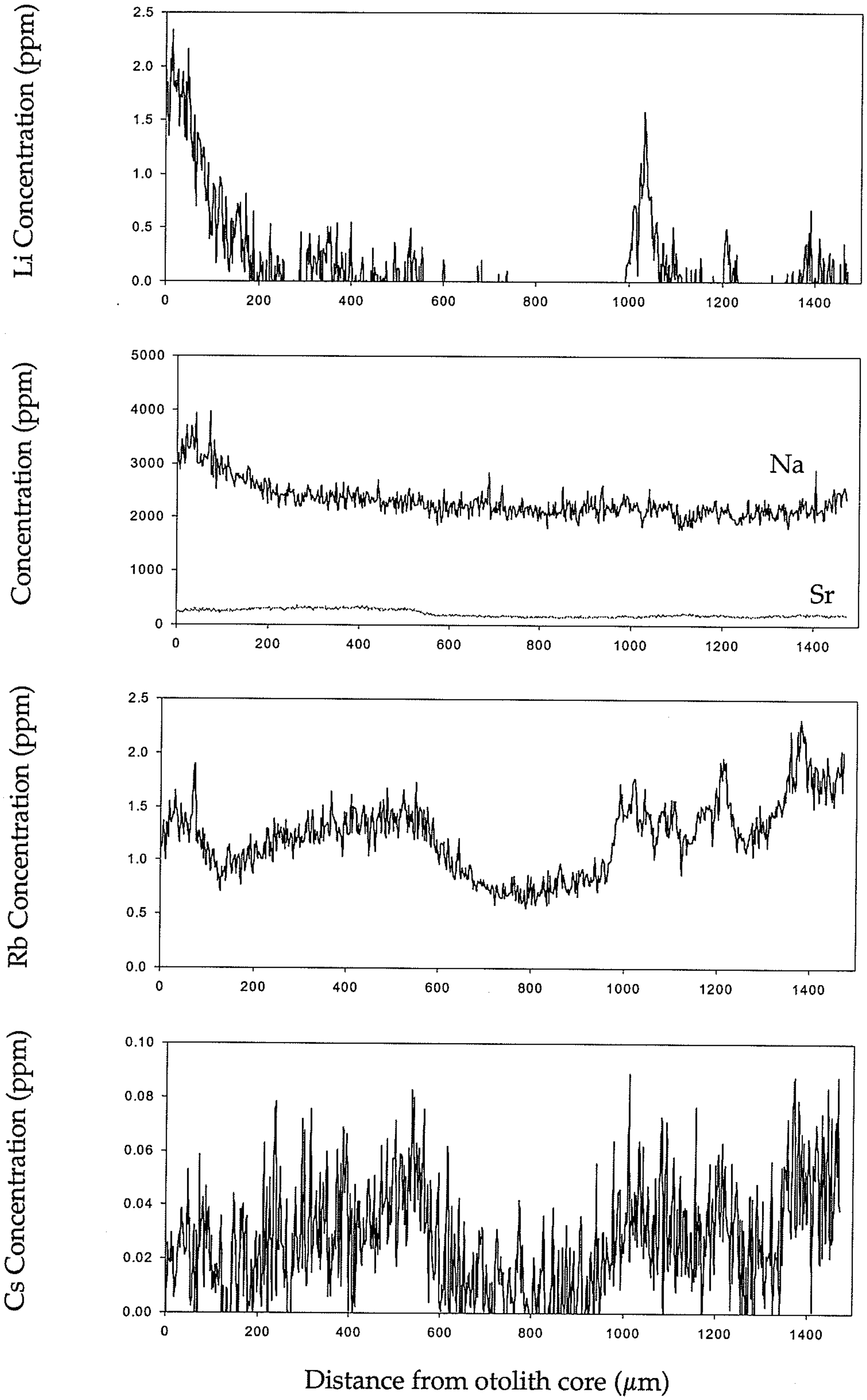
Sample Number	***Species***	***Age***
124	Walleye	2
125	Sauger	7
126	Sauger	3
127	Sauger	8
128	Sauger	4
129	Sauger	2
130	Sauger	3
131	Sauger	4
132	Sauger	4
133	Sauger	4
134	Northern Pike	10
135	Whitefish	6
136	Whitefish	11
137	Whitefish	6
BC	Black Crappie	4
140	Sauger	7
142	Sauger	4
143	Cisco	4
144	Sauger	4
145	Cisco	4
146	Yellow Perch	4
147	Yellow Perch	3
148	Northern Pike	8
149	Whitefish	6
152	Walleye	6
153	Walleye	5
154	Walleye	6
155	Northern Pike	5
156	Yellow Perch	10

157	Northern Pike	6
158	Northern Pike	9
159	Northern Pike	5
160	Whitefish	6

LDB07_124

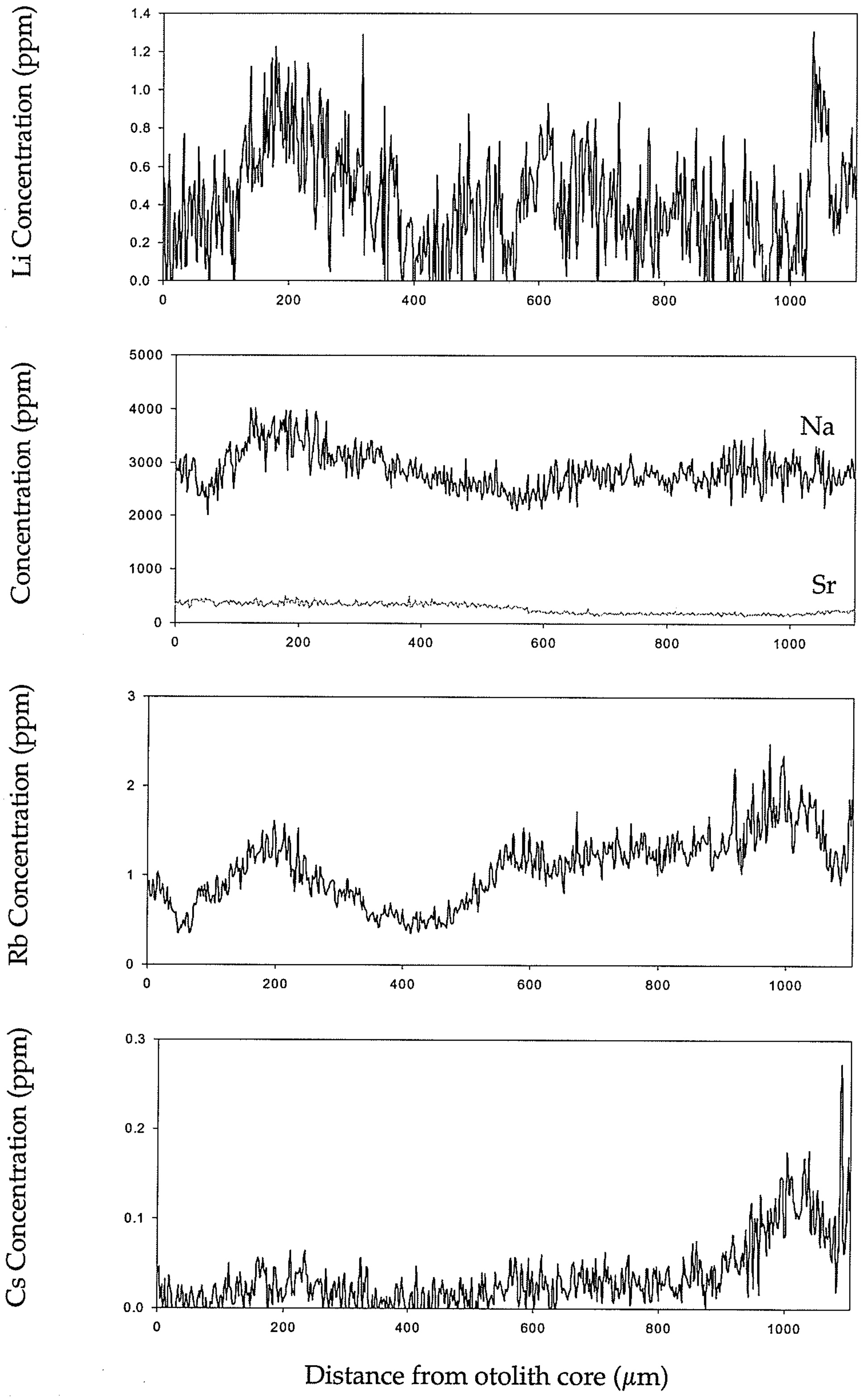

Li Concentration (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
4
3
2
1
0
Cs Concentration (ppm)
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
800
900
Distance from otolith core (μm)

LDB07_125

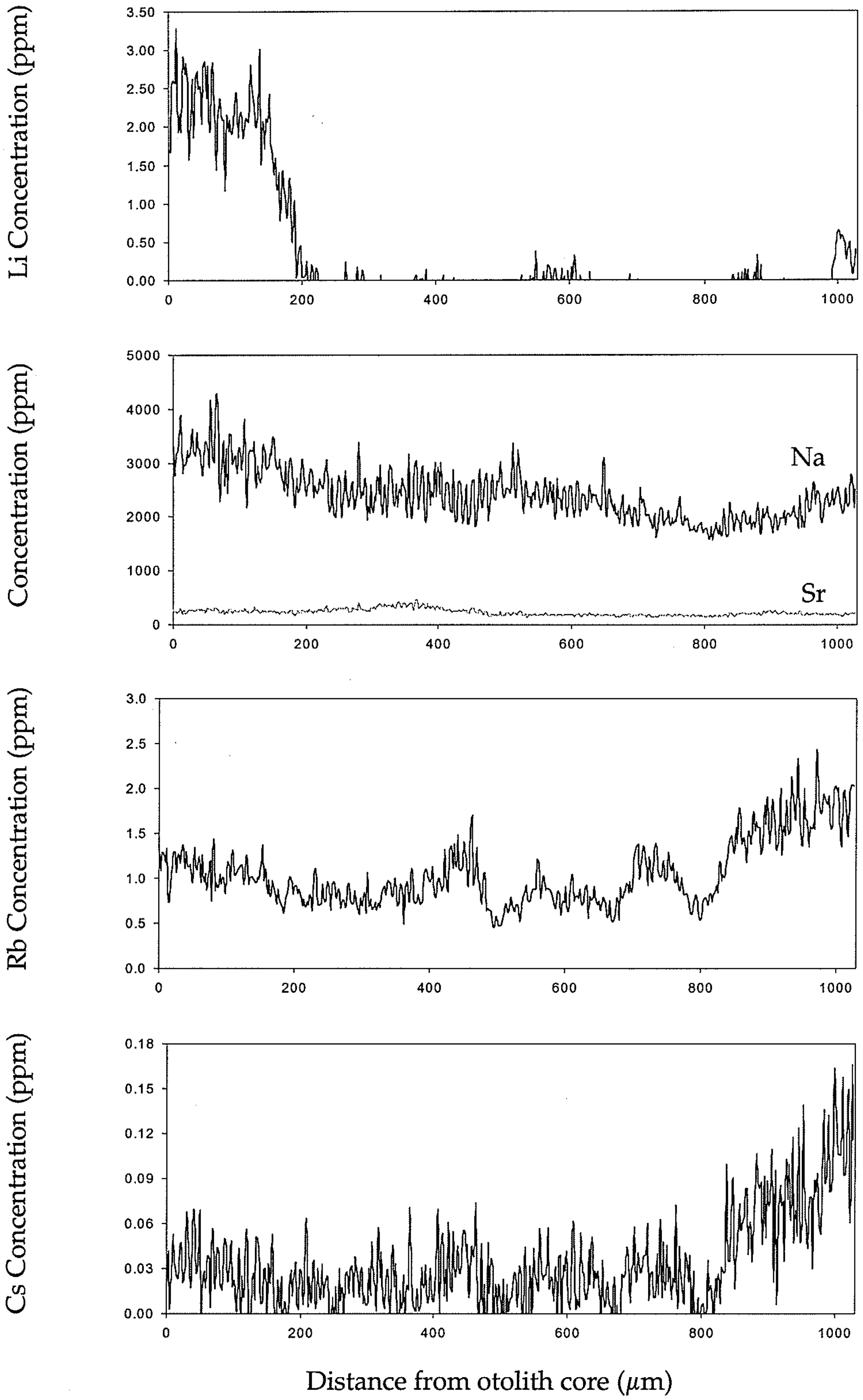


Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
0.10
0.08
0.06
0.04
0.02
0.00
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

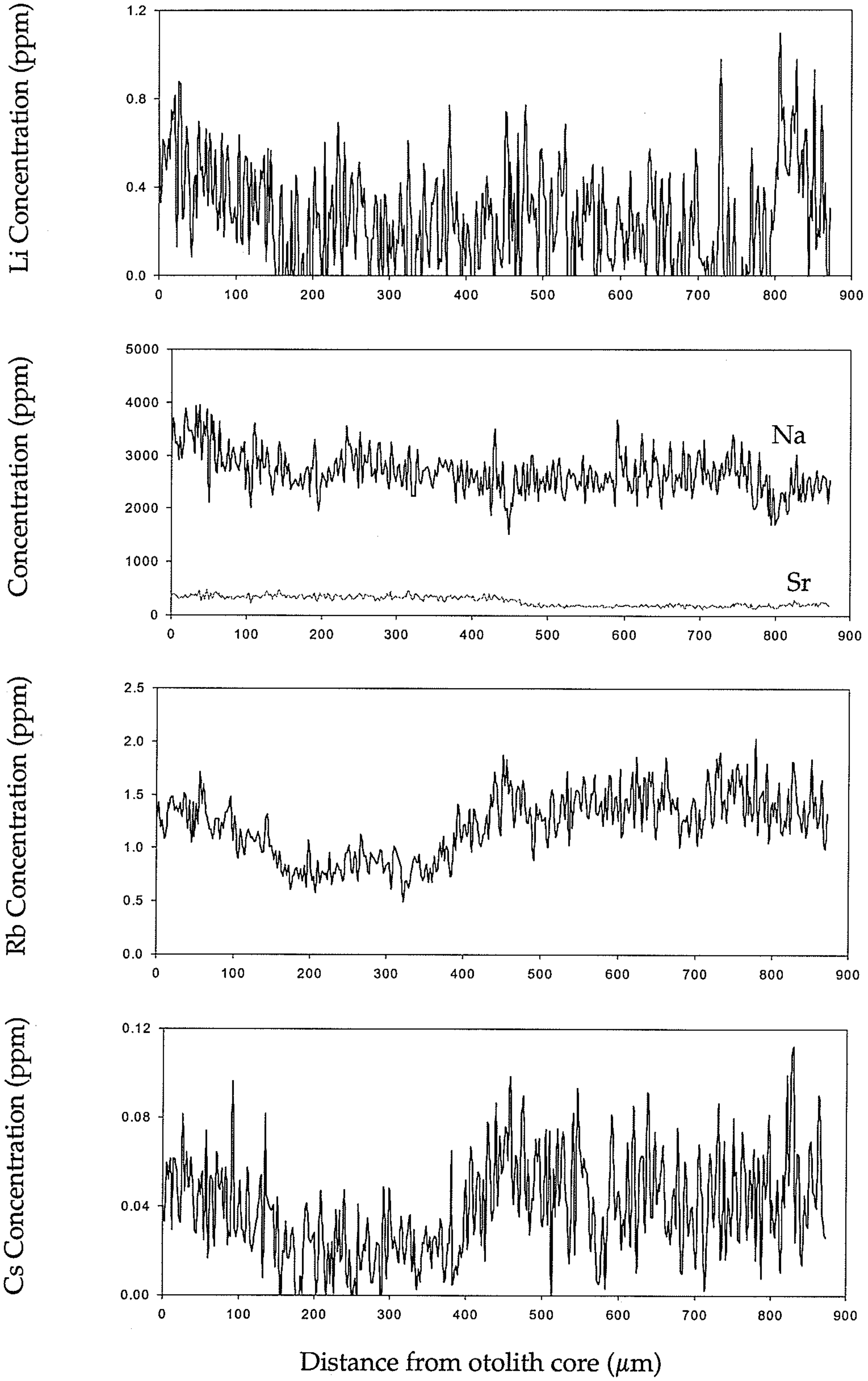
LDB07_126


Li Concentration (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
3
2
1
0
0
200
400
600
800
1000
Cs Concentration (ppm)
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

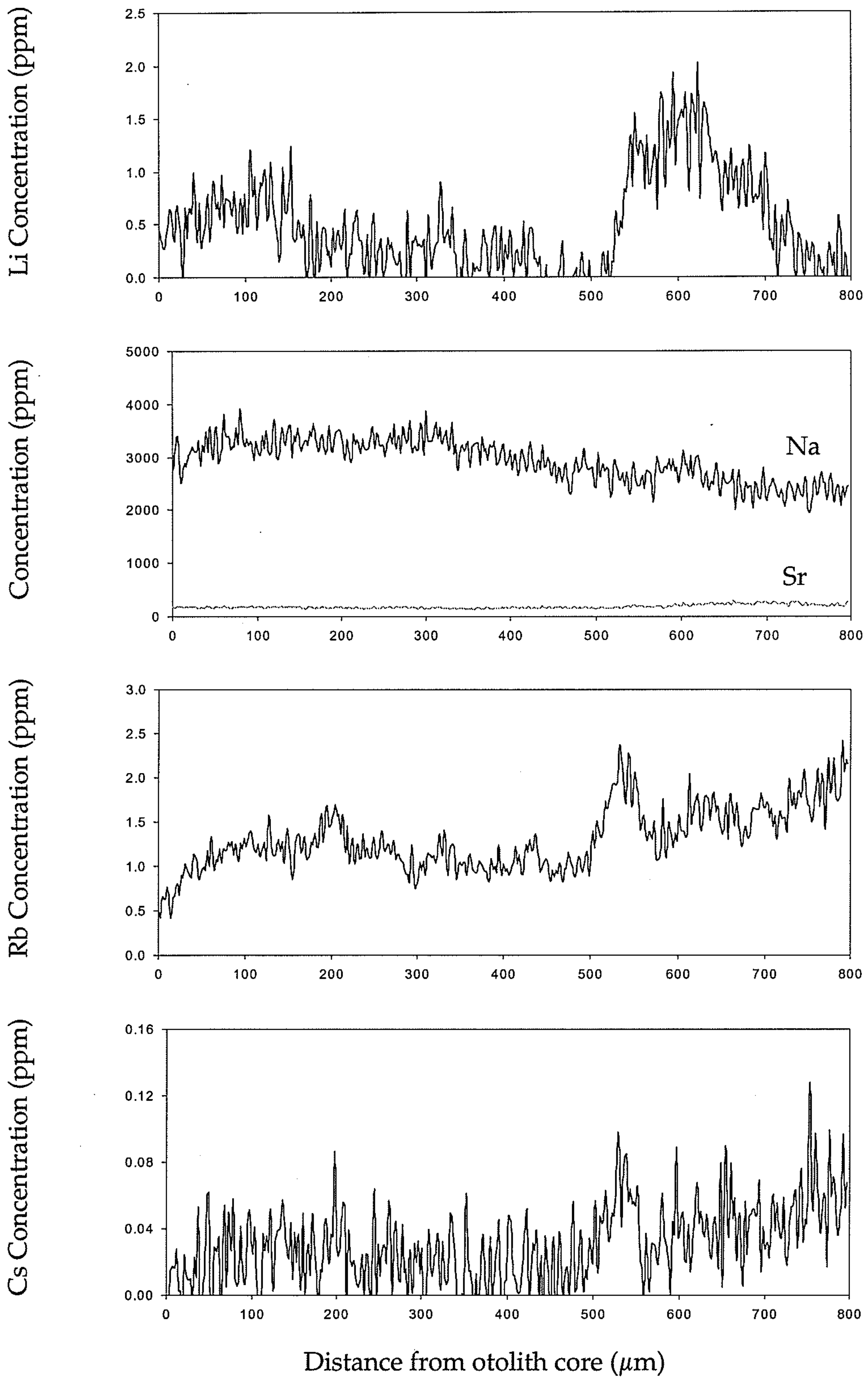
LDB07_127


Li Concentration (ppm)
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
200
400
600
800
1000
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Cs Concentration (ppm)
0.18
0.15
0.12
0.09
0.06
0.03
0.00
0
200
400
600
800
1000
Distance from otolith core (μm)

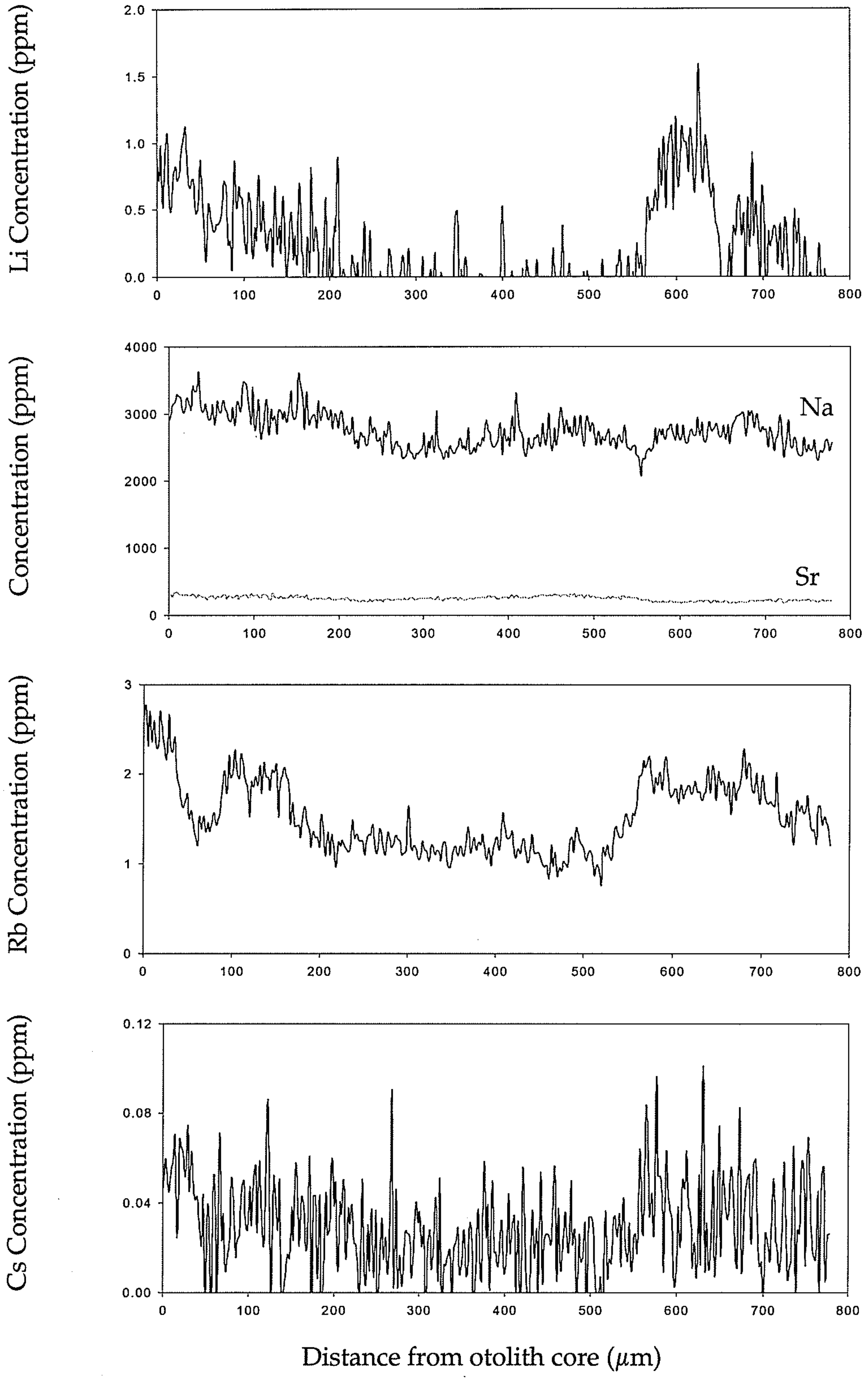
LDB07_128


Li Concentration (ppm)
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
800
900
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
800
900
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
900
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
0
100
200
300
400
500
600
700
800
900
Distance from otolith core (μm)

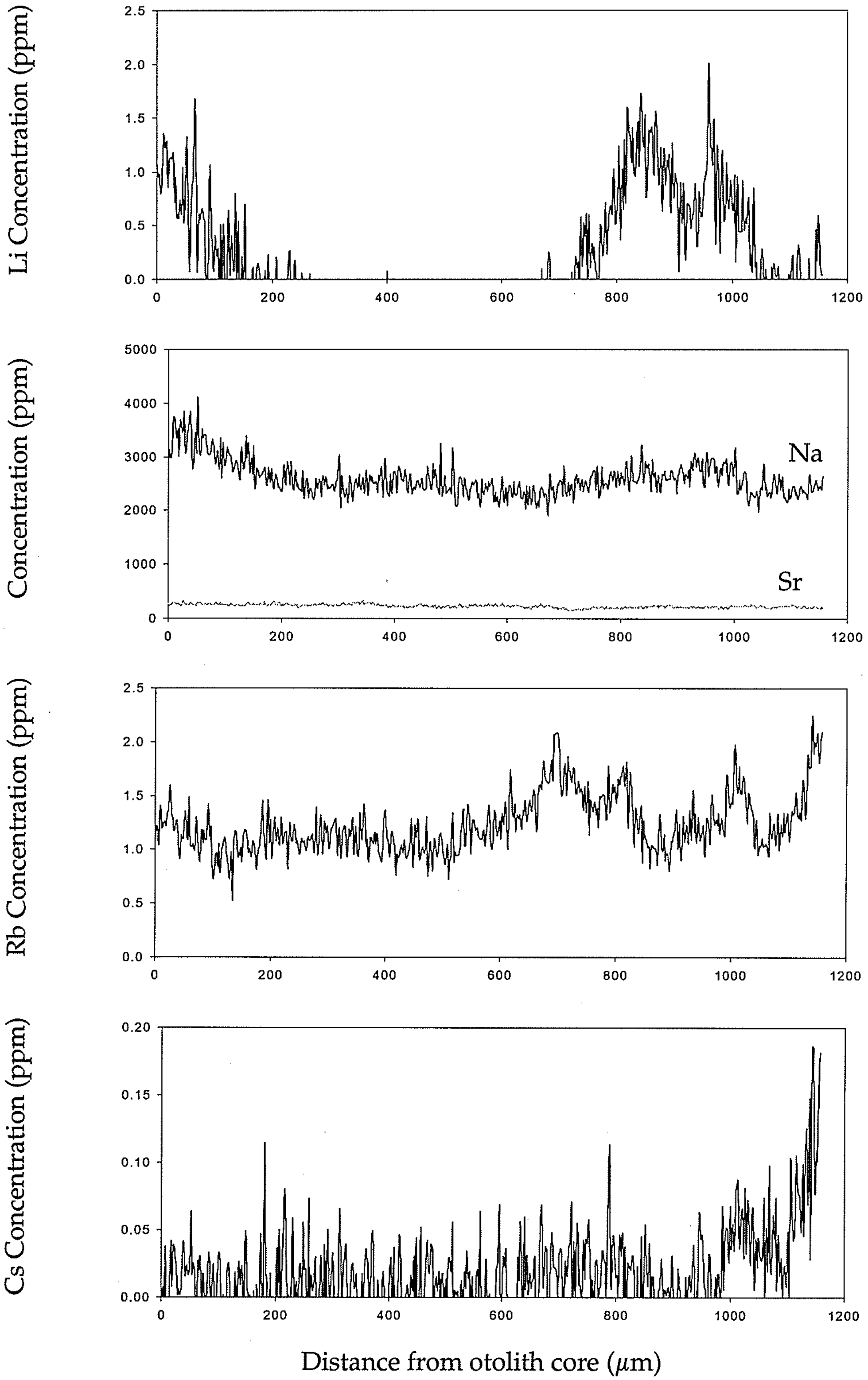
LDB07_129


Li Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
0
100
200
300
400
500
600
700
800
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
100
200
300
400
500
600
700
800
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
100
200
300
400
500
600
700
800
Cs Concentration (ppm)
0.00
0.04
0.08
0.12
0.16
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

LDB07_130

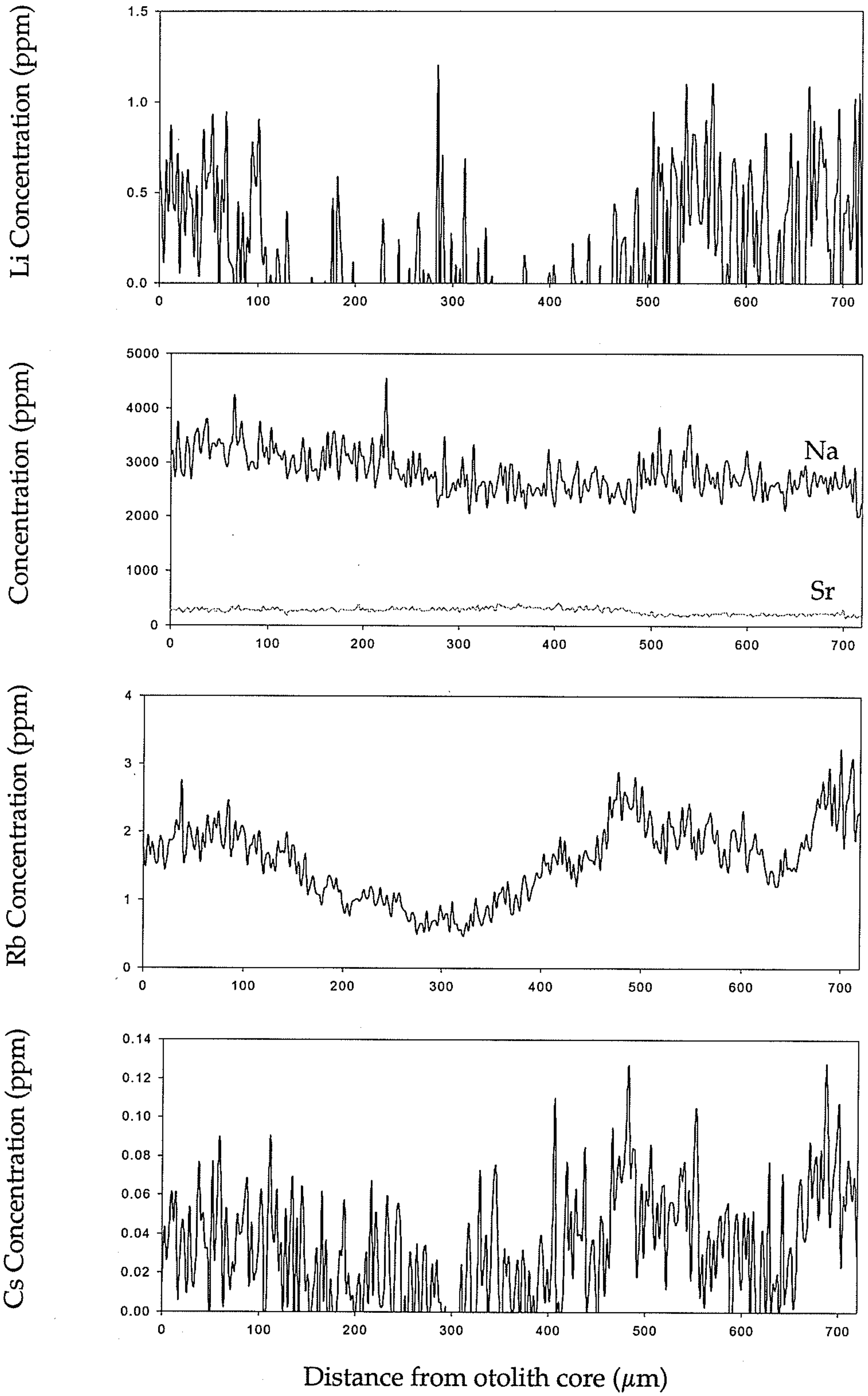

Li Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
3
2
1
0
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
Distance from otolith core (μm)

LDB07_131

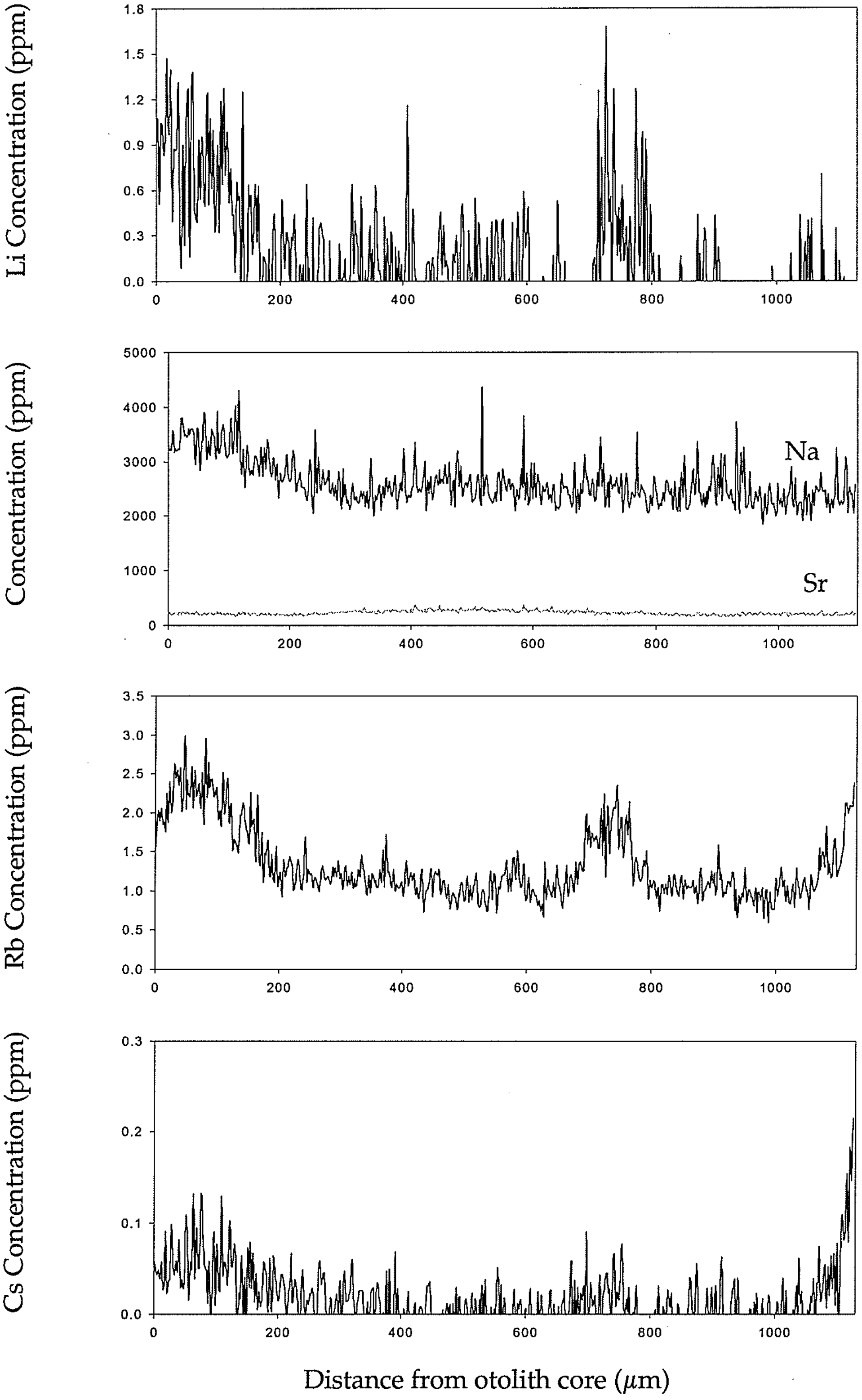


Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.20
0.15
0.10
0.05
0.00
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

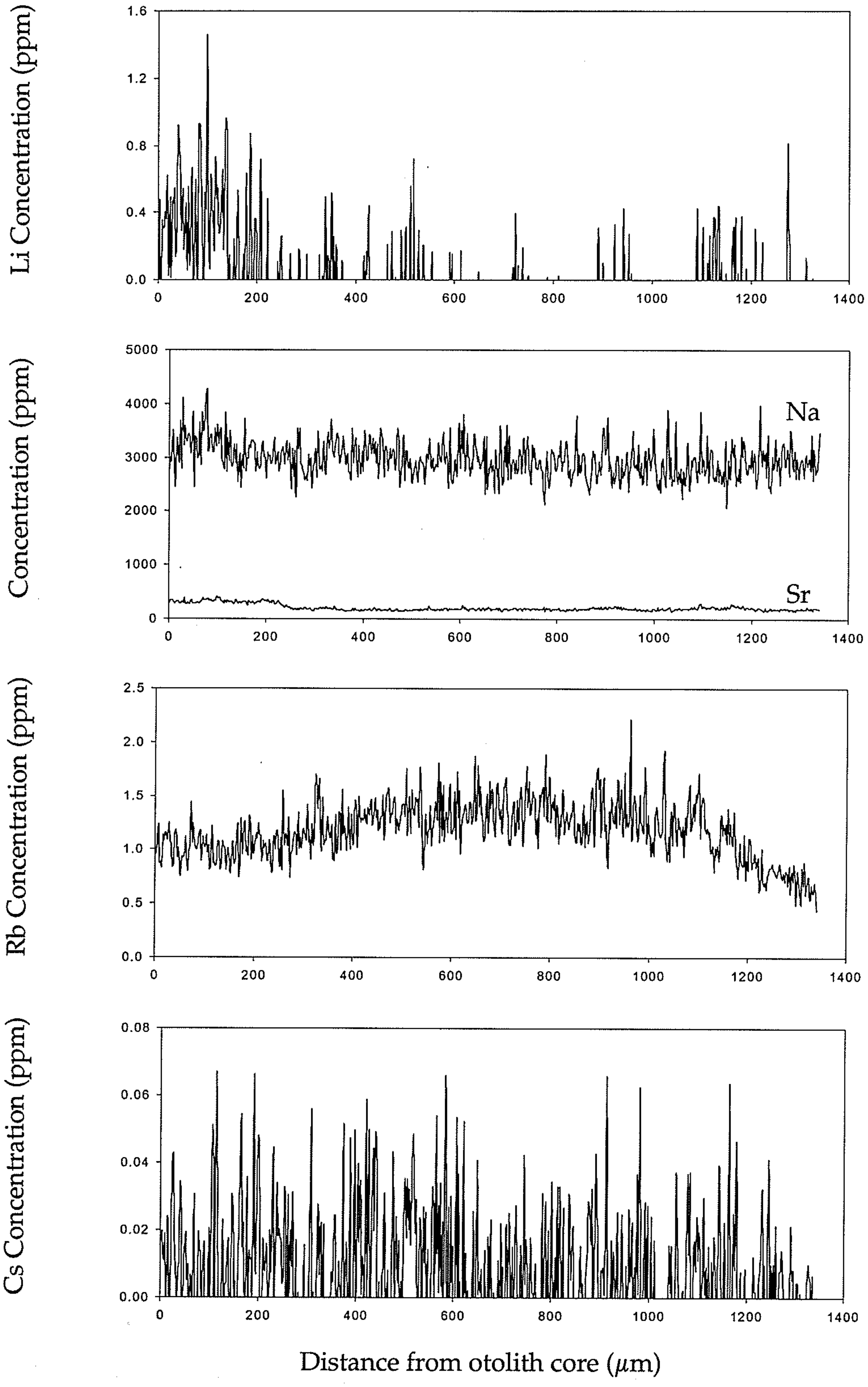
LDB07_132


Li Concentration (ppm)
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
4
3
2
1
0
Cs Concentration (ppm)
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
Distance from otolith core (μm)

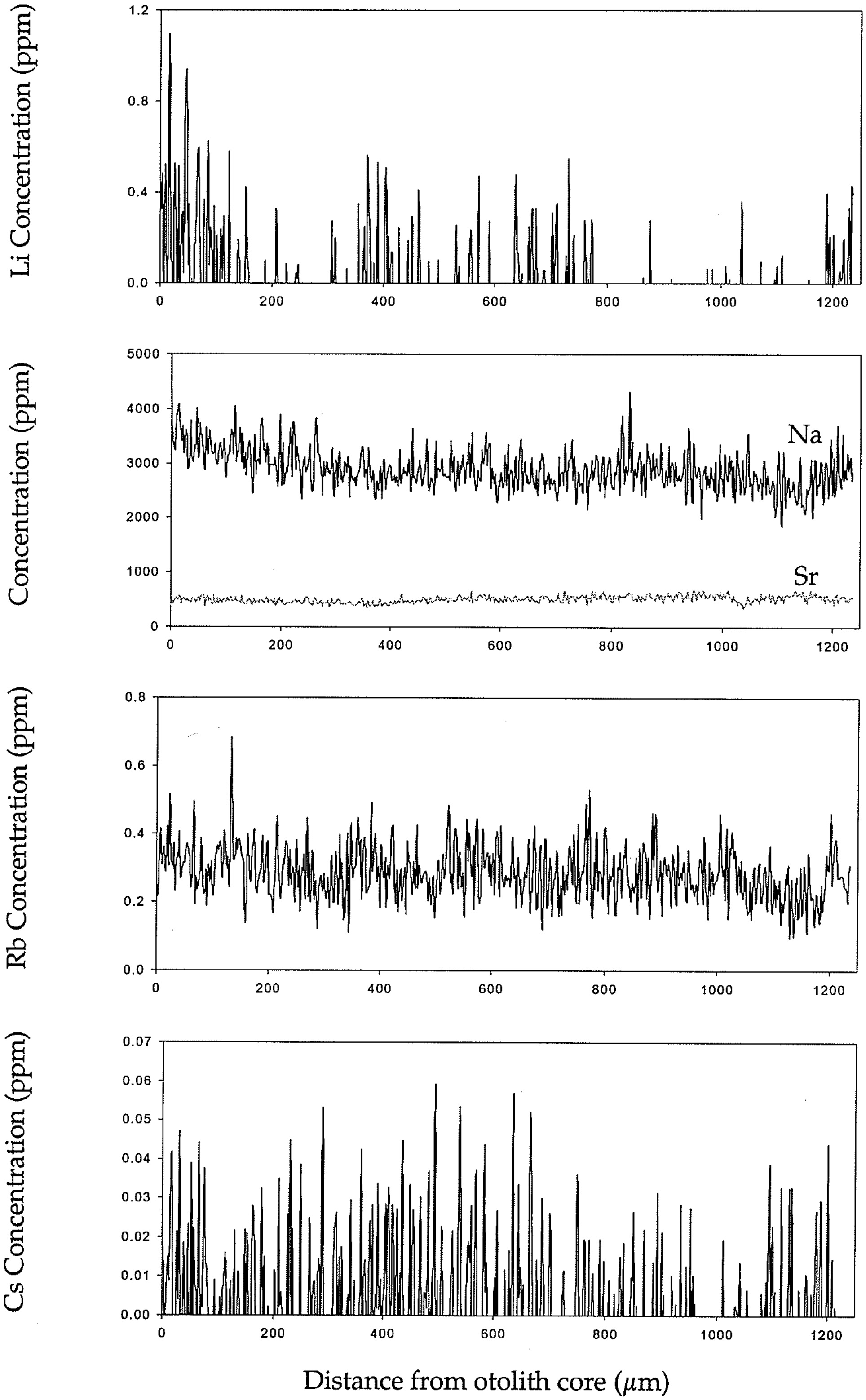
LDB07_133


Li Concentration (ppm)
0.0
0.3
0.6
0.9
1.2
1.5
1.8
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Cs Concentration (ppm)
0.0
0.1
0.2
0.3
0
200
400
600
800
1000
Distance from otolith core (μm)

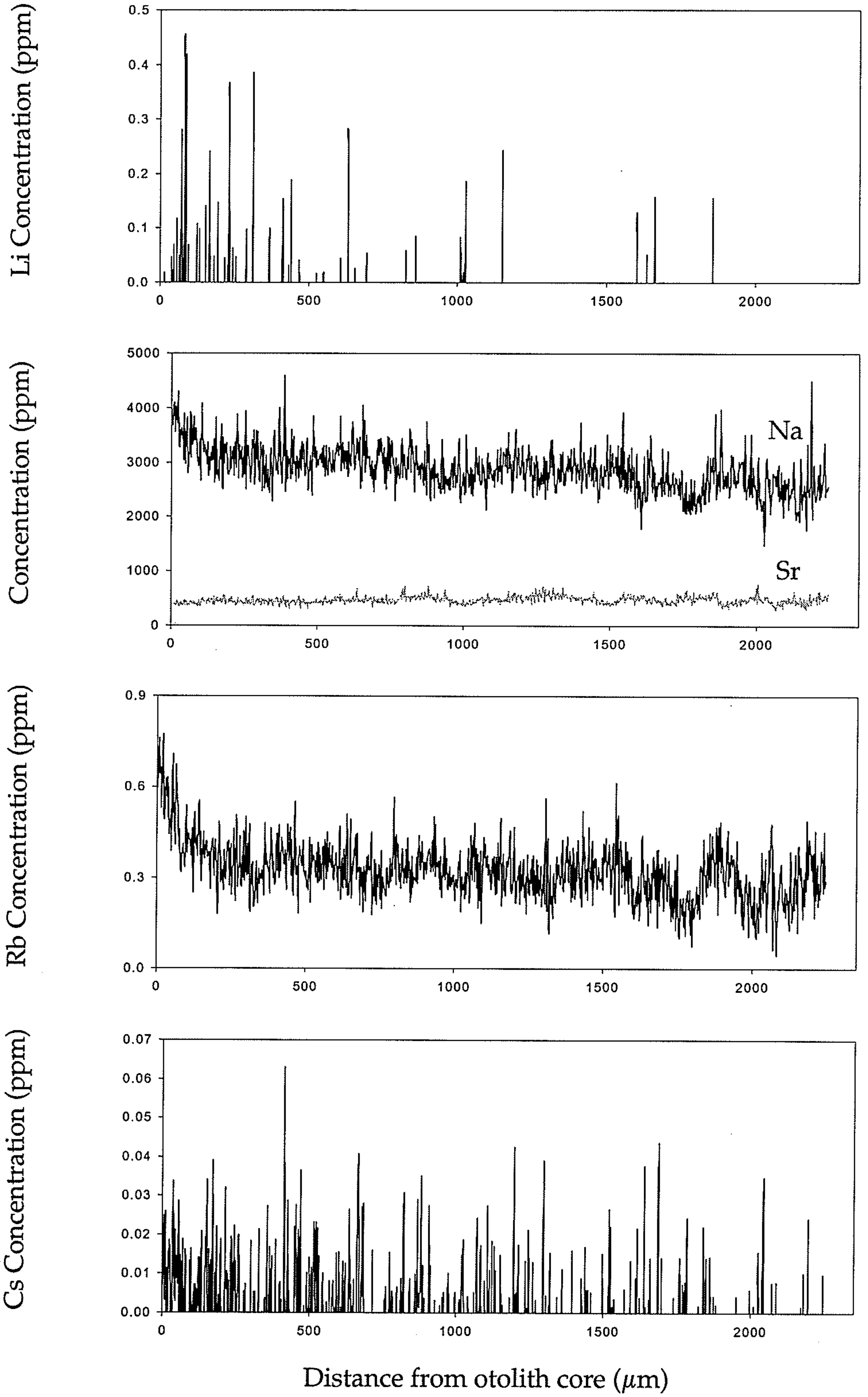
LDB07_134


Li Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
Cs Concentration (ppm)
0.08
0.06
0.04
0.02
0.00
Distance from otolith core (μm)

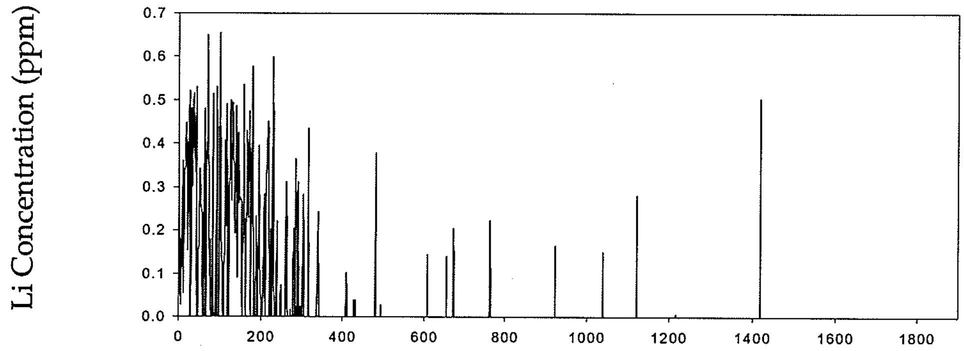
LDB07_135

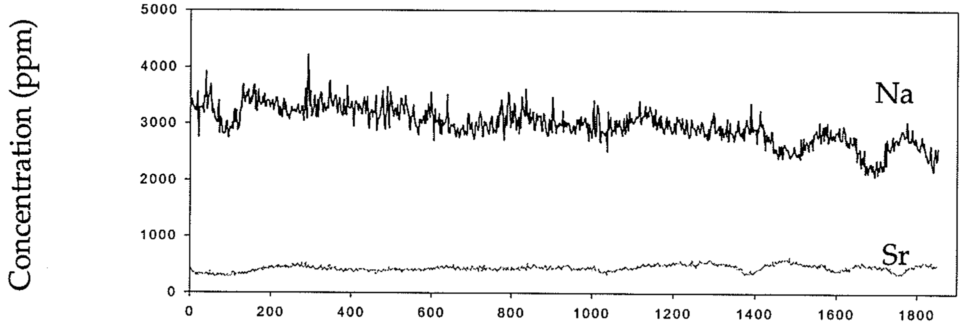

Li Concentration (ppm)
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
Cs Concentration (ppm)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Distance from otolith core (μm)

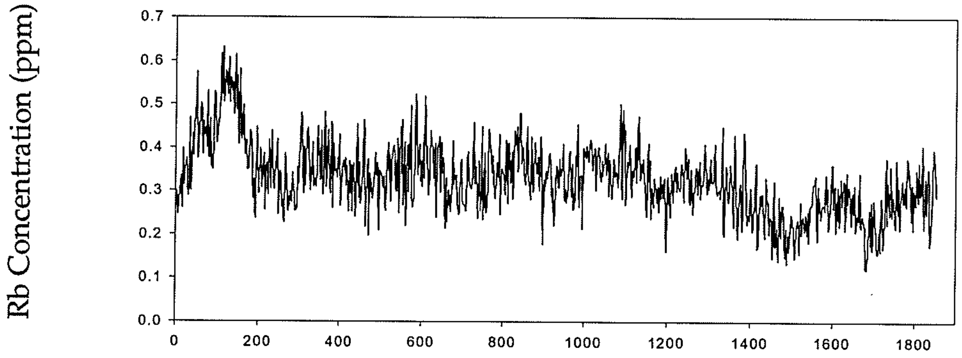
LDB07_136

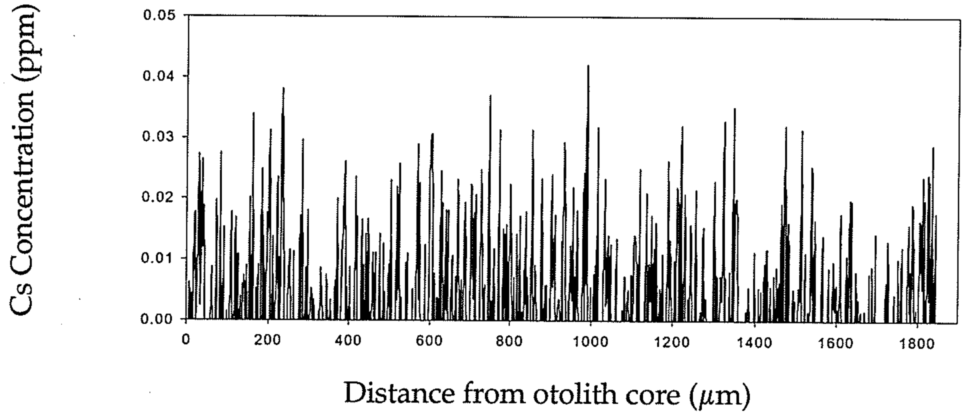

Li Concentration (ppm)
0.5
0.4
0.3
0.2
0.1
0.0
0
500
1000
1500
2000
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
0.9
0.6
0.3
0.0
Cs Concentration (ppm)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Distance from otolith core (μm)

LDB07_137

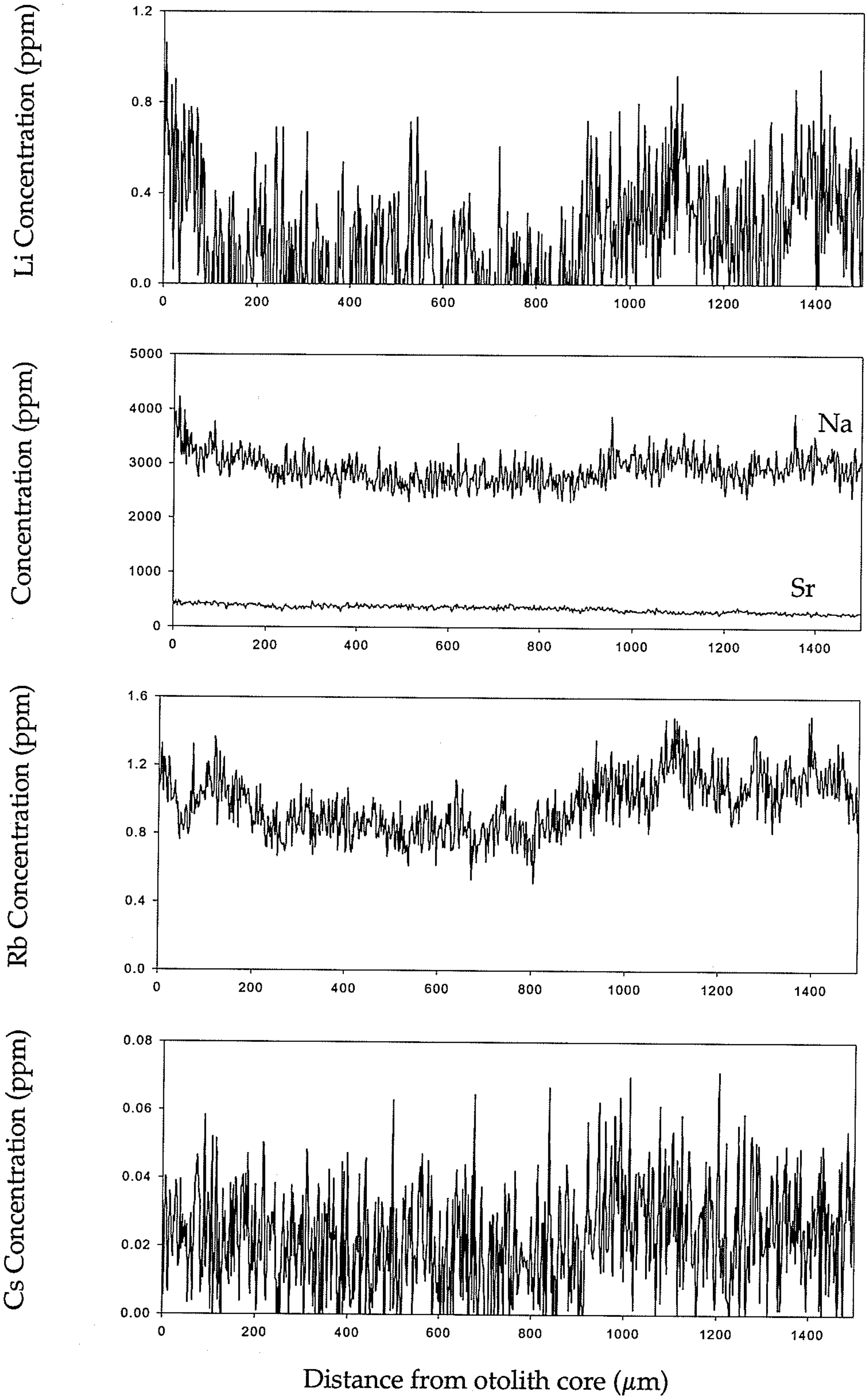

Li Concentration (ppm)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
1200
1400
1600
1800


Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
1800


Rb Concentration (ppm)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
1200
1400
1600
1800

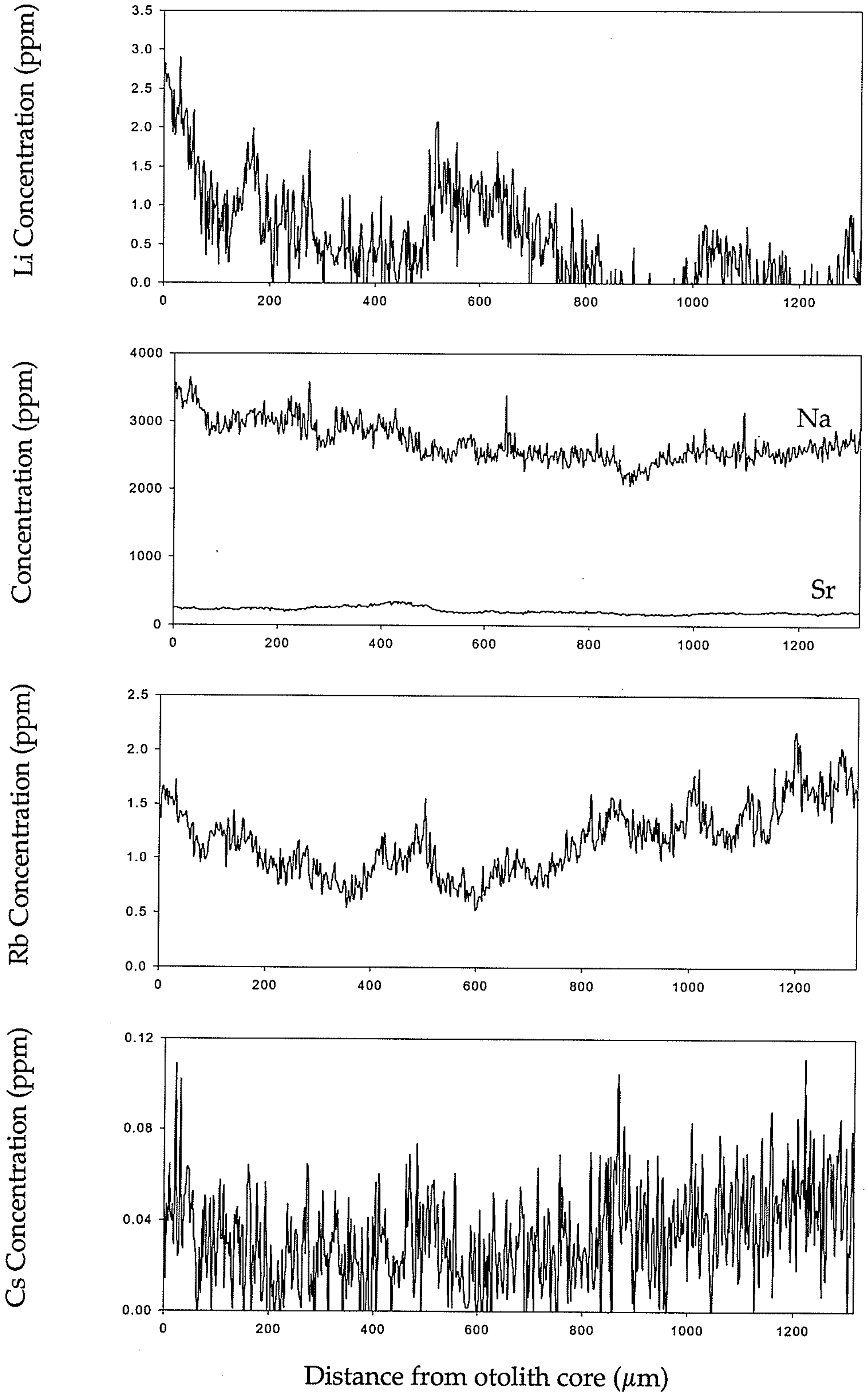

Cs Concentration (ppm)
0.05
0.04
0.03
0.02
0.01
0.00
0
200
400
600
800
1000
1200
1400
1600
1800
Distance from otolith core (μm)

LDB07_BC

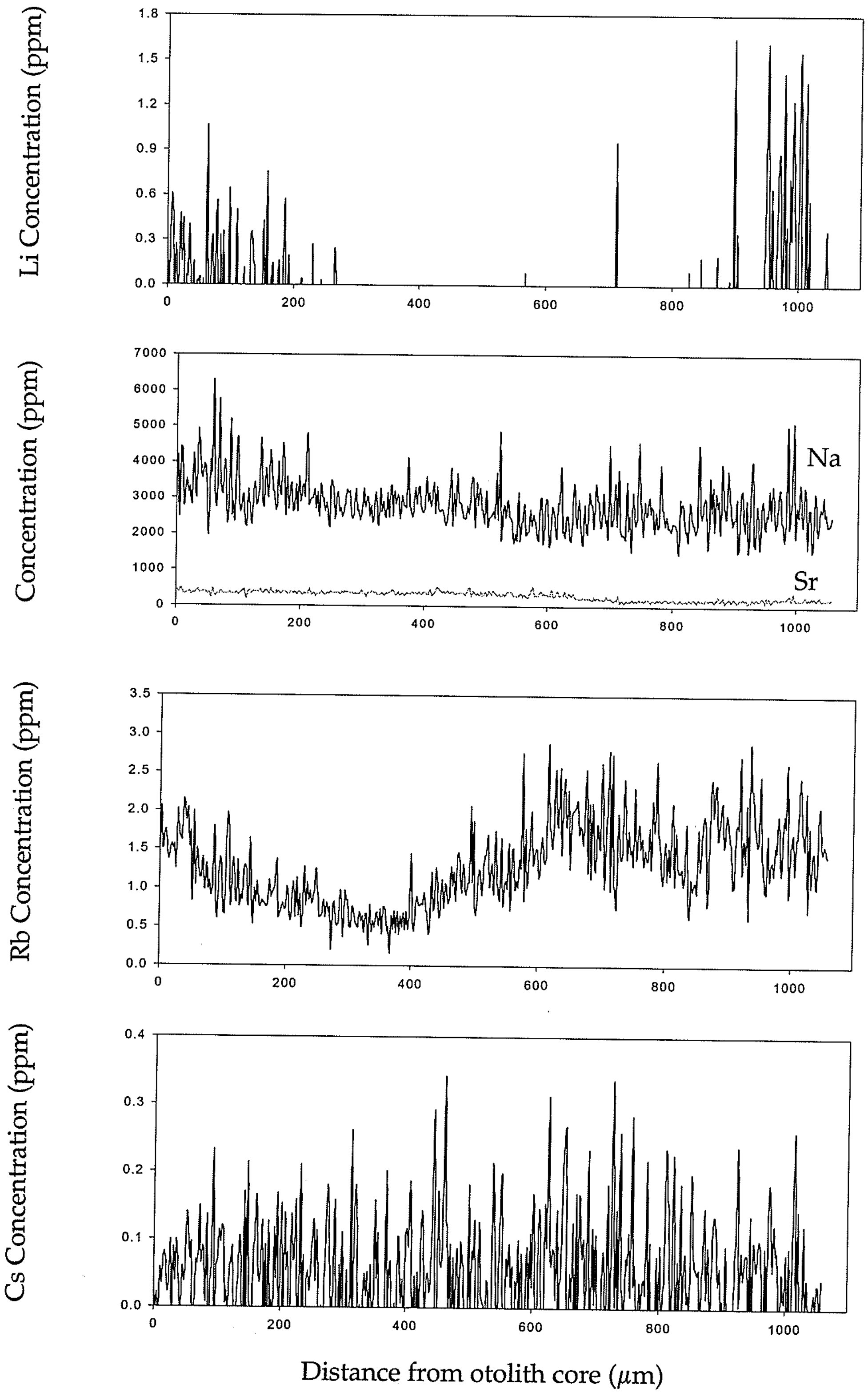


Li Concentration (ppm)
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
0.08
0.06
0.04
0.02
0.00
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

LDB07_140

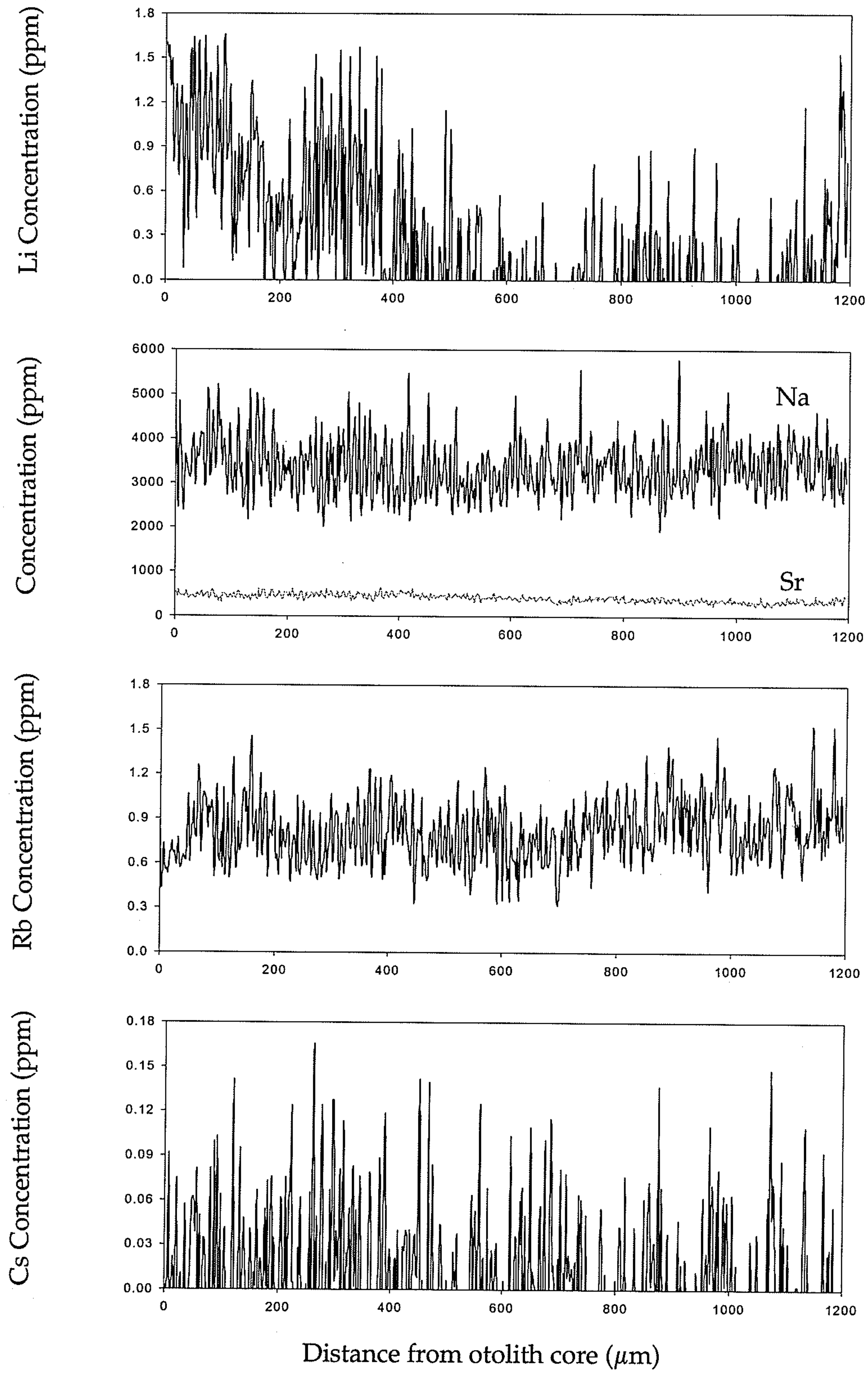

Li Concentration (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
0
200
400
600
800
1000
1200
Distance from otolith core (µm)

LDB07_142

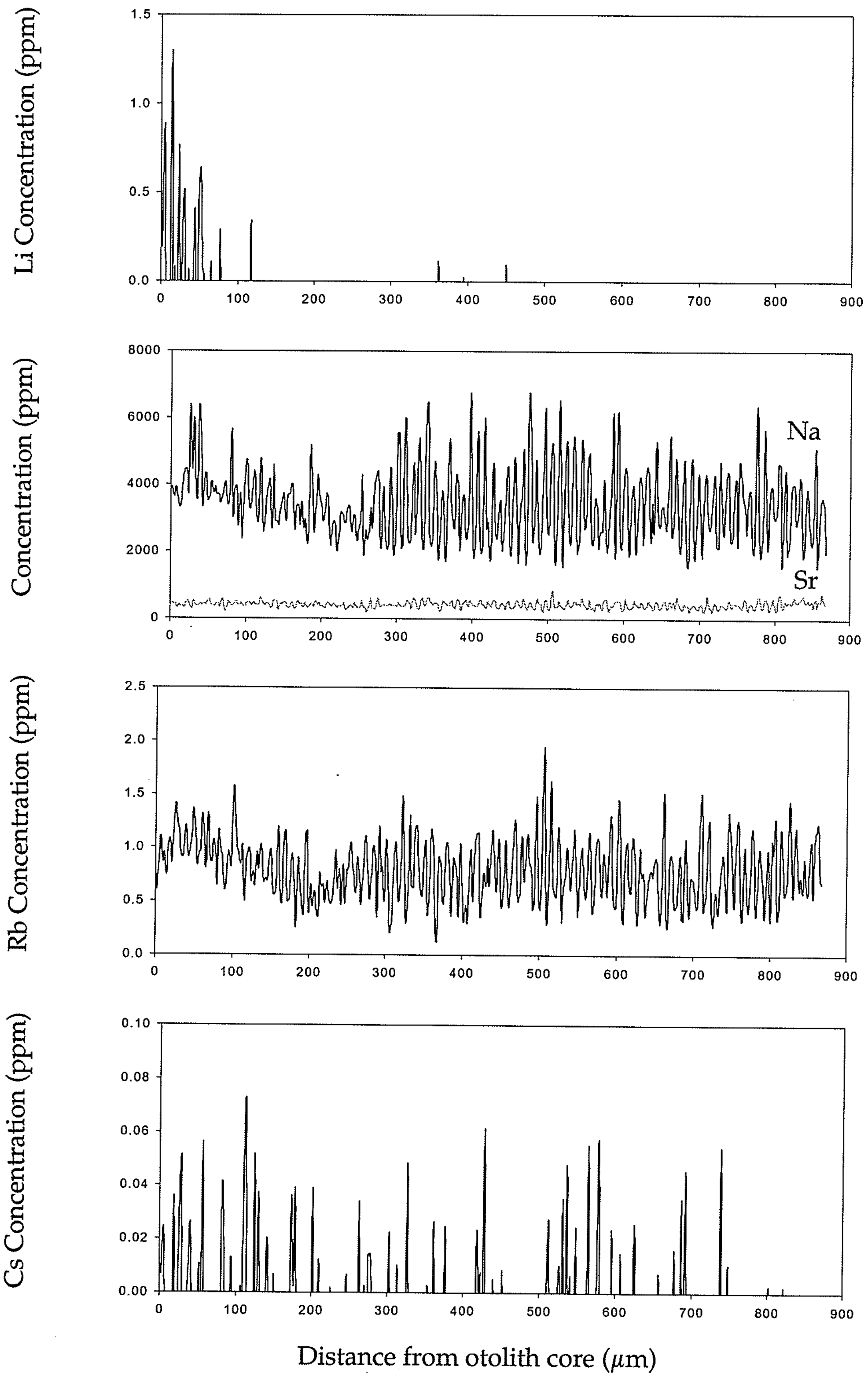


Li Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
0
200
400
600
800
1000
Concentration (ppm)
7000
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Cs Concentration (ppm)
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

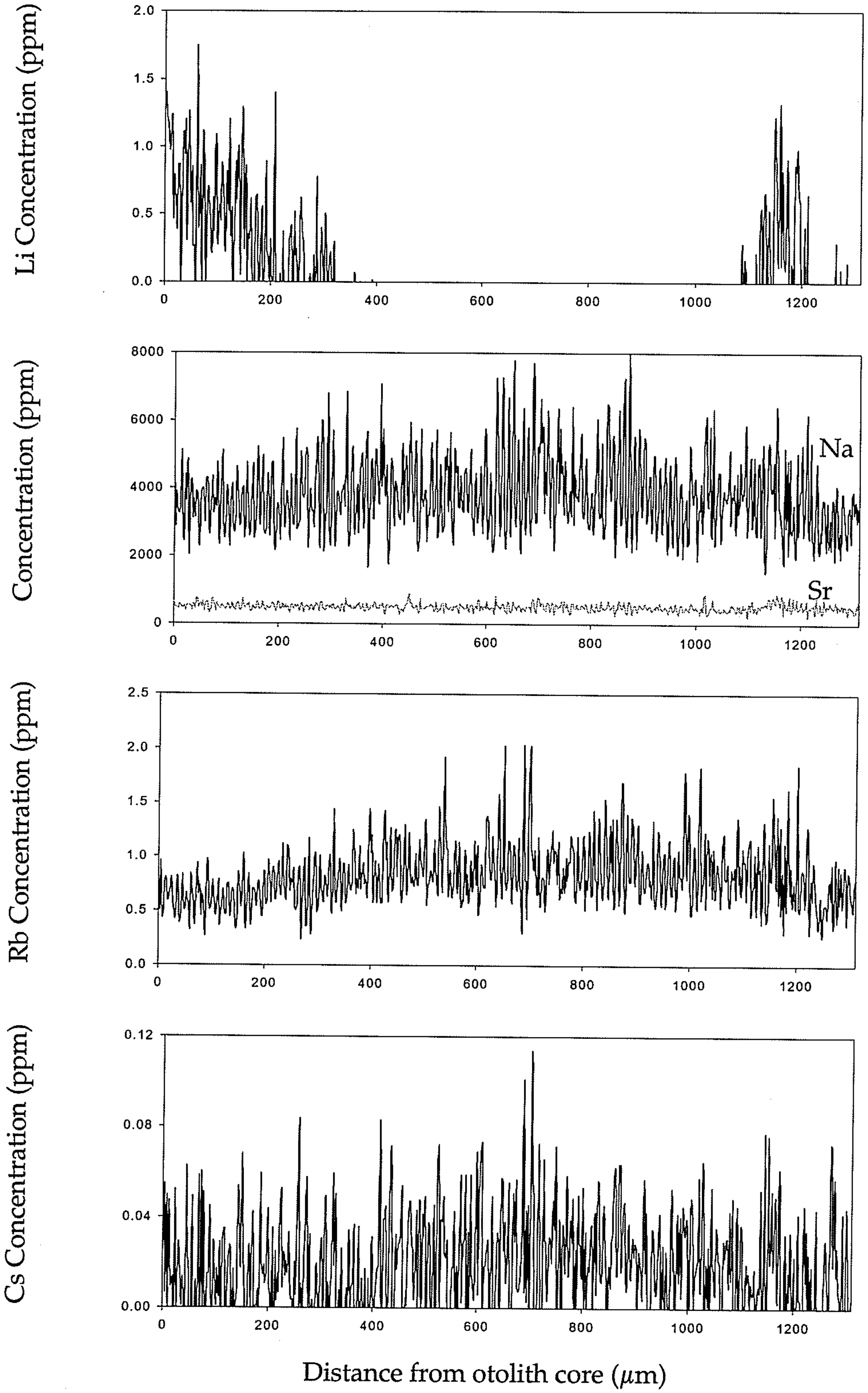
LDB07_143


Li Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.18
0.15
0.12
0.09
0.06
0.03
0.00
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

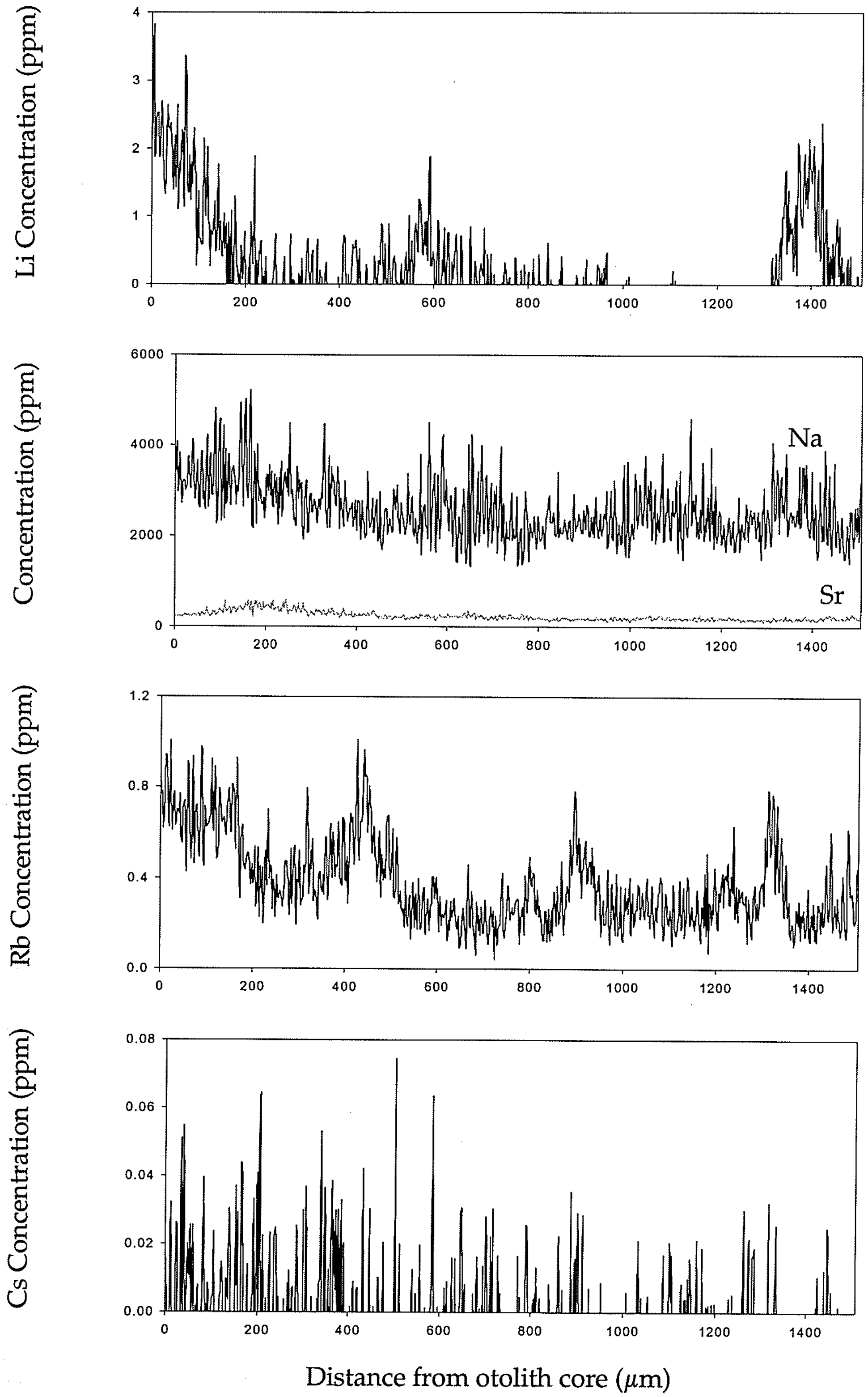
LDB07_144


Li Concentration (ppm)
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
900
Concentration (ppm)
8000
6000
4000
2000
0
Na
Sr
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
Cs Concentration (ppm)
0.10
0.08
0.06
0.04
0.02
0.00
Distance from otolith core (μm)

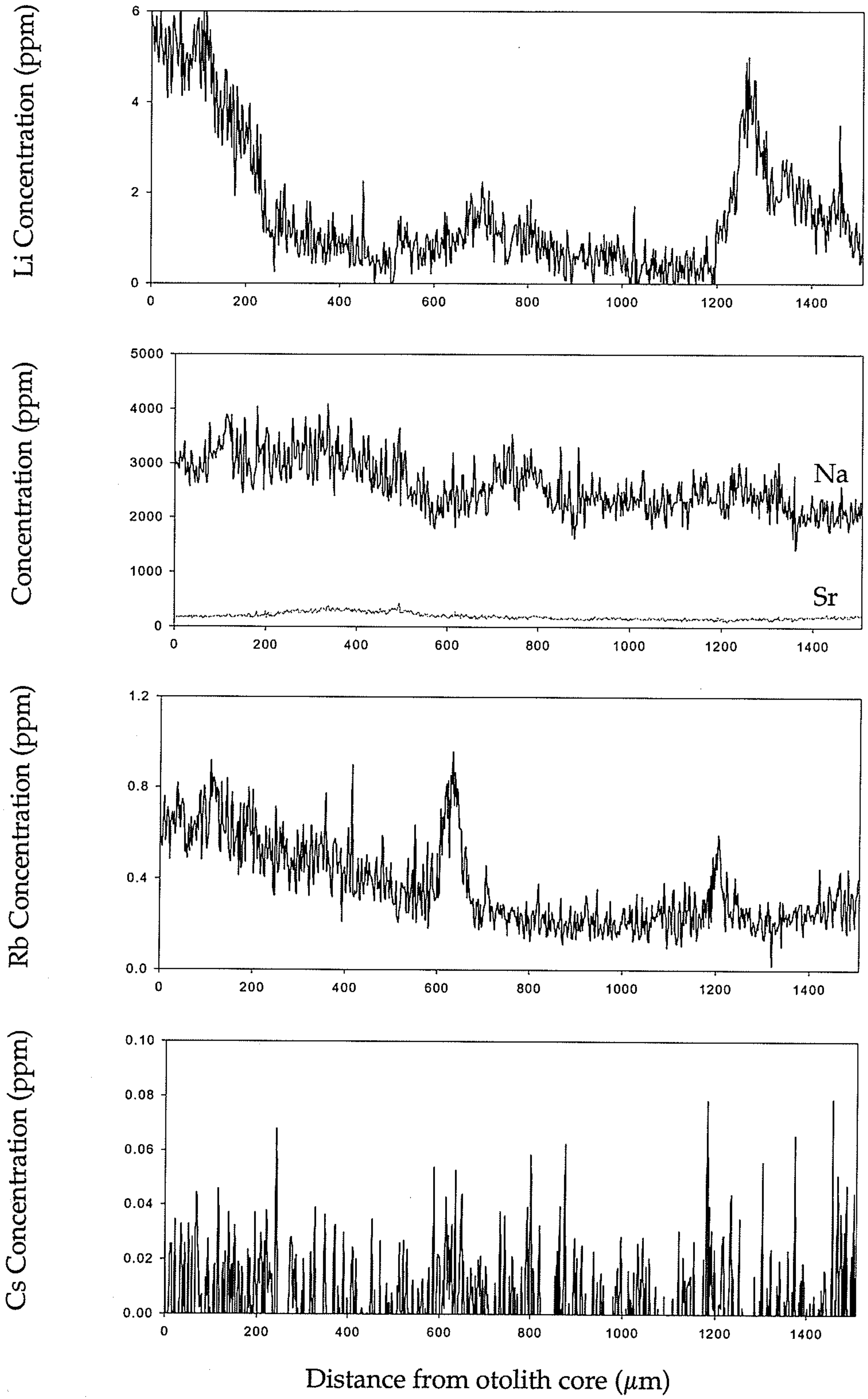
LDB07_145


Li Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
8000
6000
4000
2000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.12
0.08
0.04
0.00
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

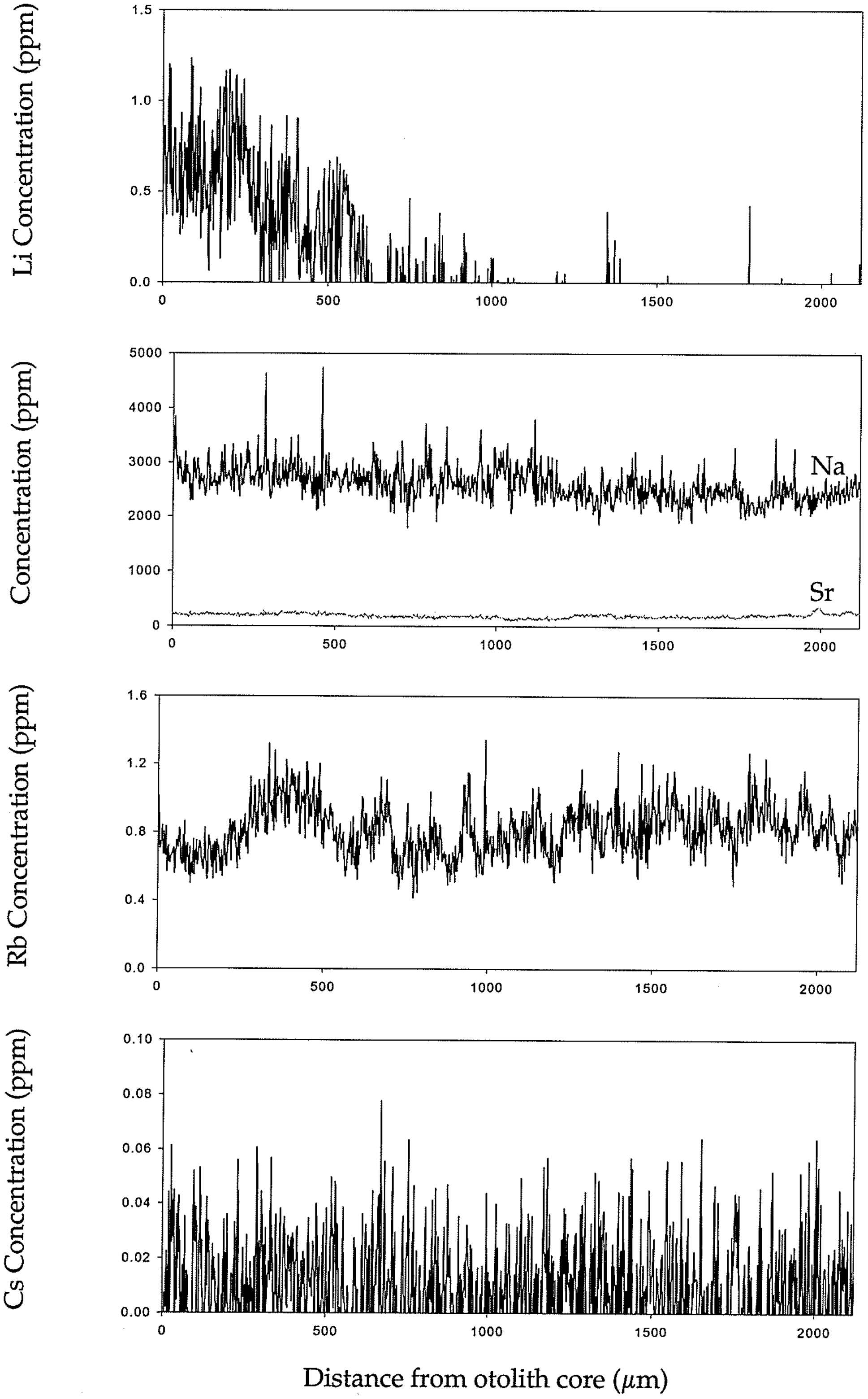
LDB07_146


Li Concentration (ppm)
4
3
2
1
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
6000
4000
2000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
0.08
0.06
0.04
0.02
0.00
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

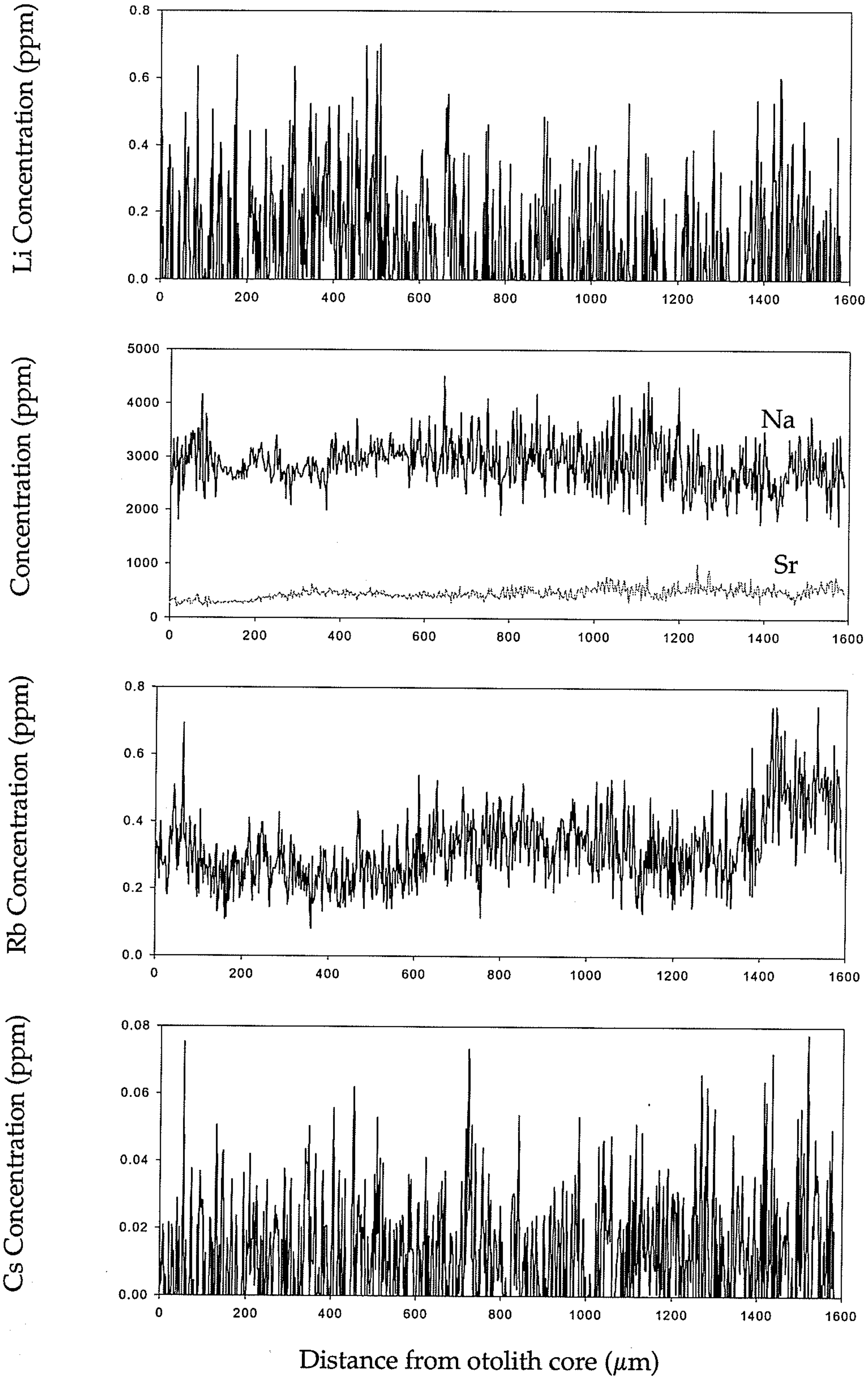
LDB07_147


Li Concentration (ppm)
0
2
4
6
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
0.0
0.4
0.8
1.2
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
0.00
0.02
0.04
0.06
0.08
0.10
0
200
400
600
800
1000
1200
1400
Distance from otolith core (µm)

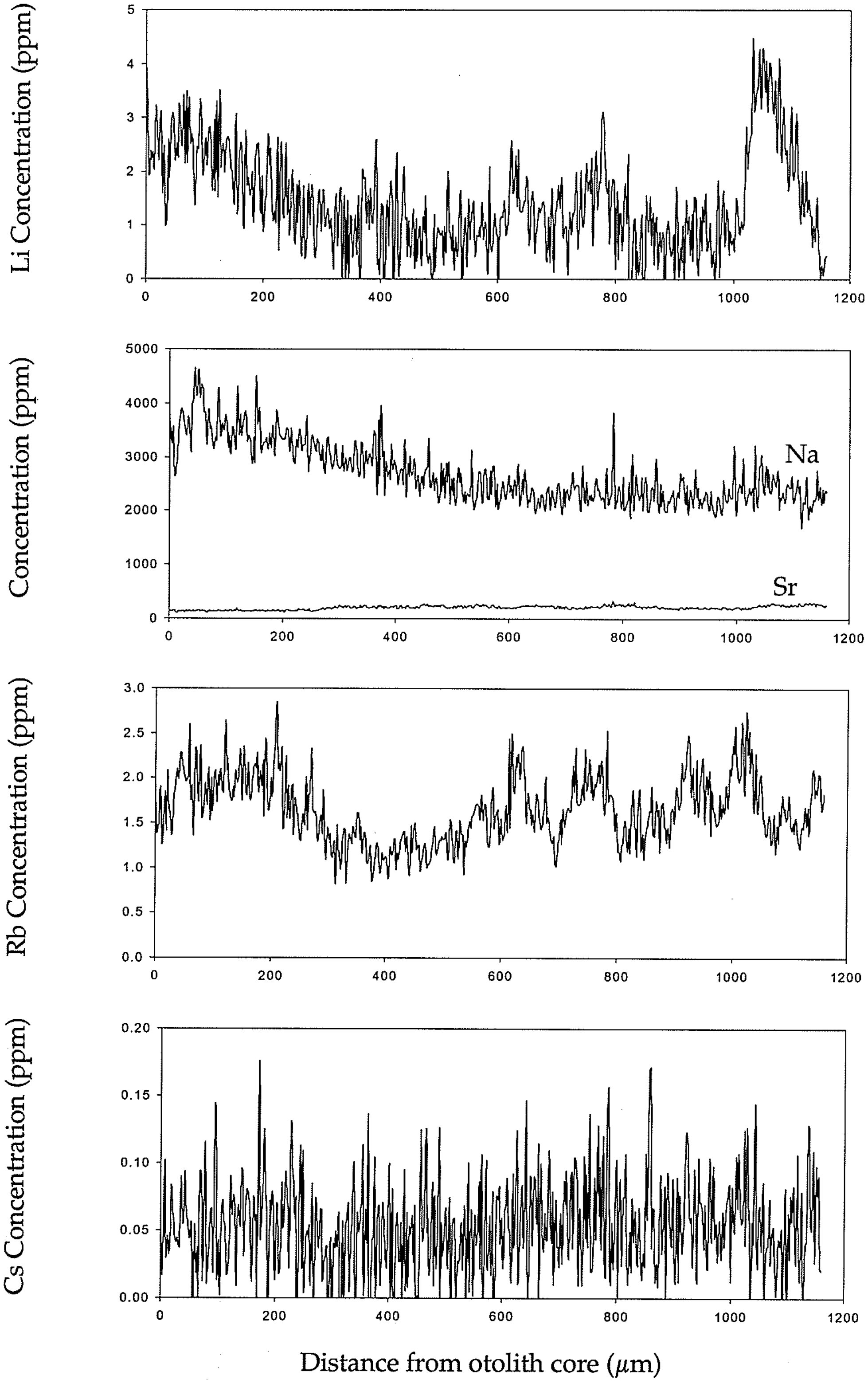
LDB07_148


Li Concentration (ppm)
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
500
1000
1500
2000
Cs Concentration (ppm)
0.10
0.08
0.06
0.04
0.02
0.00
0
500
1000
1500
2000
Distance from otolith core (μm)

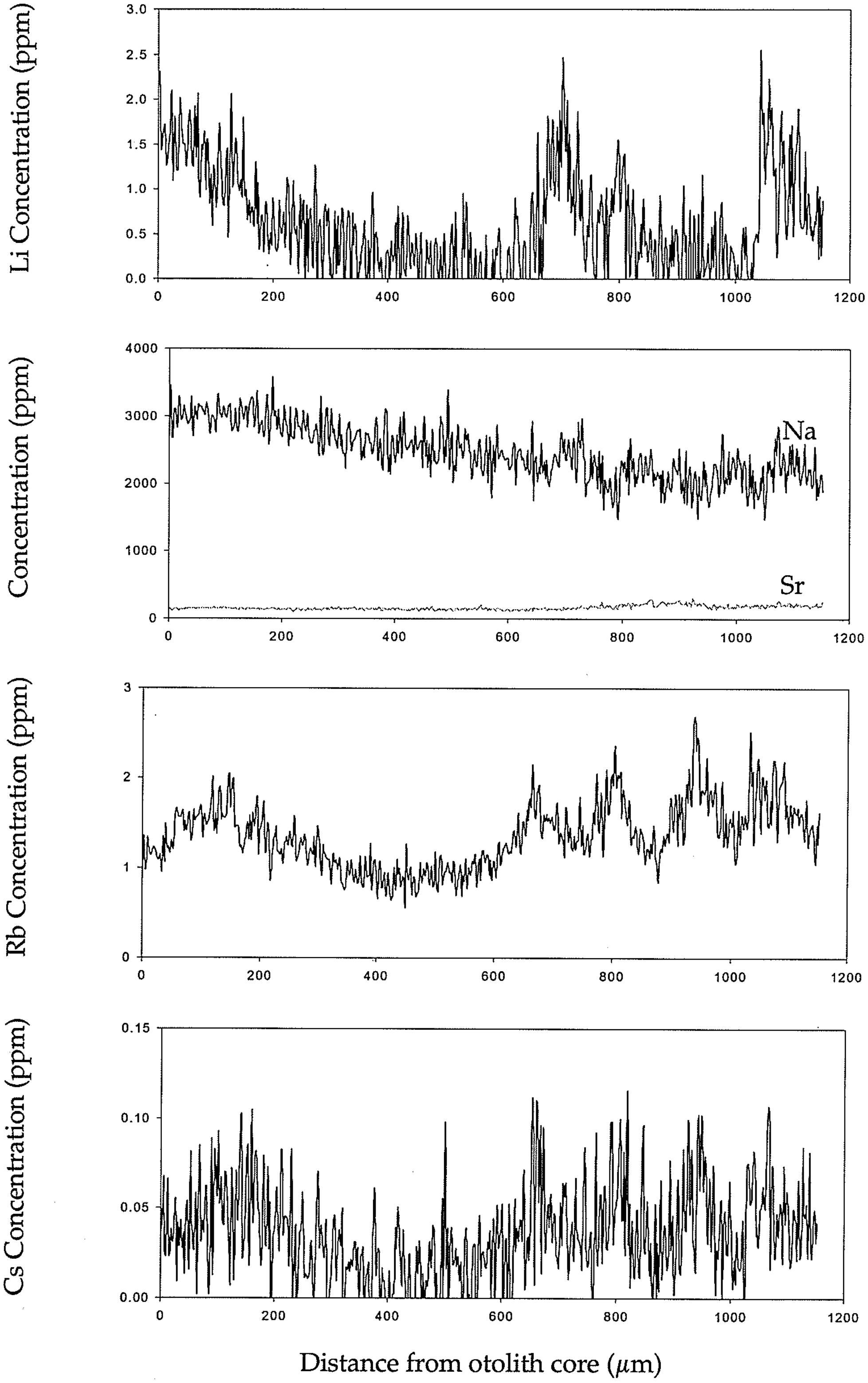
LDB07_149


Li Concentration (ppm)
0.0
0.2
0.4
0.6
0.8
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
Rb Concentration (ppm)
0.0
0.2
0.4
0.6
0.8
Cs Concentration (ppm)
0.00
0.02
0.04
0.06
0.08
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

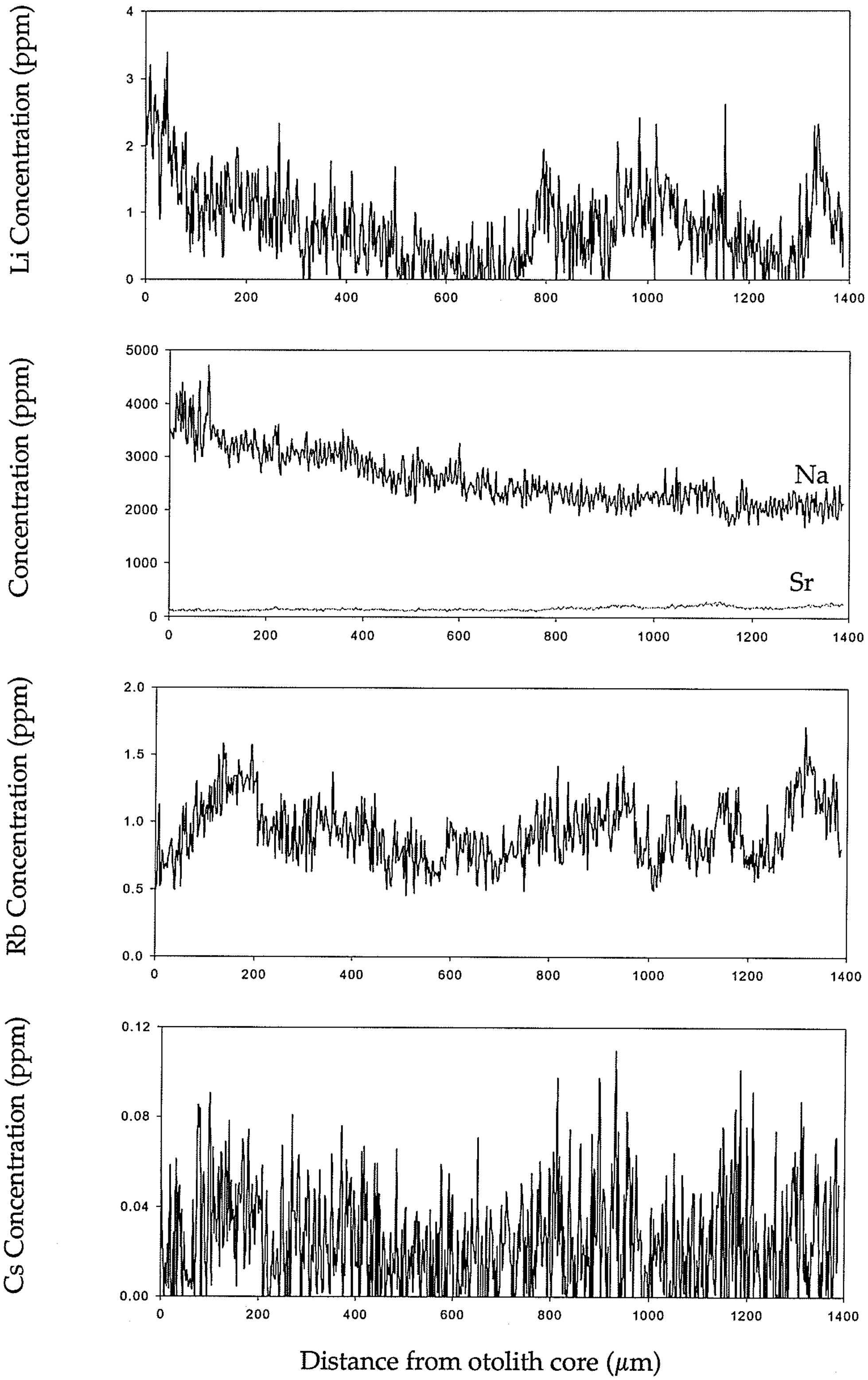
LDB07_152


Li Concentration (ppm)
0
1
2
3
4
5
0
200
400
600
800
1000
1200
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.00
0.05
0.10
0.15
0.20
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

LDB07_153

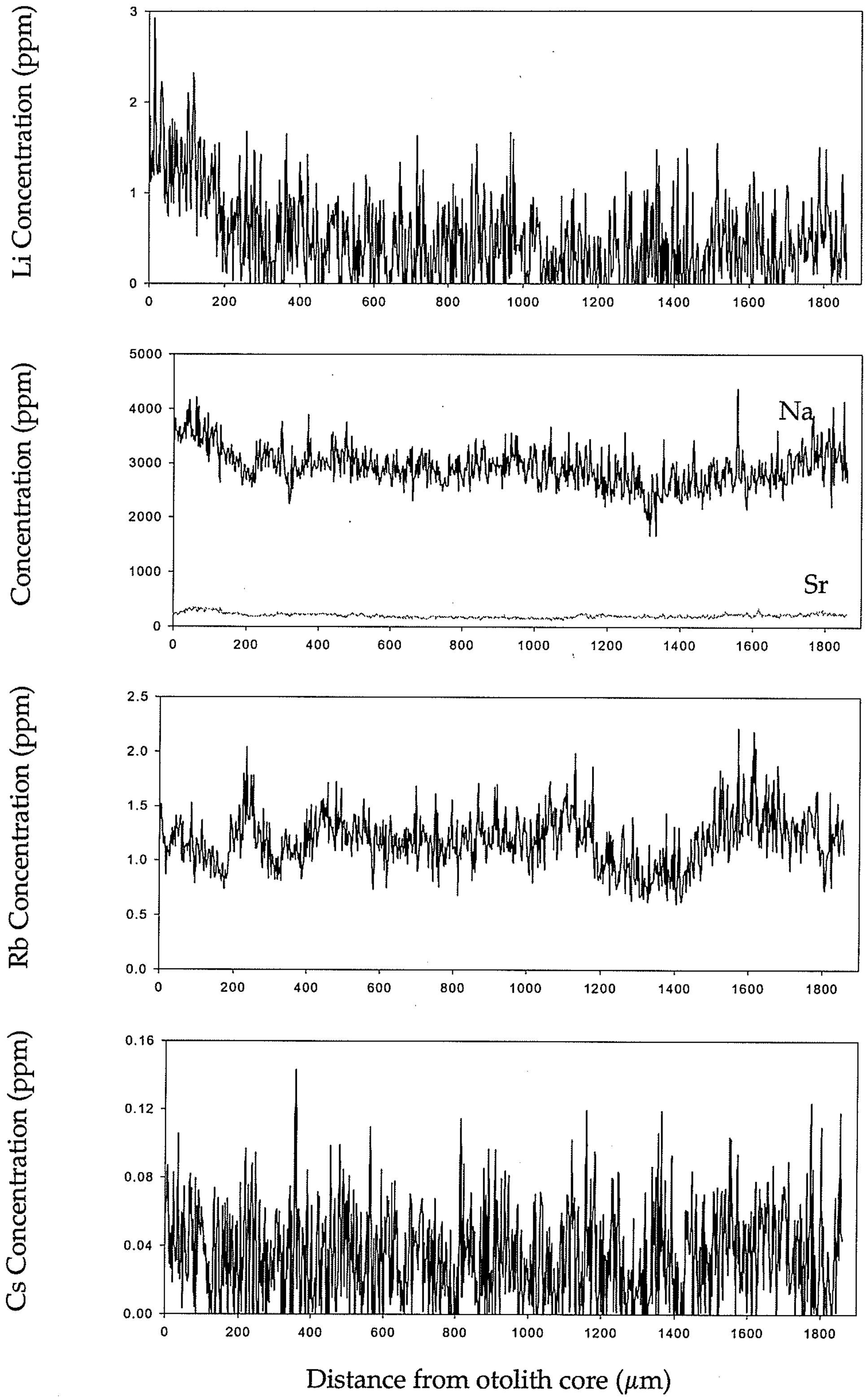

Li Concentration (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
3
2
1
0
Cs Concentration (ppm)
0.15
0.10
0.05
0.00
Distance from otolith core (μm)

LDB07_154

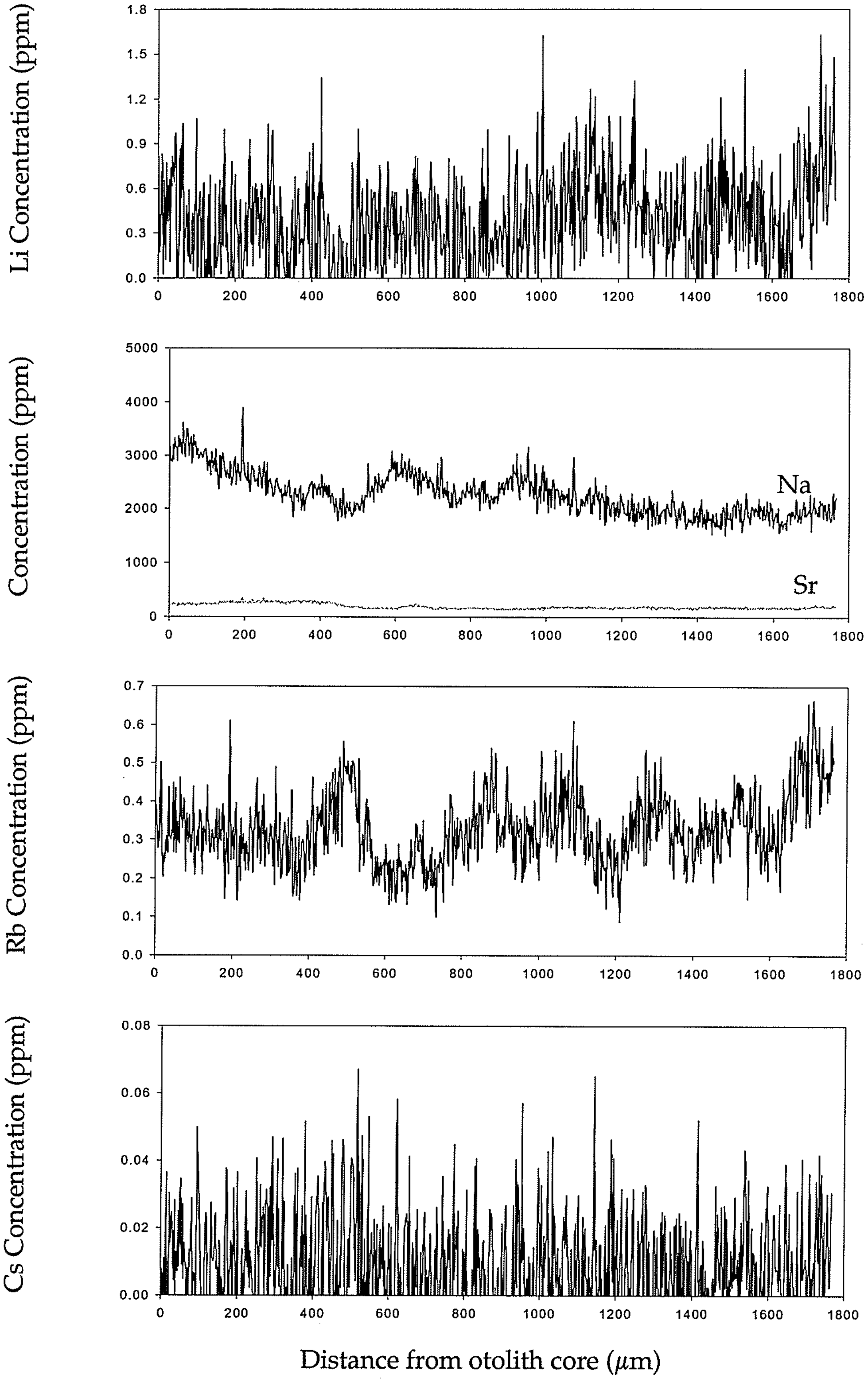


Li Concentration (ppm)
0
1
2
3
4
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
Cs Concentration (ppm)
0.00
0.04
0.08
0.12
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

LDB07_155

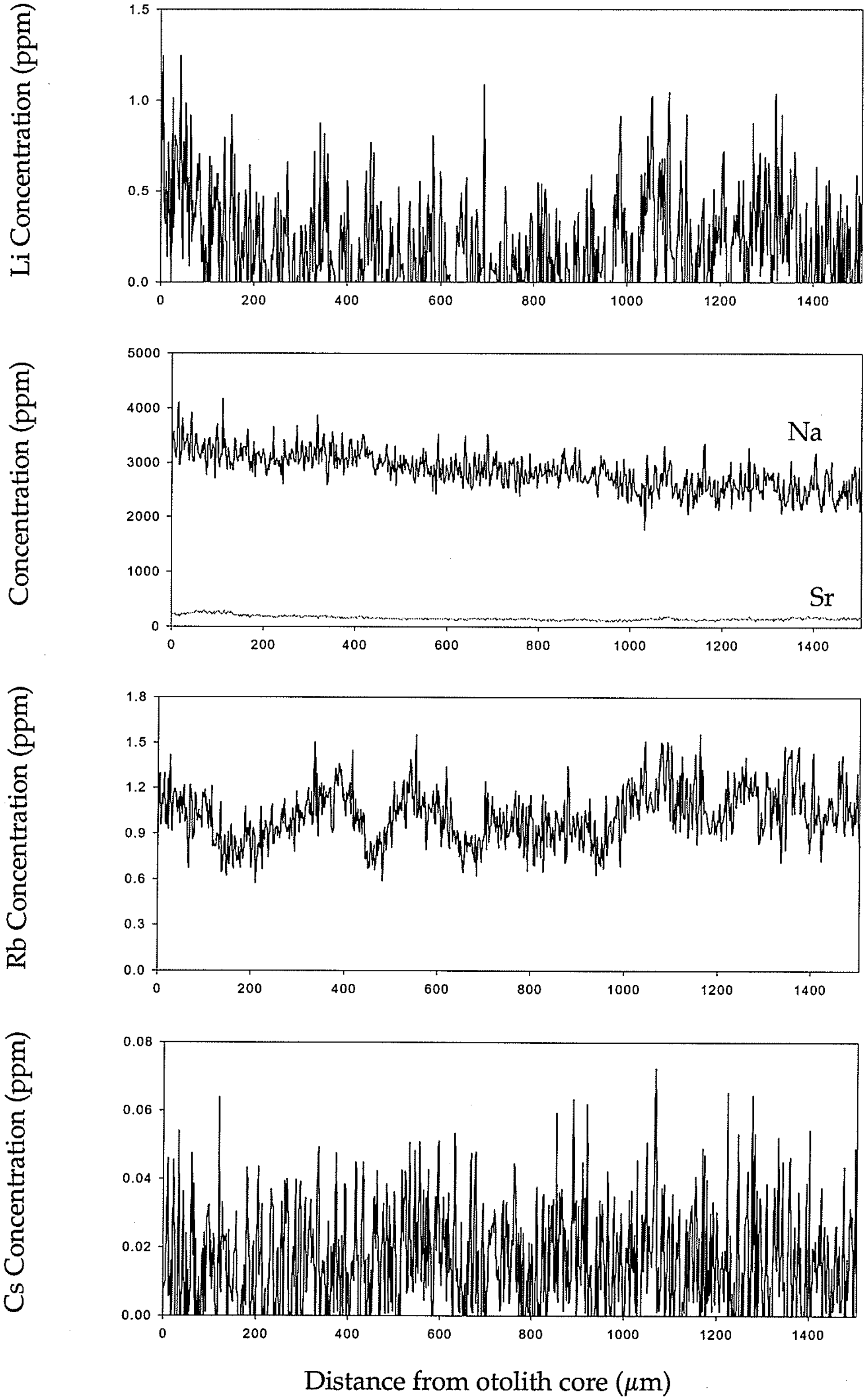

Li Concentration (ppm)
0
1
2
3
0
200
400
600
800
1000
1200
1400
1600
1800
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
1800
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
0
200
400
600
800
1000
1200
1400
1600
1800
Cs Concentration (ppm)
0.00
0.04
0.08
0.12
0.16
0
200
400
600
800
1000
1200
1400
1600
1800
Distance from otolith core (μm)

LDB07_156

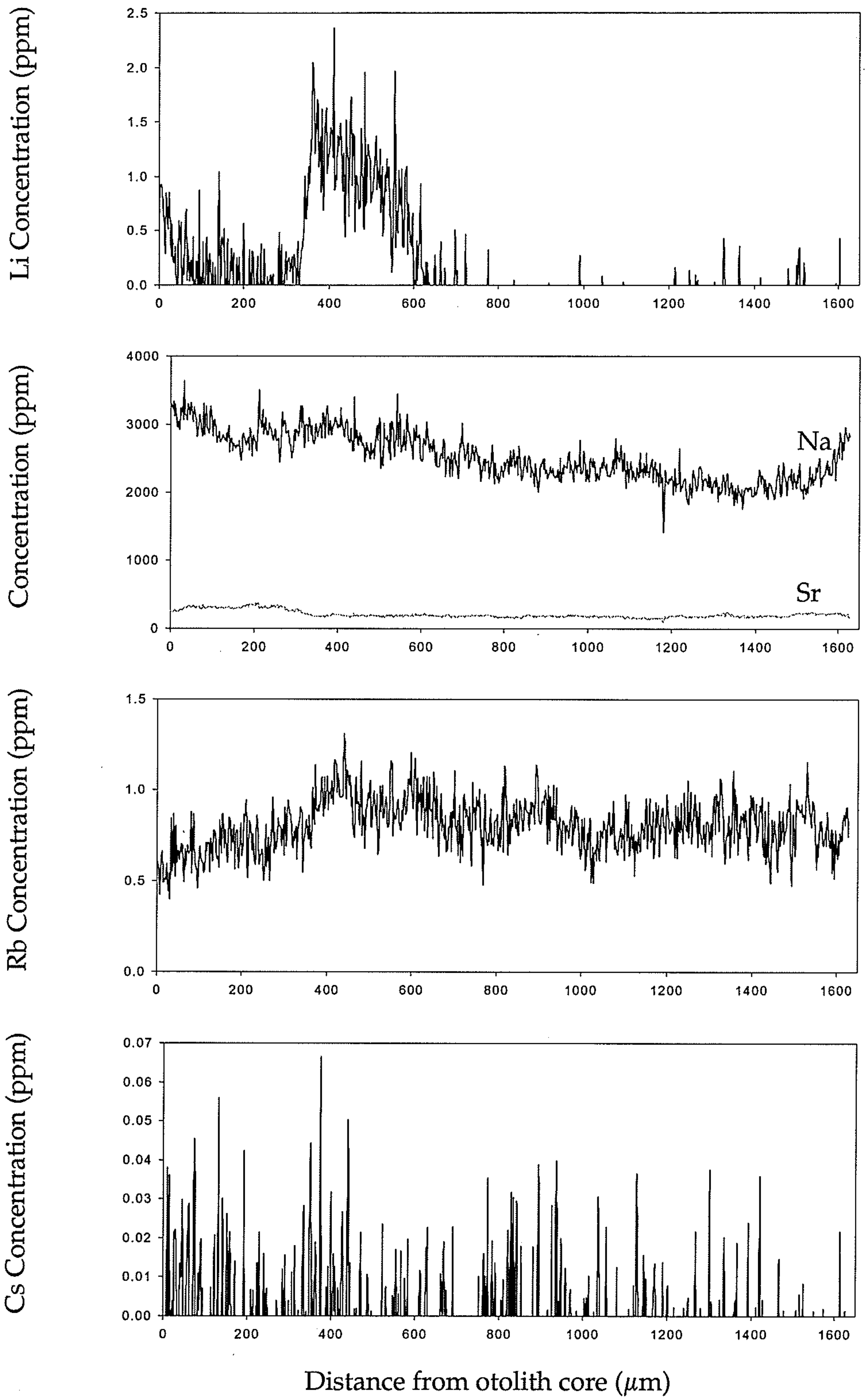


Li Concentration (ppm)
0.0
0.3
0.6
0.9
1.2
1.5
1.8
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
Rb Concentration (ppm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Cs Concentration (ppm)
0.00
0.02
0.04
0.06
0.08
0
200
400
600
800
1000
1200
1400
1600
1800
Distance from otolith core (μm)

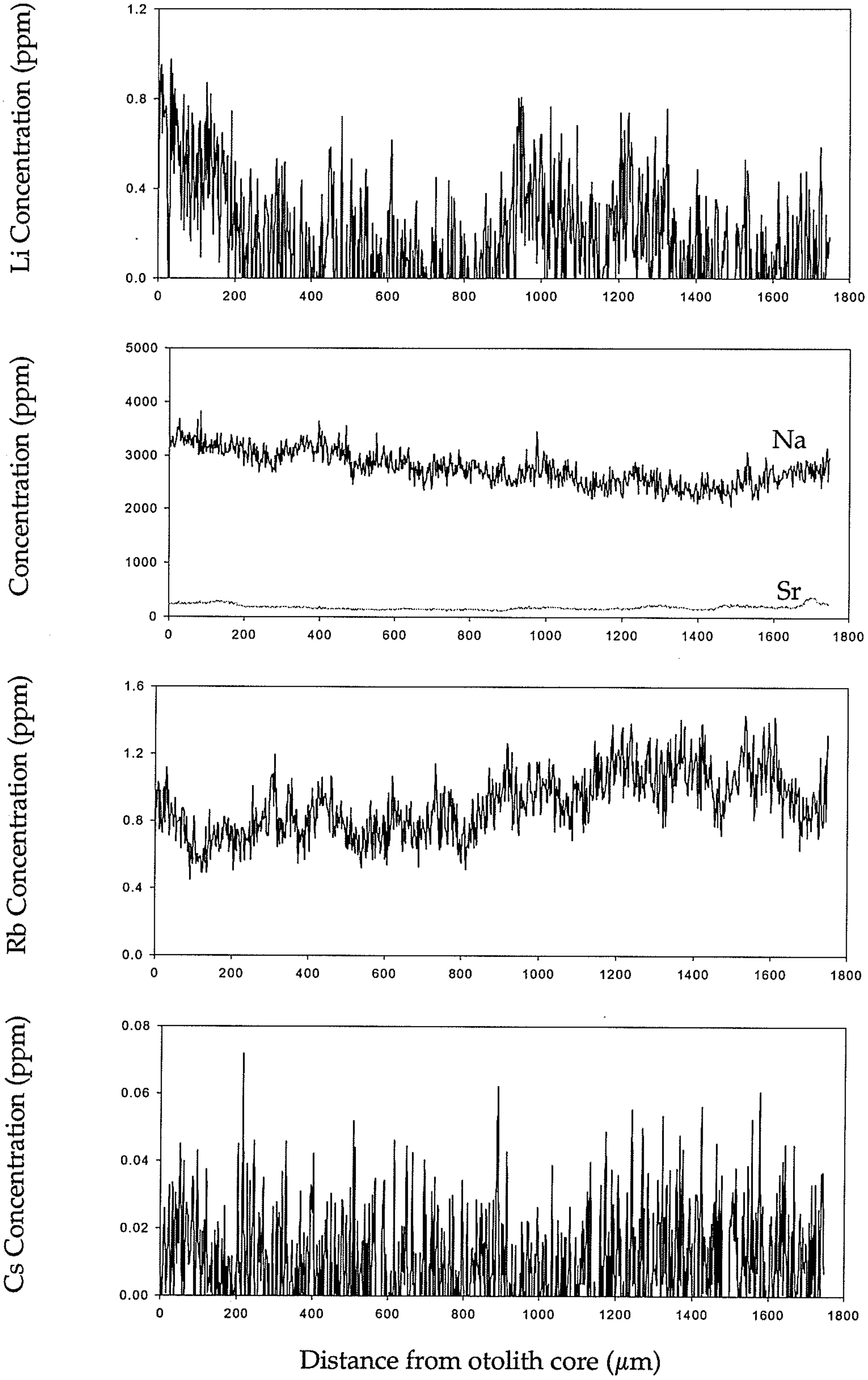
LDB07_157


Li Concentration (ppm)
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
Cs Concentration (ppm)
0.08
0.06
0.04
0.02
0.00
Distance from otolith core (μm)

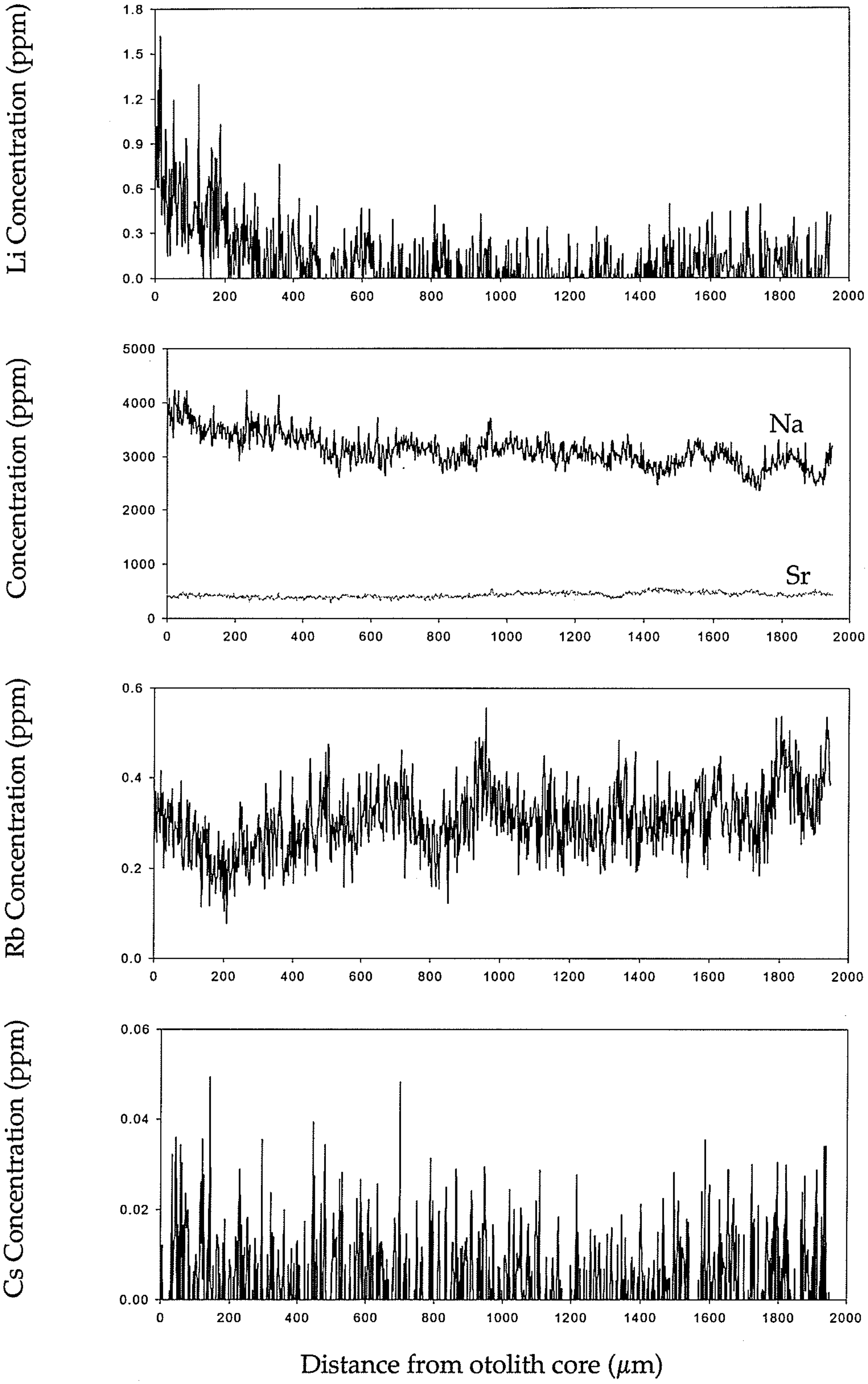
LDB07_158


Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.5
1.0
0.5
0.0
Cs Concentration (ppm)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Distance from otolith core (μm)

LDB07_159


Li Concentration (ppm)
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
Cs Concentration (ppm)
0.08
0.06
0.04
0.02
0.00
Distance from otolith core (μm)

LDB07_160


Li Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
0.6
0.4
0.2
0.0
Cs Concentration (ppm)
0.06
0.04
0.02
0.00
Distance from otolith core (μm)

Appendix G LA-ICP-MS data for Lac du Bonnet otoliths *continued*

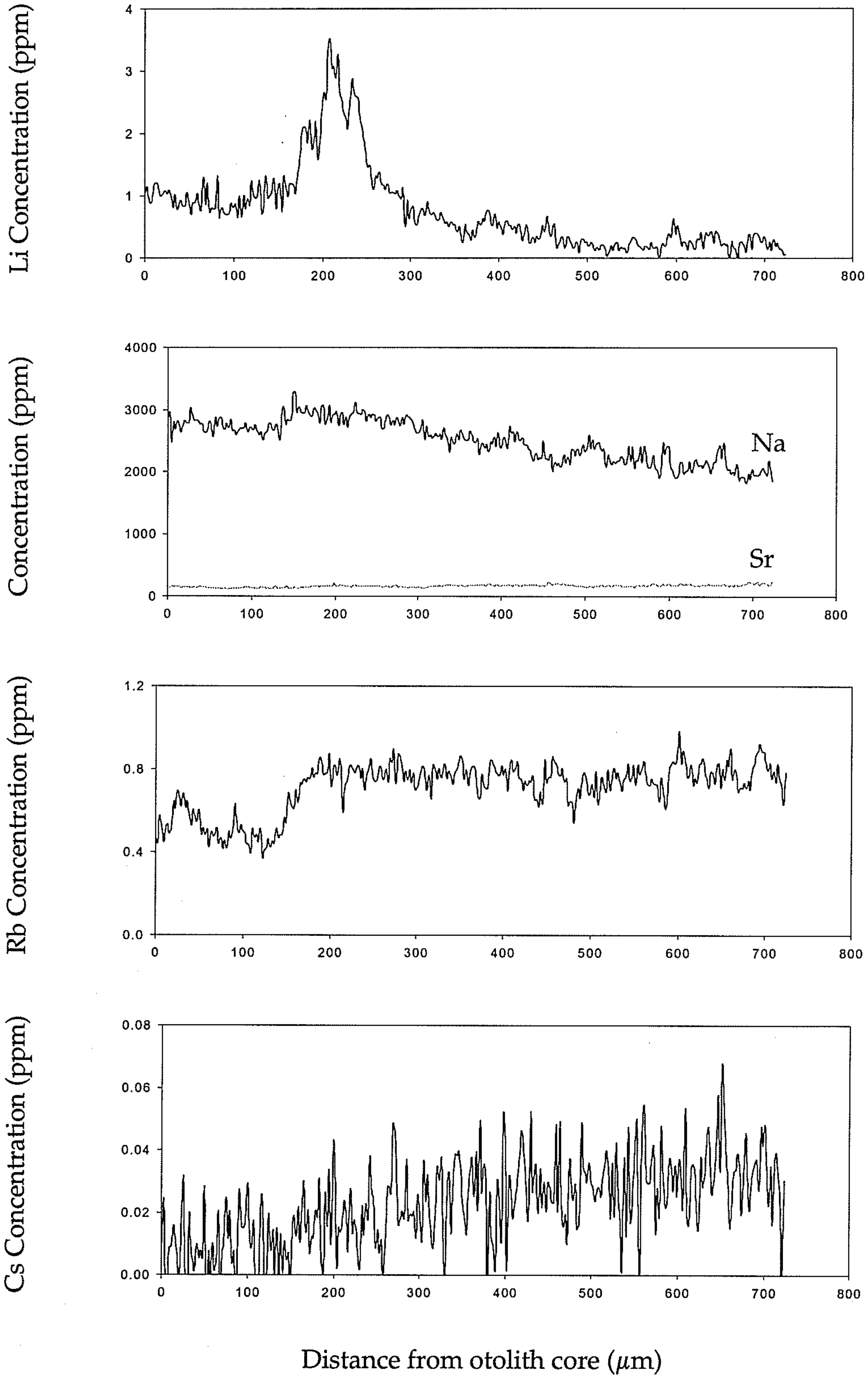
Species: Walleye (*Sander vitreous*)

Captured: 2006 (Manitoba Conservation Archives)

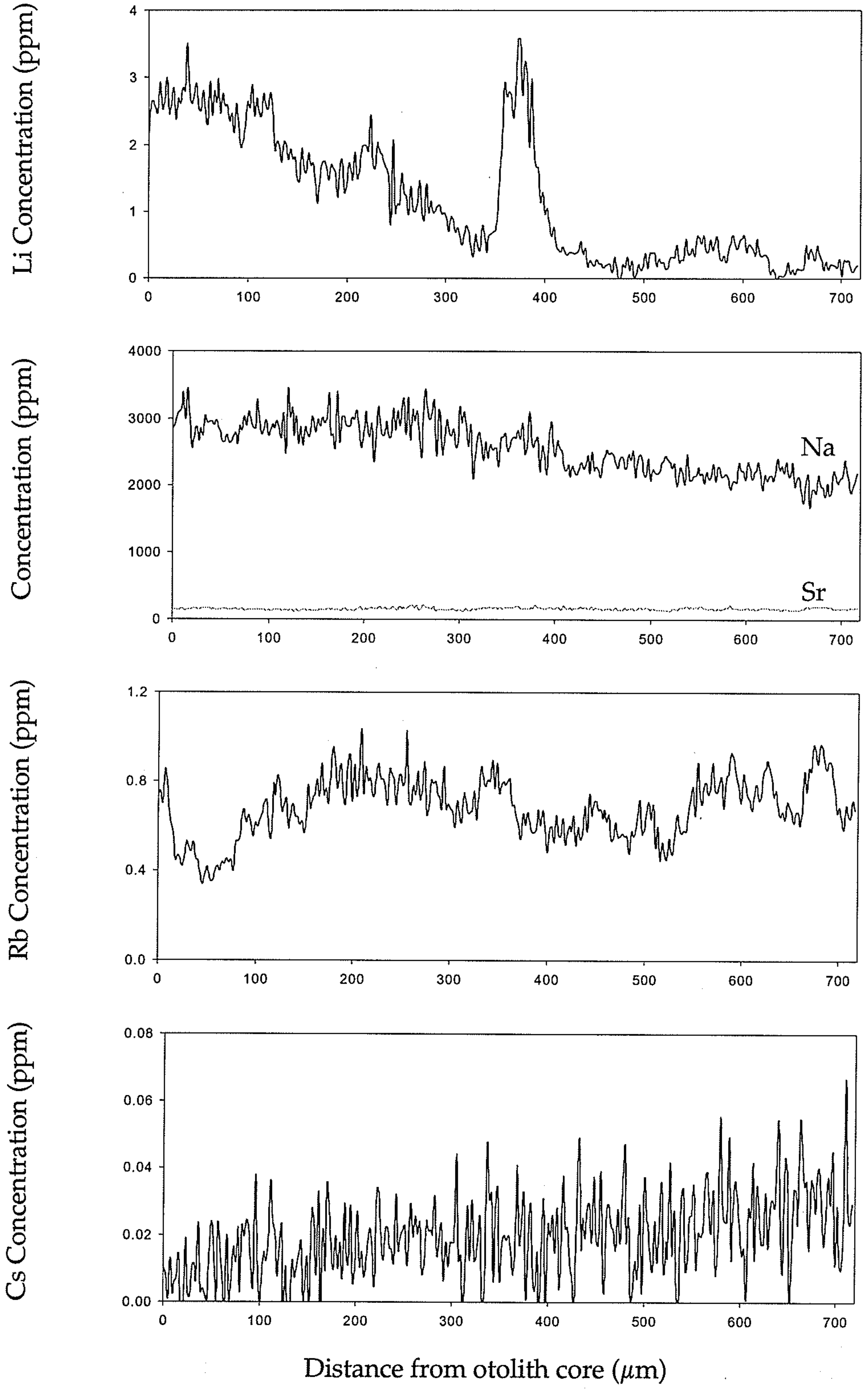
Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
01	Walleye	13
02	Walleye	11
03	Walleye	11
04	Walleye	7

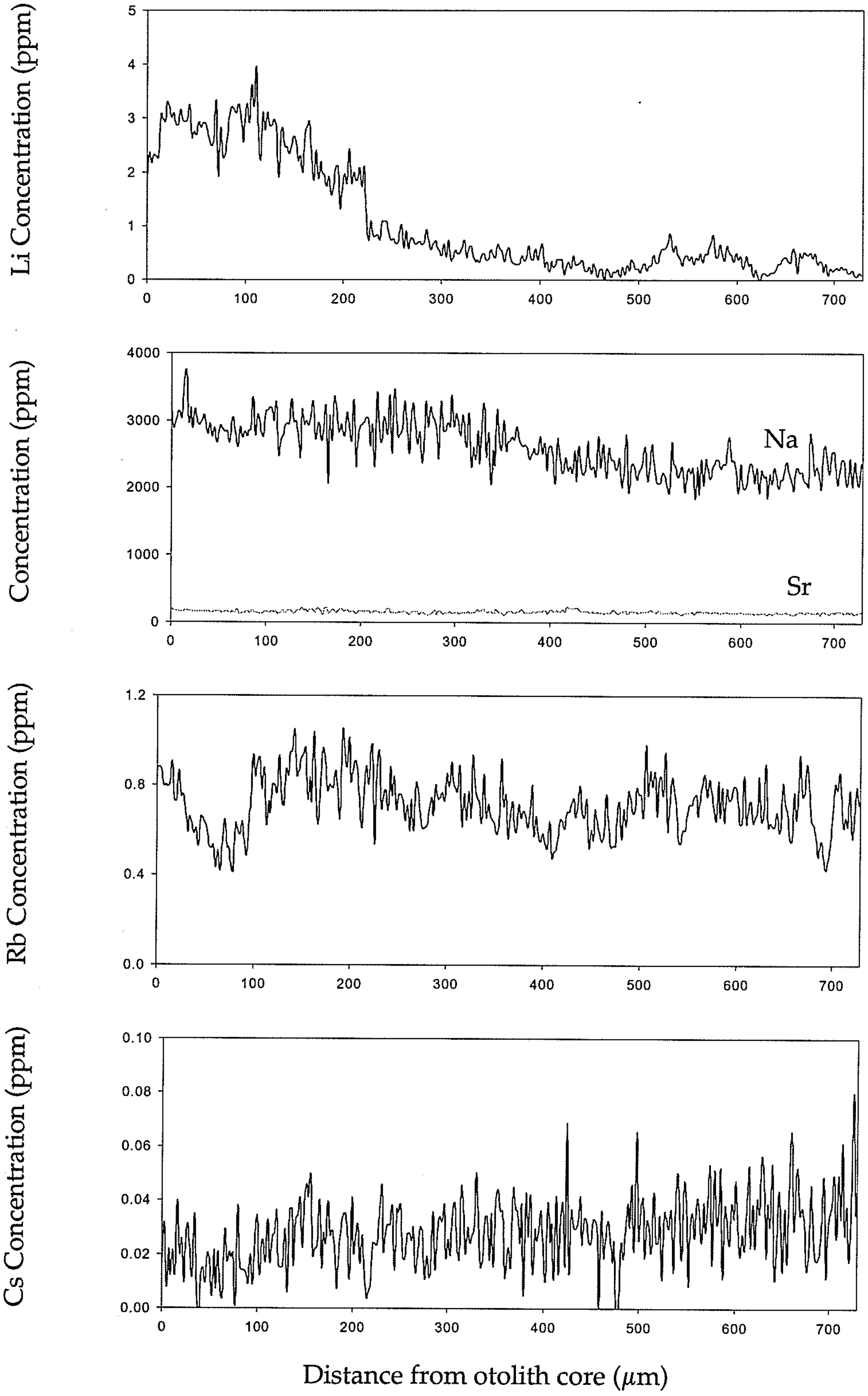
LDB06_01


Li Concentration (ppm)
4
3
2
1
0
0
100
200
300
400
500
600
700
800
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
800
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
800
Cs Concentration (ppm)
0.08
0.06
0.04
0.02
0.00
0
100
200
300
400
500
600
700
800
Distance from otolith core (µm)

LDB06_02

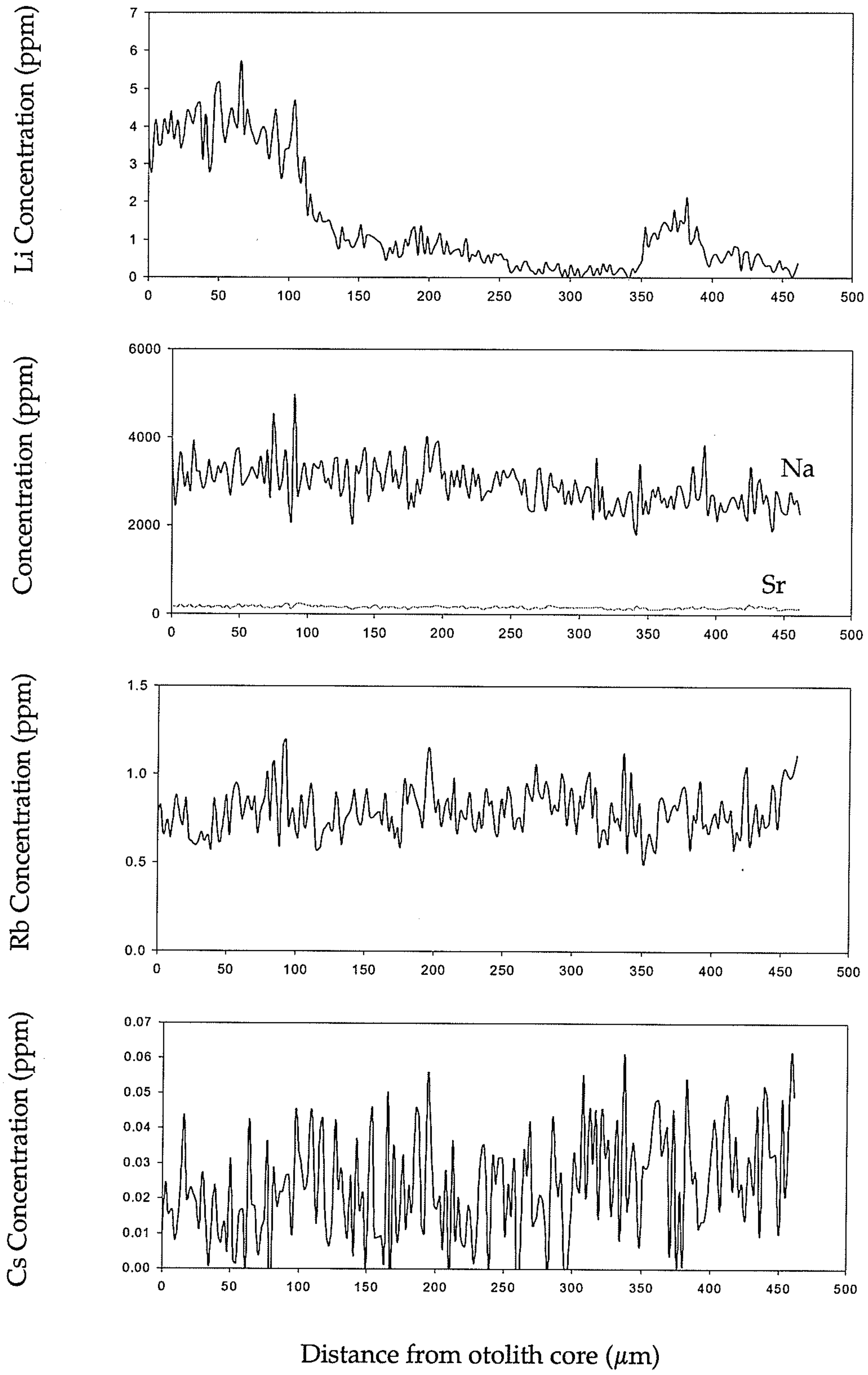

Li Concentration (ppm)
4
3
2
1
0
0
100
200
300
400
500
600
700
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
Cs Concentration (ppm)
0.08
0.06
0.04
0.02
0.00
0
100
200
300
400
500
600
700
Distance from otolith core (μm)

LDB06_03



Li Concentration (ppm)
5
4
3
2
1
0
0
100
200
300
400
500
600
700
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
Cs Concentration (ppm)
0.10
0.08
0.06
0.04
0.02
0.00
0
100
200
300
400
500
600
700
Distance from otolith core (μm)

LDB06_04



Li Concentration (ppm)
0
1
2
3
4
5
6
7
Concentration (ppm)
0
2000
4000
6000
Na
Sr
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
Cs Concentration (ppm)
0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0
50
100
150
200
250
300
350
400
450
500
Distance from otolith core (μm)

Appendix G LA-ICP-MS data for Lac du Bonnet otoliths *continued*

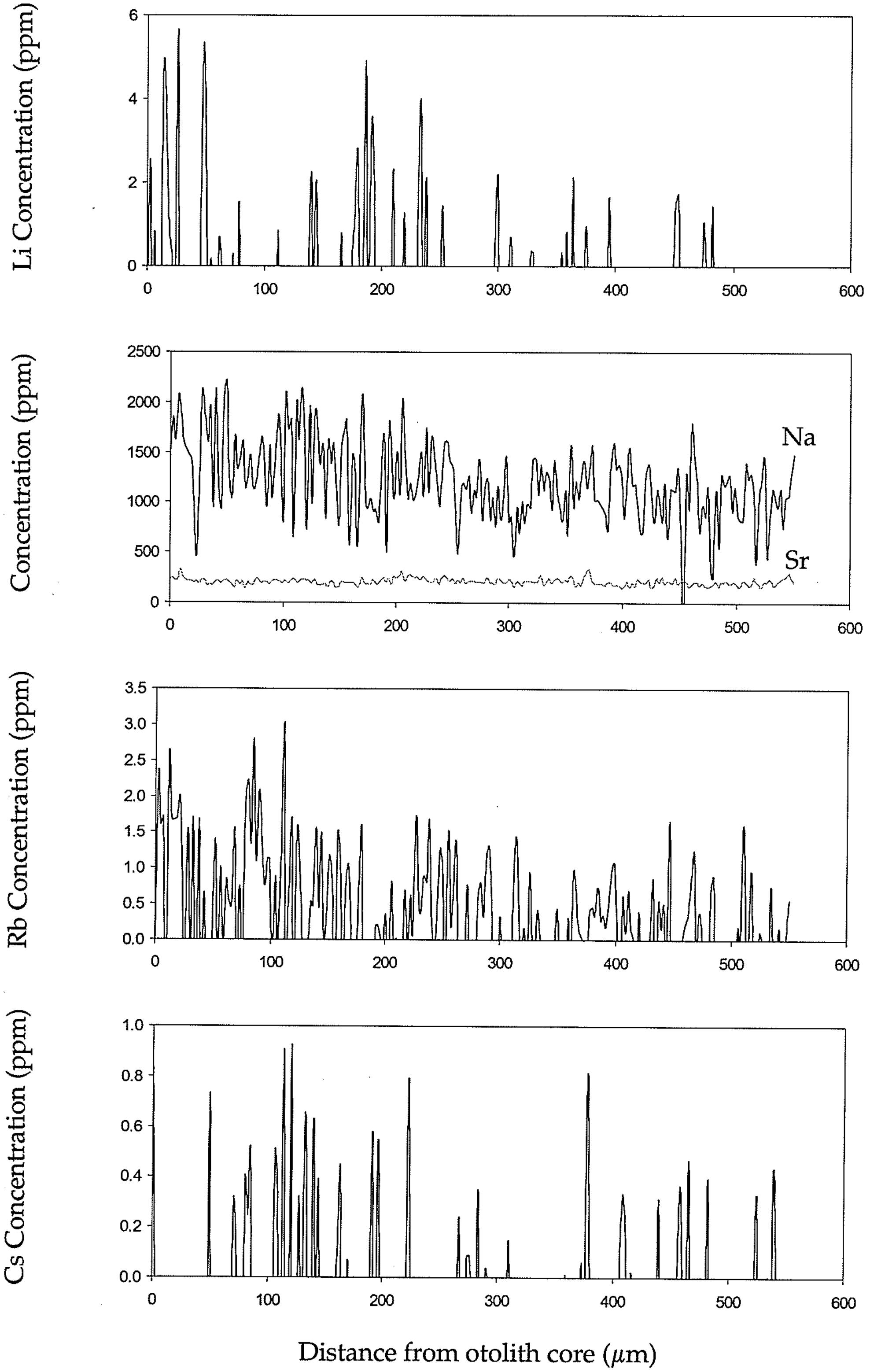
Species: Walleye (*Sander vitreous*), Sauger (*Stizostedion canadense*)

Captured: 2005 (Manitoba Conservation Archives)

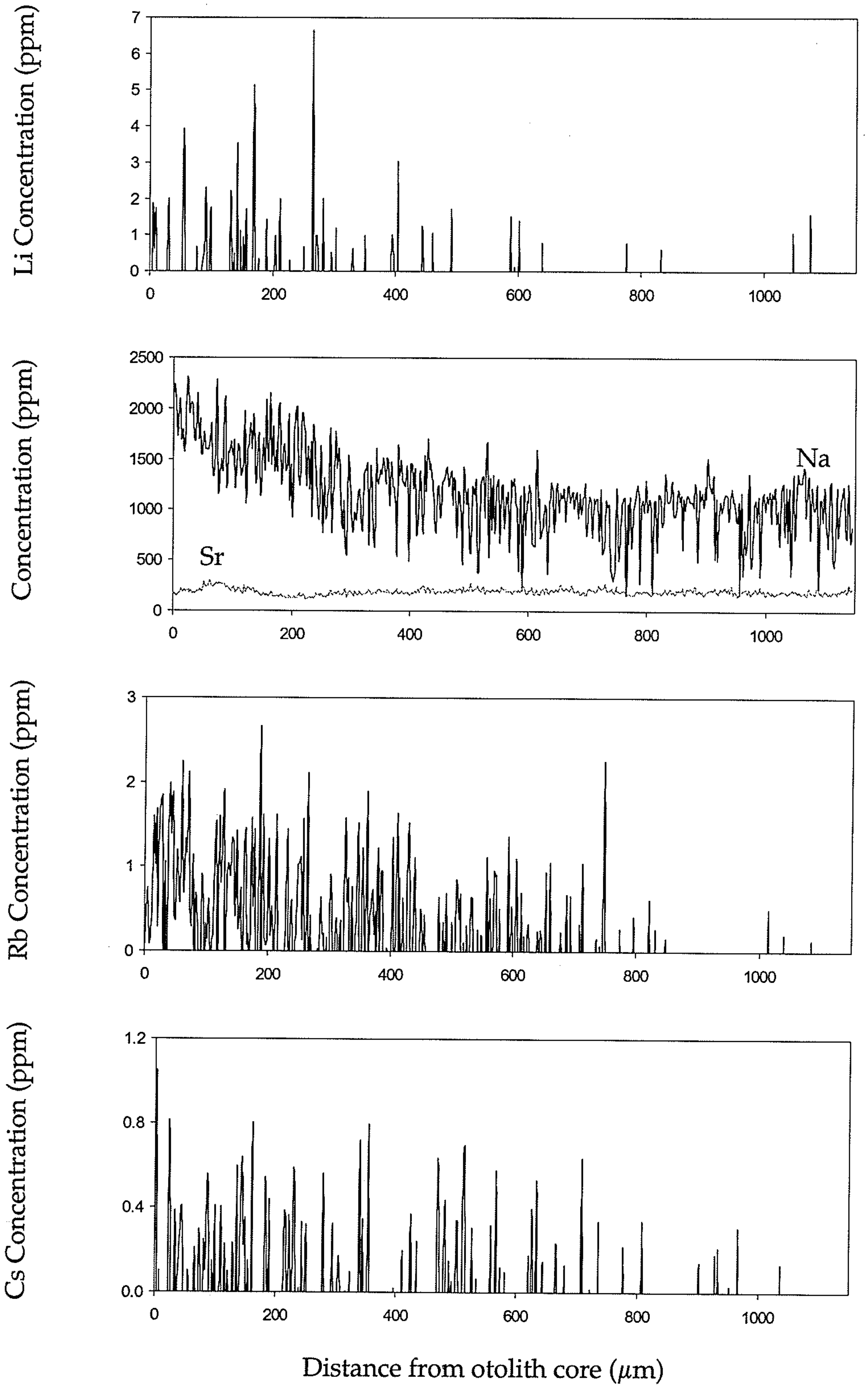
Isotopes	**Li^{7}**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
73	Walleye	7
74	Walleye	12
75	Walleye	10
77	Walleye	5
79	Sauger	11
80	Sauger	5

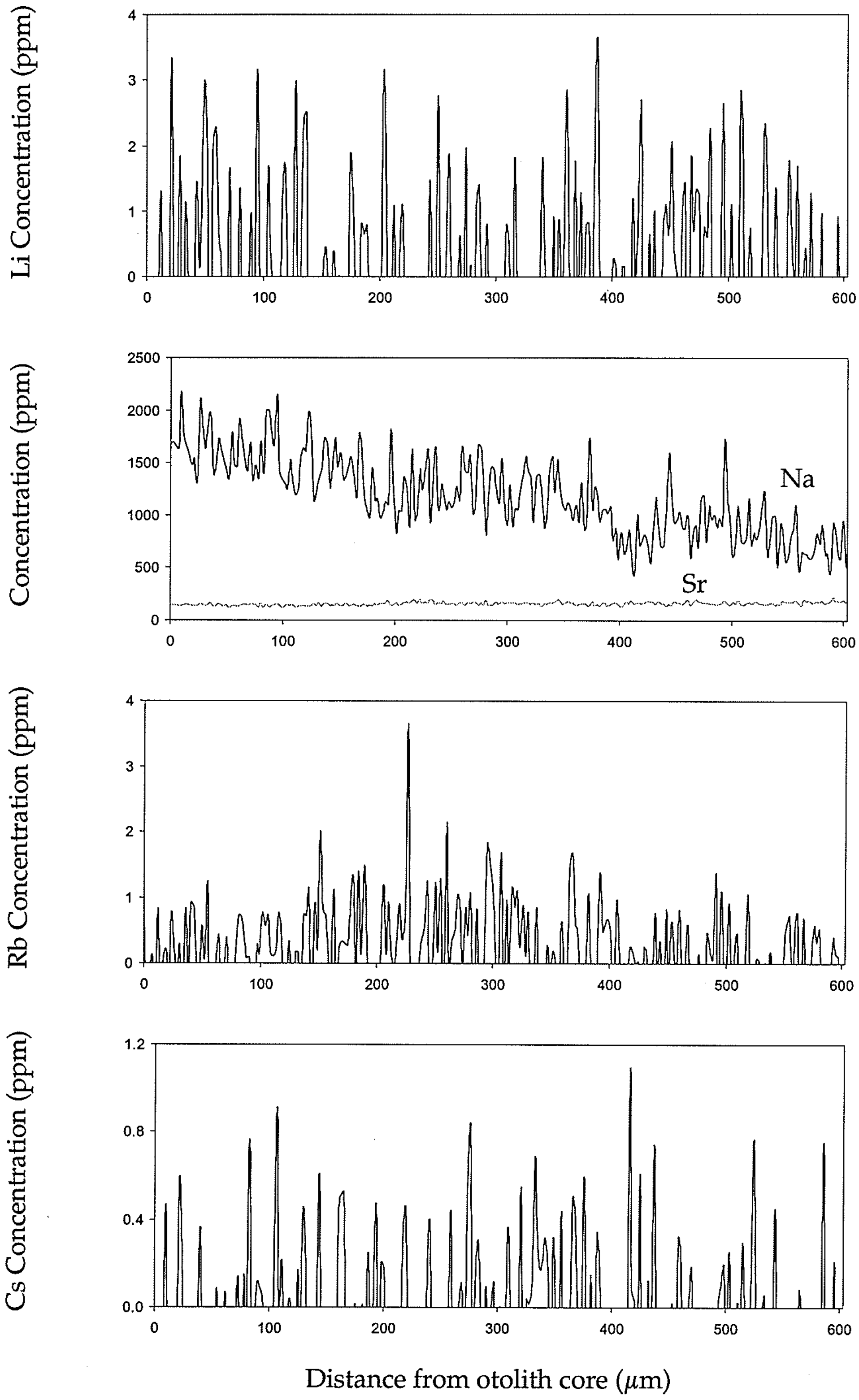
LDB05_73


Li Concentration (ppm)
0
2
4
6
0
100
200
300
400
500
600
Concentration (ppm)
0
500
1000
1500
2000
2500
Na
Sr
0
100
200
300
400
500
600
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0
100
200
300
400
500
600
Cs Concentration (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
0
100
200
300
400
500
600
Distance from otolith core (μm)

LDB05_74

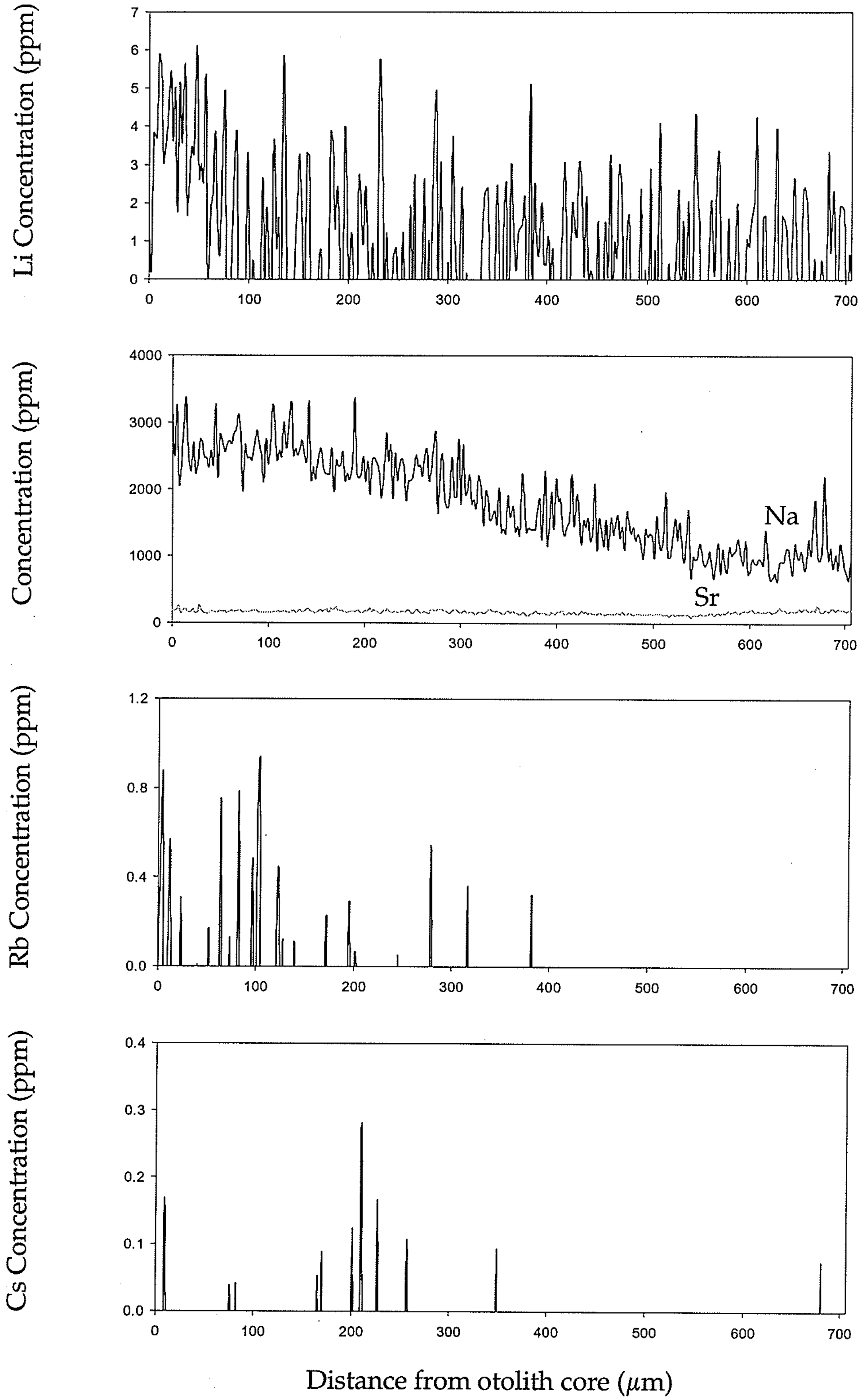

Li Concentration (ppm)
7
6
5
4
3
2
1
0
0
200
400
600
800
1000
Concentration (ppm)
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
3
2
1
0
0
200
400
600
800
1000
Cs Concentration (ppm)
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

LDB05_75



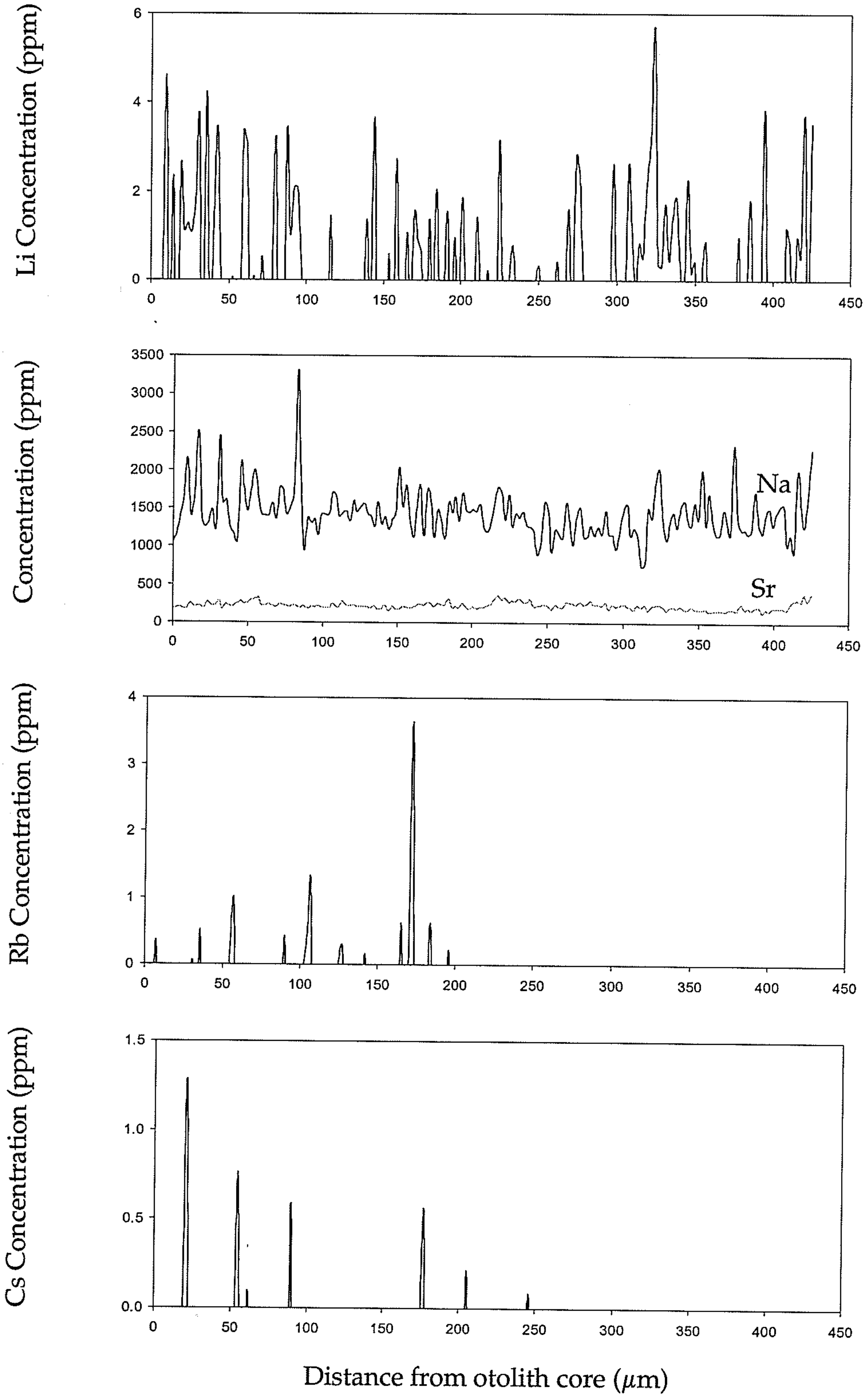
Li Concentration (ppm)
4
3
2
1
0
0
100
200
300
400
500
600
Concentration (ppm)
2500
2000
1500
1000
500
0
Na
Sr
0
100
200
300
400
500
600
Rb Concentration (ppm)
4
3
2
1
0
0
100
200
300
400
500
600
Cs Concentration (ppm)
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
Distance from otolith core (μm)

LDB05_77

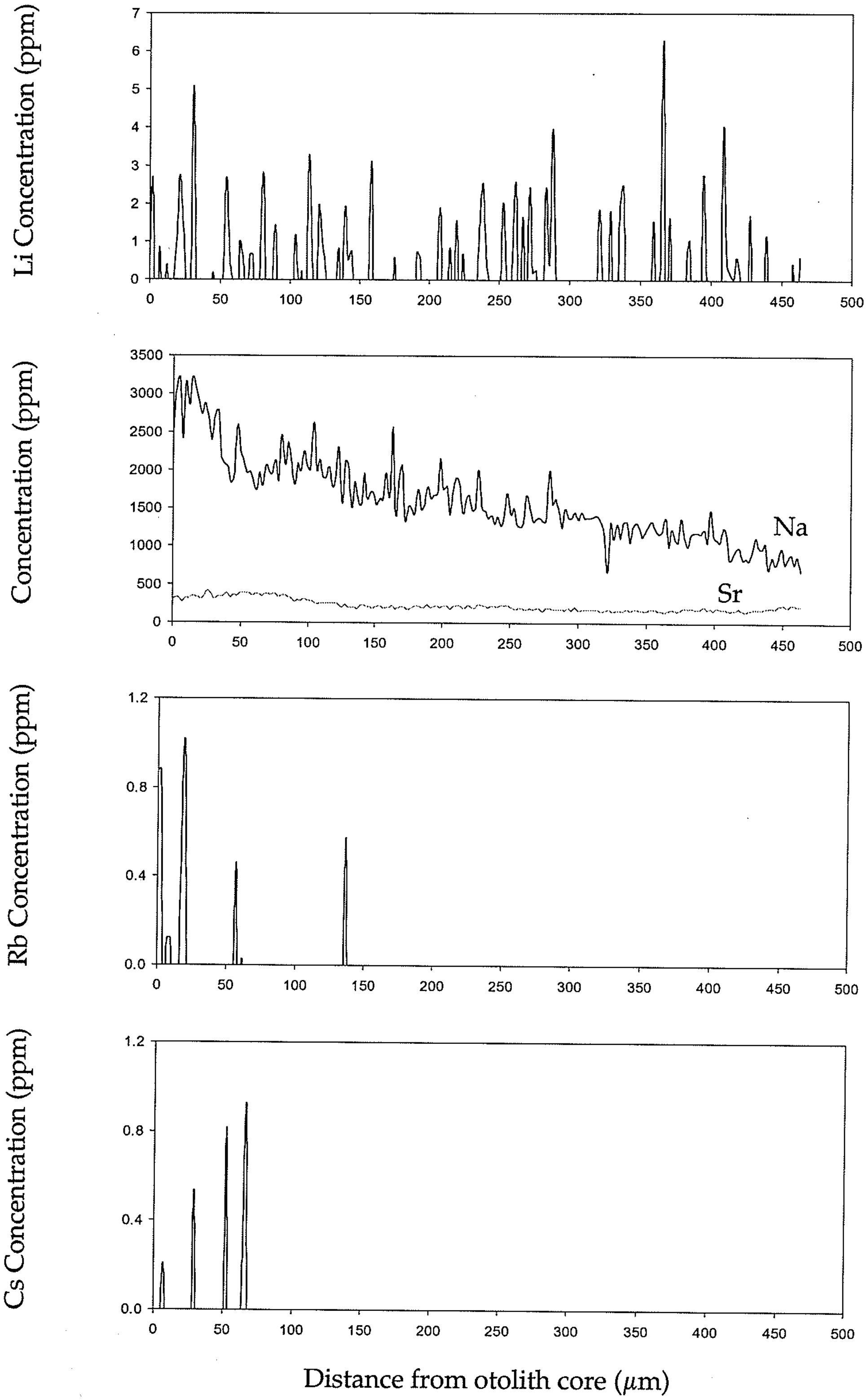


Li Concentration (ppm)
0
1
2
3
4
5
6
7
0
100
200
300
400
500
600
700
Concentration (ppm)
0
1000
2000
3000
4000
Na
Sr
0
100
200
300
400
500
600
700
Rb Concentration (ppm)
0.0
0.4
0.8
1.2
0
100
200
300
400
500
600
700
Cs Concentration (ppm)
0.0
0.1
0.2
0.3
0.4
0
100
200
300
400
500
600
700
Distance from otolith core (μm)

LDB05_79


Li Concentration (ppm)
0
2
4
6
0
50
100
150
200
250
300
350
400
450
Concentration (ppm)
0
500
1000
1500
2000
2500
3000
3500
Na
Sr
0
50
100
150
200
250
300
350
400
450
Rb Concentration (ppm)
0
1
2
3
4
0
50
100
150
200
250
300
350
400
450
Cs Concentration (ppm)
0.0
0.5
1.0
1.5
0
50
100
150
200
250
300
350
400
450
Distance from otolith core (μm)

LDB05_80


Li Concentration (ppm)
7
6
5
4
3
2
1
0
0
50
100
150
200
250
300
350
400
450
500
Concentration (ppm)
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
50
100
150
200
250
300
350
400
450
500
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
50
100
150
200
250
300
350
400
450
500
Cs Concentration (ppm)
1.2
0.8
0.4
0.0
0
50
100
150
200
250
300
350
400
450
500
Distance from otolith core (μm)

Appendix G LA-ICP-MS data for Lac du Bonnet otoliths *continued*

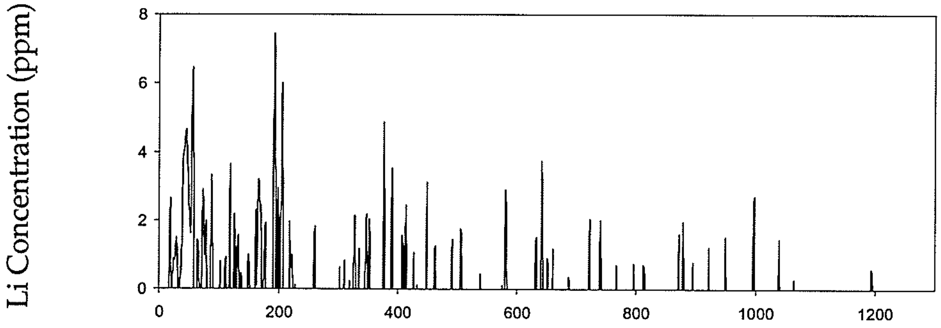
Species: Walleye (*Sander vitreous*)

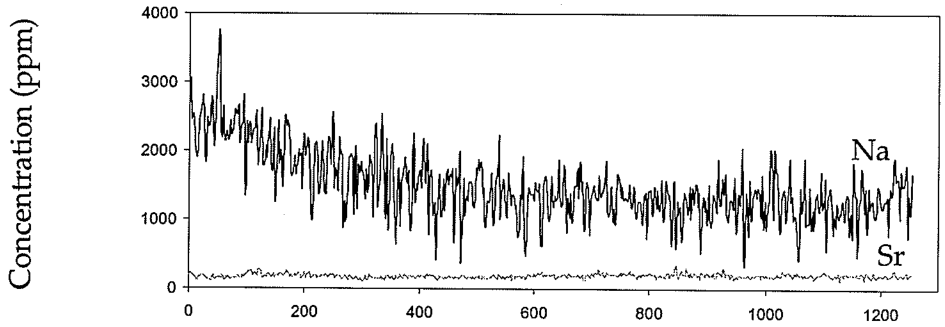
Captured: 2004 (Manitoba Conservation Archives)

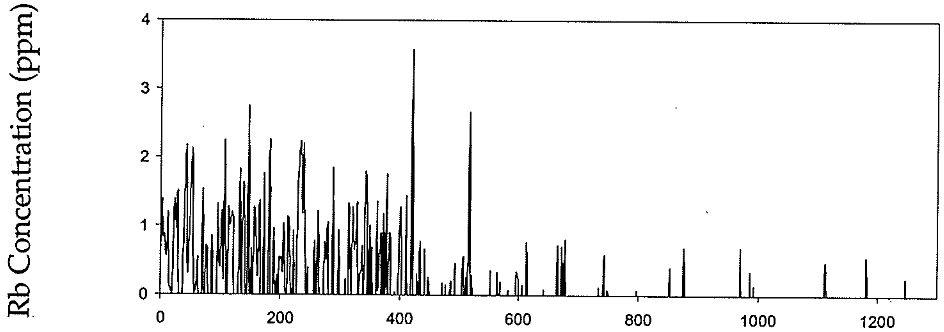
Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

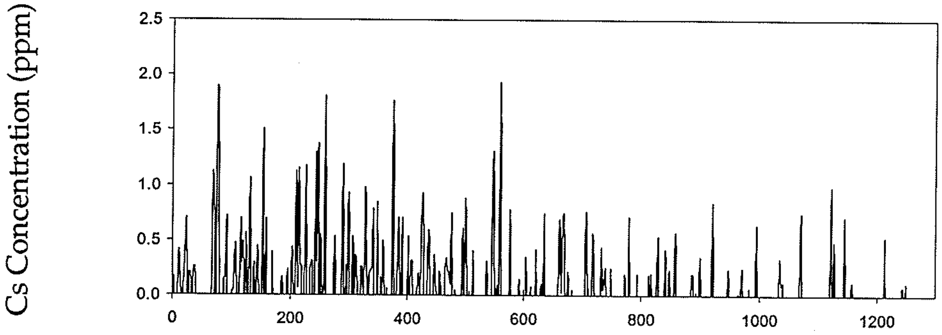
Sample Number	***Species***	***Age***
114	Walleye	14
115	Walleye	13
116	Walleye	17
118	Walleye	5
119	Walleye	2

LDB04_114



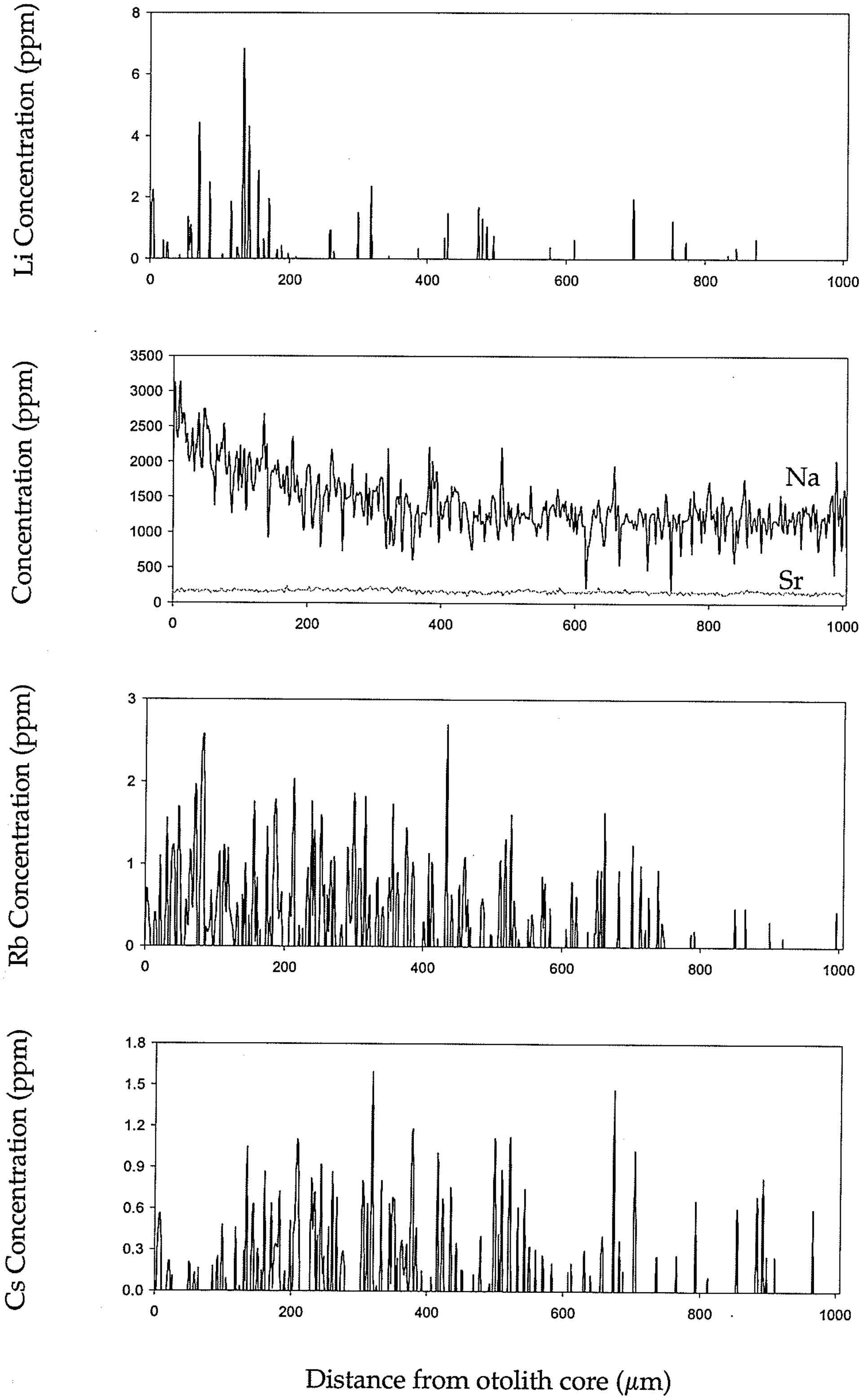




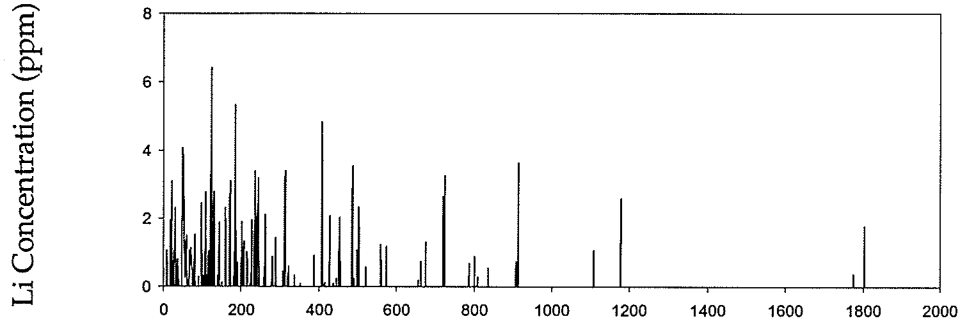


Distance from otolith core (μm)

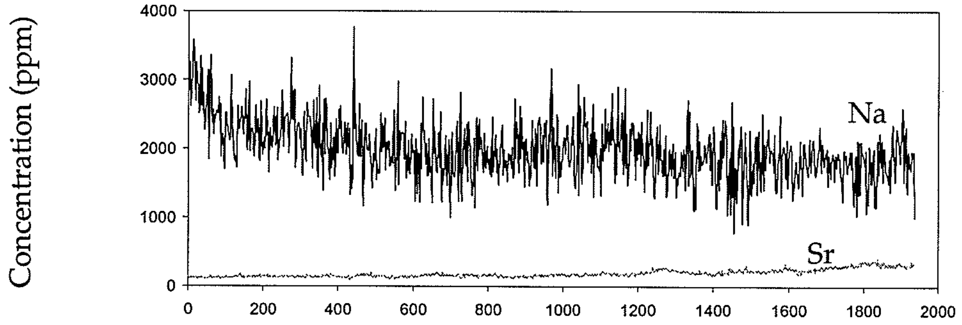
LDB04_115


Li Concentration (ppm)
0
2
4
6
8
0
200
400
600
800
1000
Concentration (ppm)
0
500
1000
1500
2000
2500
3000
3500
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
0
1
2
3
0
200
400
600
800
1000
Cs Concentration (ppm)
0.0
0.3
0.6
0.9
1.2
1.5
1.8
0
200
400
600
800
1000
Distance from otolith core (μm)

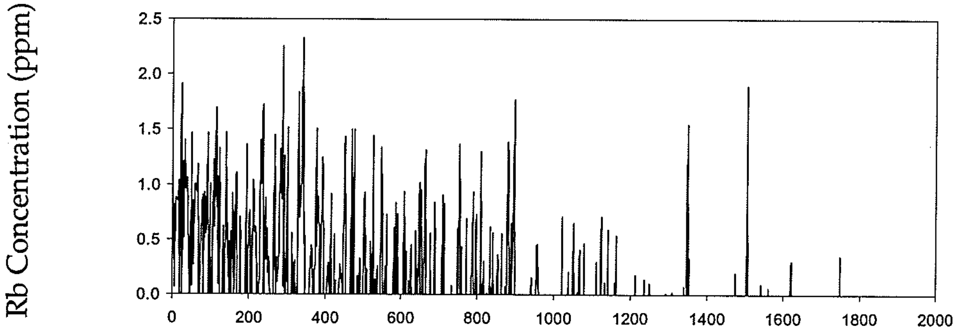
LDB04_116



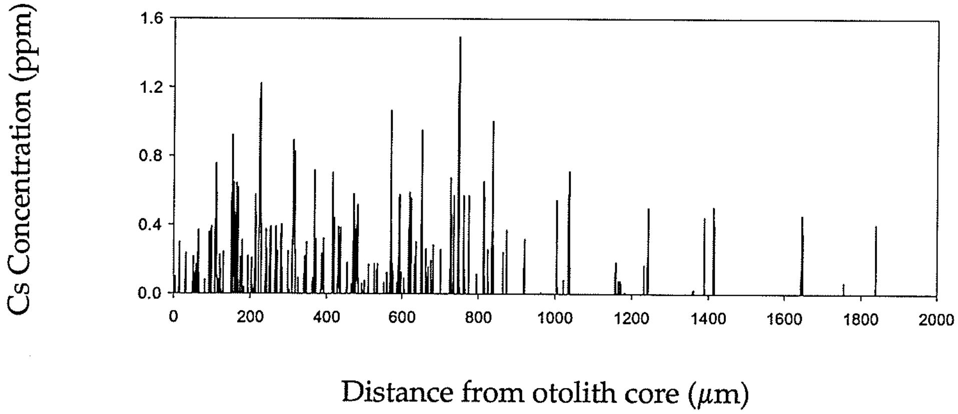
Li Concentration (ppm)
8
6
4
2
0
0
200
400
600
800
1000
1200
1400
1600
1800
2000



Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
1800
2000

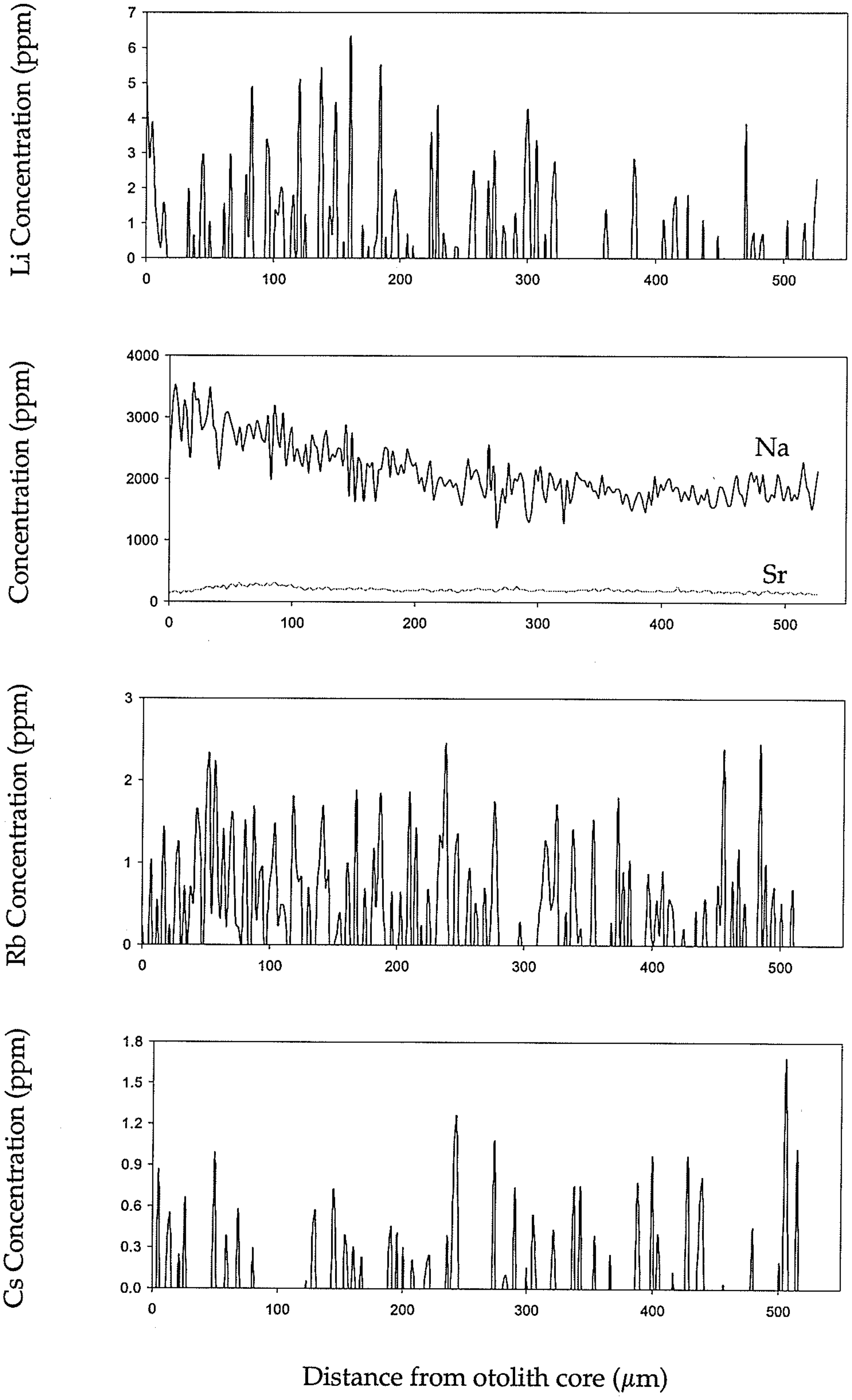


Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
2000



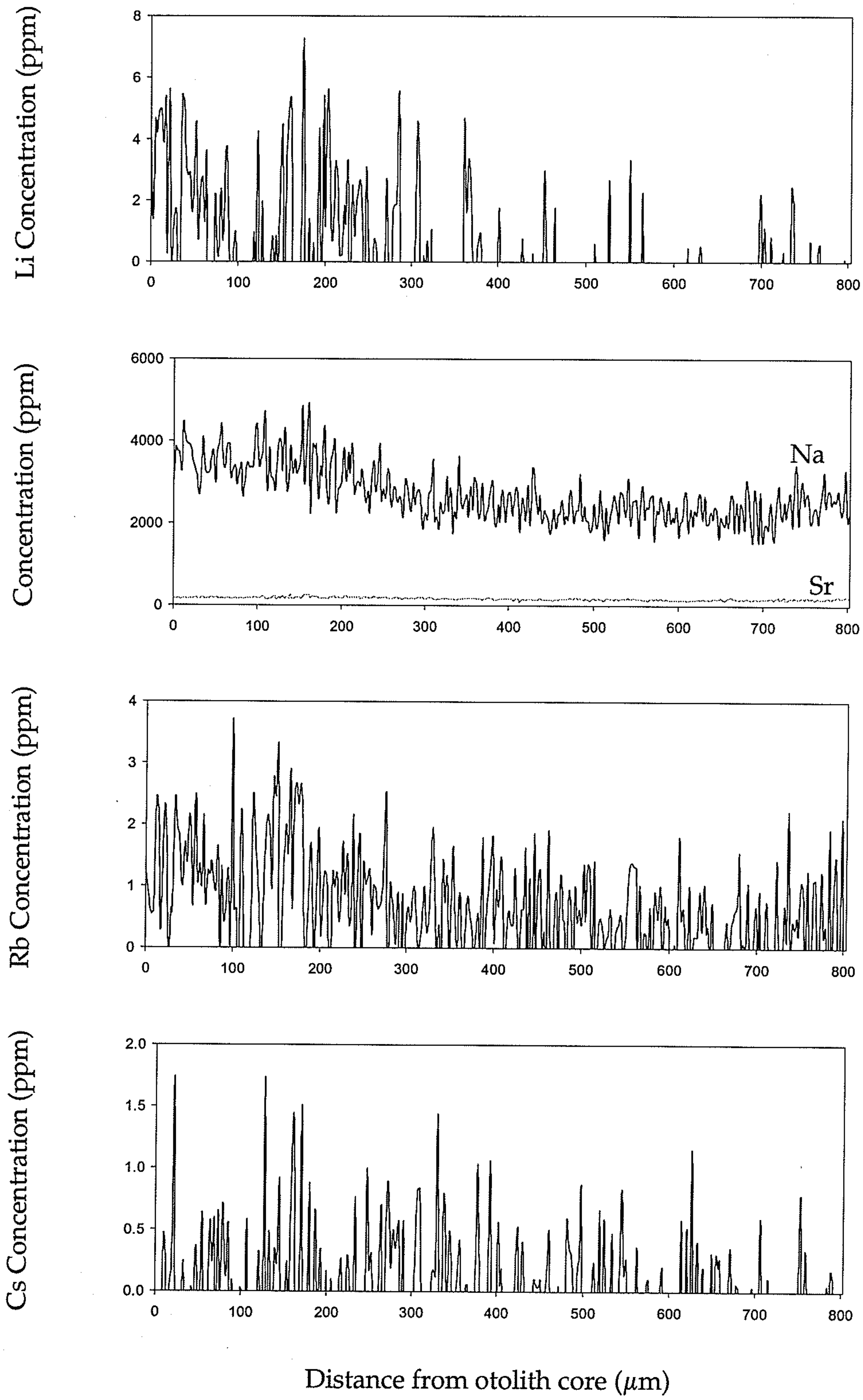
Cs Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Distance from otolith core (μm)

LDB04_118



Li Concentration (ppm)
0
1
2
3
4
5
6
7
Concentration (ppm)
0
1000
2000
3000
4000
Na
Sr
Rb Concentration (ppm)
0
1
2
3
Cs Concentration (ppm)
0.0
0.3
0.6
0.9
1.2
1.5
1.8
0
100
200
300
400
500
Distance from otolith core (μm)

LDB04_119


Li Concentration (ppm)
0
2
4
6
8
0
100
200
300
400
500
600
700
800
Concentration (ppm)
0
2000
4000
6000
Na
Sr
0
100
200
300
400
500
600
700
800
Rb Concentration (ppm)
0
1
2
3
4
0
100
200
300
400
500
600
700
800
Cs Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
0
100
200
300
400
500
600
700
800
Distance from otolith core (µm)

Appendix G LA-ICP-MS data for Lac du Bonnet otoliths *continued*

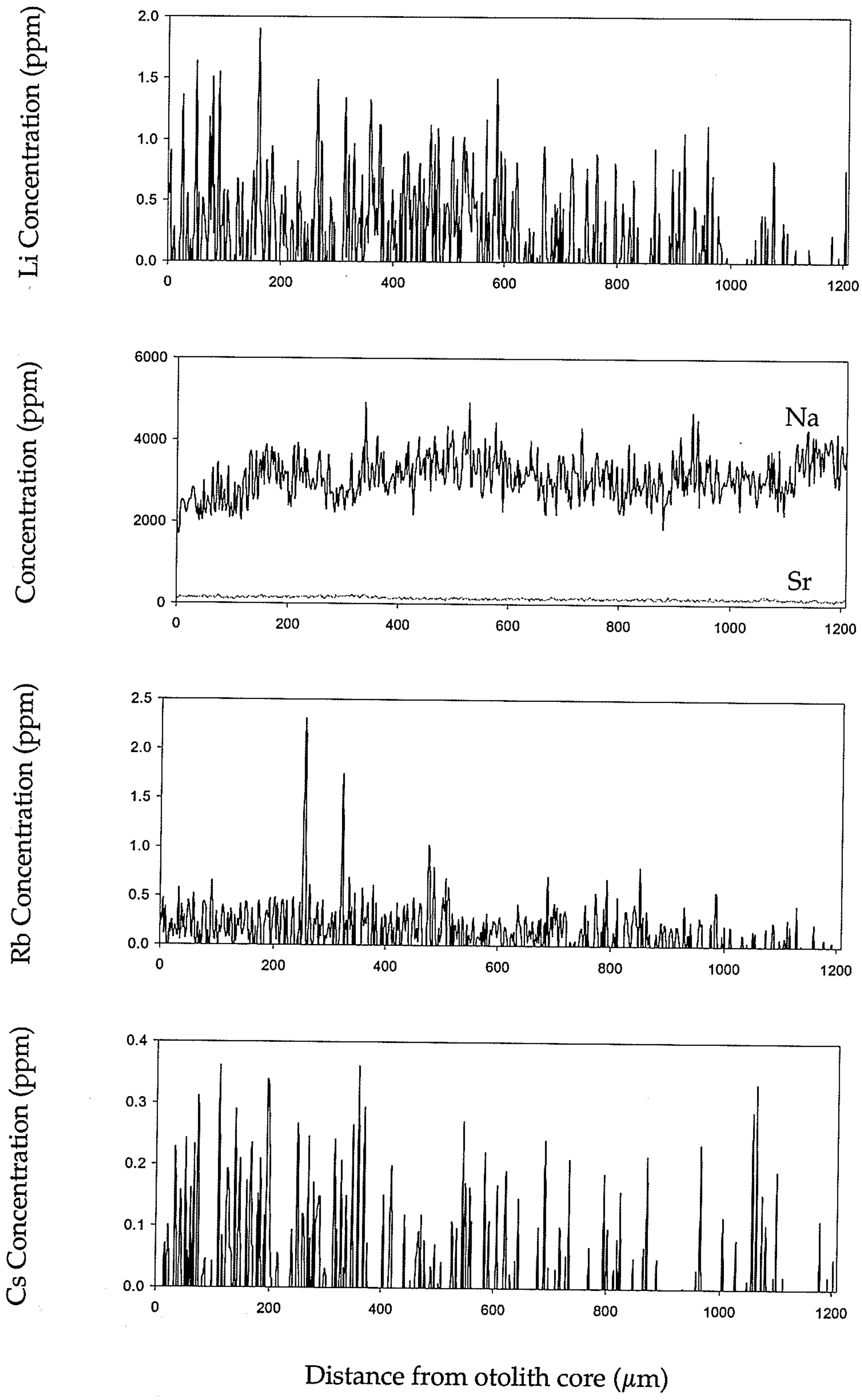
Species: Walleye (*Sander vitreous*), Sauger (*Stizostedion canadense*)

Captured: 2003 (Manitoba Conservation Archives)

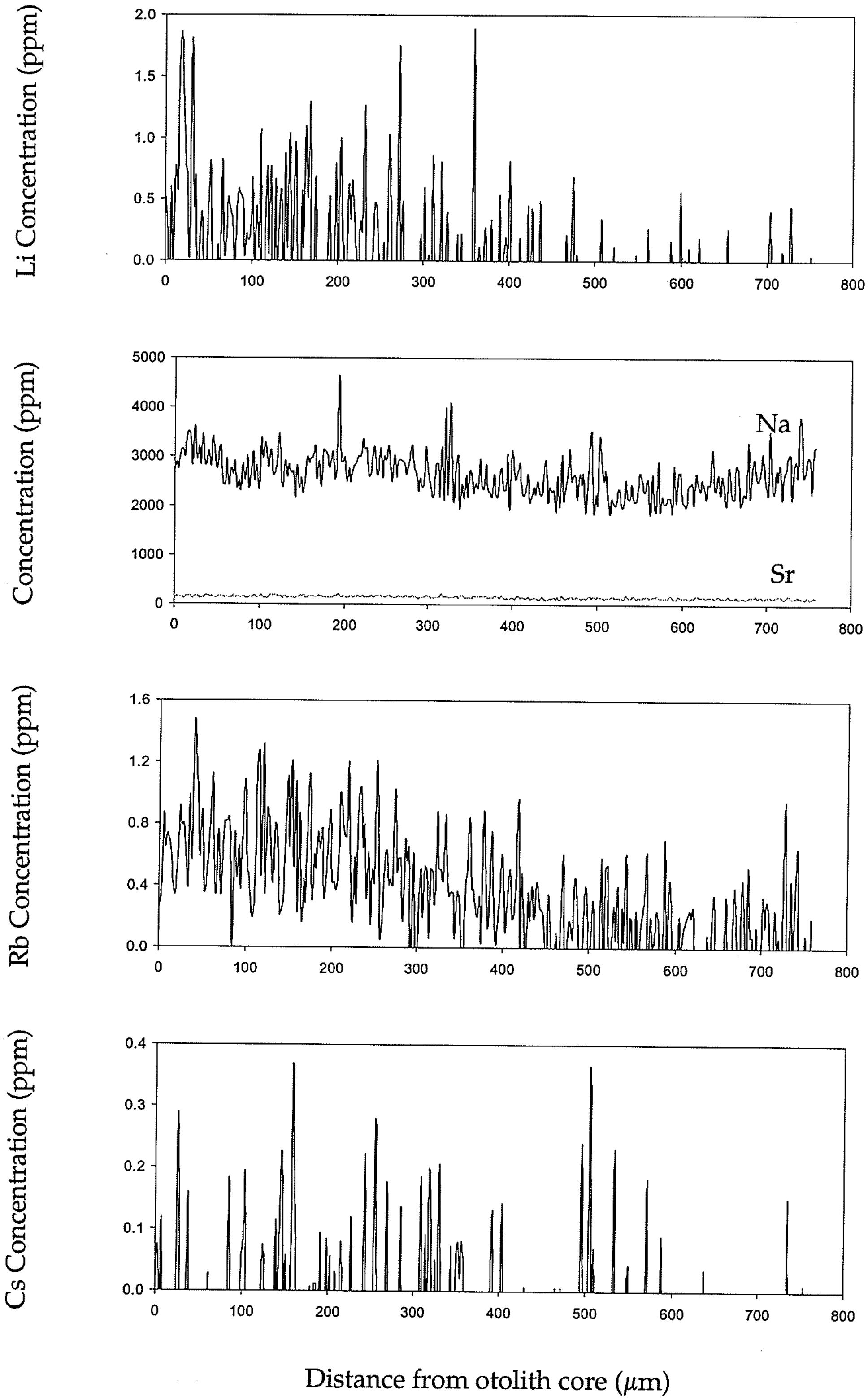
Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
61	Walleye	1
62	Walleye	1
63	Walleye	0
65	Sauger	4
66	Sauger	4
67	Sauger	2

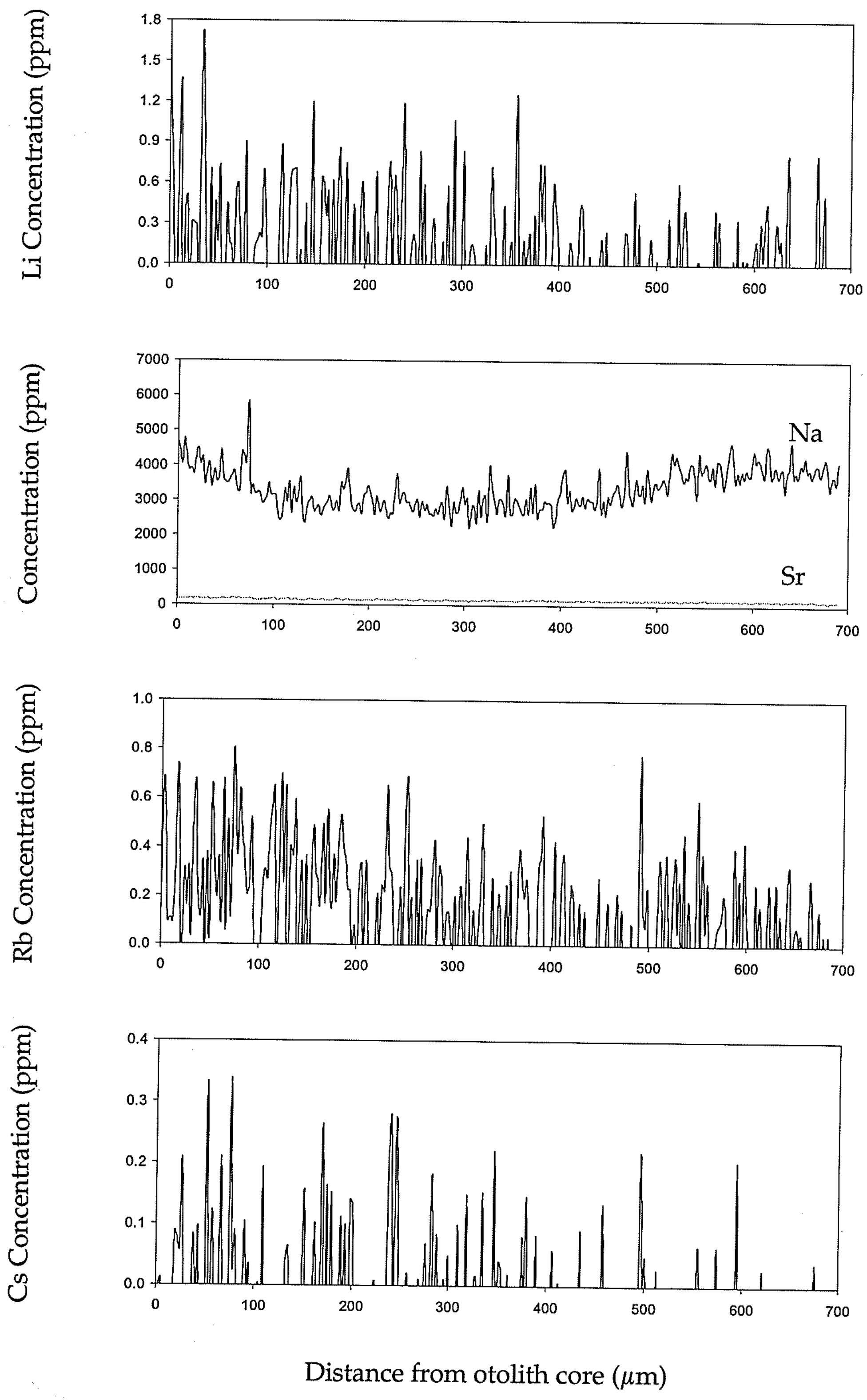
LDB03_61


Li Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
6000
4000
2000
0
Na
Sr
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
Cs Concentration (ppm)
0.4
0.3
0.2
0.1
0.0
Distance from otolith core (μm)

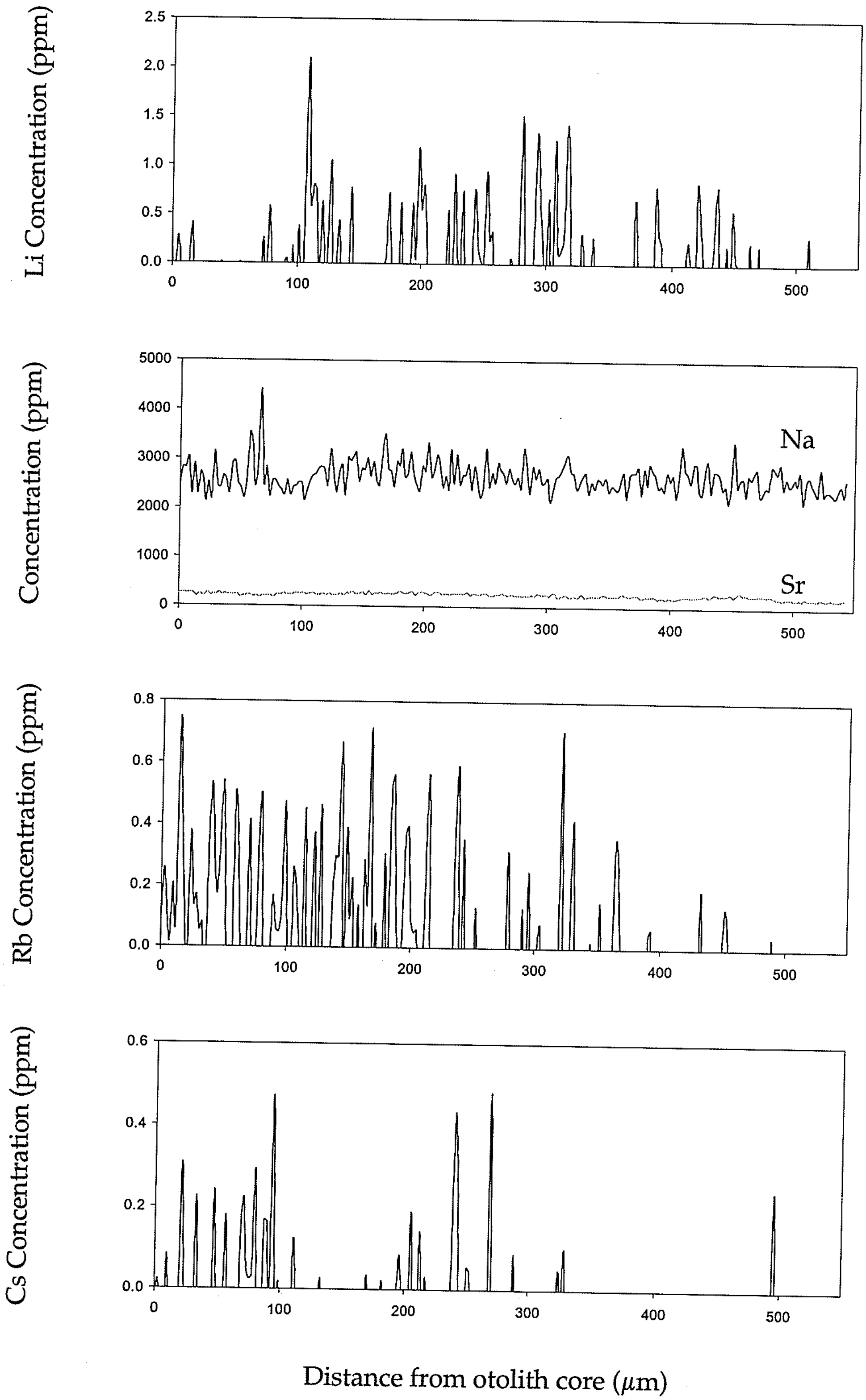
LDB03_62


Li Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
800
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
800
Cs Concentration (ppm)
0.4
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

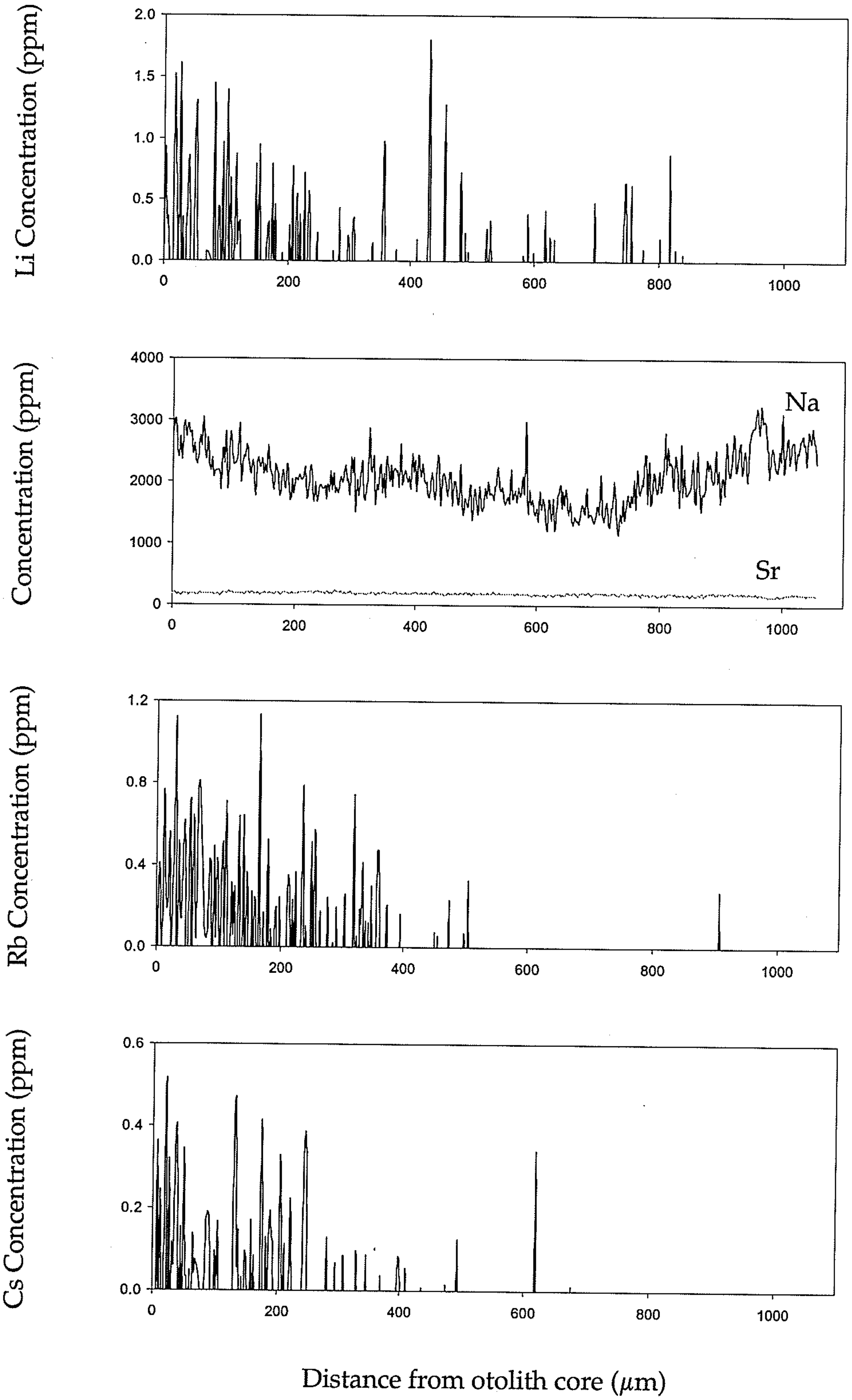
LDB03_63


Li Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
Concentration (ppm)
7000
6000
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
Cs Concentration (ppm)
0.4
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
Distance from otolith core (μm)

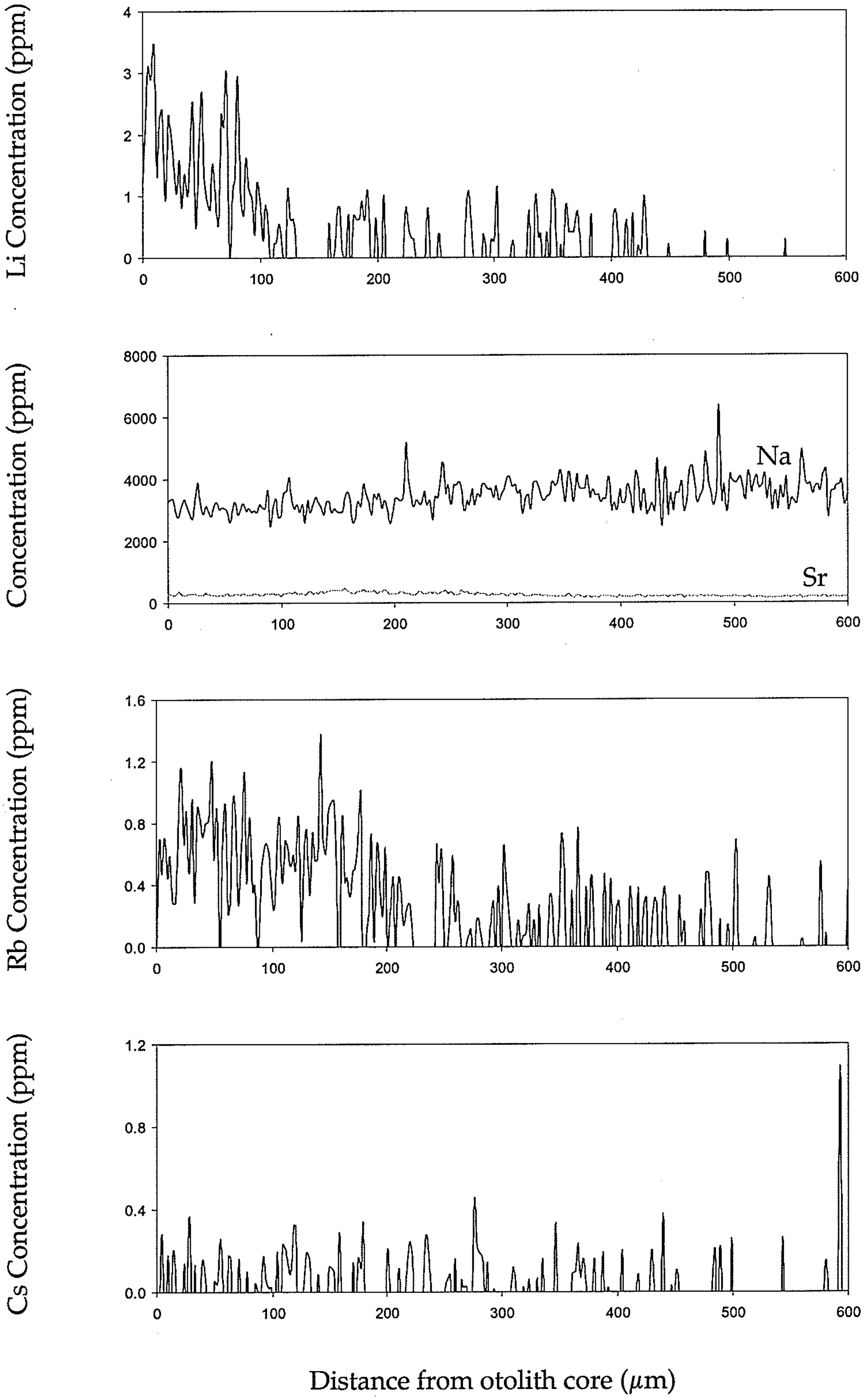
LDB03_65


Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
Rb Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
Cs Concentration (ppm)
0.6
0.4
0.2
0.0
0
100
200
300
400
500
Distance from otolith core (μm)

LDB03_66


Li Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
Cs Concentration (ppm)
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

LDB03_67


Li Concentration (ppm)
4
3
2
1
0
0
100
200
300
400
500
600
Concentration (ppm)
8000
6000
4000
2000
0
Na
Sr
0
100
200
300
400
500
600
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
Cs Concentration (ppm)
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
Distance from otolith core (μm)

Appendix G LA-ICP-MS data for Lac du Bonnet otoliths *continued*

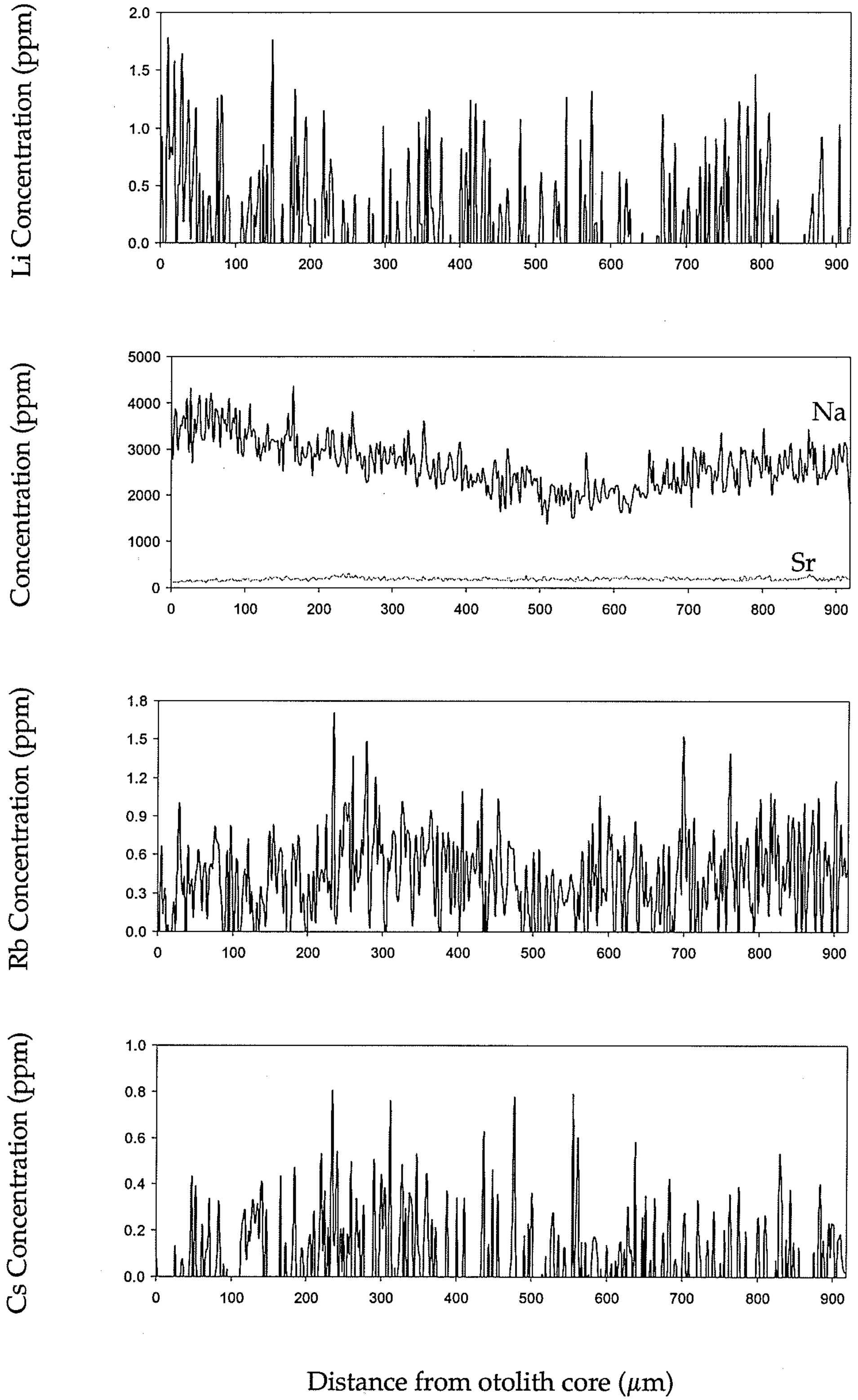
Species: Walleye (*Sander vitreous*), Sauger (*Stizostedion canadense*)

Captured: 2002 (Manitoba Conservation Archives)

Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

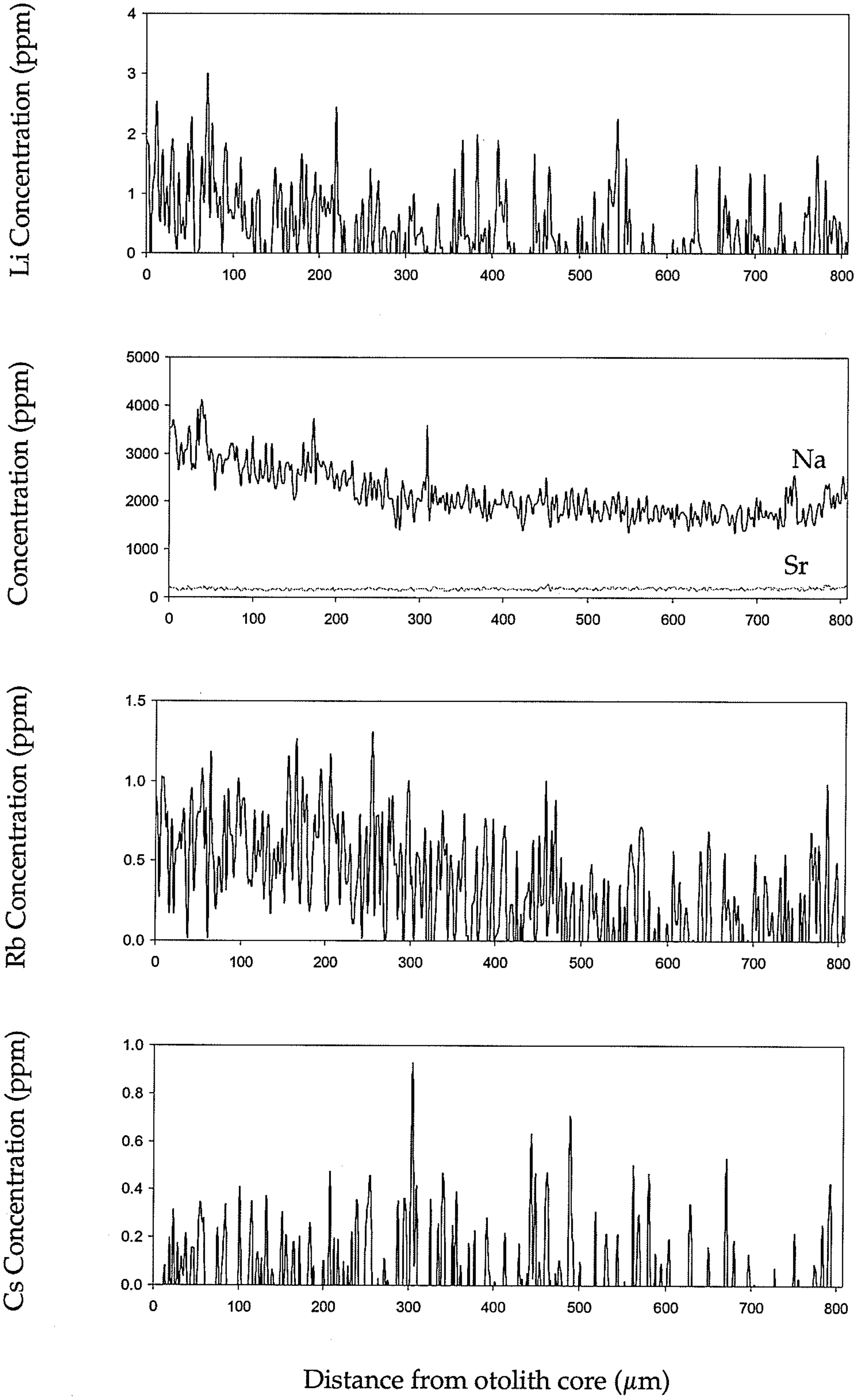
Sample Number	***Species***	***Age***
107	Walleye	11
108	Walleye	9
113	Walleye	8
114	Walleye	8
119	Sauger	4
120	Sauger	2

LDB02_107

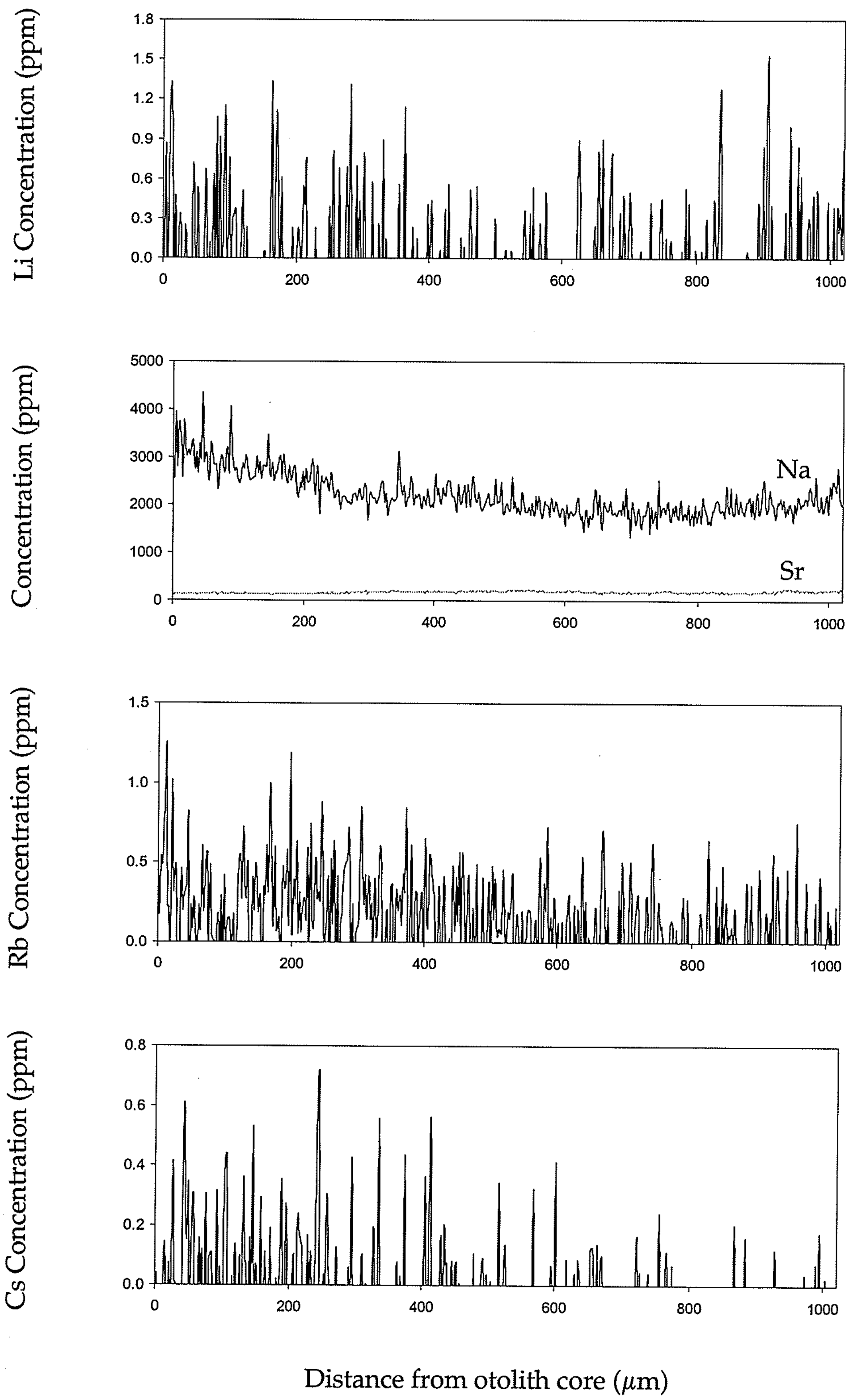


Li Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
900
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
Cs Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
Distance from otolith core (μm)

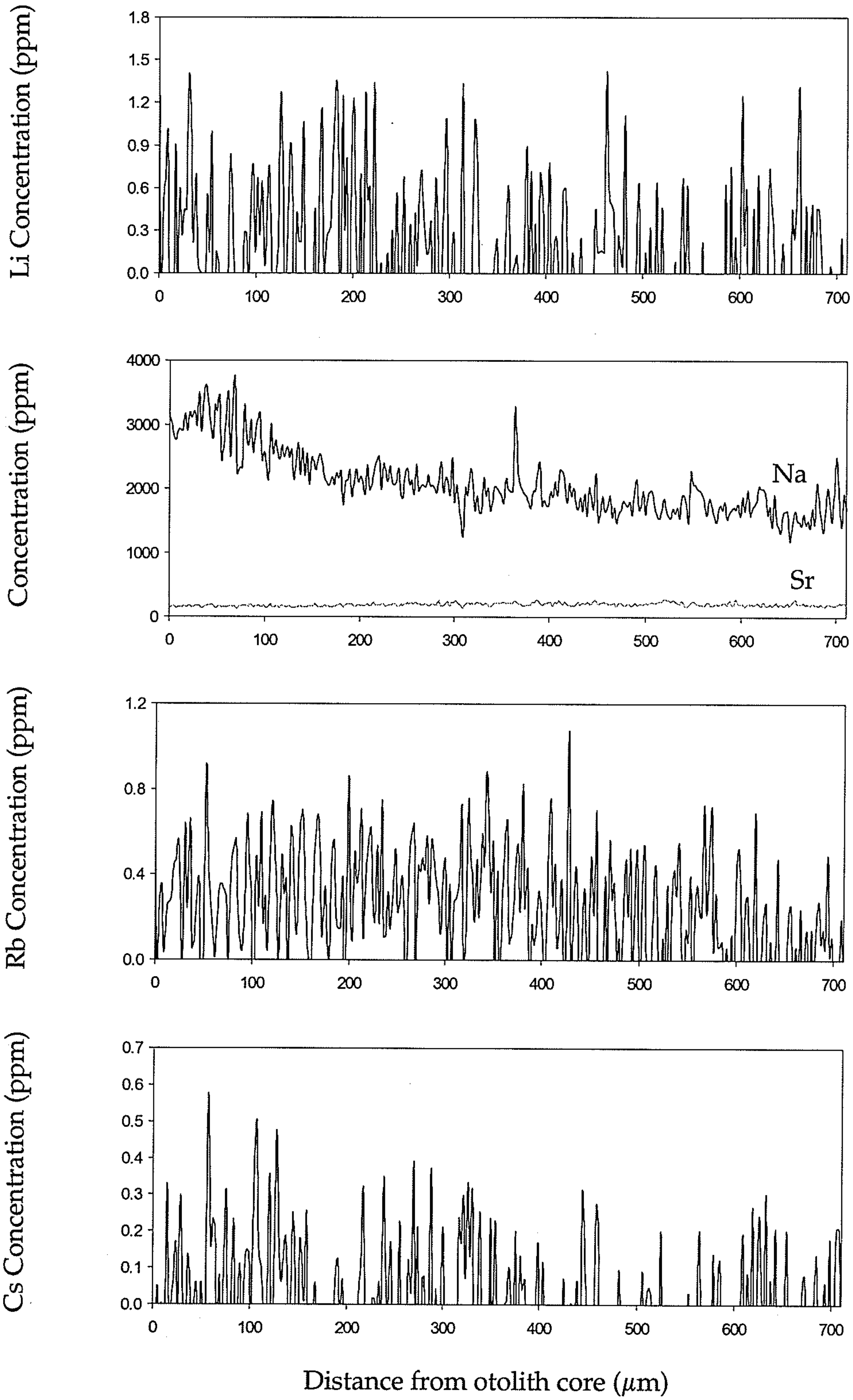
LDB02_108


Li Concentration (ppm)
0
1
2
3
4
0
100
200
300
400
500
600
700
800
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
100
200
300
400
500
600
700
800
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
0
100
200
300
400
500
600
700
800
Cs Concentration (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

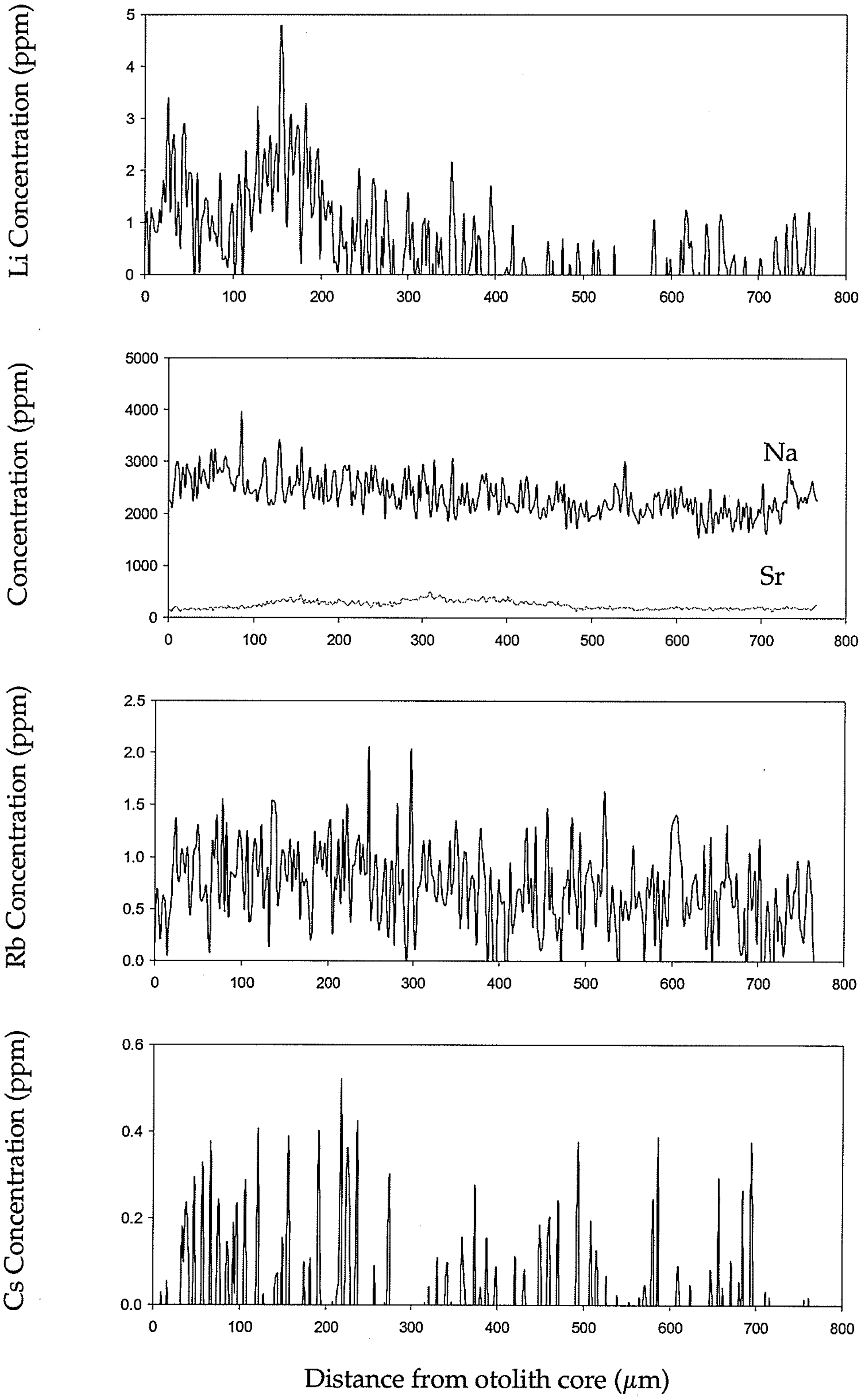
LDB02_113


Li Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
0
200
400
600
800
1000
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Cs Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

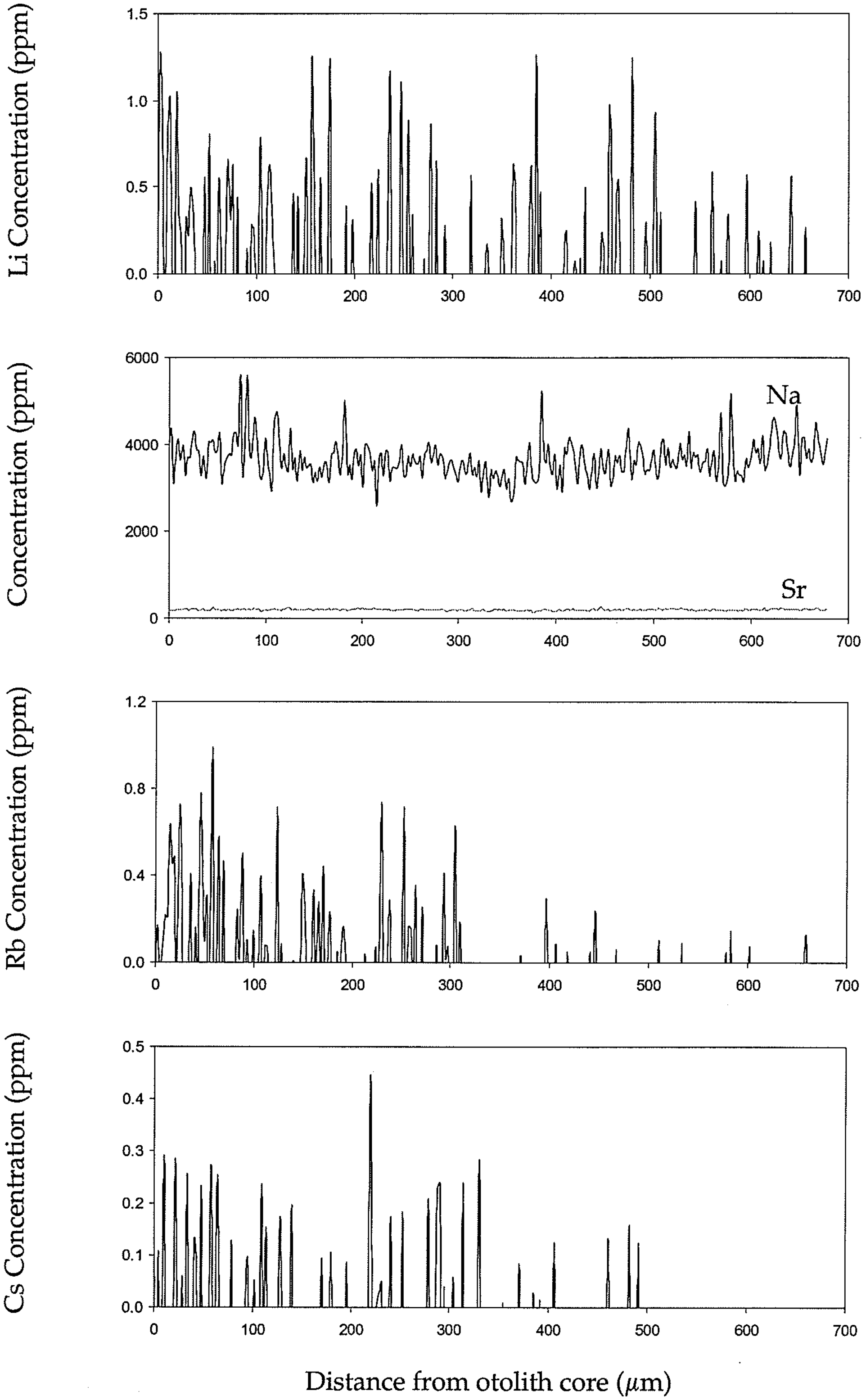
LDB02_114


Li Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
0
100
200
300
400
500
600
700
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
Cs Concentration (ppm)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
Distance from otolith core (μm)

LDB02_119


Li Concentration (ppm)
5
4
3
2
1
0
0
100
200
300
400
500
600
700
800
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
800
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
Cs Concentration (ppm)
0.6
0.4
0.2
0.0
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

LDB02_120



Li Concentration (ppm)
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
Concentration (ppm)
6000
4000
2000
0
Na
Sr
0
100
200
300
400
500
600
700
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
Cs Concentration (ppm)
0.5
0.4
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
Distance from otolith core (μm)

Appendix G LA-ICP-MS data for Lac du Bonnet otoliths *continued*

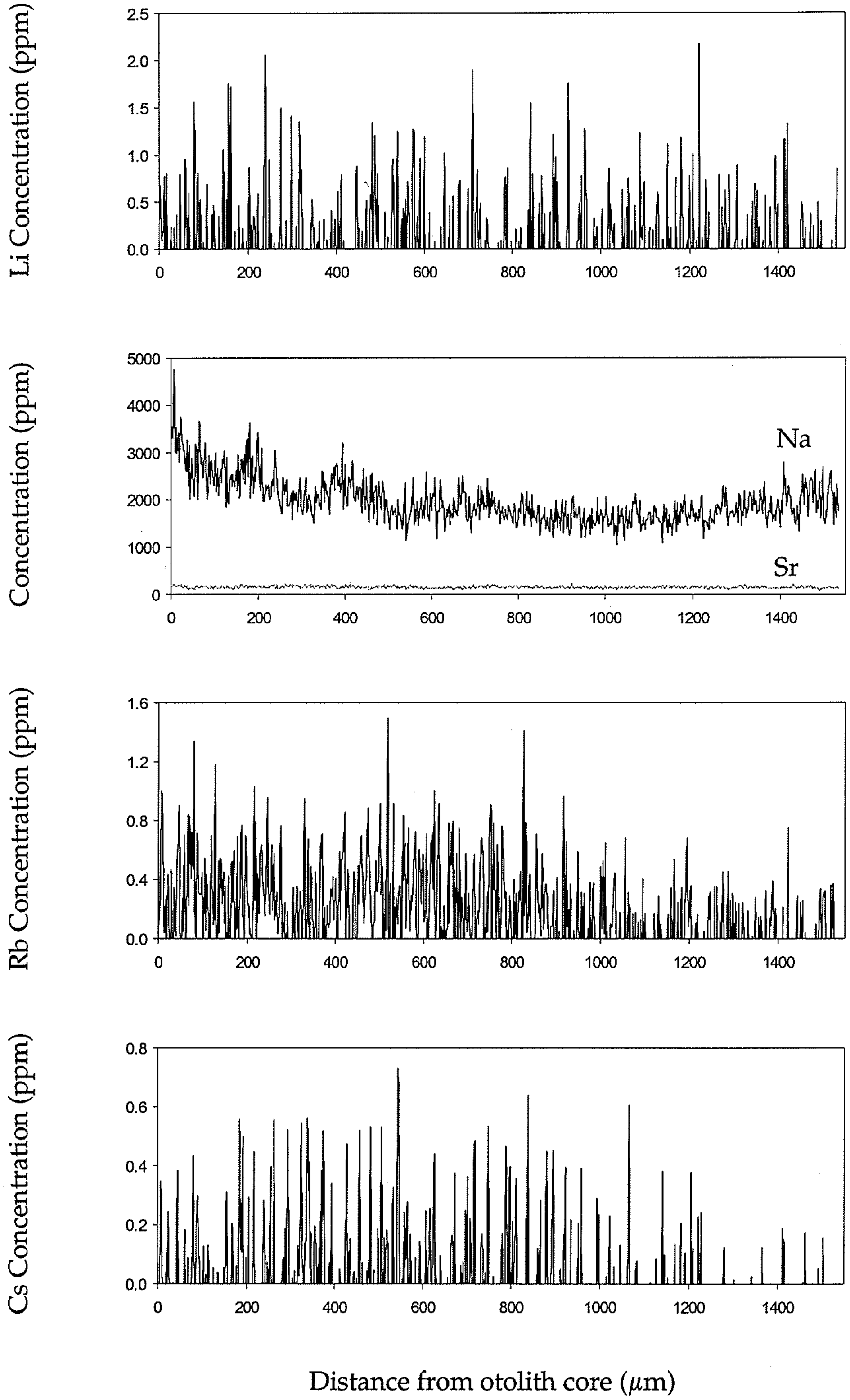
Species: Sauger (*Stizostedion canadense*)

Captured: 2001 (Manitoba Conservation Archives)

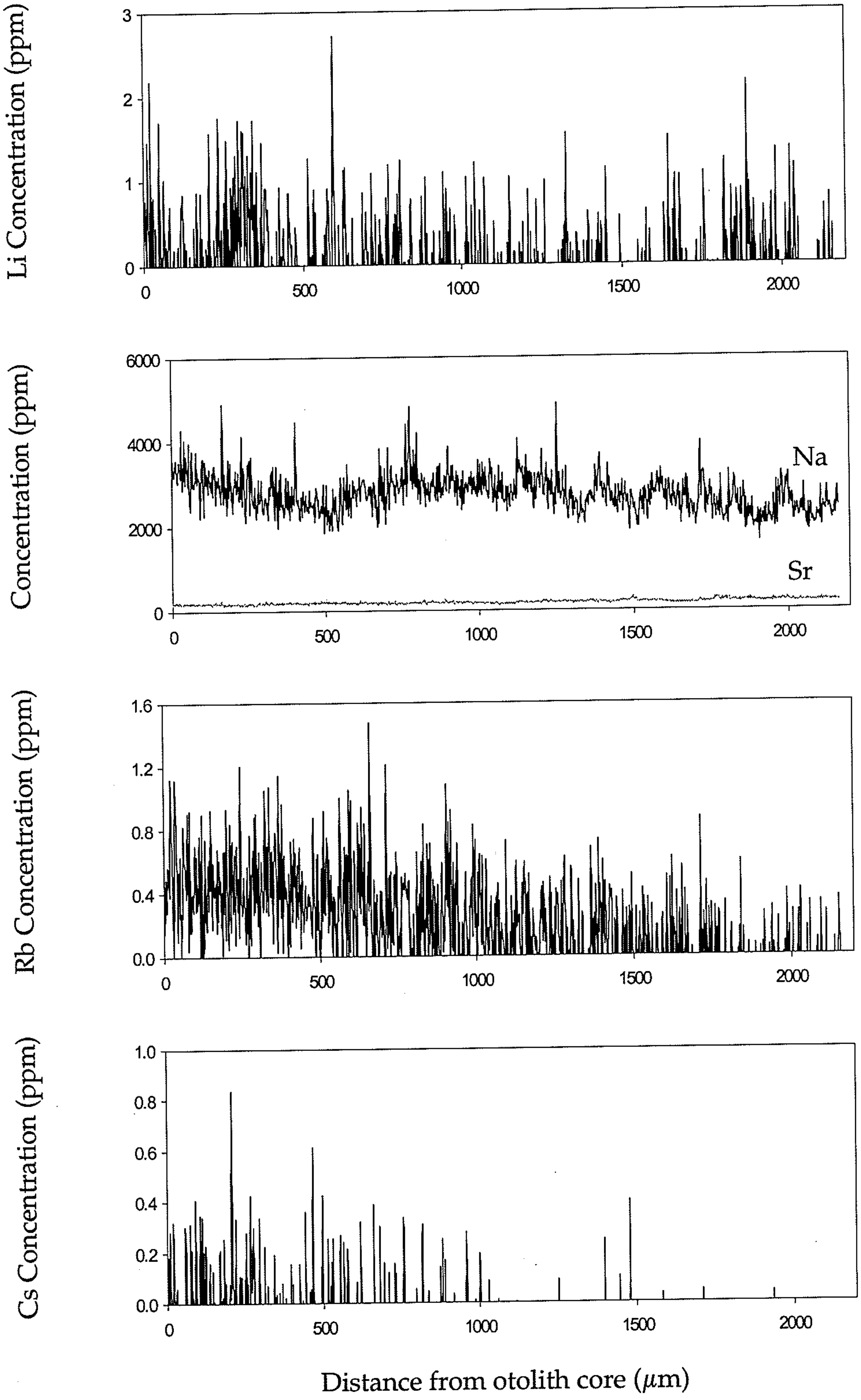
Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
41	Sauger	14
42	Sauger	9
43	Sauger	6
44	Sauger	8
45	Sauger	6
46	Sauger	2

LDB01_41

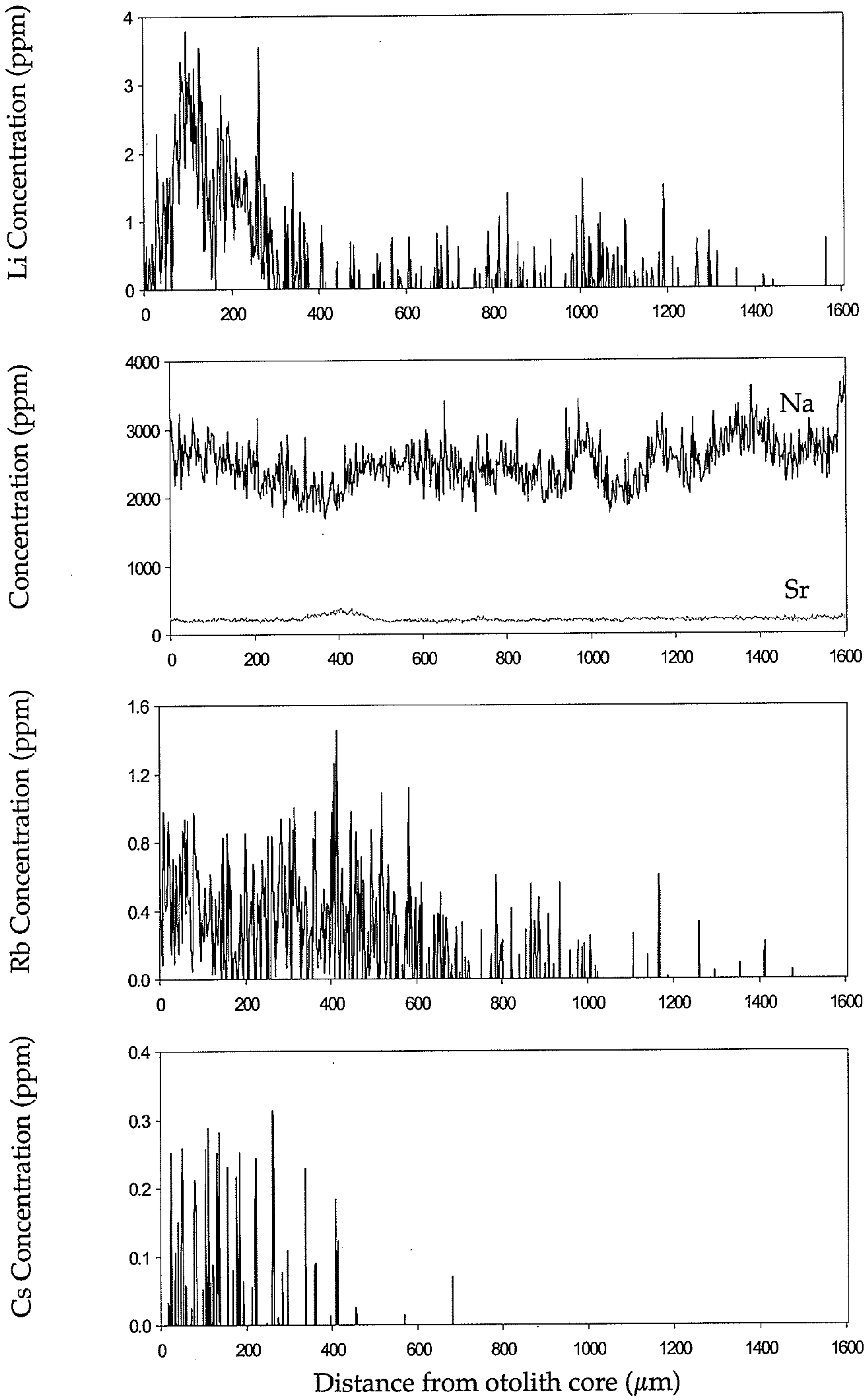

Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
Cs Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
Distance from otolith core (µm)

LDB01_42

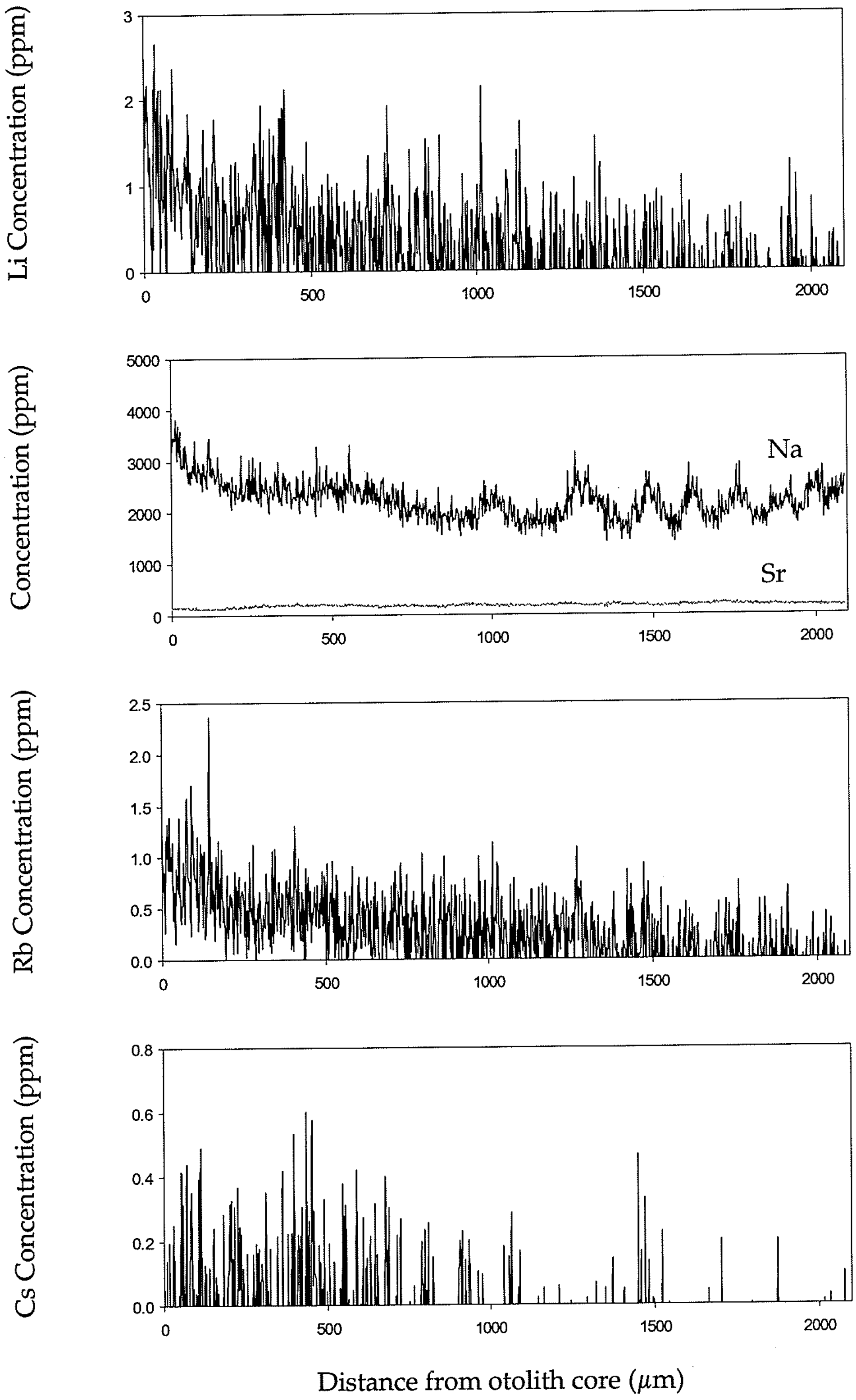


Li Concentration (ppm)
3
2
1
0
0
500
1000
1500
2000
Concentration (ppm)
6000
4000
2000
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
500
1000
1500
2000
Cs Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500
2000
Distance from otolith core (μm)

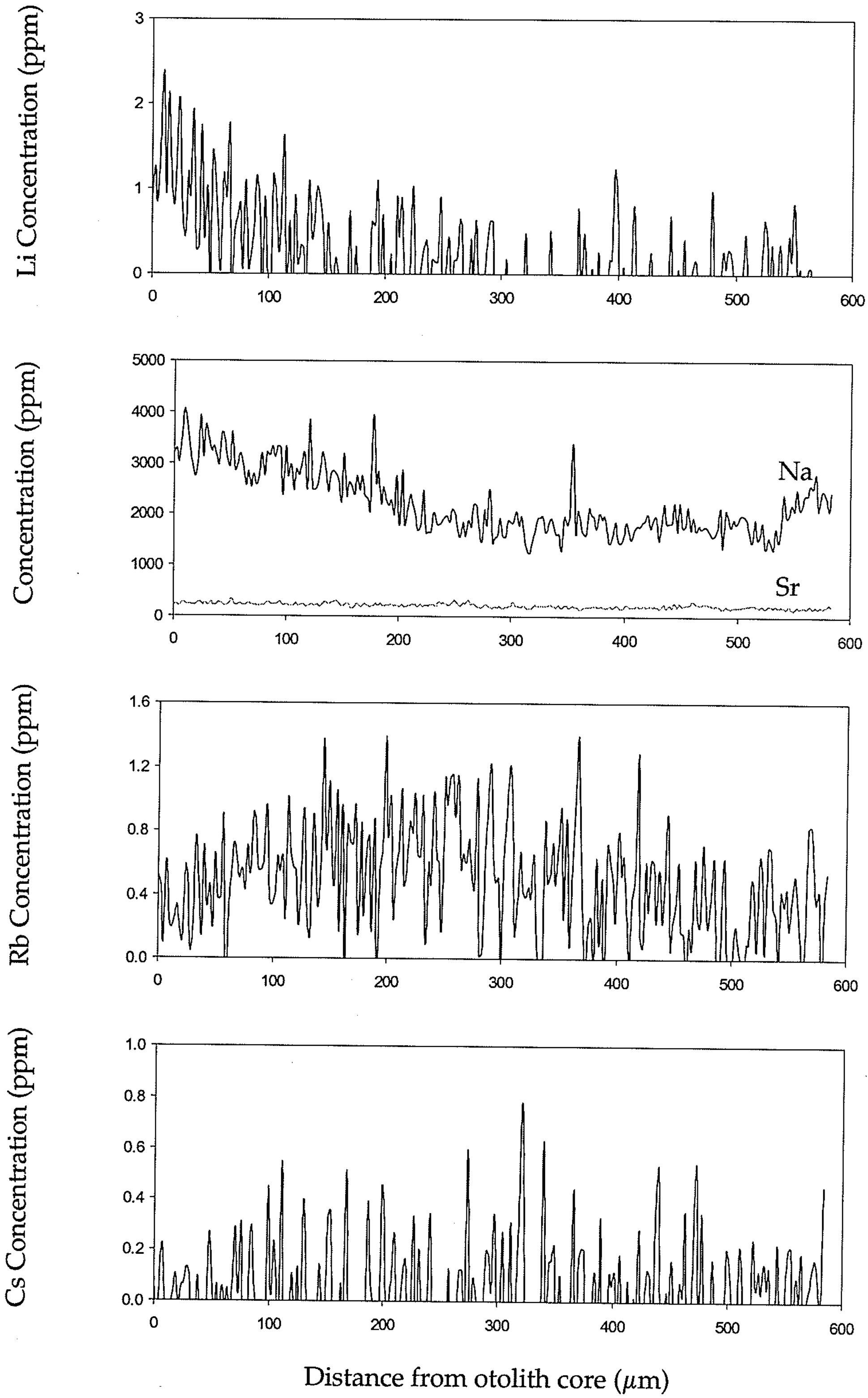
LDB01_43


Li Concentration (ppm)
0
1
2
3
4
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
Na
Sr
0
1000
2000
3000
4000
0
200
400
600
800
1000
1200
1400
1600
Rb Concentration (ppm)
0.0
0.4
0.8
1.2
1.6
0
200
400
600
800
1000
1200
1400
1600
Cs Concentration (ppm)
0.0
0.1
0.2
0.3
0.4
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

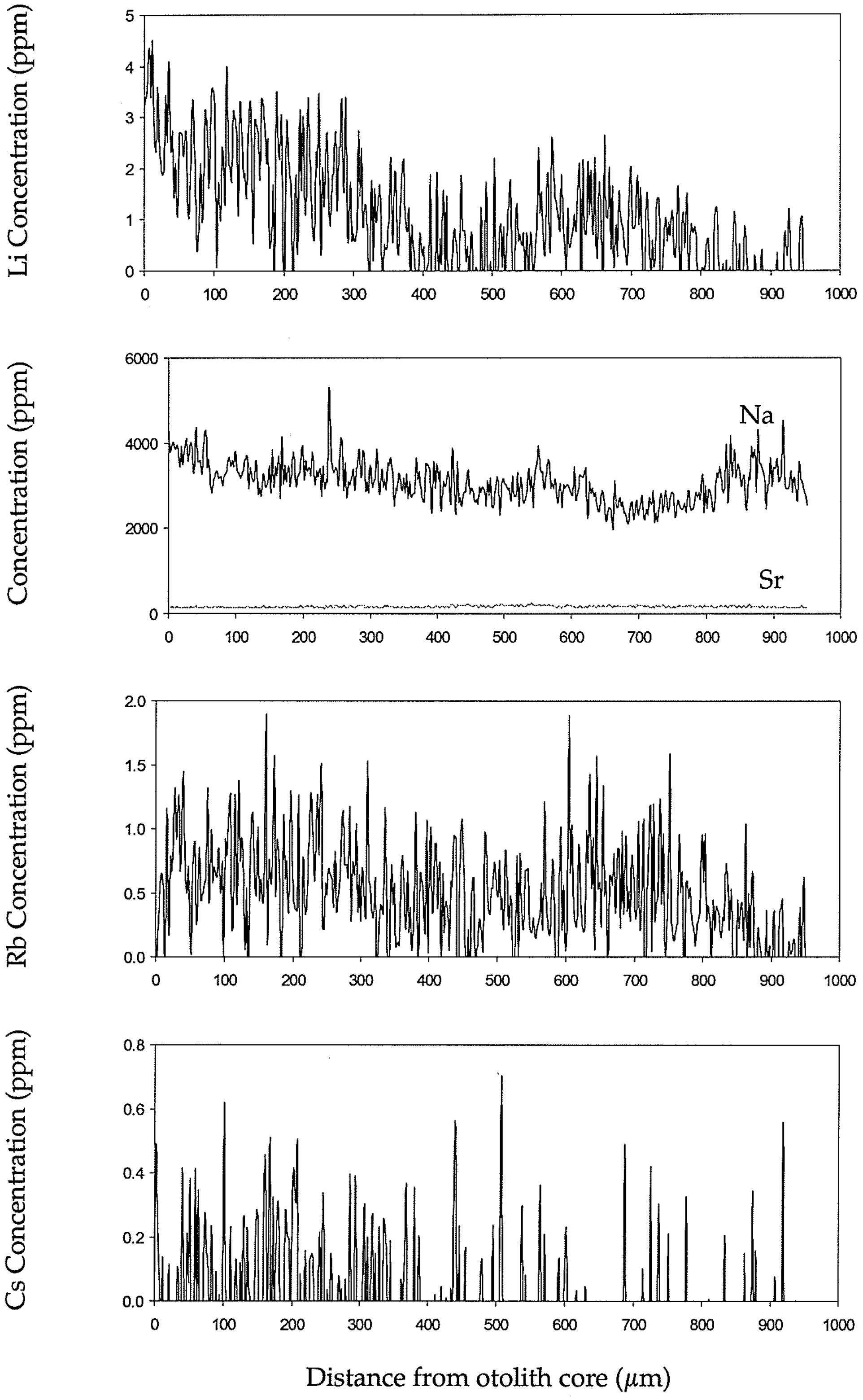
LDB01_44


Li Concentration (ppm)
0
1
2
3
0
500
1000
1500
2000
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
0
500
1000
1500
2000
Cs Concentration (ppm)
0.0
0.2
0.4
0.6
0.8
0
500
1000
1500
2000
Distance from otolith core (μm)

LDB01_45


Li Concentration (ppm)
3
2
1
0
0
100
200
300
400
500
600
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
Cs Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
600
Distance from otolith core (μm)

LDB01_46


Li Concentration (ppm)
0
1
2
3
4
5
0
100
200
300
400
500
600
700
800
900
1000
Concentration (ppm)
0
2000
4000
6000
Na
Sr
0
100
200
300
400
500
600
700
800
900
1000
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
0
100
200
300
400
500
600
700
800
900
1000
Cs Concentration (ppm)
0.0
0.2
0.4
0.6
0.8
0
100
200
300
400
500
600
700
800
900
1000
Distance from otolith core (μm)

Appendix G LA-ICP-MS data for Lac du Bonnet otoliths *continued*

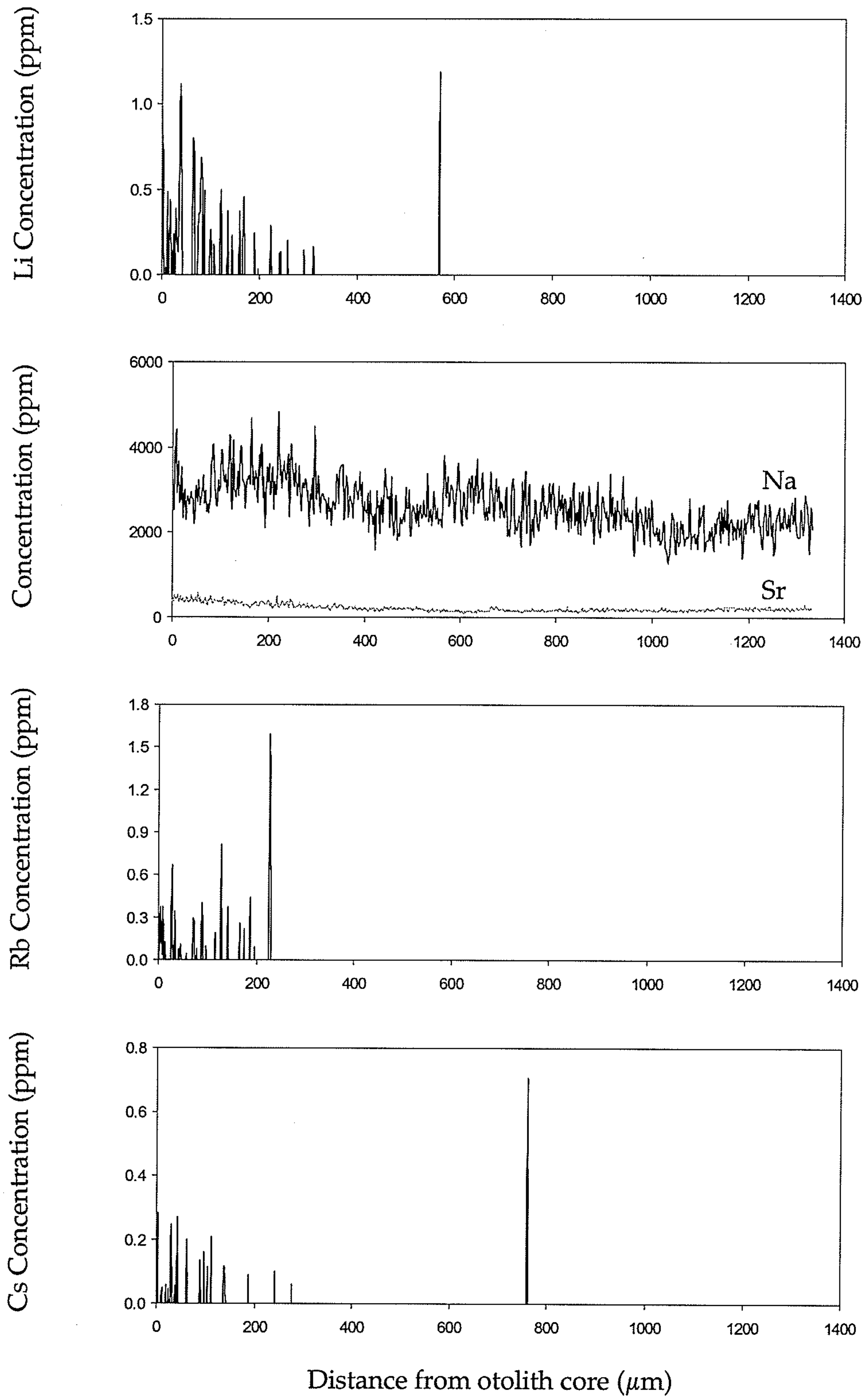
Species: Sauger (*Stizostedion canadense*)

Captured: 2000 (Manitoba Conservation Archives)

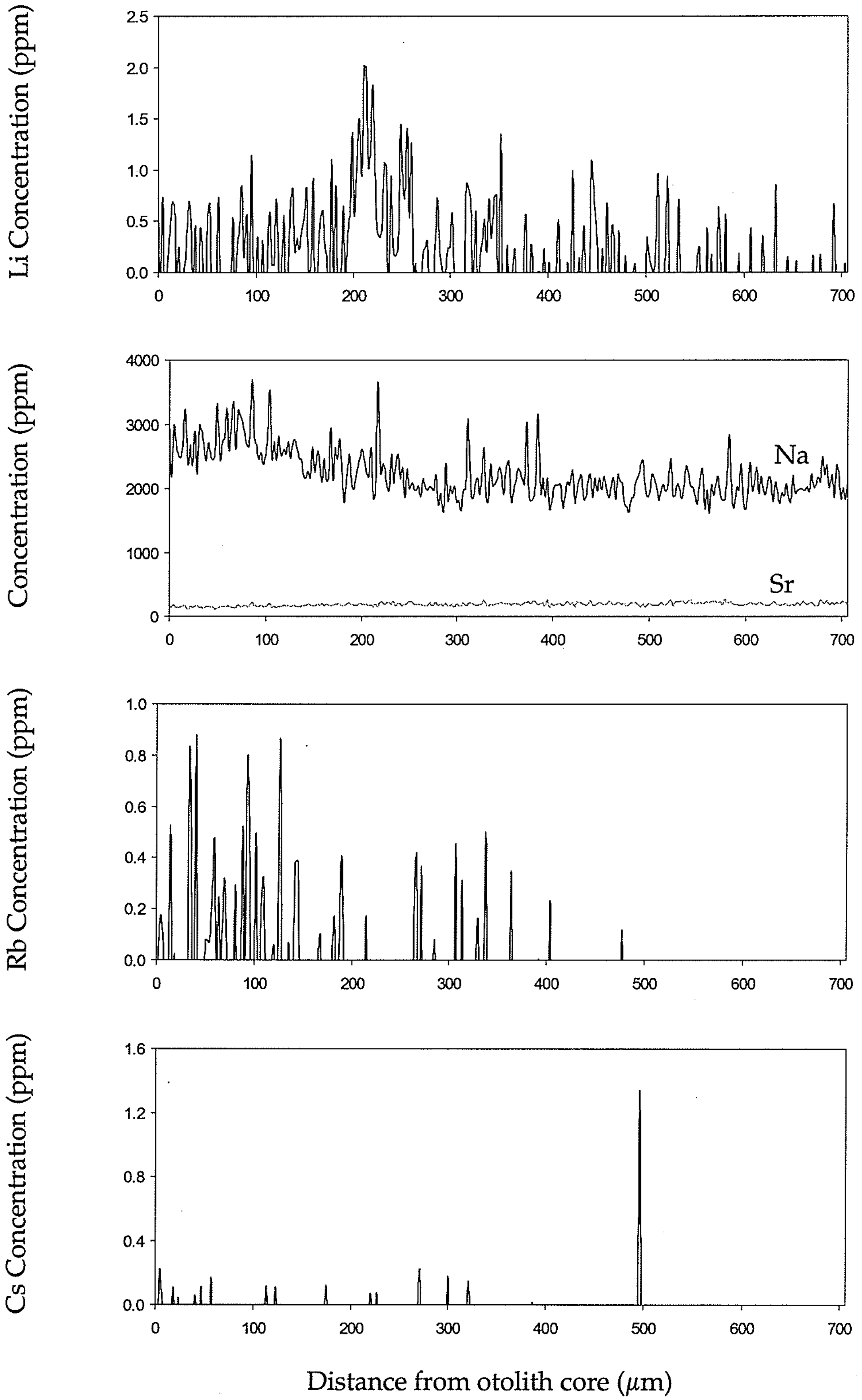
Isotopes	**Li^{7}**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
57	Walleye	21
58	Walleye	8
59	Walleye	7
60	Walleye	8
66	Sauger	6
67	Sauger	5

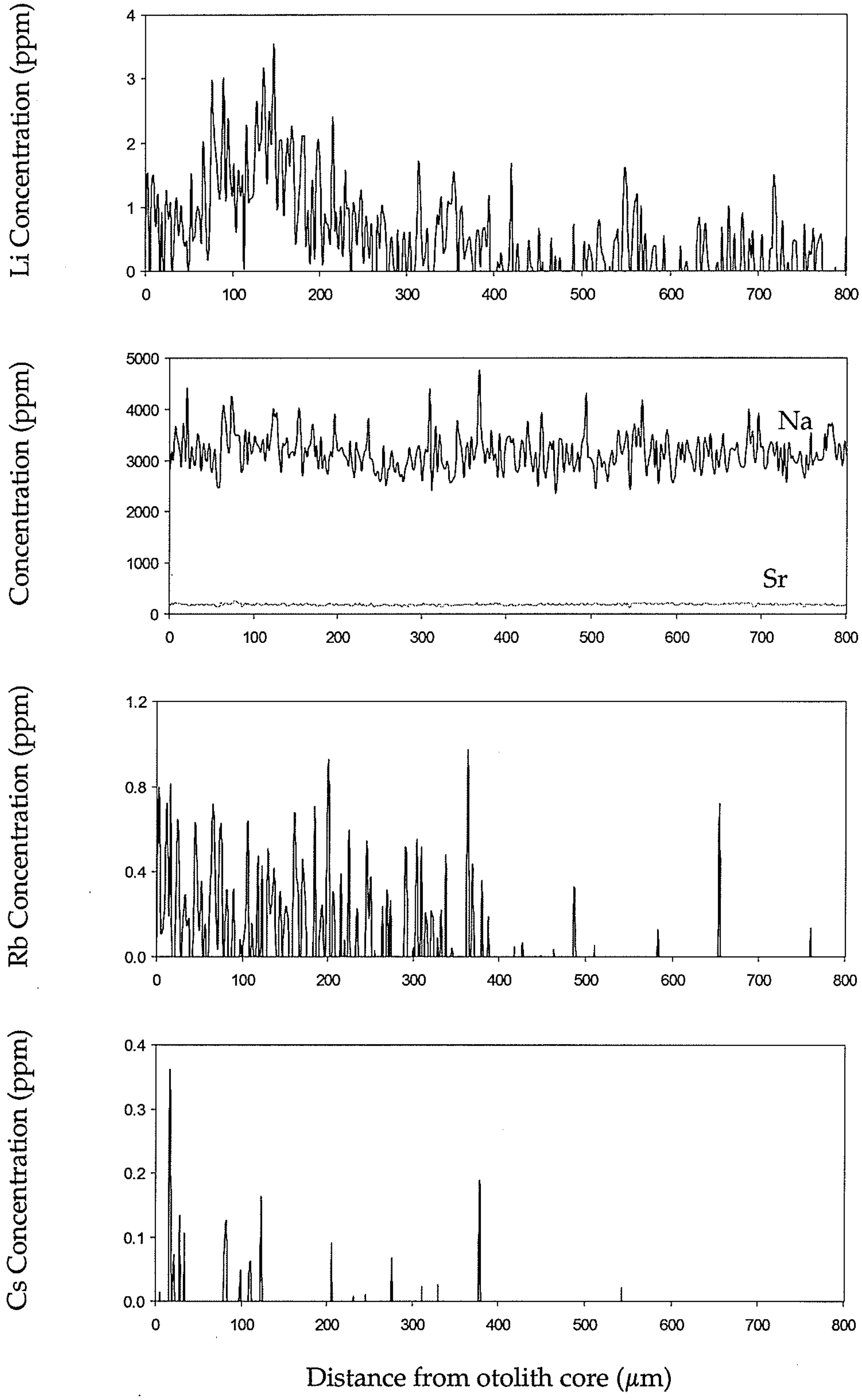
LDB00_57


Li Concentration (ppm)
1.5
1.0
0.5
0.0
Concentration (ppm)
6000
4000
2000
0
Na
Sr
Rb Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
Cs Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (µm)

LDB00_58

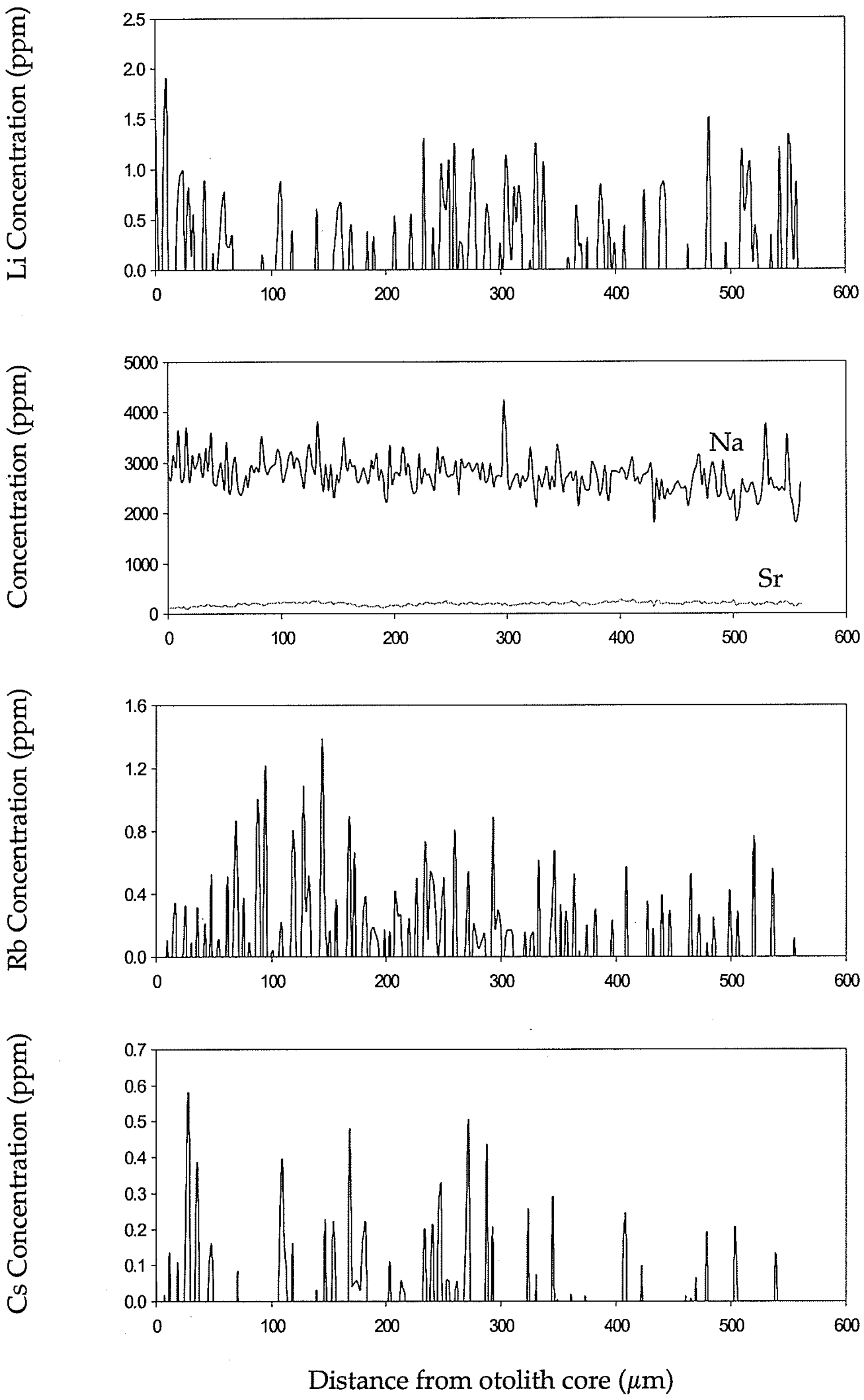

Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
Cs Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
Distance from otolith core (μm)

LDB00_59



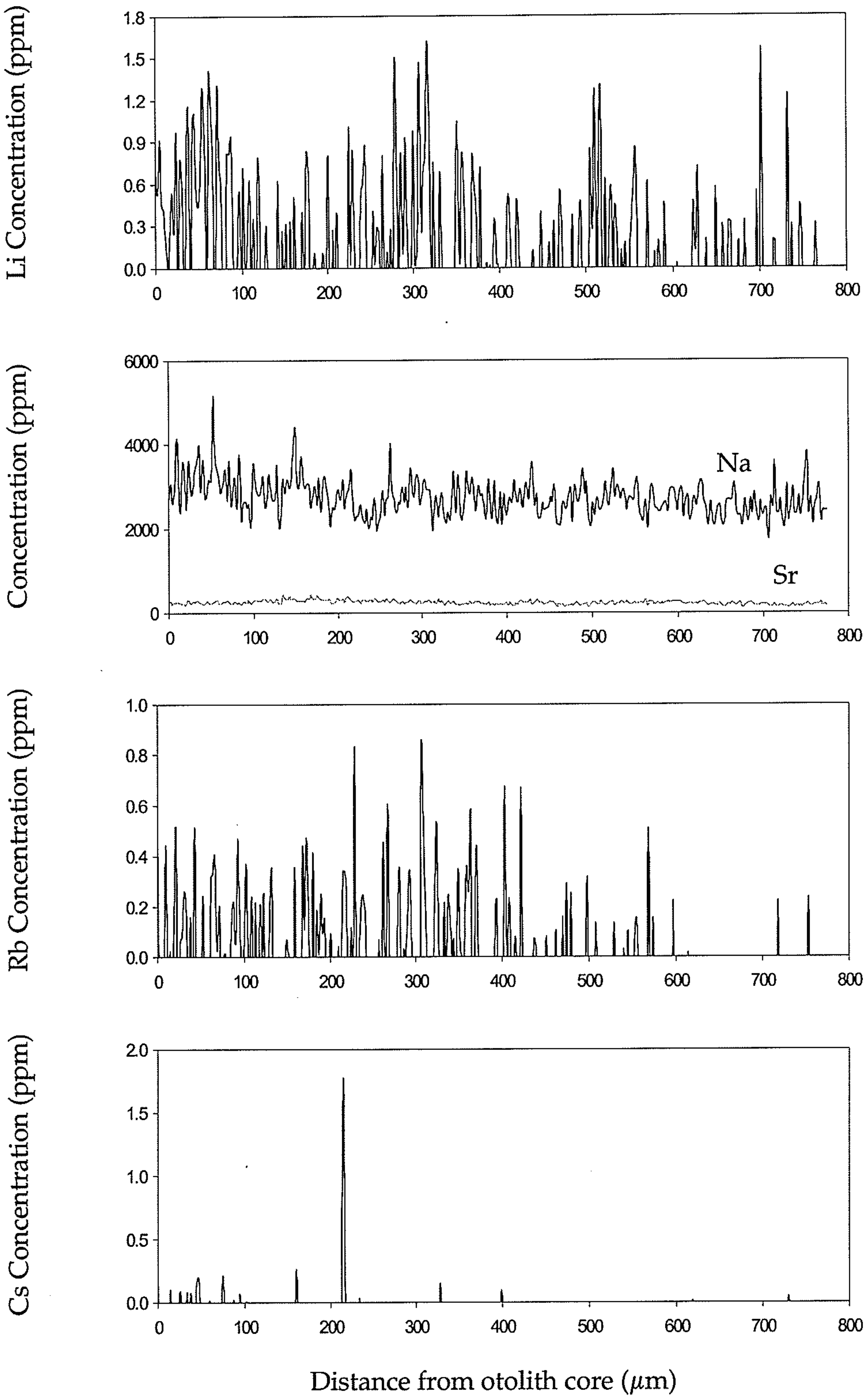
Li Concentration (ppm)
0
1
2
3
4
0
100
200
300
400
500
600
700
800
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
100
200
300
400
500
600
700
800
Rb Concentration (ppm)
0.0
0.4
0.8
1.2
0
100
200
300
400
500
600
700
800
Cs Concentration (ppm)
0.0
0.1
0.2
0.3
0.4
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

LDB00_60



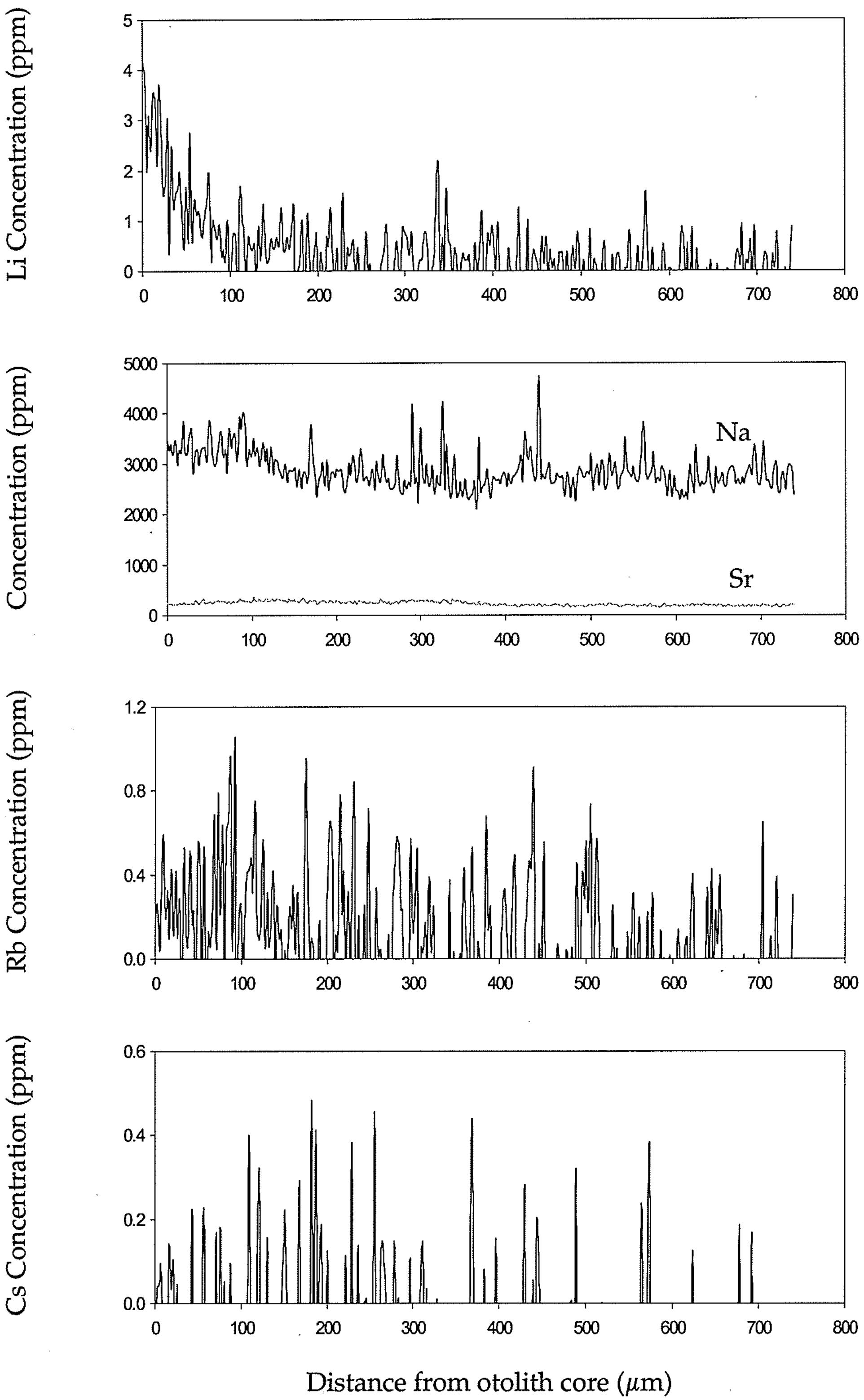
Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
Cs Concentration (ppm)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Distance from otolith core (μm)

LDB00_66



Li Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
0
100
200
300
400
500
600
700
800
Concentration (ppm)
6000
4000
2000
0
Na
Sr
0
100
200
300
400
500
600
700
800
Rb Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
600
700
800
Cs Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

LDB00_67


Li Concentration (ppm)
5
4
3
2
1
0
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
Cs Concentration (ppm)
0.6
0.4
0.2
0.0
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

Appendix G LA-ICP-MS data for Lac du Bonnet otoliths *continued*

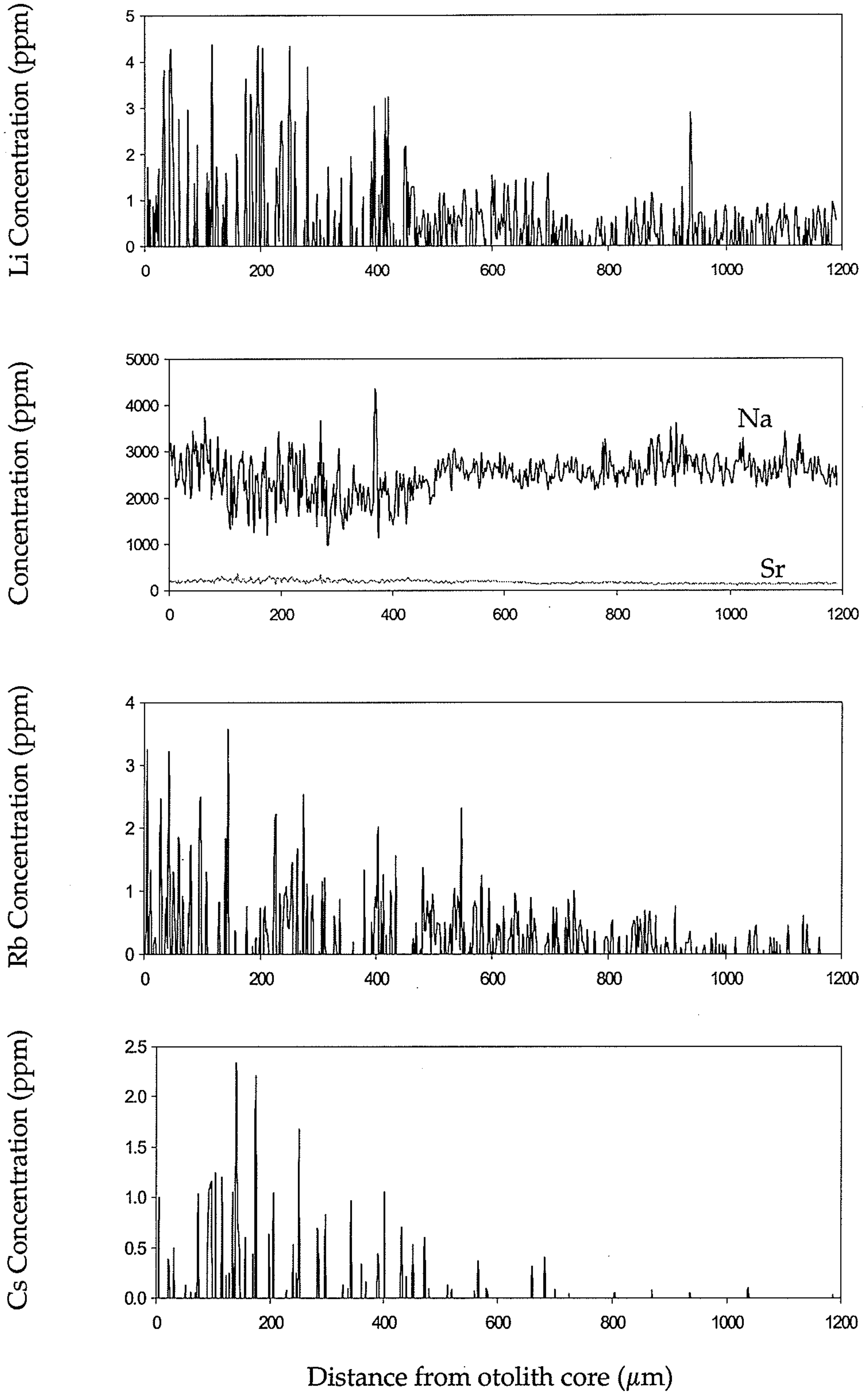
Species: Walleye (*Sander vitreous*)

Captured: 1999 (Manitoba Conservation Archives)

Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
01	Walleye	5

LDB99_01


Li Concentration (ppm)
0
1
2
3
4
5
0
200
400
600
800
1000
1200
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
0
1
2
3
4
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

Appendix G LA-ICP-MS data for Lac du Bonnet otoliths *continued*

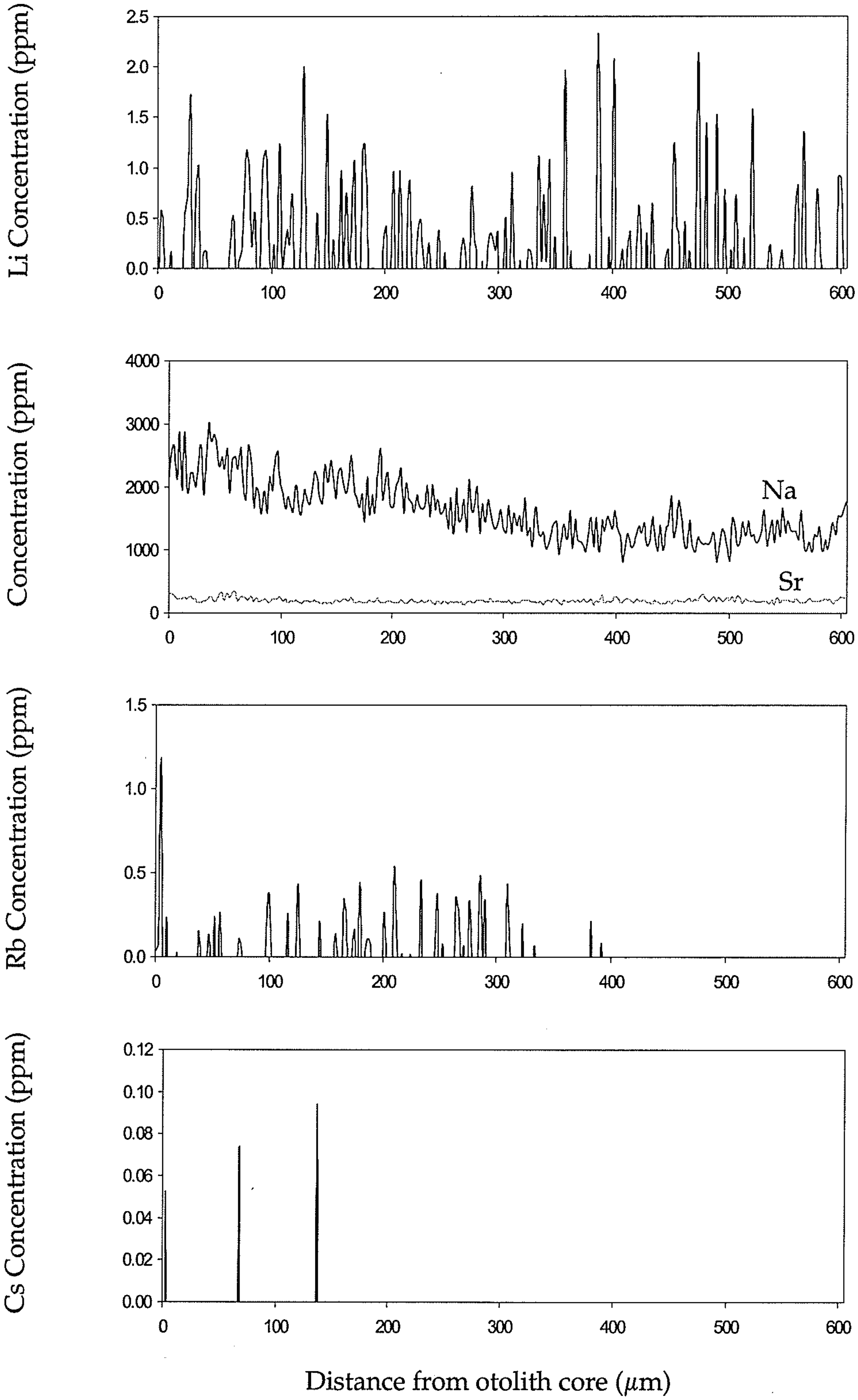
Species: Walleye (*Sander vitreous*)

Captured: 1998 (Manitoba Conservation Archives)

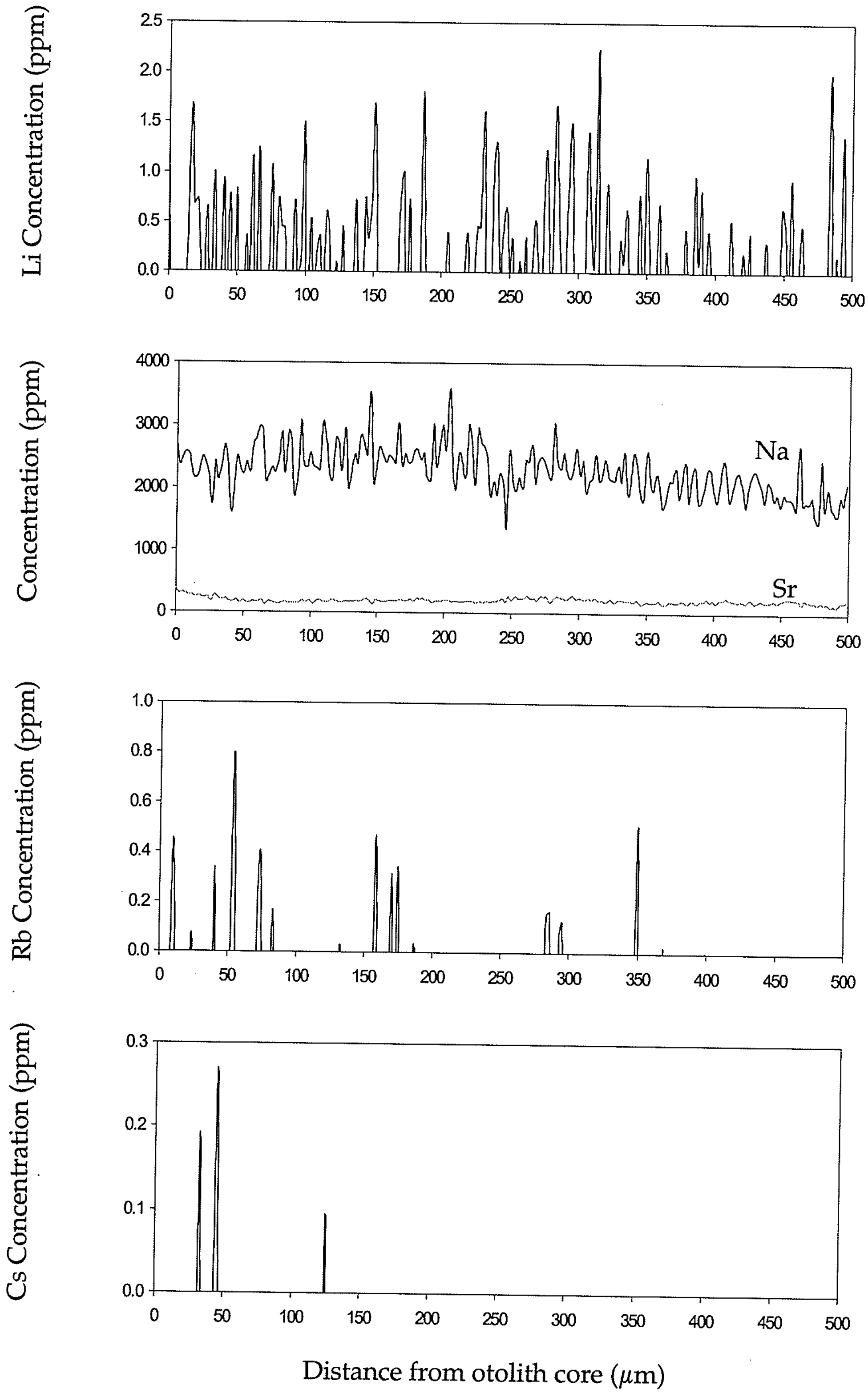
Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
56	Walleye	4
57	Walleye	5
58	Walleye	4
59	Walleye	4
60	Walleye	4
61	Walleye	3

LDB98_56

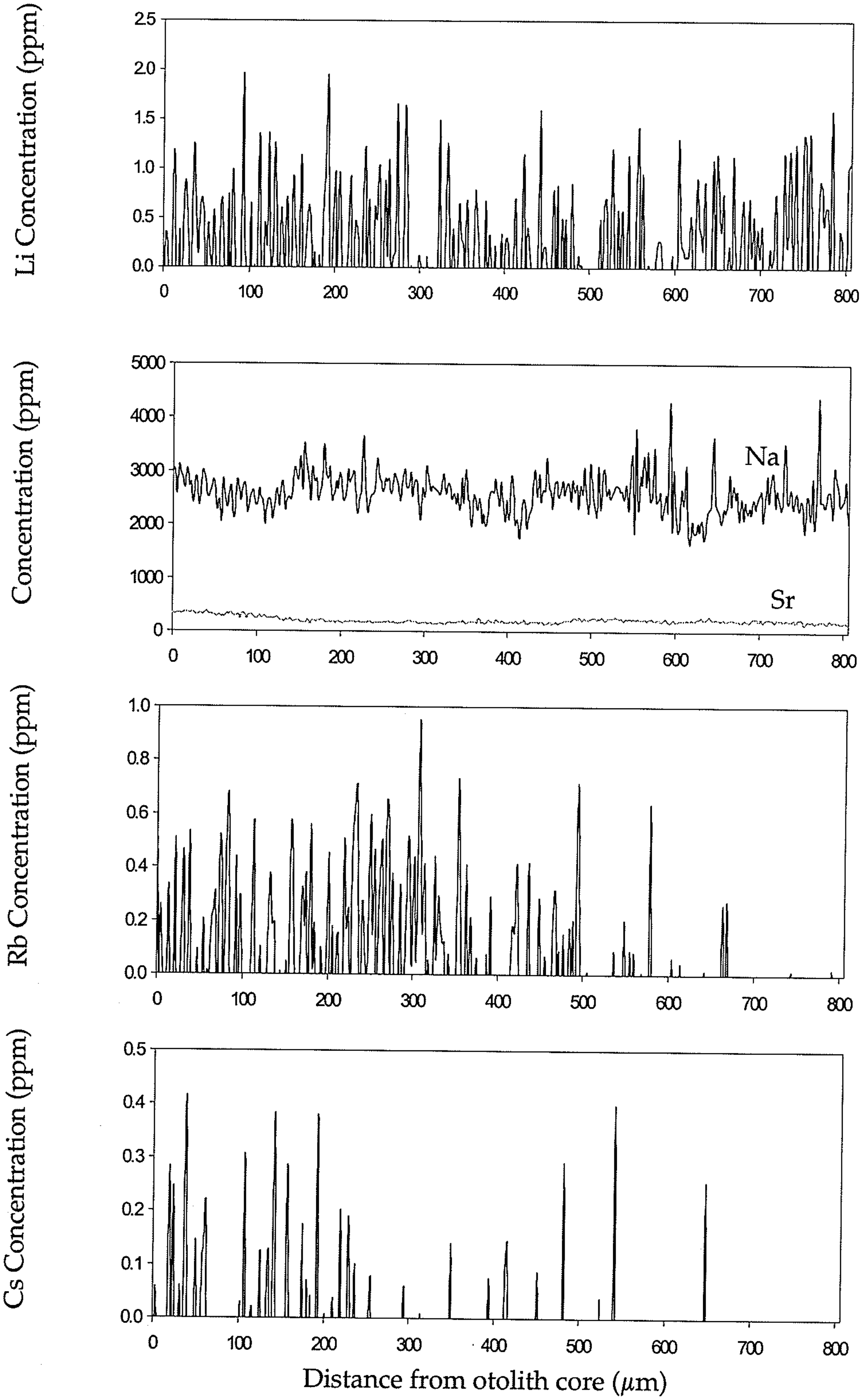

Li Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
0
100
200
300
400
500
600
Concentration (ppm)
0
1000
2000
3000
4000
Na
Sr
0
100
200
300
400
500
600
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
0
100
200
300
400
500
600
Cs Concentration (ppm)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0
100
200
300
400
500
600
Distance from otolith core (μm)

LDB98_57

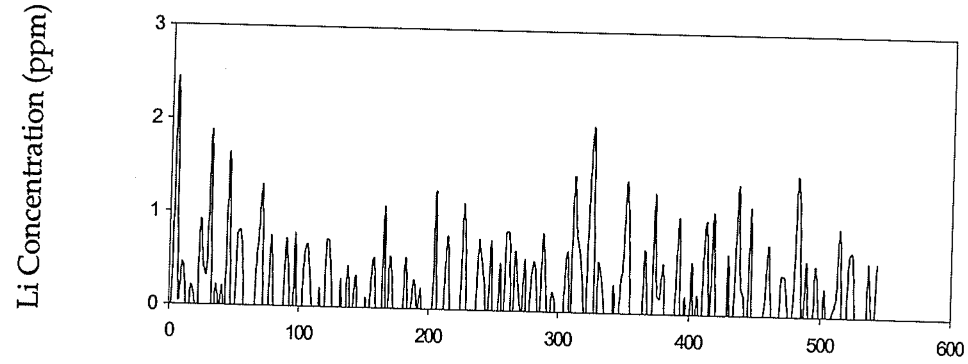


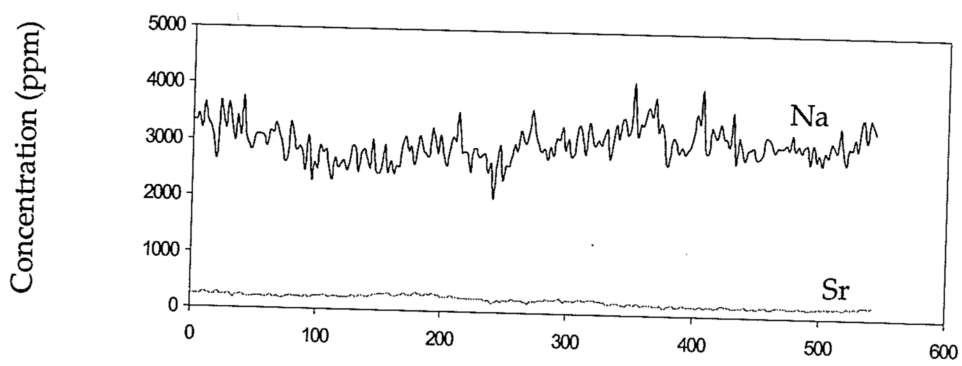
Li Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
Concentration (ppm)
0
1000
2000
3000
4000
Na
Sr
Rb Concentration (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
Cs Concentration (ppm)
0.0
0.1
0.2
0.3
0
50
100
150
200
250
300
350
400
450
500
Distance from otolith core (μm)

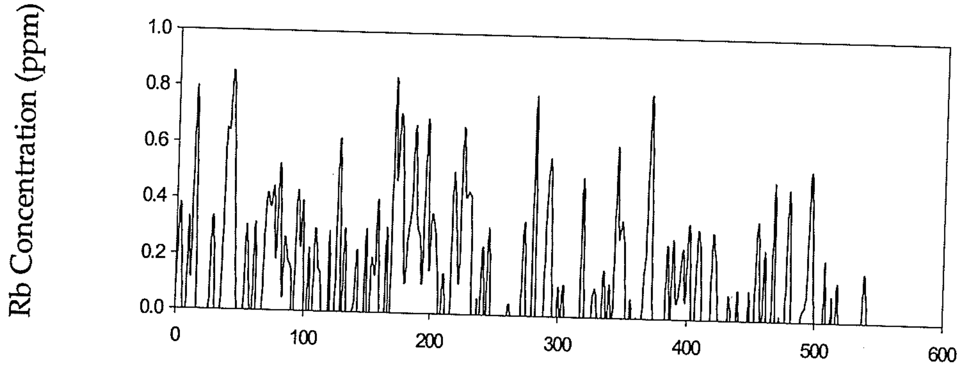
LDB98_58

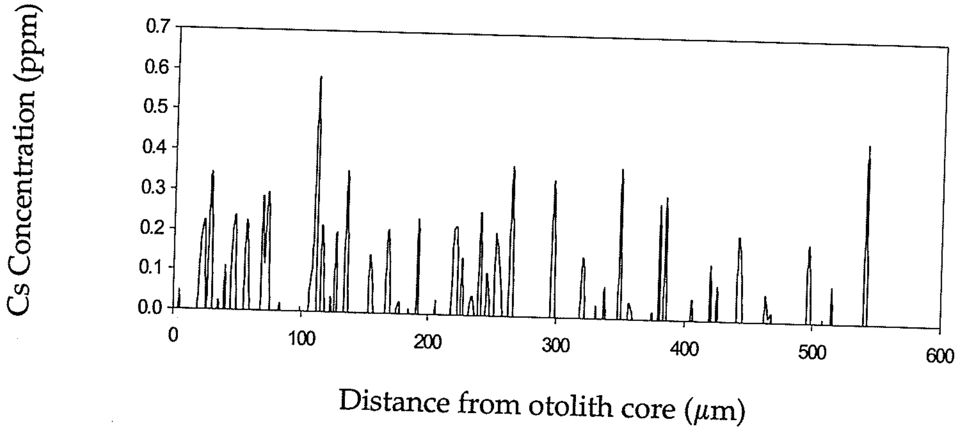

Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
Cs Concentration (ppm)
0.5
0.4
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

LDB98_59

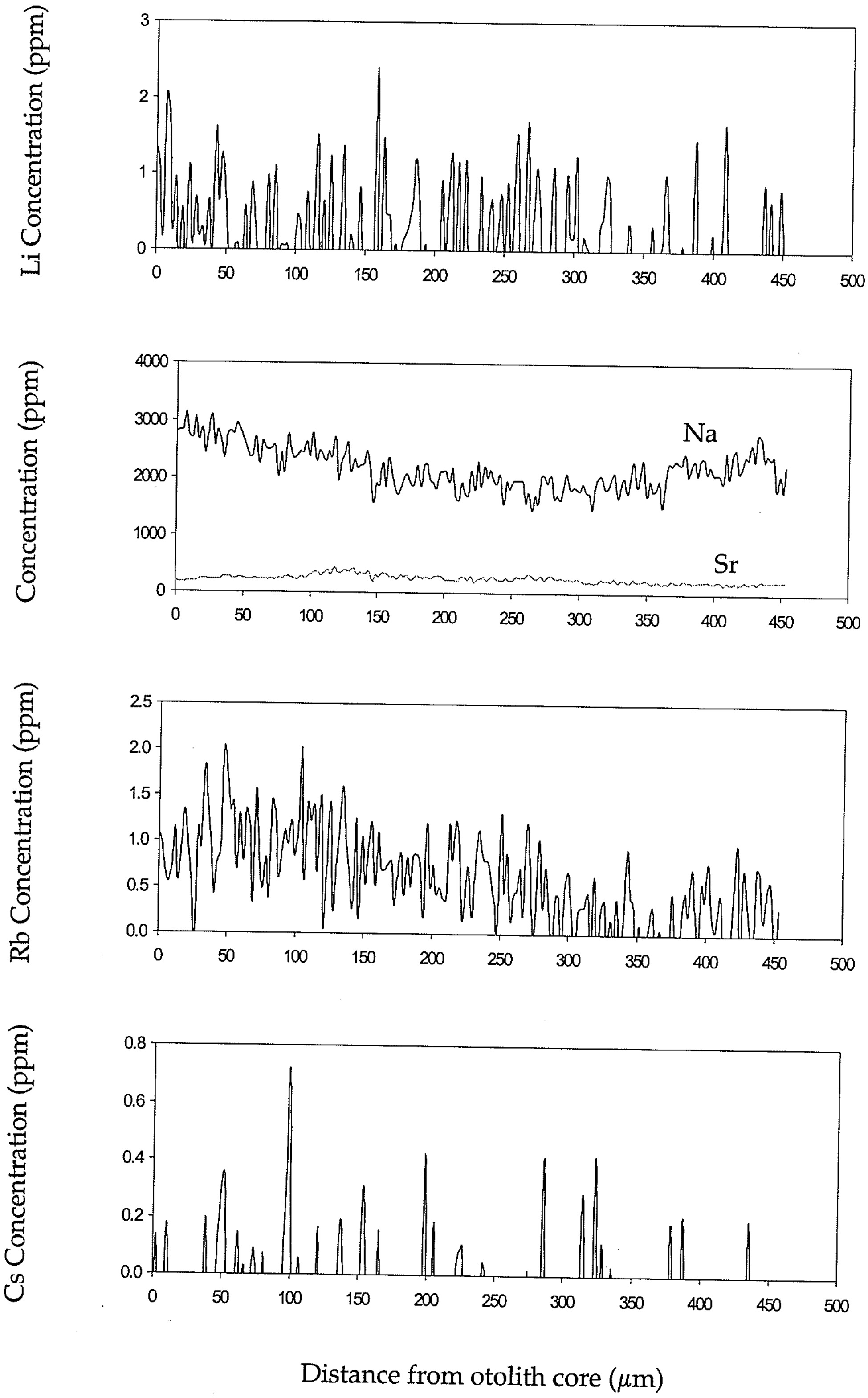

Li Concentration (ppm)
0
1
2
3
0
100
200
300
400
500
600


Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
100
200
300
400
500
600

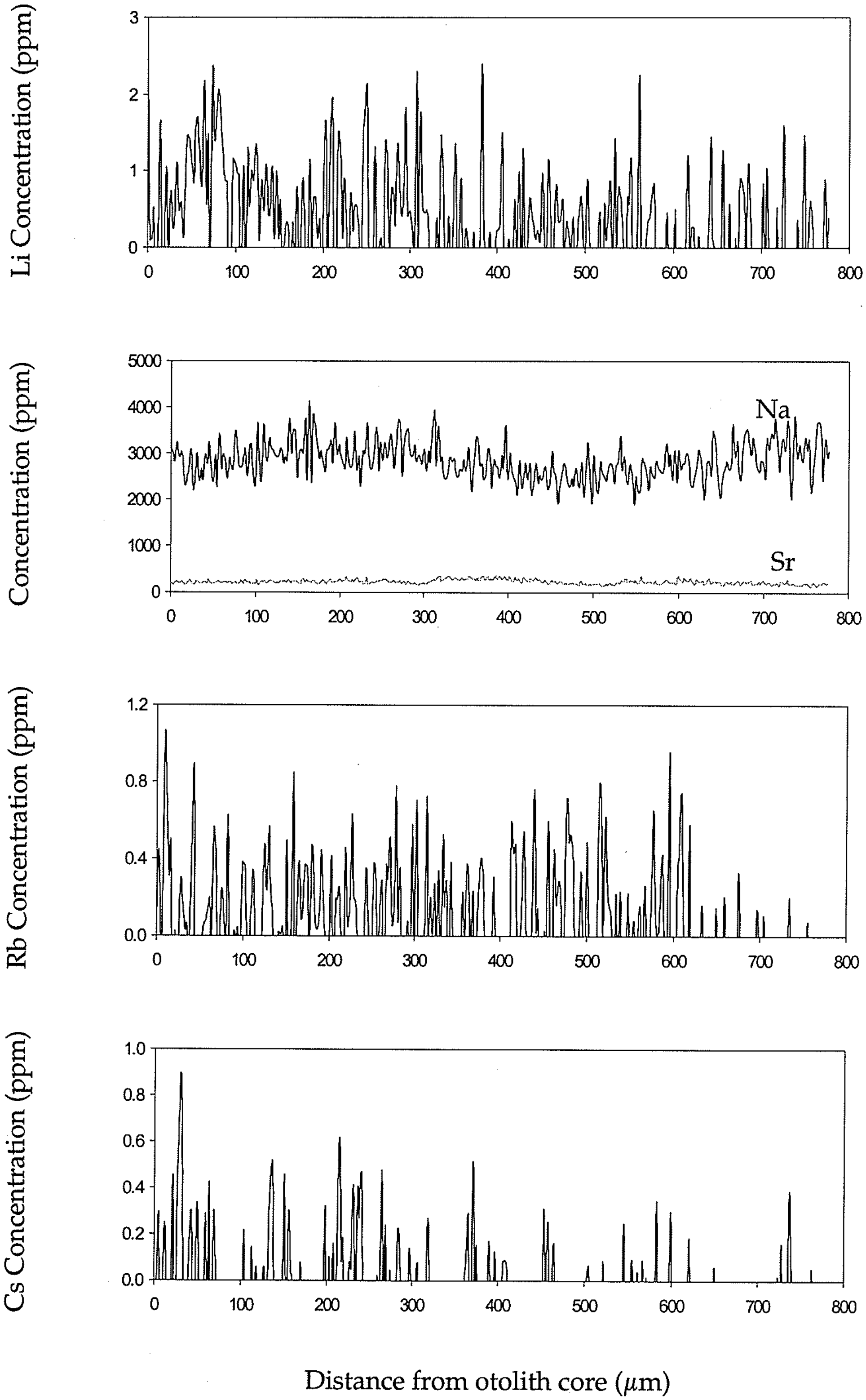

Rb Concentration (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
0
100
200
300
400
500
600


Cs Concentration (ppm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0
100
200
300
400
500
600
Distance from otolith core (μm)

LDB98_60


Li Concentration (ppm)
3
2
1
0
0
50
100
150
200
250
300
350
400
450
500
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
50
100
150
200
250
300
350
400
450
500
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
50
100
150
200
250
300
350
400
450
500
Cs Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
300
350
400
450
500
Distance from otolith core (μm)

LDB98_61


Li Concentration (ppm)
3
2
1
0
0
100
200
300
400
500
600
700
800
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
800
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
800
Cs Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

Appendix G LA-ICP-MS data for Lac du Bonnet otoliths *continued*

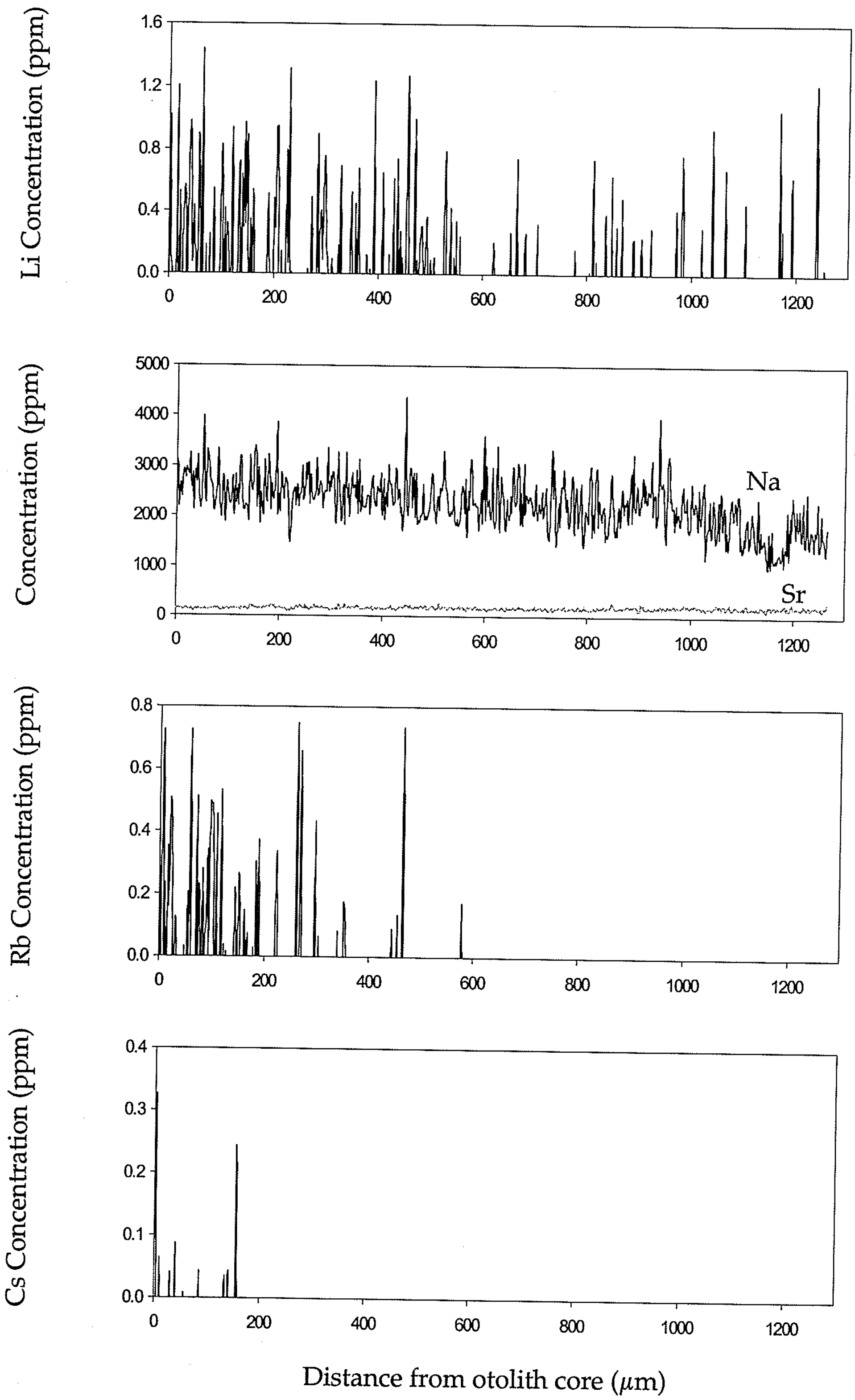
Species: Walleye (*Sander vitreous*), Sauger (*Stizostedion canadense*)

Captured: 1997 (Manitoba Conservation Archives)

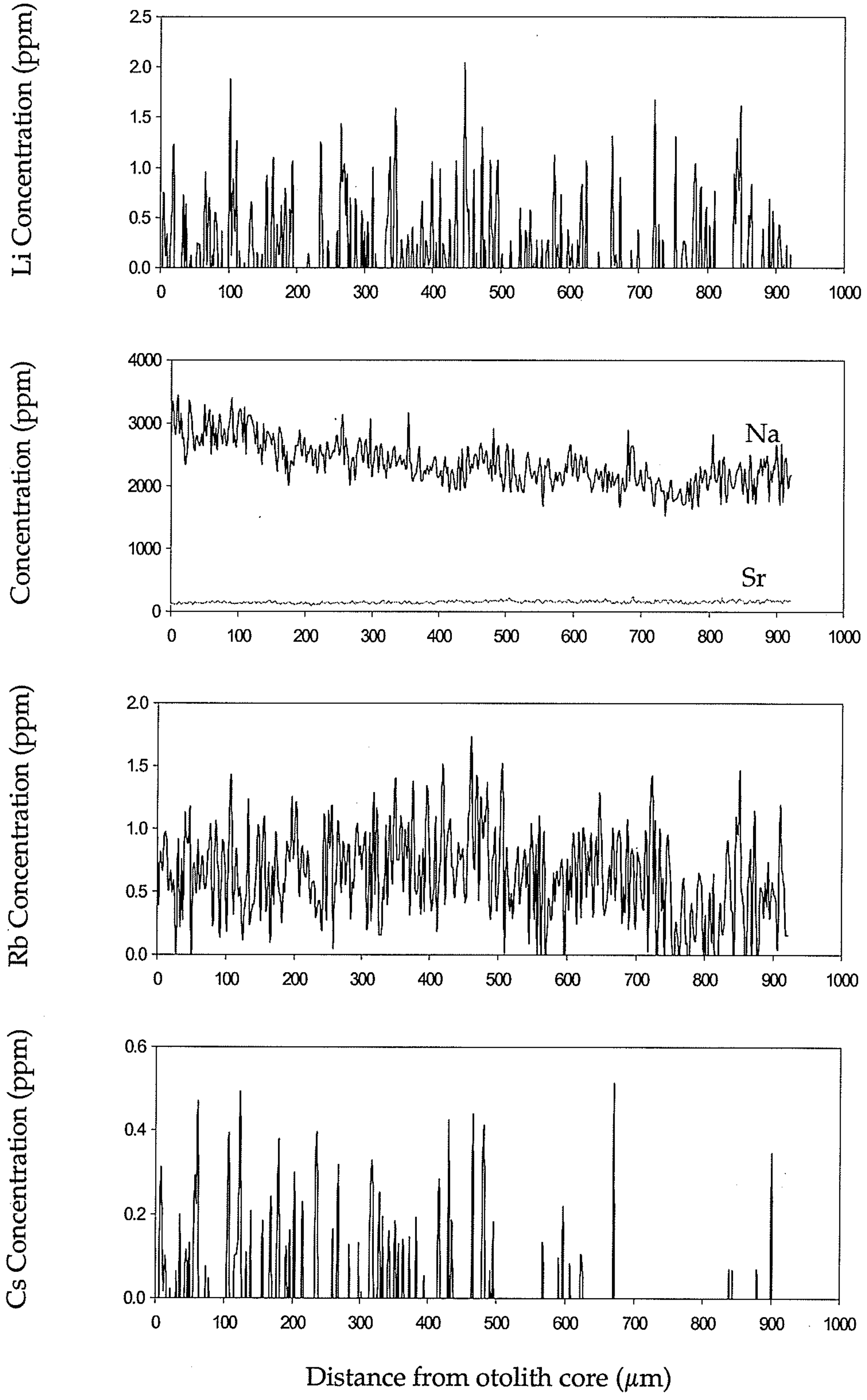
Isotopes	**Li^{7}**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
129	Walleye	9
130	Walleye	8
131	Walleye	9
136	Sauger	7
137	Sauger	9
138	Walleye	6

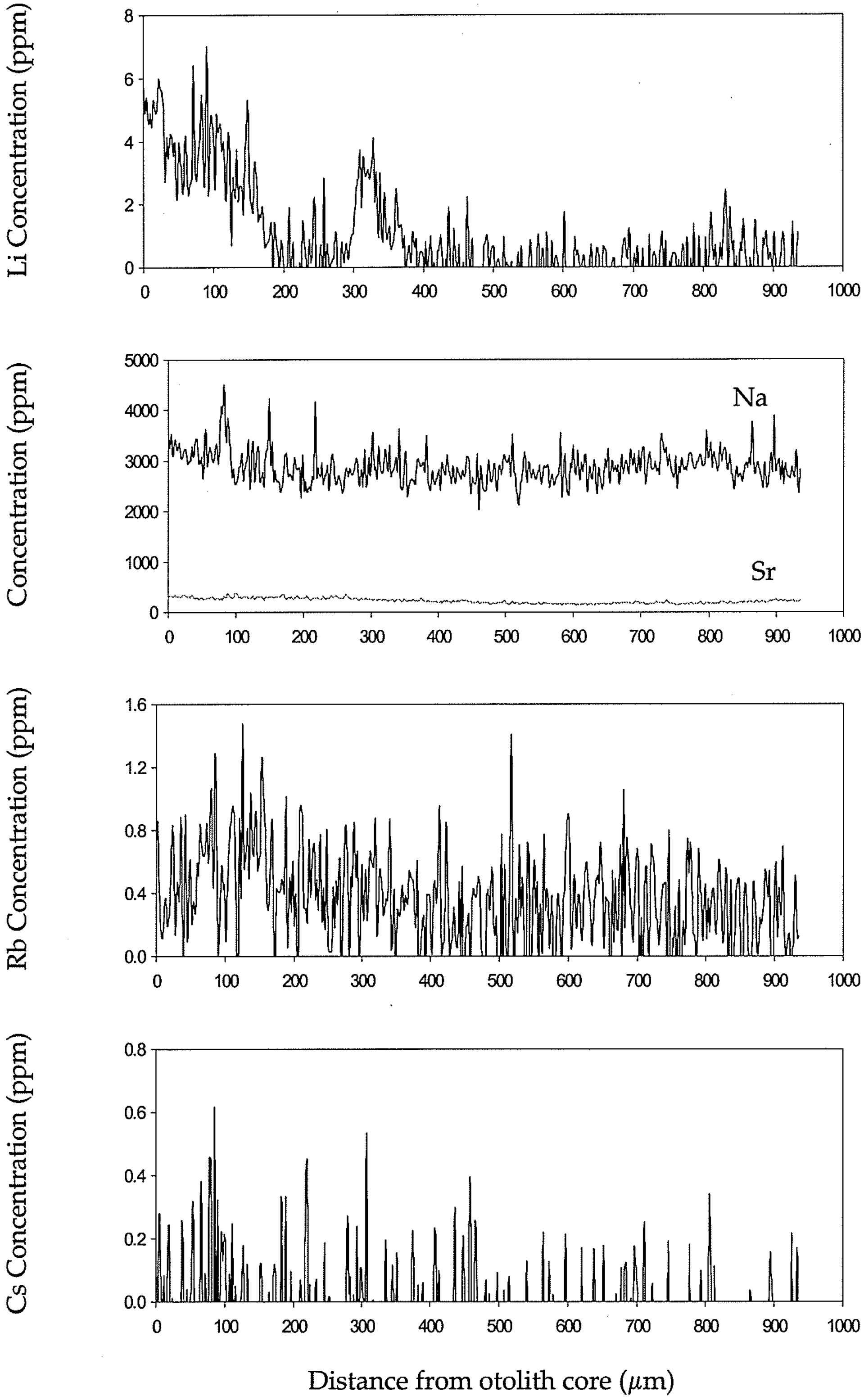
LDB97_129


Li Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
Cs Concentration (ppm)
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

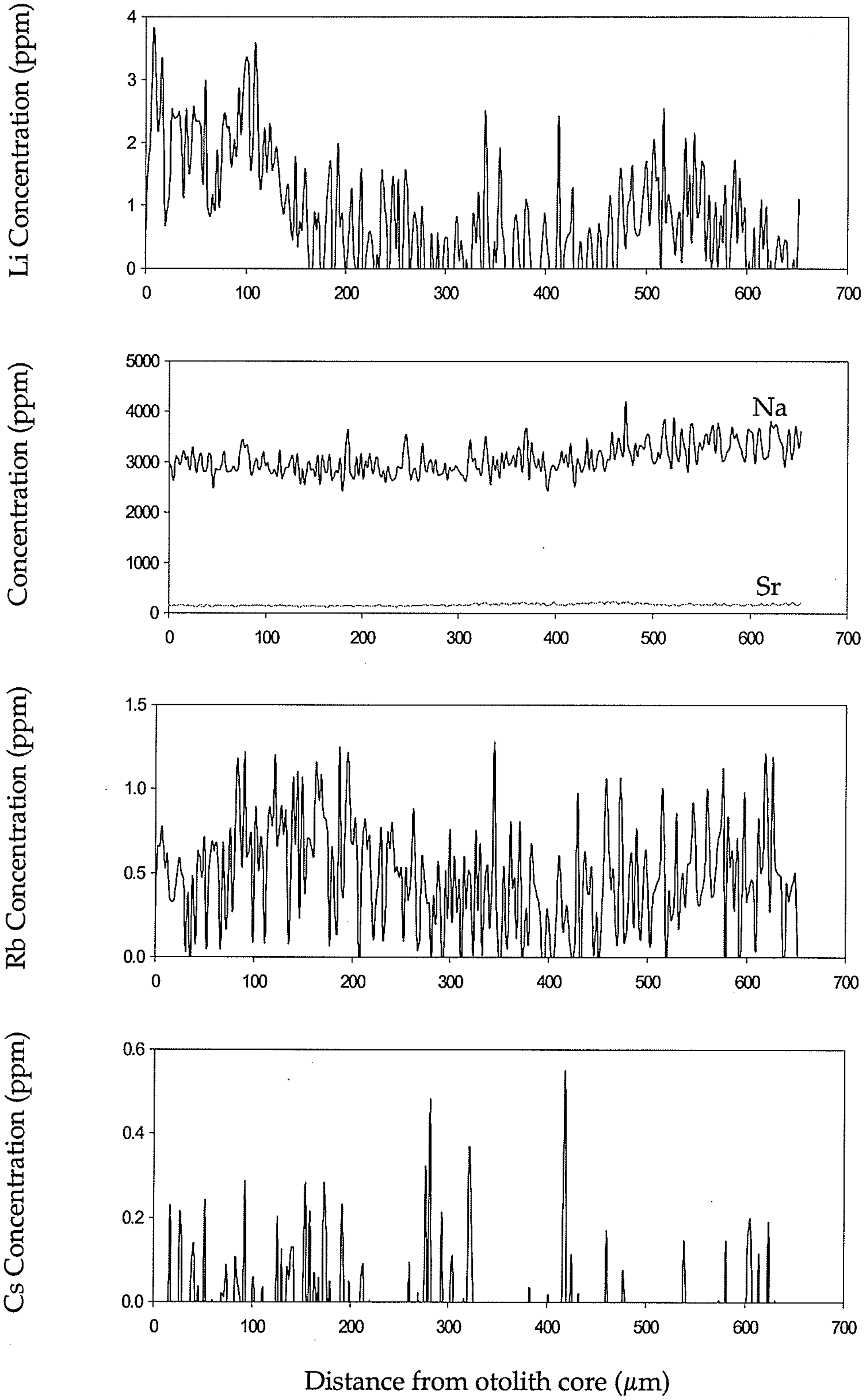
LDB97_130


Li Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
Concentration (ppm)
0
1000
2000
3000
4000
Na
Sr
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
Cs Concentration (ppm)
0.0
0.2
0.4
0.6
0
100
200
300
400
500
600
700
800
900
1000
Distance from otolith core (μm)

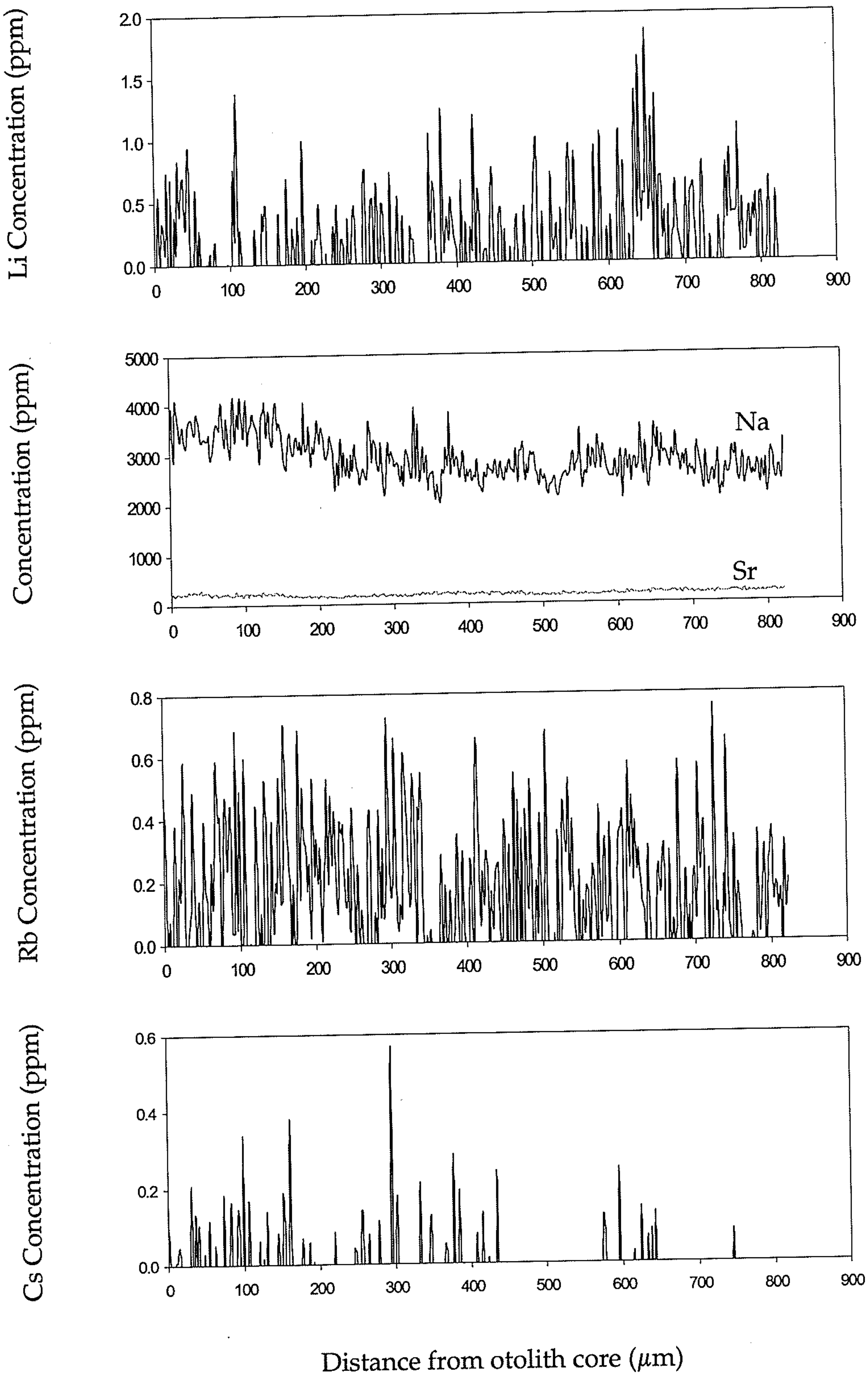
LDB97_131


Li Concentration (ppm)
8
6
4
2
0
0 100 200 300 400 500 600 700 800 900 1000
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0 100 200 300 400 500 600 700 800 900 1000
Rb Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0 100 200 300 400 500 600 700 800 900 1000
Cs Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
0 100 200 300 400 500 600 700 800 900 1000
Distance from otolith core (μm)

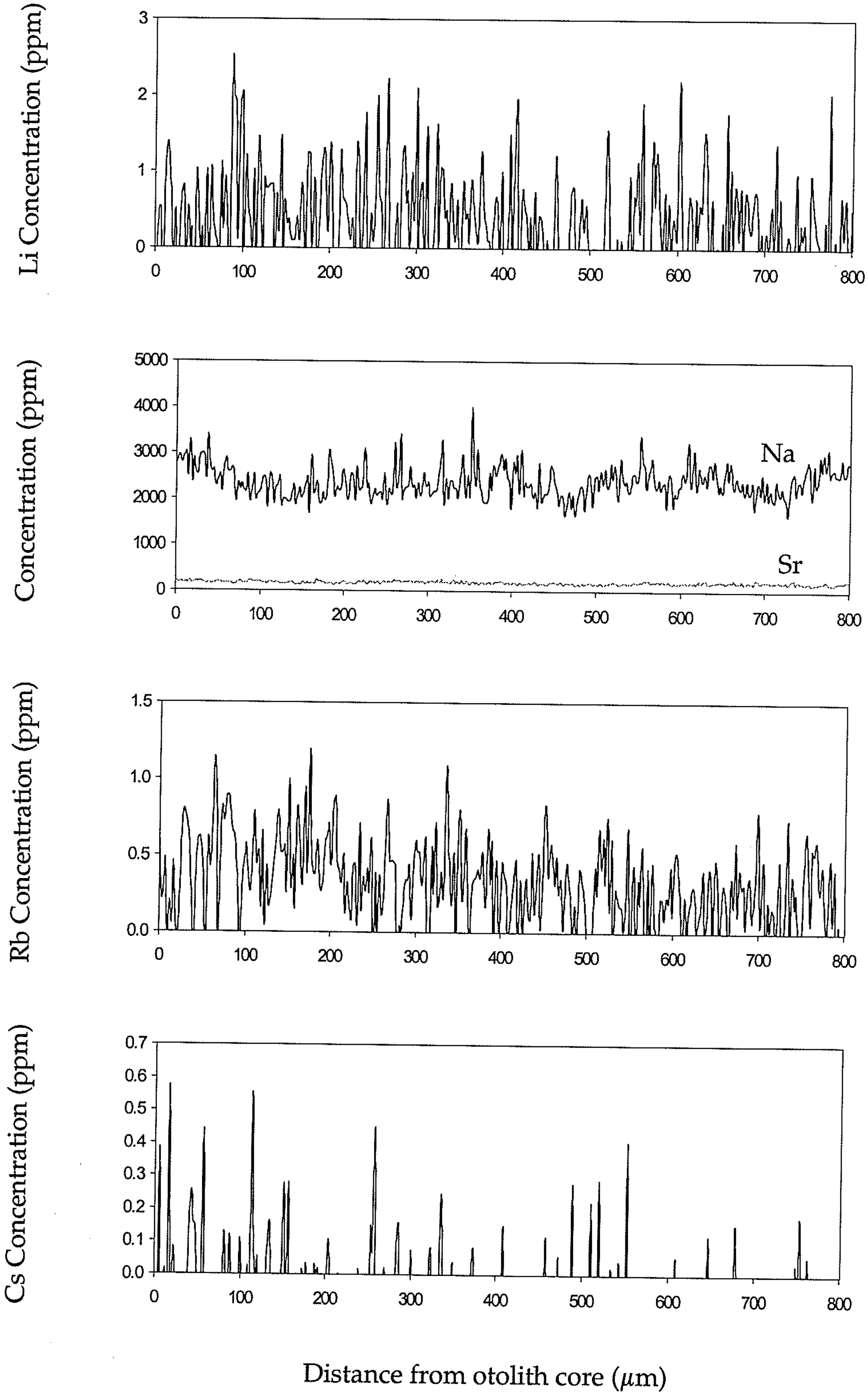
LDB97_136


Li Concentration (ppm)
0
1
2
3
4
0
100
200
300
400
500
600
700
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
Rb Concentration (ppm)
0.0
0.5
1.0
1.5
Cs Concentration (ppm)
0.0
0.2
0.4
0.6
Distance from otolith core (μm)

LDB97_137


Li Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
Rb Concentration (ppm)
0.0
0.2
0.4
0.6
0.8
Cs Concentration (ppm)
0.0
0.2
0.4
0.6
0
100
200
300
400
500
600
700
800
900
Distance from otolith core (μm)

LDB97_138


Li Concentration (ppm)
3
2
1
0
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.5
1.0
0.5
0.0
Cs Concentration (ppm)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

Appendix G LA-ICP-MS data for Lac du Bonnet otoliths *continued*

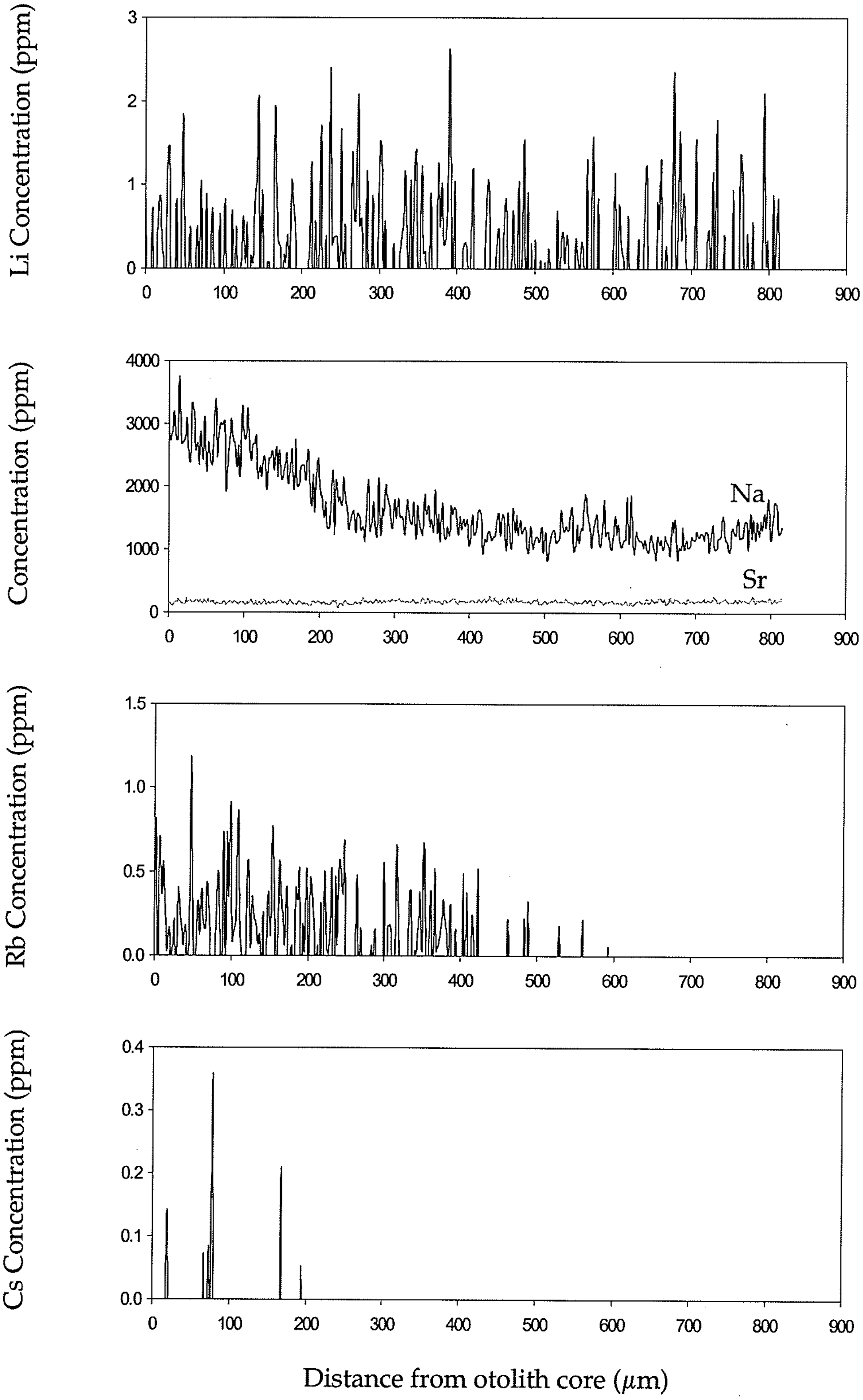
Species: Walleye (*Sander vitreous*)

Captured: 1996 (Manitoba Conservation Archives)

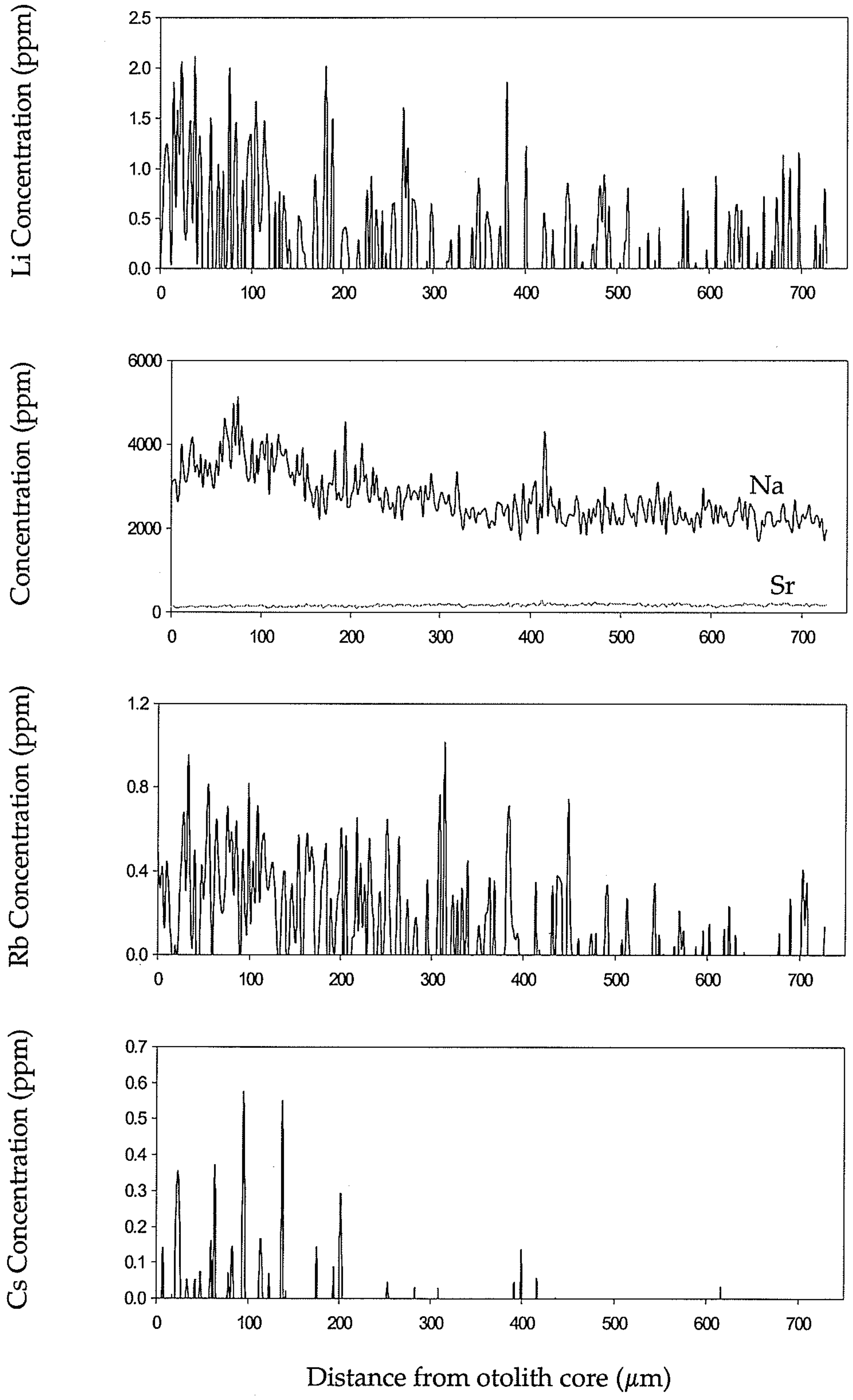
Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
137	Walleye	7
140	Walleye	7
149	Walleye	7
150	Walleye	12
151	Walleye	10
152	Walleye	8

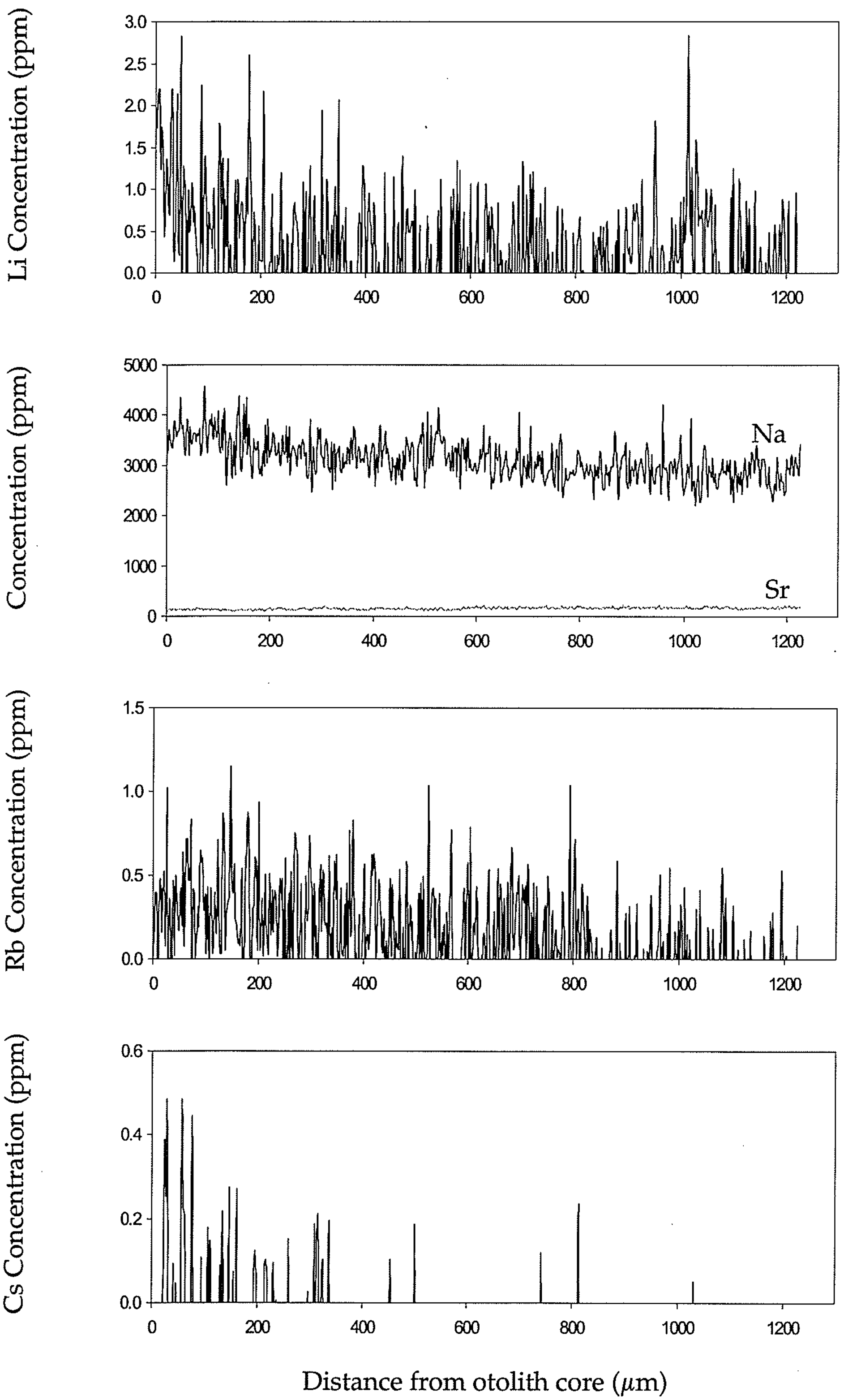
LDB96_137


Li Concentration (ppm)
3
2
1
0
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.5
1.0
0.5
0.0
Cs Concentration (ppm)
0.4
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
800
900
Distance from otolith core (μm)

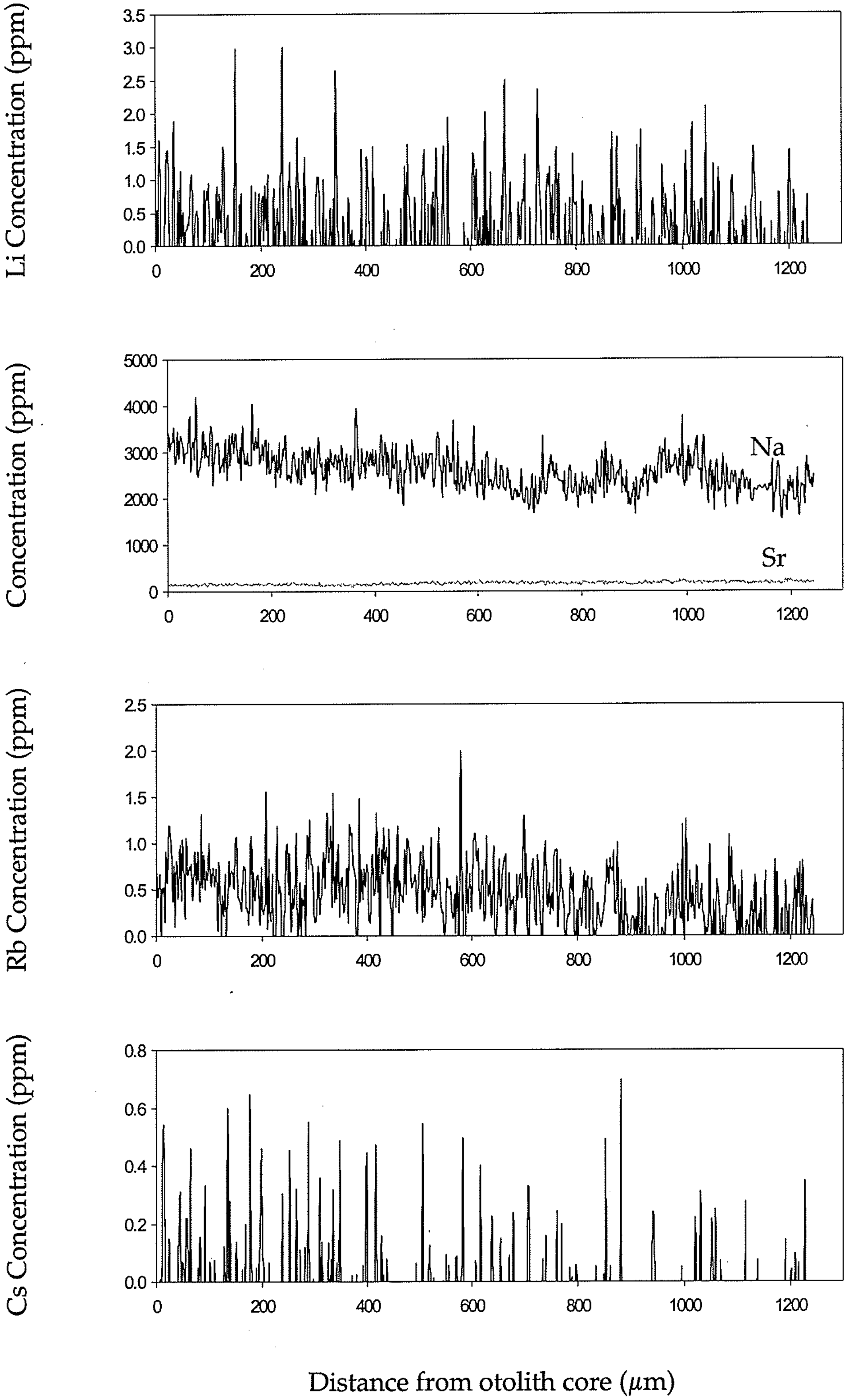
LDB96_140


Li Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
Concentration (ppm)
6000
4000
2000
0
Na
Sr
0
100
200
300
400
500
600
700
Rb Concentration (ppm)
1.2
0.8
0.4
0.0
0
100
200
300
400
500
600
700
Cs Concentration (ppm)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
Distance from otolith core (μm)

LDB96_149

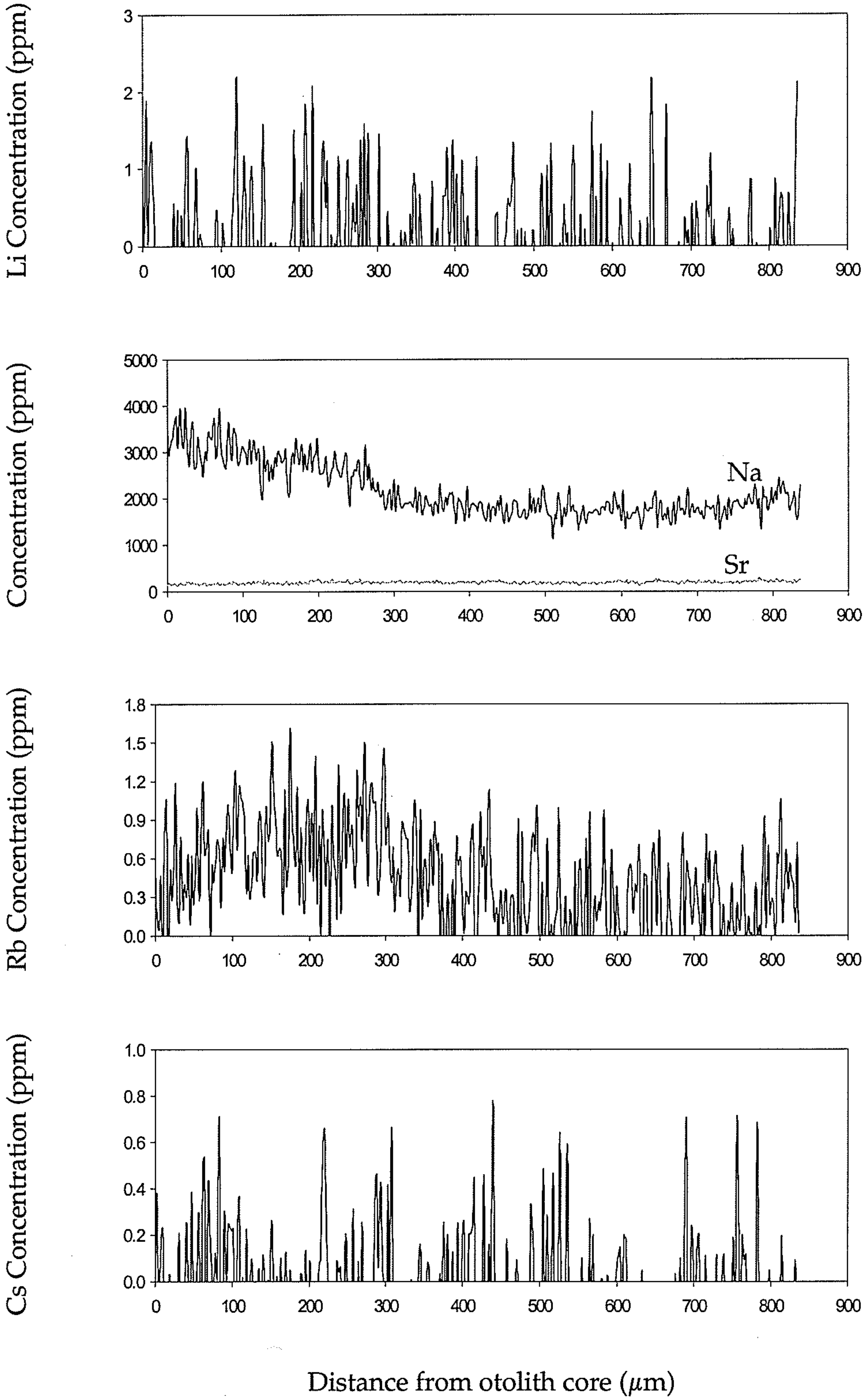

Li Concentration (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

LDB96_150

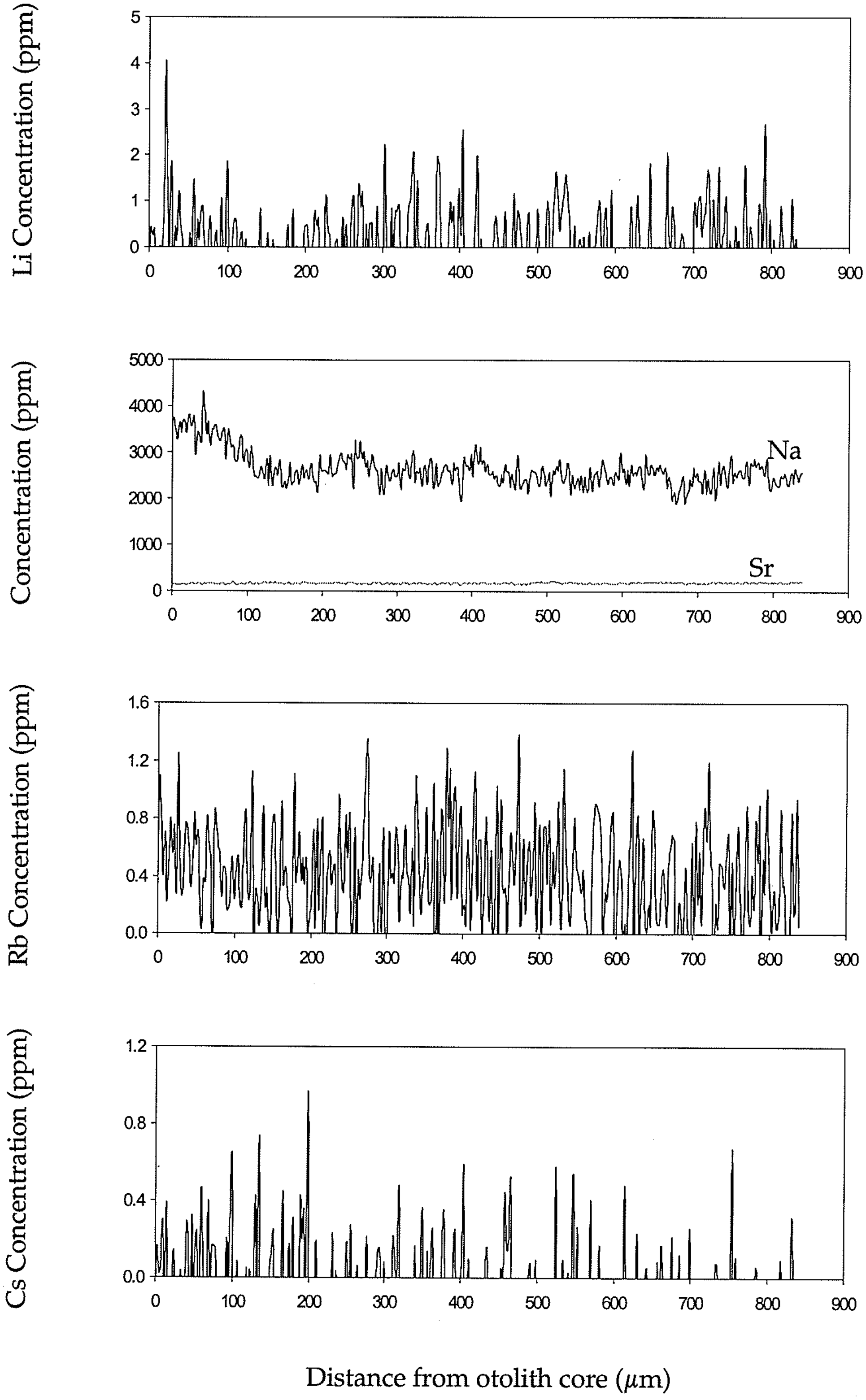


Li Concentration (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
Cs Concentration (ppm)
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

LDB96_151


Li Concentration (ppm)
3
2
1
0
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
Cs Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
600
700
800
900
Distance from otolith core (μm)

LDB96_152


Li Concentration (ppm)
0
1
2
3
4
5
0
100
200
300
400
500
600
700
800
900
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
100
200
300
400
500
600
700
800
900
Rb Concentration (ppm)
0.0
0.4
0.8
1.2
1.6
0
100
200
300
400
500
600
700
800
900
Cs Concentration (ppm)
0.0
0.4
0.8
1.2
0
100
200
300
400
500
600
700
800
900
Distance from otolith core (μm)

Appendix H LA-ICP-MS data for Bird River Downstream otoliths

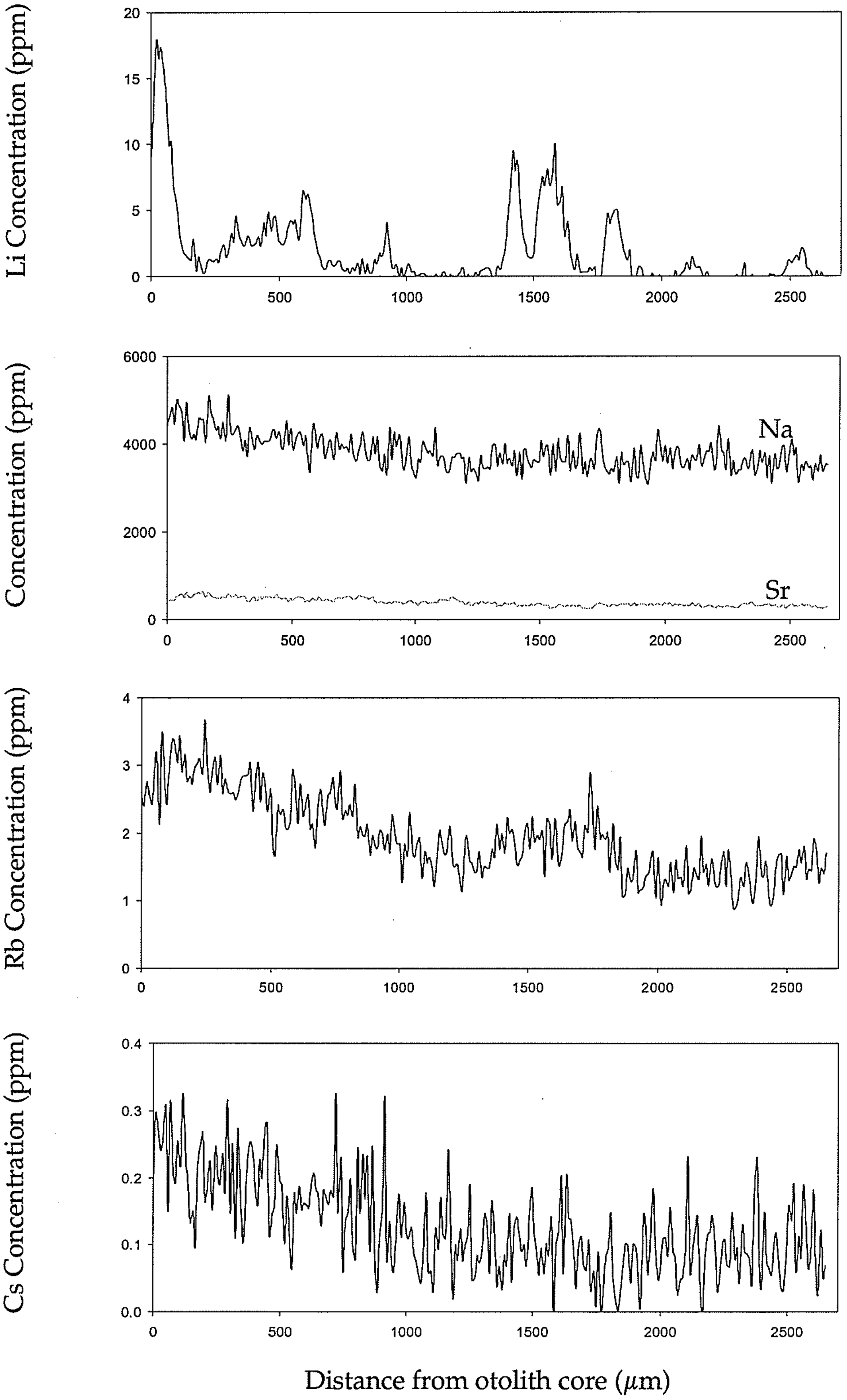
Species: Walleye (*Sander vitreous*), Northern Pike (*Esox lucius*)

Captured: 1998 (TetrES Consultants, Inc.)

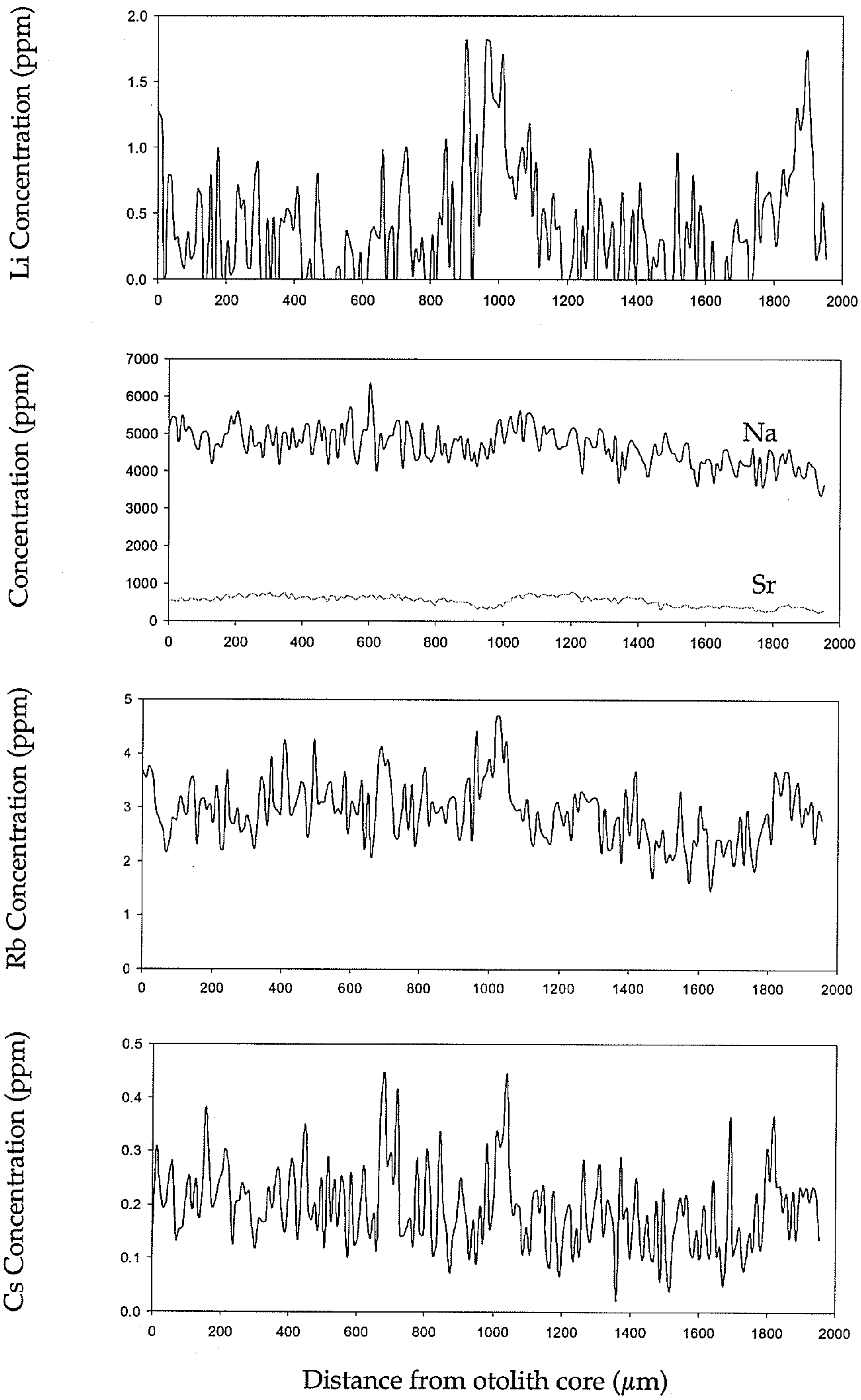
Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
04	Northern Pike	7
05	Walleye	6
06	Walleye	5
07	Walleye	4
08	Northern Pike	9
10	Northern Pike	4

BRDown98_04

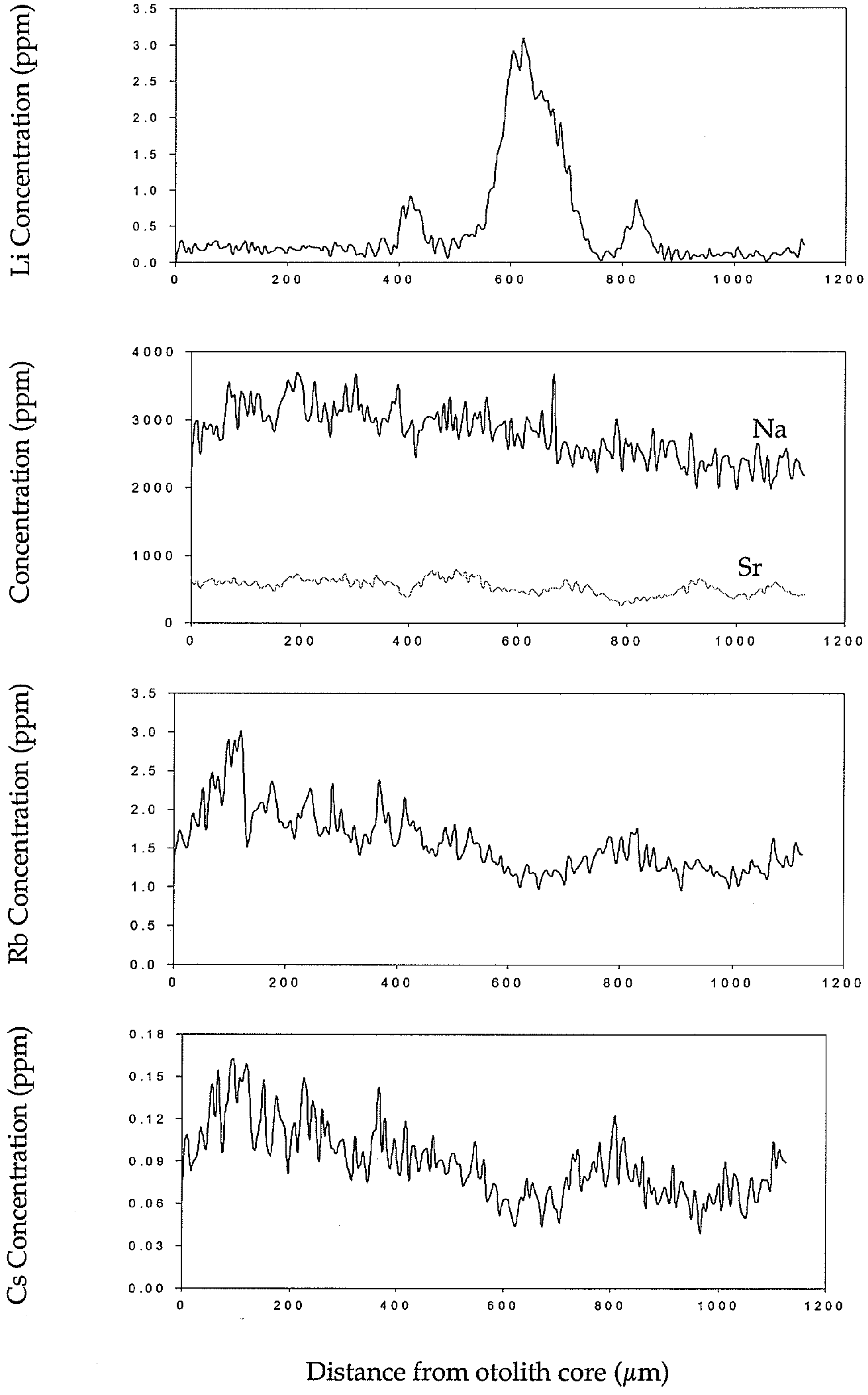

Li Concentration (ppm)
20
15
10
5
0
0
500
1000
1500
2000
2500
Concentration (ppm)
6000
4000
2000
0
Na
Sr
0
500
1000
1500
2000
2500
Rb Concentration (ppm)
4
3
2
1
0
0
500
1000
1500
2000
2500
Cs Concentration (ppm)
0.4
0.3
0.2
0.1
0.0
0
500
1000
1500
2000
2500
Distance from otolith core (μm)

BRDown98_05

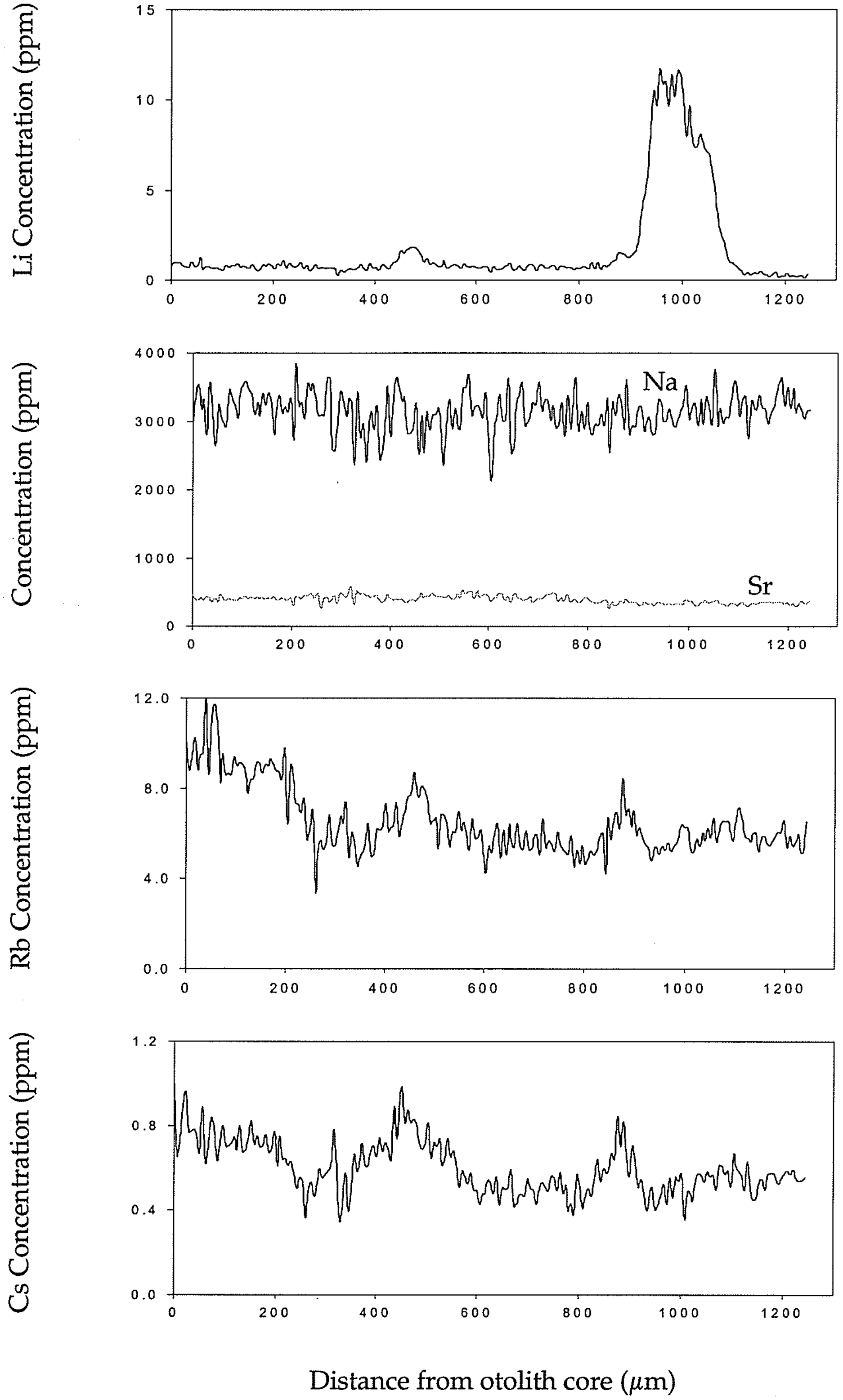


Li Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
Concentration (ppm)
7000
6000
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
5
4
3
2
1
0
Cs Concentration (ppm)
0.5
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Distance from otolith core (μm)

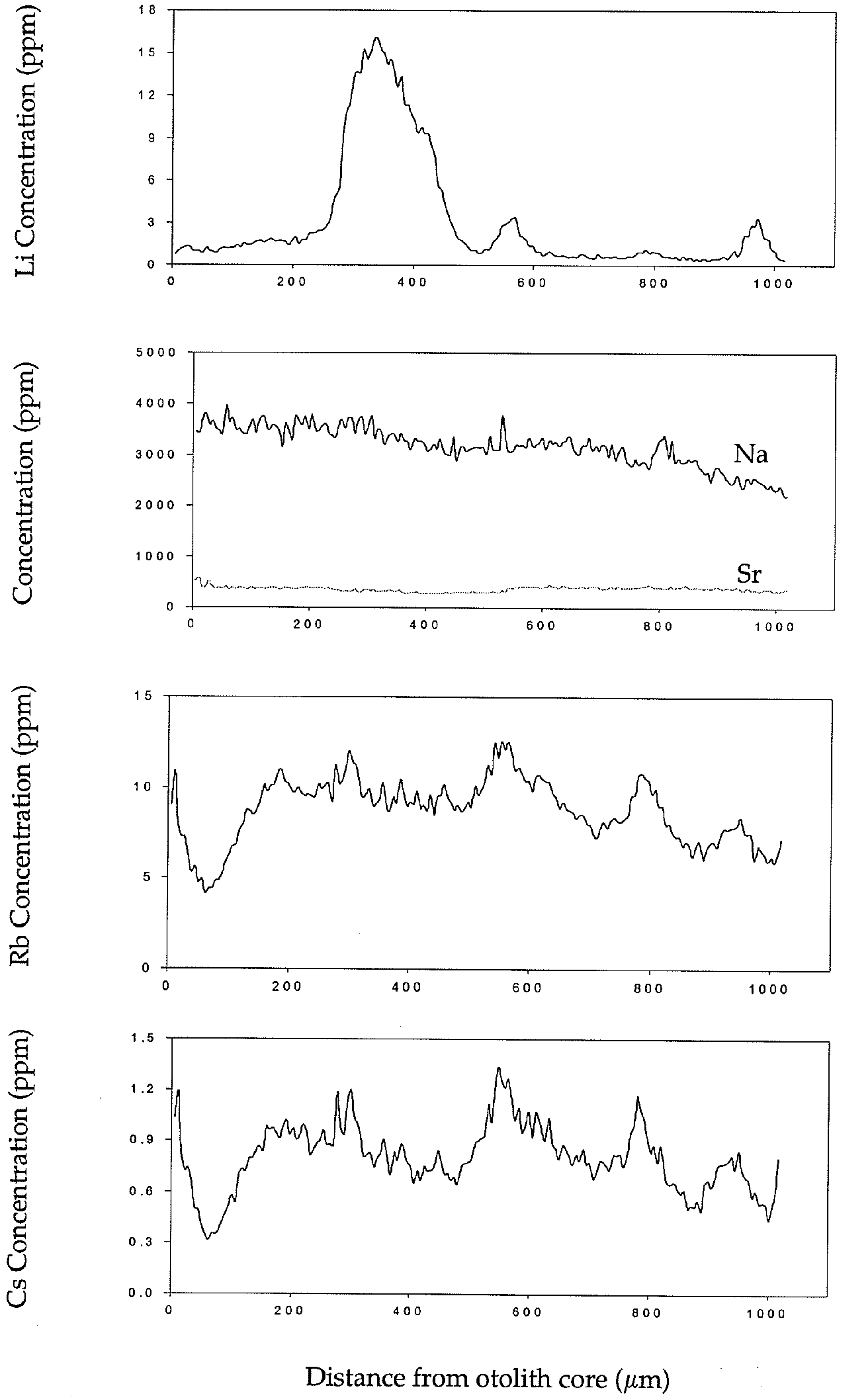
BRDown98_06


Li Concentration (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
Cs Concentration (ppm)
0.18
0.15
0.12
0.09
0.06
0.03
0.00
Distance from otolith core (µm)

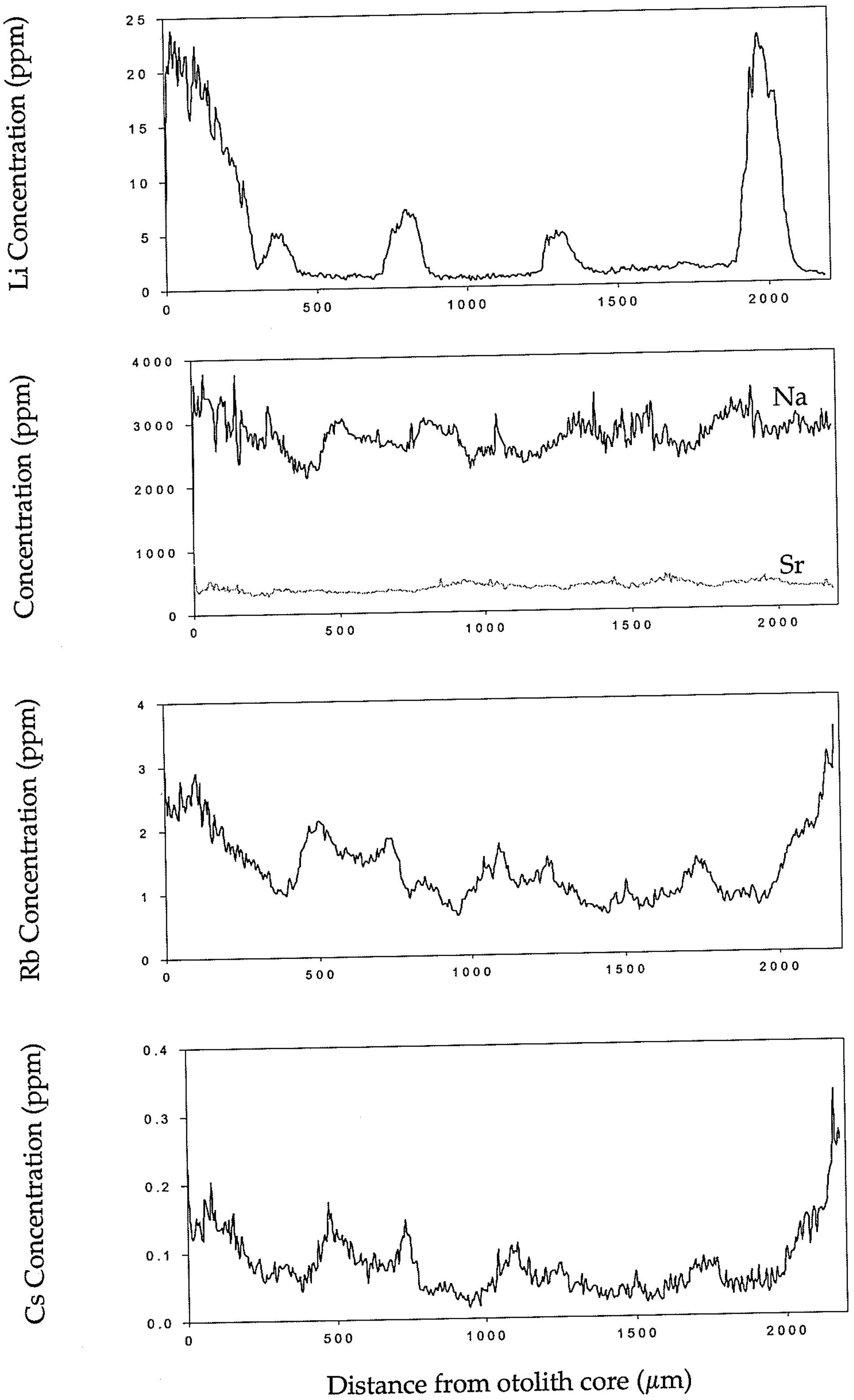
BRDown98_07


Li Concentration (ppm)
15
10
5
0
0
200
400
600
800
1000
1200
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
12.0
8.0
4.0
0.0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

BRDown98_08


Li Concentration (ppm)
0
3
6
9
12
15
18
0
200
400
600
800
1000
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
0
5
10
15
0
200
400
600
800
1000
Cs Concentration (ppm)
0.0
0.3
0.6
0.9
1.2
1.5
0
200
400
600
800
1000
Distance from otolith core (μm)

BRDown98_10


Li Concentration (ppm)
25
20
15
10
5
0
0
500
1000
1500
2000
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
4
3
2
1
0
0
500
1000
1500
2000
Cs Concentration (ppm)
0.4
0.3
0.2
0.1
0.0
0
500
1000
1500
2000
Distance from otolith core (μm)

Appendix I LA-ICP-MS data for Bernic Lake otoliths

Species: Northern Pike (*Esox lucius*), Cisco (*Coregonus artedii*), Yellow Perch (*Perca flavescens*), White Sucker (*Catostomus commersoni*)

Captured: 2008

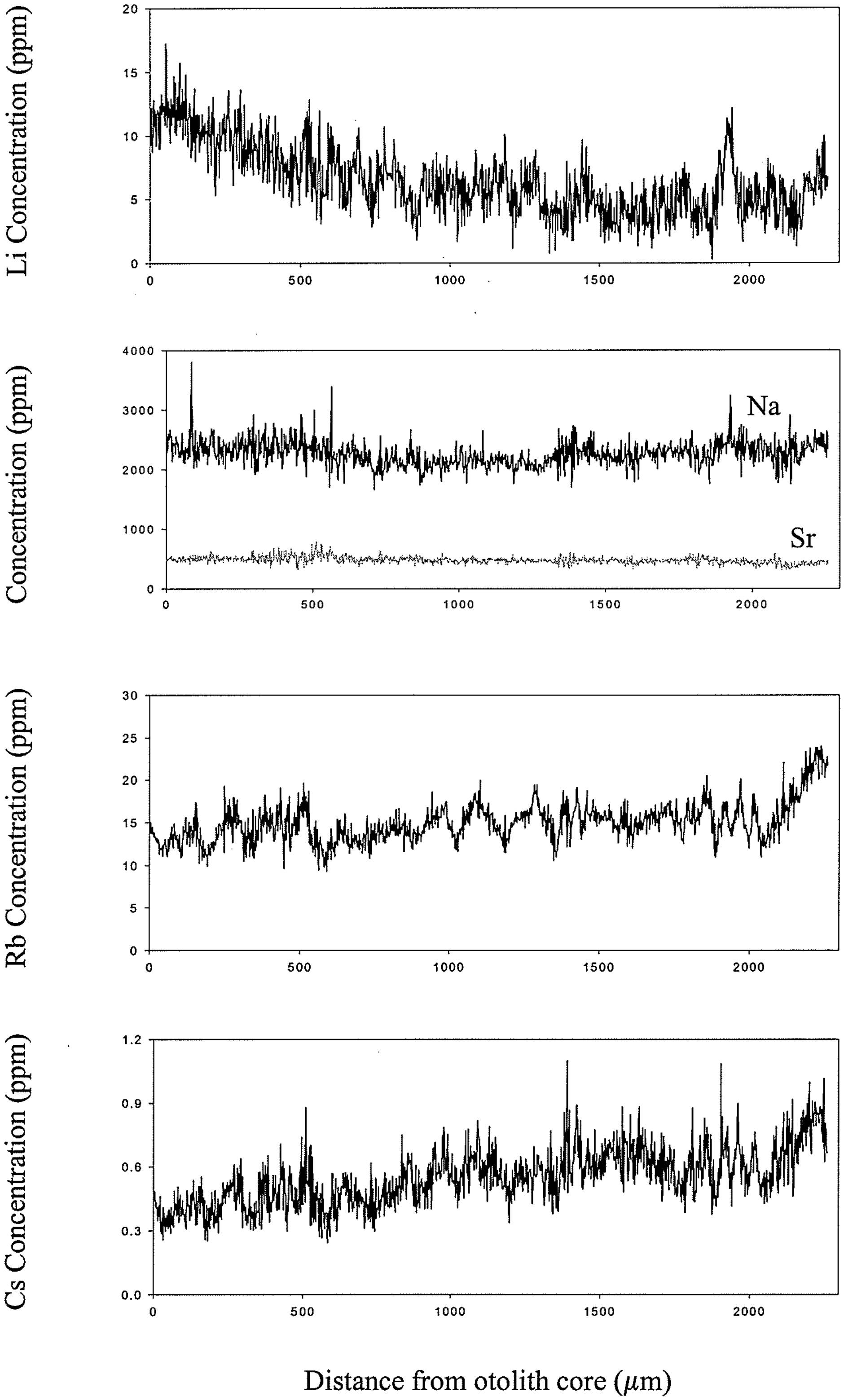
Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Location***	***Age***
BSS08-01	White Sucker	South Shore	9
BSS08-02	White Sucker	South Shore	8
BSS08-03	White Sucker	South Shore	8
BSS08-04	White Sucker	South Shore	11
BSS08-05	White Sucker	South Shore	6
BSS08-06	White Sucker	South Shore	11
BSS08-07	White Sucker	South Shore	9
BSS08-08	White Sucker	South Shore	8
BSS08-09	White Sucker	South Shore	8
BSS08-10	White Sucker	South Shore	7
BSS08-11	White Sucker	South Shore	4
BSS08-12	White Sucker	South Shore	12
BSS08-13	White Sucker	South Shore	8
BSS08-14	White Sucker	South Shore	14
BSS08-15	White Sucker	South Shore	11
BSS08-16	Yellow Perch	South Shore	5
BSS08-17	Yellow Perch	South Shore	5
BSS08-18	Yellow Perch	South Shore	8
BSS08-19	Yellow Perch	South Shore	5
BSS08-20	Yellow Perch	South Shore	7
BSS08-21	Yellow Perch	South Shore	8
BSS08-22	Yellow Perch	South Shore	8
BSS08-23	Yellow Perch	South Shore	8
BSS08-24	Yellow Perch	South Shore	7
BSS08-25	Yellow Perch	South Shore	10
BSS08-26	Yellow Perch	South Shore	9
BSS08-27	Yellow Perch	South Shore	5
BSS08-28	Yellow Perch	South Shore	6
BSS08-29	Yellow Perch	South Shore	5
BSS08-30	Yellow Perch	South Shore	7

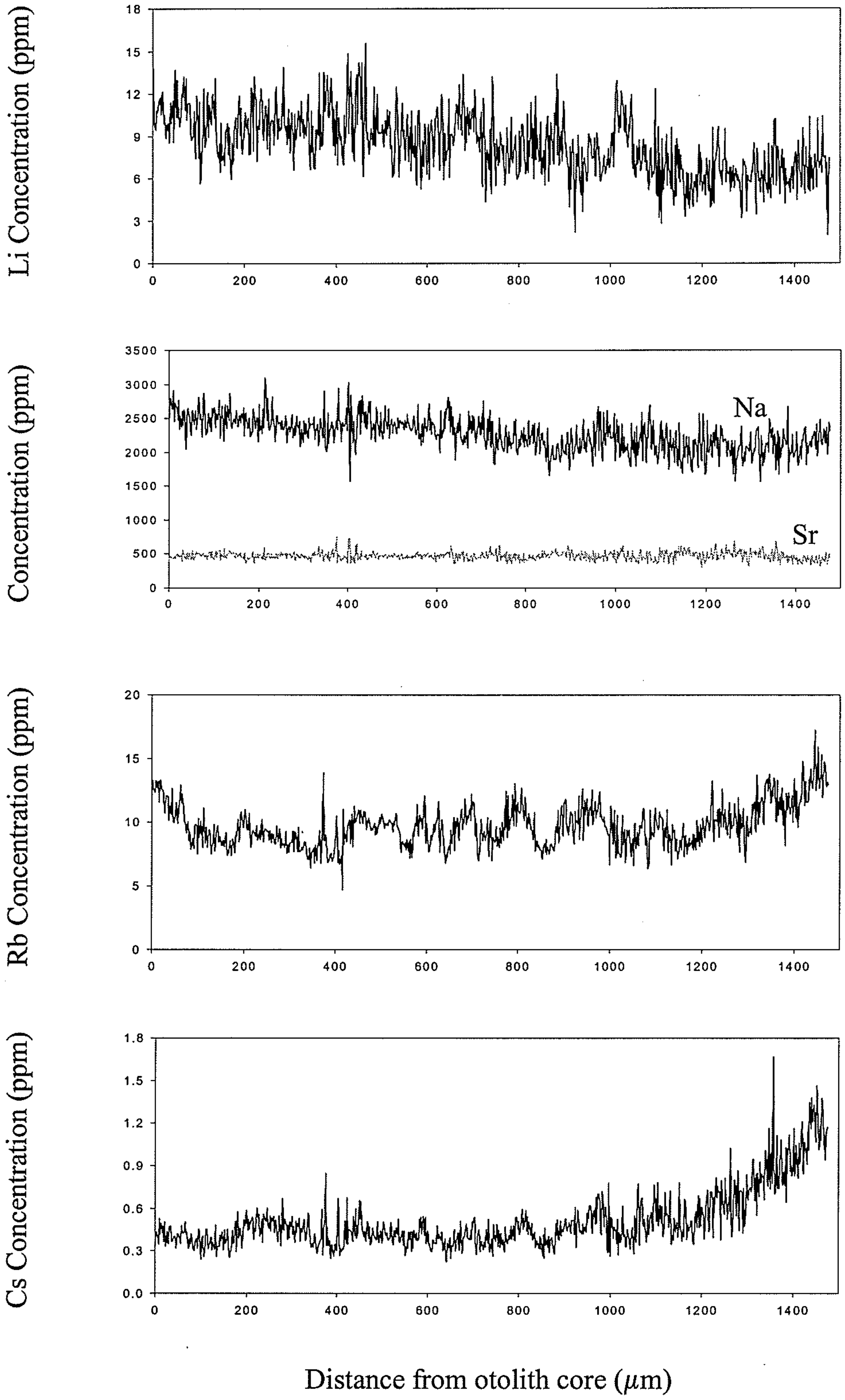
BSS08-31	Yellow Perch	South Shore	5
BSS08-32	Yellow Perch	South Shore	5
BSS08-33	Yellow Perch	South Shore	8
BSS08-34	Yellow Perch	South Shore	6
B08-01	Yellow Perch	Narrows	5
B08-02	Yellow Perch	Narrows	3
B08-03	Yellow Perch	Narrows	3
B08-04	Yellow Perch	Narrows	3
B08-05	Yellow Perch	Narrows	5
B08-06	Yellow Perch	Narrows	4
B08-07	Yellow Perch	Narrows	4
B08-08	Yellow Perch	Narrows	5
B08-09	Yellow Perch	Narrows	6
B08-10	Yellow Perch	Narrows	5
B08-11	Yellow Perch	Narrows	8
B08-12	Yellow Perch	Narrows	5
B08-13	Yellow Perch	Narrows	4
B08-14	Yellow Perch	Narrows	5
B08-15	Yellow Perch	Narrows	6
B08-16	Yellow Perch	Narrows	4
B08-17	Yellow Perch	Narrows	3
B08-18	Yellow Perch	Narrows	3
B08-19	Yellow Perch	Narrows	8
B08-20	Yellow Perch	Narrows	3
B08-21	Yellow Perch	Narrows	3
B08-22	Yellow Perch	Narrows	8
B08-23	Yellow Perch	Narrows	5
B08-24	Cisco	Narrows	3
B08-25	Yellow Perch	Narrows	7
B08-26	Yellow Perch	Narrows	5
B08-27	Yellow Perch	Narrows	4
B08-28	Yellow Perch	Narrows	6
B08-29	Yellow Perch	Narrows	8
B08-30	Northern Pike	Narrows	10
B08-31	White Sucker	Narrows	9
B08-32	White Sucker	Narrows	7
B08-33	White Sucker	Narrows	7
B08-34	White Sucker	Narrows	8
B08-35	Northern Pike	Narrows	7
B08-36	White Sucker	Narrows	7
B08-37	White Sucker	Narrows	8
B08-38	White Sucker	Narrows	6
B08-39	Yellow Perch	Narrows	4
B08-40	White Sucker	Narrows	9
B08-41	White Sucker	Narrows	8

BM08-01	Yellow Perch	Across from Mine	8
BM08-02	Yellow Perch	Across from Mine	5
BM08-03	Yellow Perch	Across from Mine	4
BM08-04	Yellow Perch	Across from Mine	4
BM08-05	Yellow Perch	Across from Mine	3
BM08-06	Yellow Perch	Across from Mine	4
BM08-07	Yellow Perch	Across from Mine	4
BM08-08	Yellow Perch	Across from Mine	4
BM08-09	Yellow Perch	Across from Mine	4
BL08-01	White Sucker	Across from Mine	10
BL08-02	White Sucker	Across from Mine	9
BL08-03	White Sucker	Across from Mine	9
BL08-04	Yellow Perch	Across from Mine	8
BL08-05	Yellow Perch	Across from Mine	3
BL08-06	Yellow Perch	Across from Mine	2
BL08-07	Yellow Perch	Across from Mine	3

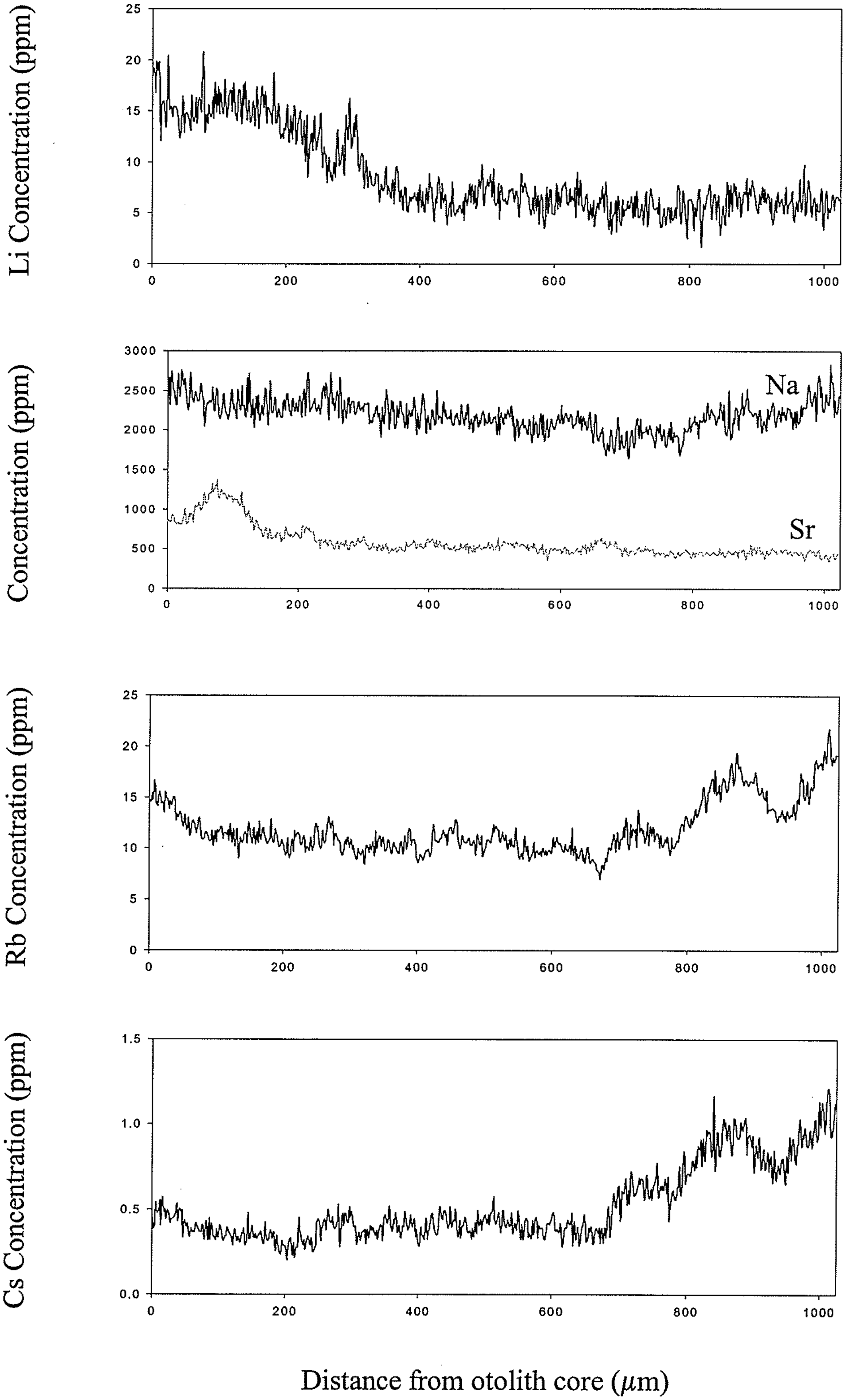
BSS08_01


Li Concentration (ppm)
20
15
10
5
0
0
500
1000
1500
2000
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
30
25
20
15
10
5
0
0
500
1000
1500
2000
Cs Concentration (ppm)
1.2
0.9
0.6
0.3
0.0
0
500
1000
1500
2000
Distance from otolith core (μm)

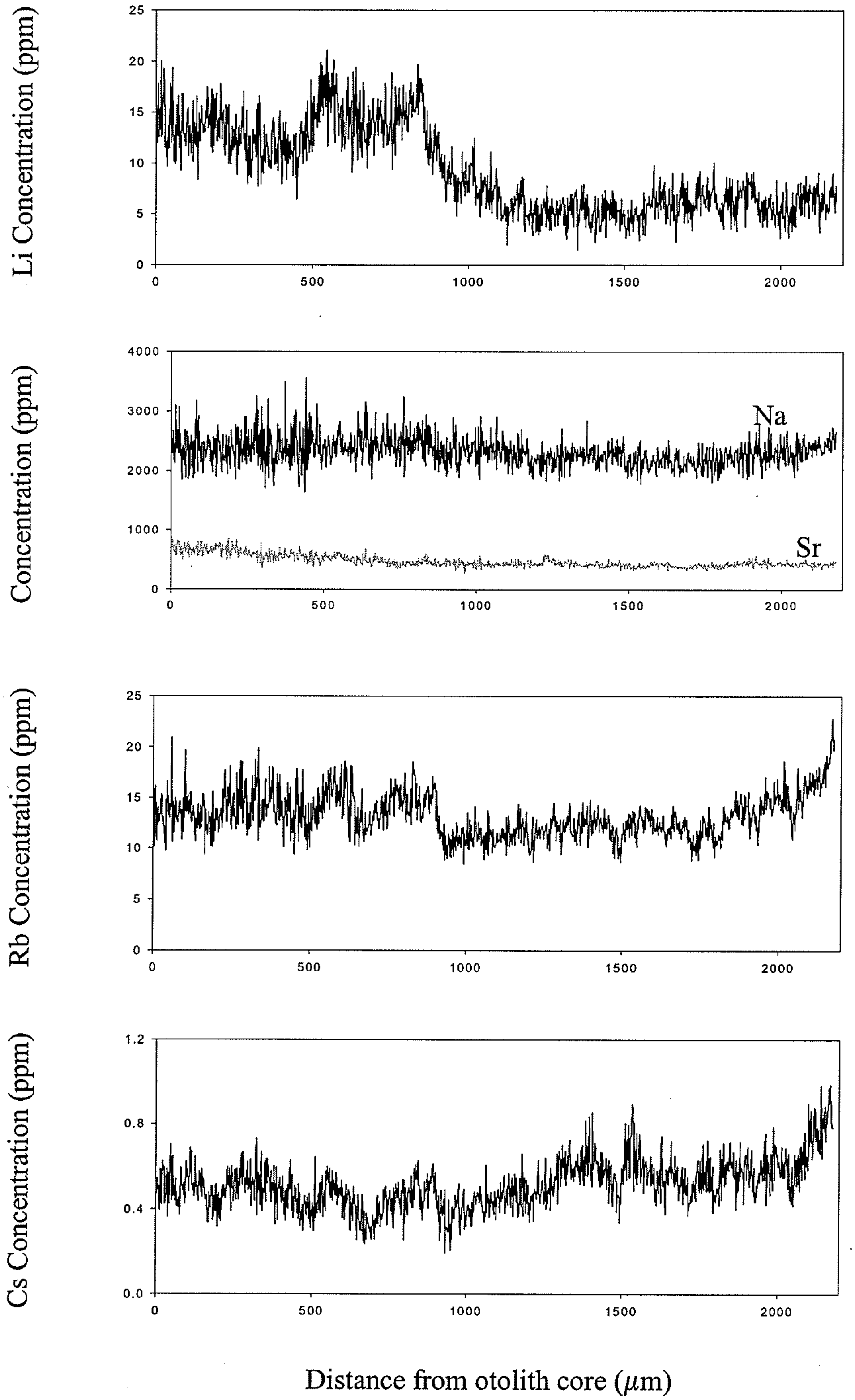
BSS08_02


Li Concentration (ppm)
18
15
12
9
6
3
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

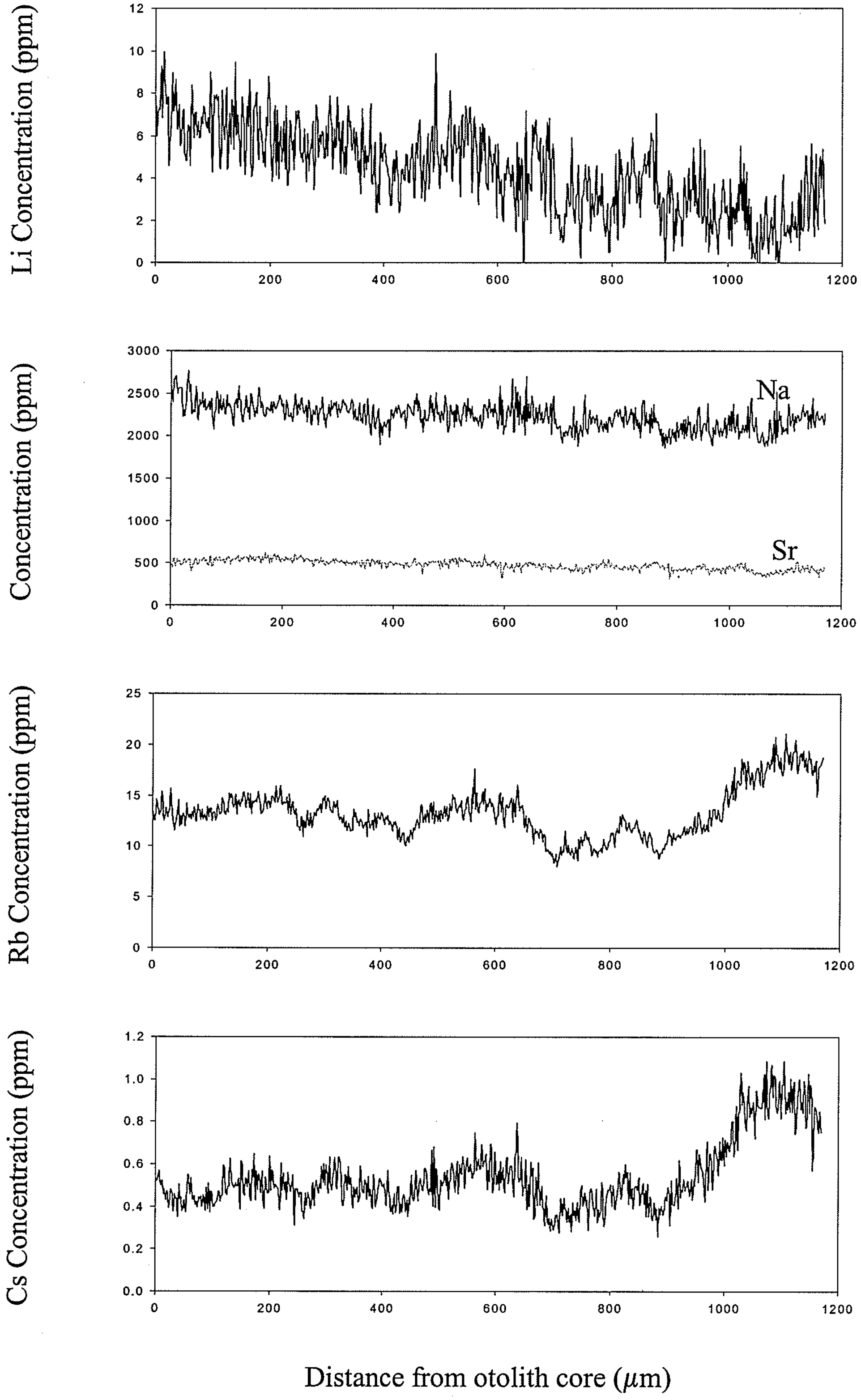
BSS08_03


Li Concentration (ppm)
25
20
15
10
5
0
0
200
400
600
800
1000
Concentration (ppm)
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
25
20
15
10
5
0
0
200
400
600
800
1000
Cs Concentration (ppm)
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Distance from otolith core (µm)

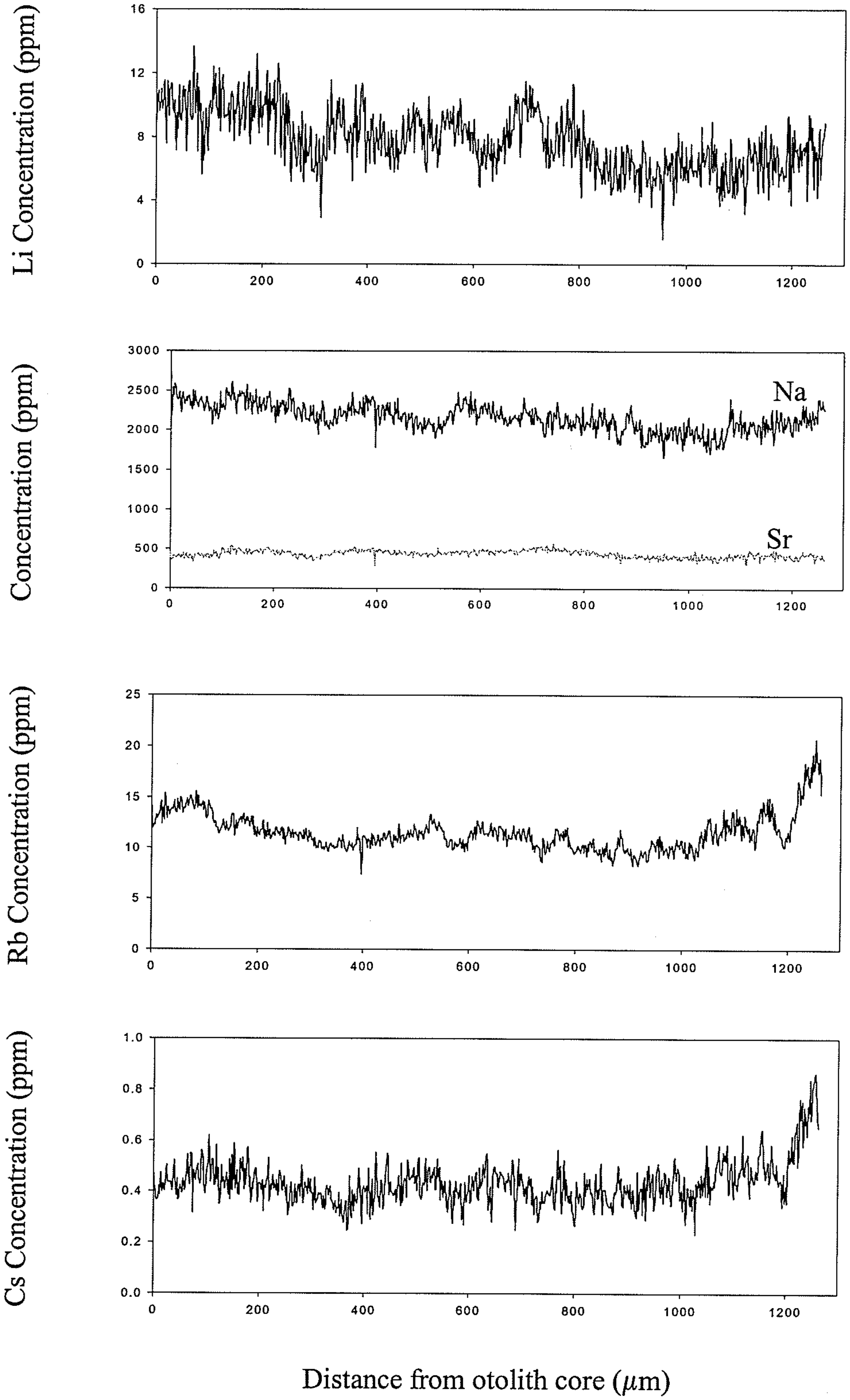
BSS08_04


Li Concentration (ppm)
25
20
15
10
5
0
0
500
1000
1500
2000
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
25
20
15
10
5
0
0
500
1000
1500
2000
Cs Concentration (ppm)
1.2
0.8
0.4
0.0
0
500
1000
1500
2000
Distance from otolith core (μm)

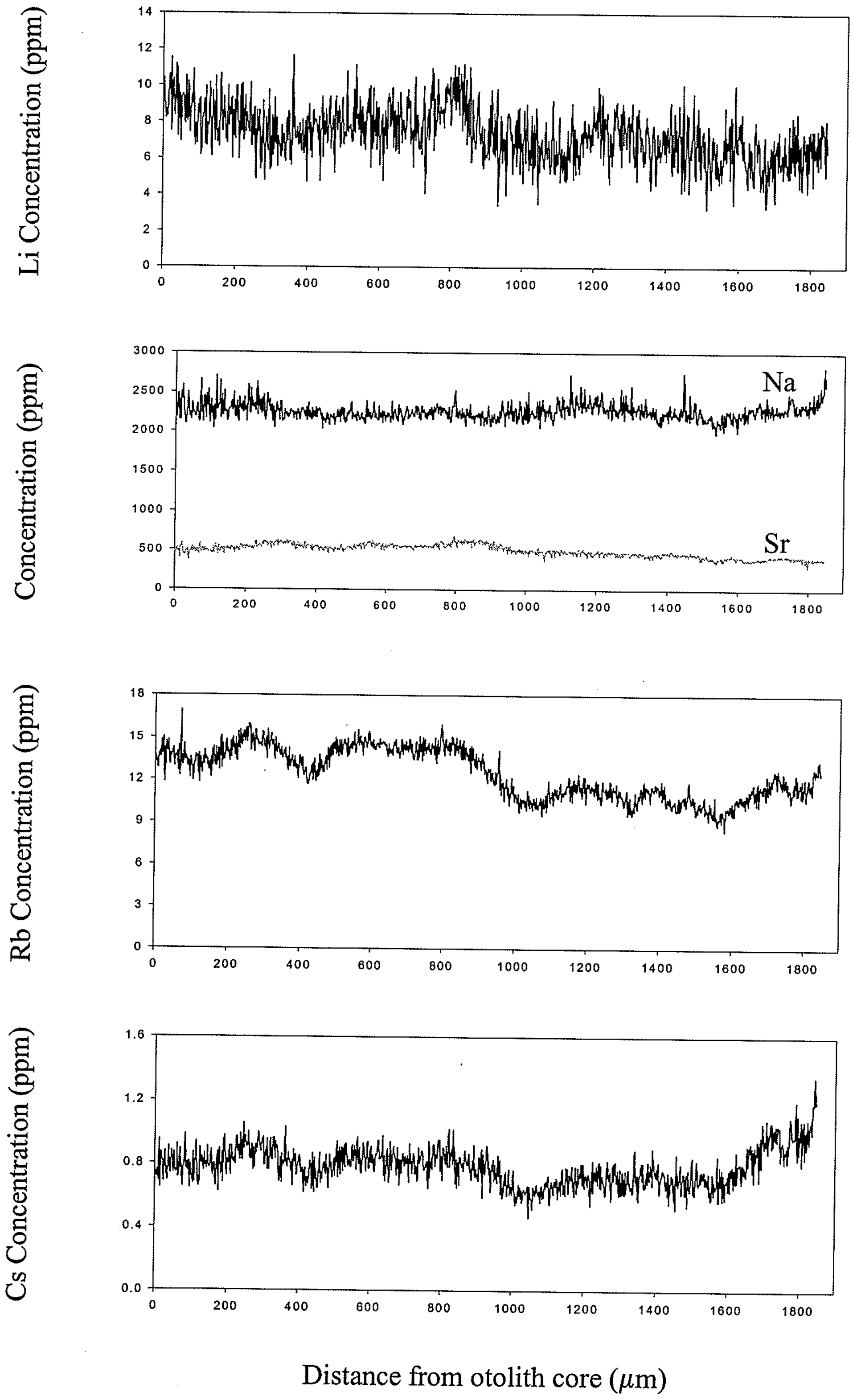
BSS08_05


Li Concentration (ppm)
0
2
4
6
8
10
12
Concentration (ppm)
0
500
1000
1500
2000
2500
3000
Na
Sr
Rb Concentration (ppm)
0
5
10
15
20
25
Cs Concentration (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

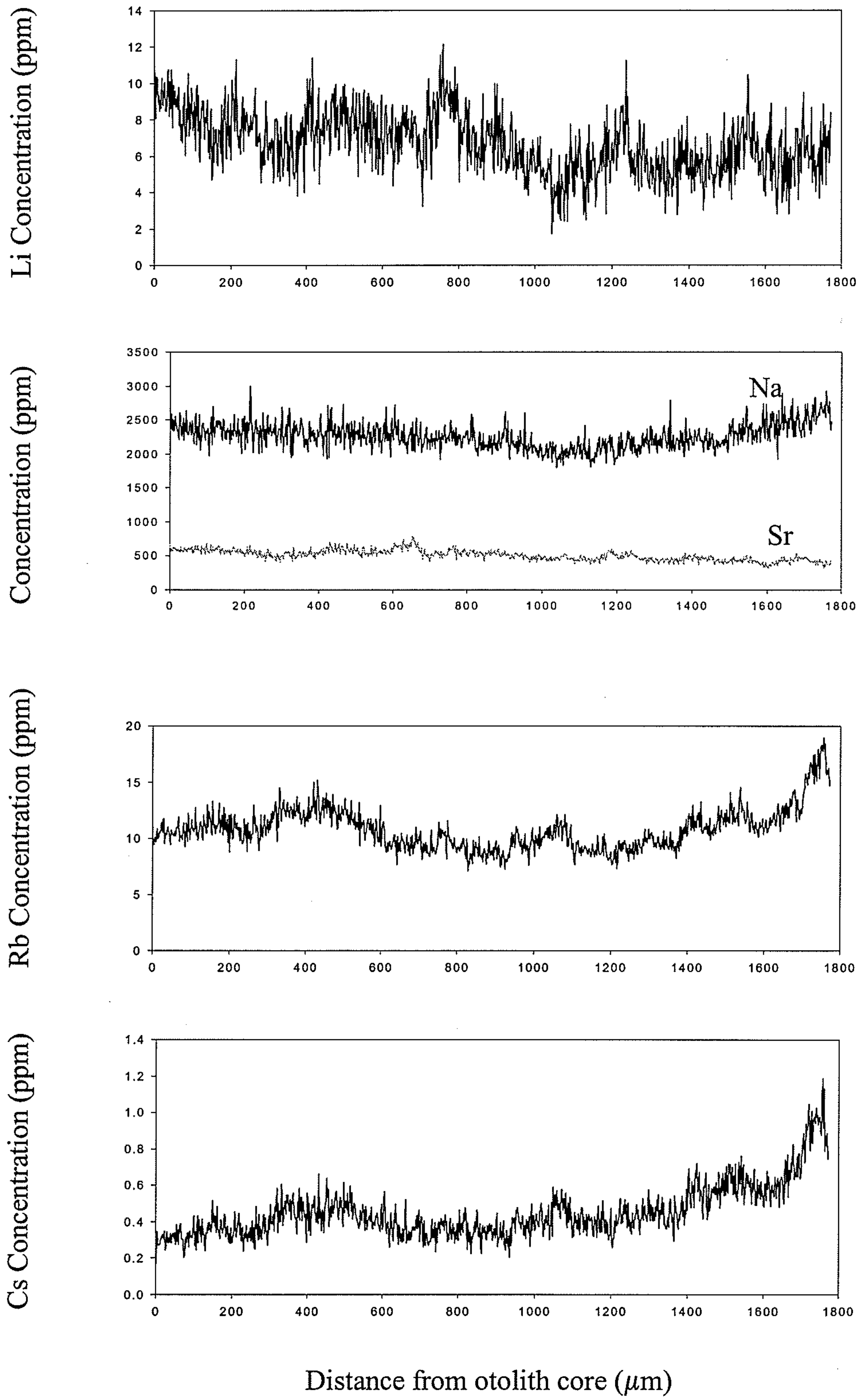
BSS08_06


Li Concentration (ppm)
16
12
8
4
0
0
200
400
600
800
1000
1200
Concentration (ppm)
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
25
20
15
10
5
0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

BSS08_07

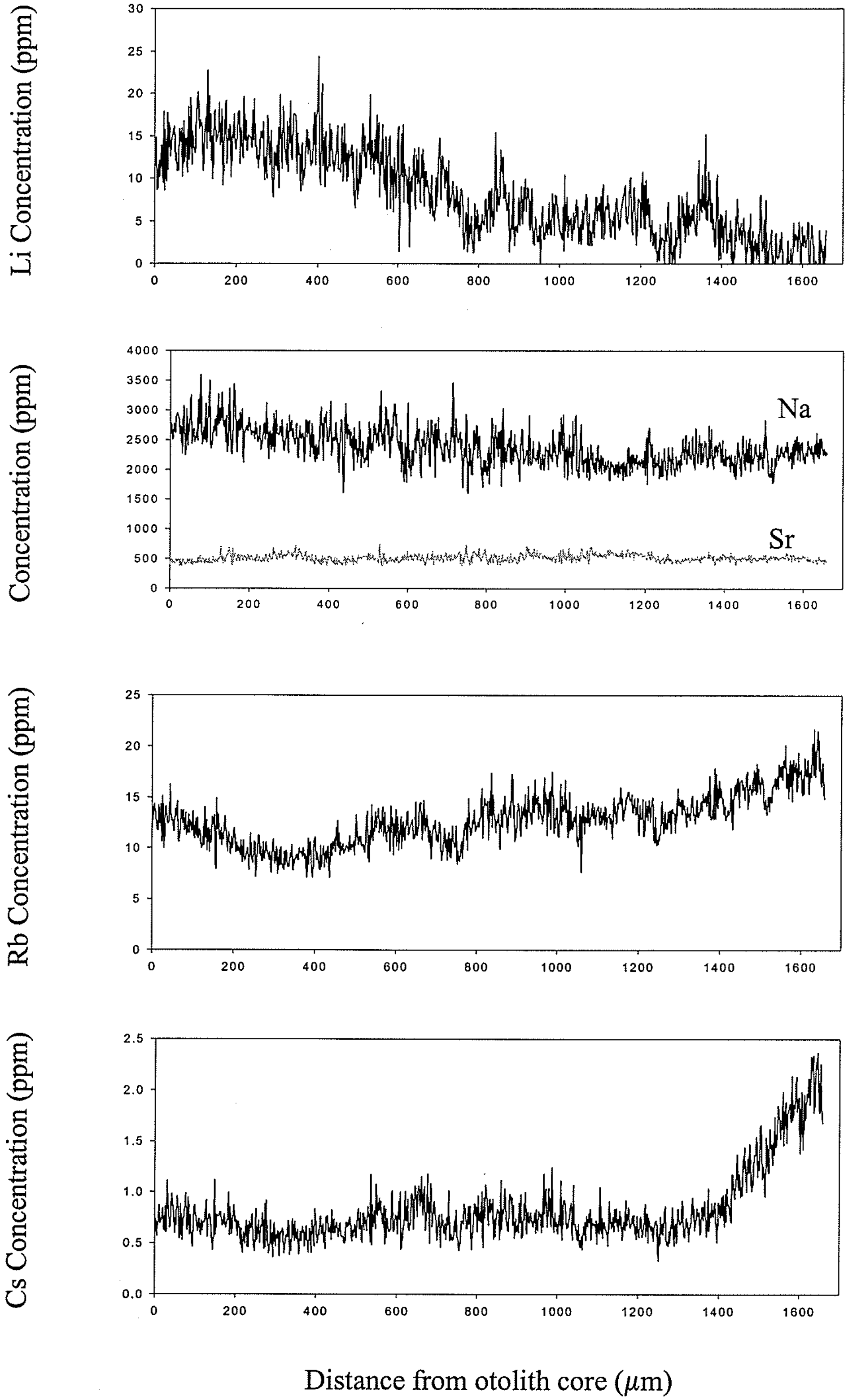

Li Concentration (ppm)
14
12
10
8
6
4
2
0
0
200
400
600
800
1000
1200
1400
1600
1800
Concentration (ppm)
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
1800
Rb Concentration (ppm)
18
15
12
9
6
3
0
0
200
400
600
800
1000
1200
1400
1600
1800
Cs Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
Distance from otolith core (μm)

BSS08_08

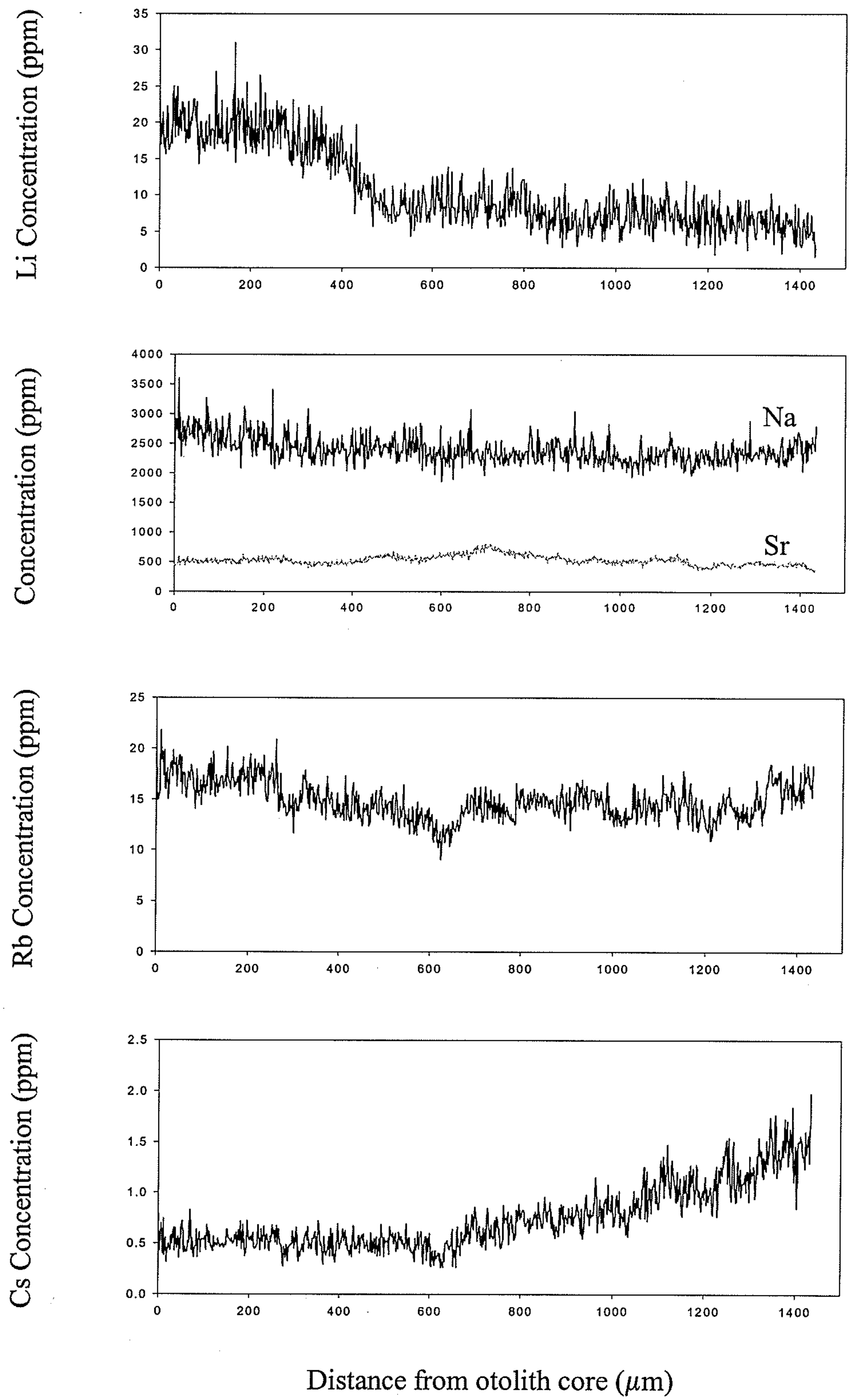


Li Concentration (ppm)
14
12
10
8
6
4
2
0
Concentration (ppm)
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
Rb Concentration (ppm)
20
15
10
5
0
Cs Concentration (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
Distance from otolith core (μm)

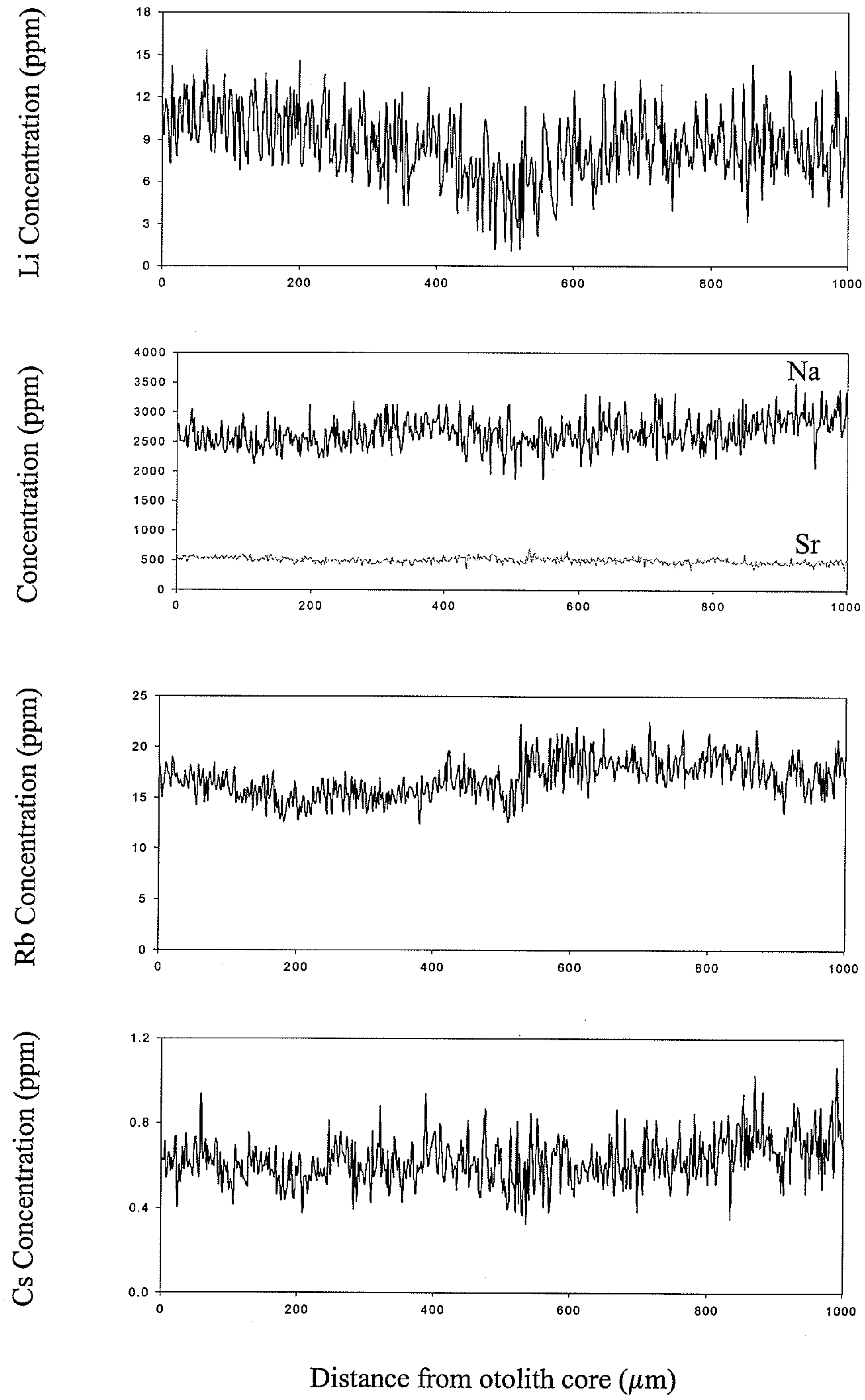
BSS08_09


Li Concentration (ppm)
0
5
10
15
20
25
30
Concentration (ppm)
0
500
1000
1500
2000
2500
3000
3500
4000
Na
Sr
Rb Concentration (ppm)
0
5
10
15
20
25
Cs Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

BSS08_10

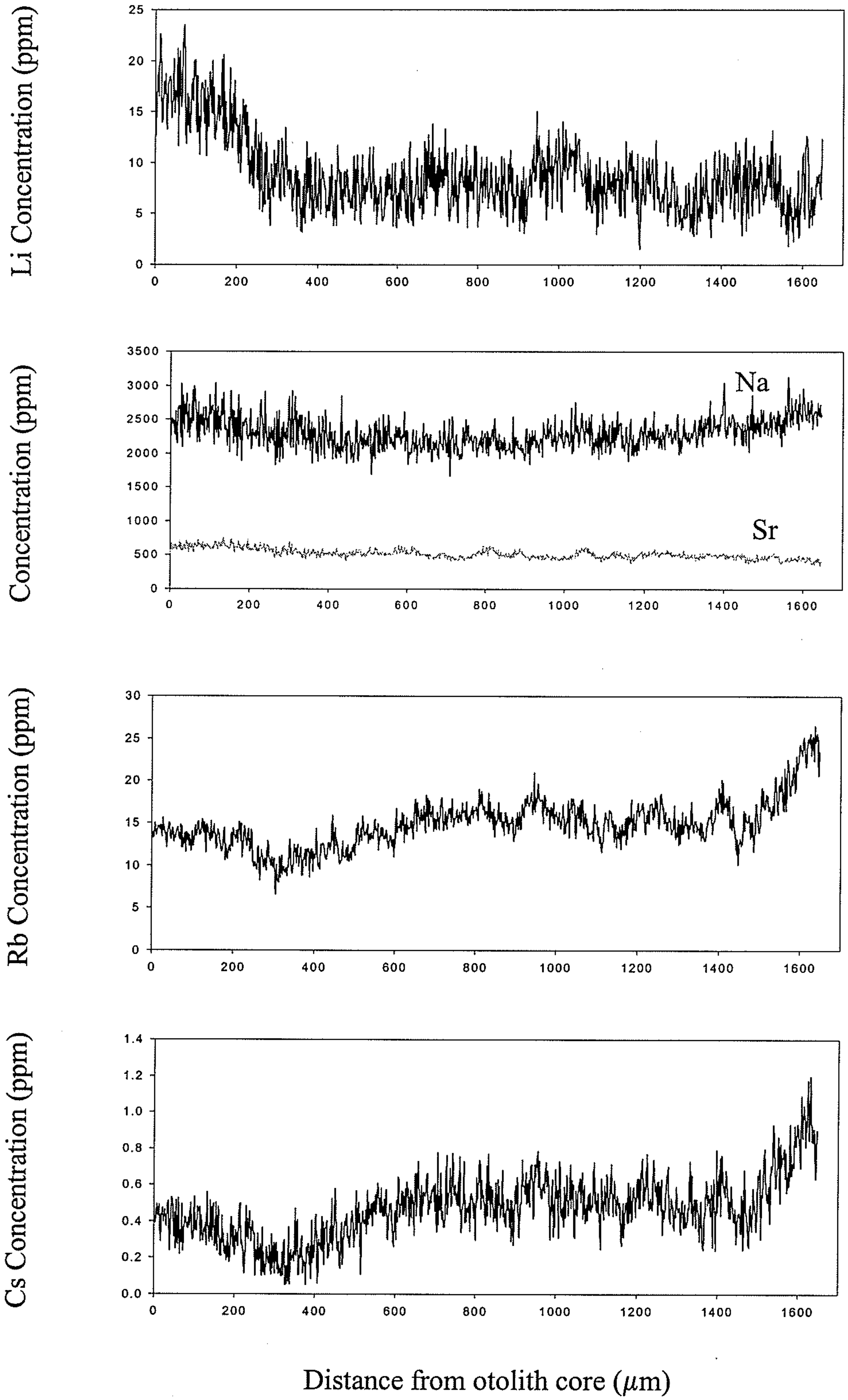

Li Concentration (ppm)
0
5
10
15
20
25
30
35
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
Na
Sr
0
500
1000
1500
2000
2500
3000
3500
4000
Rb Concentration (ppm)
0
5
10
15
20
25
Cs Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
Distance from otolith core (μm)

BSS08_11

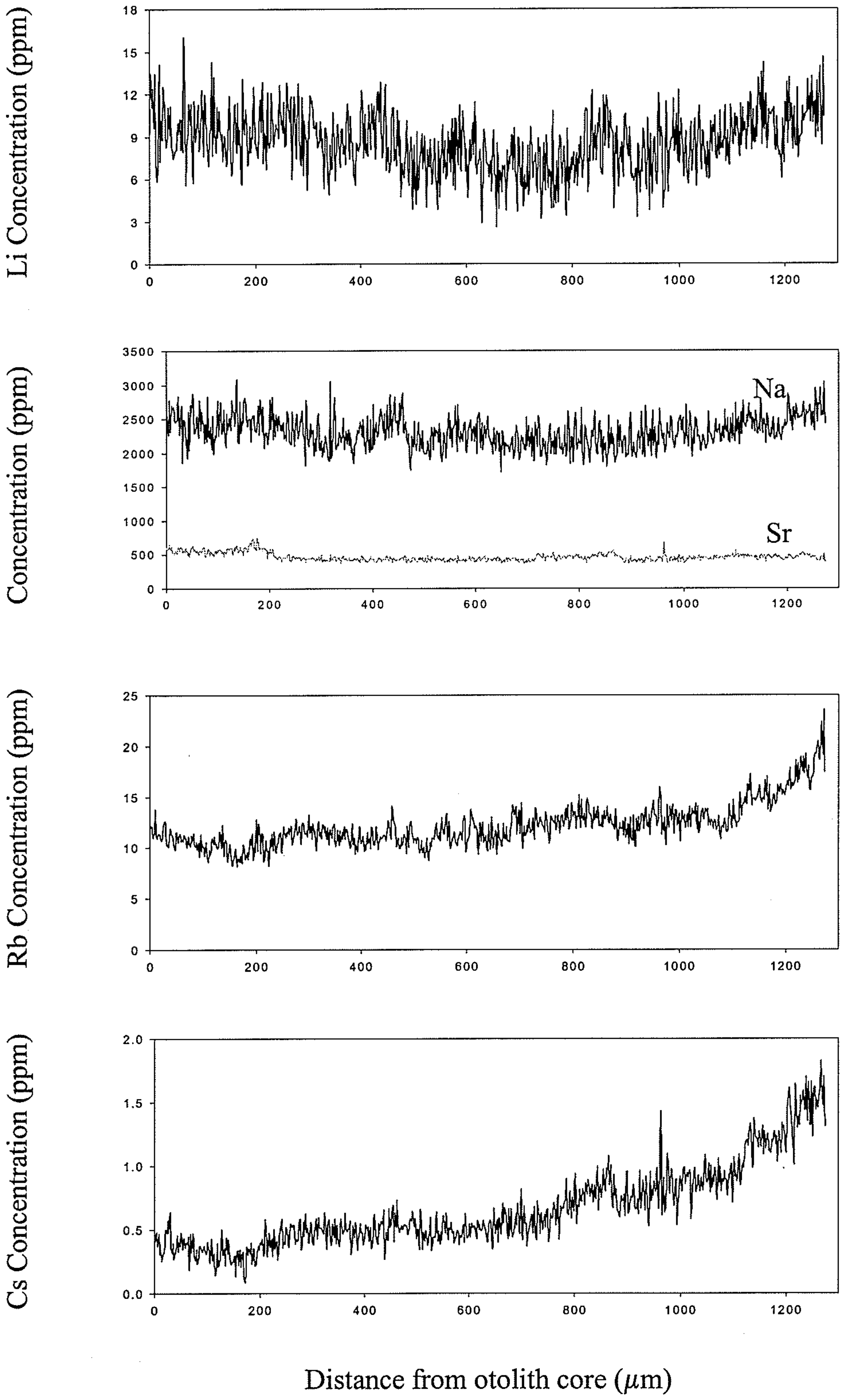


Li Concentration (ppm)
18
15
12
9
6
3
0
Concentration (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
Rb Concentration (ppm)
25
20
15
10
5
0
Cs Concentration (ppm)
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

BSS08_12

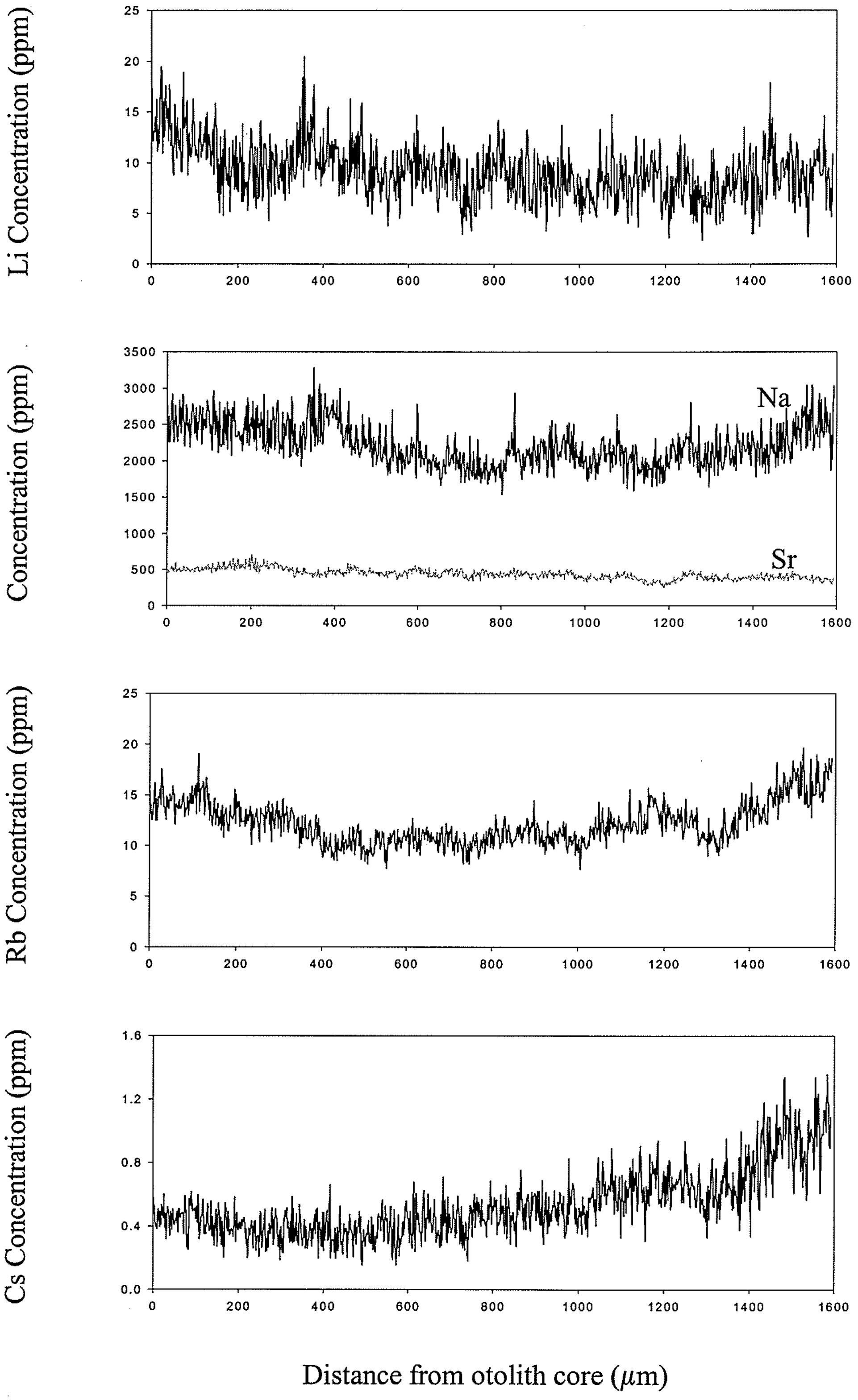

Li Concentration (ppm)
0
5
10
15
20
25
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
Na
Sr
0
500
1000
1500
2000
2500
3000
3500
Rb Concentration (ppm)
0
5
10
15
20
25
30
Cs Concentration (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
Distance from otolith core (μm)

BSS08_13

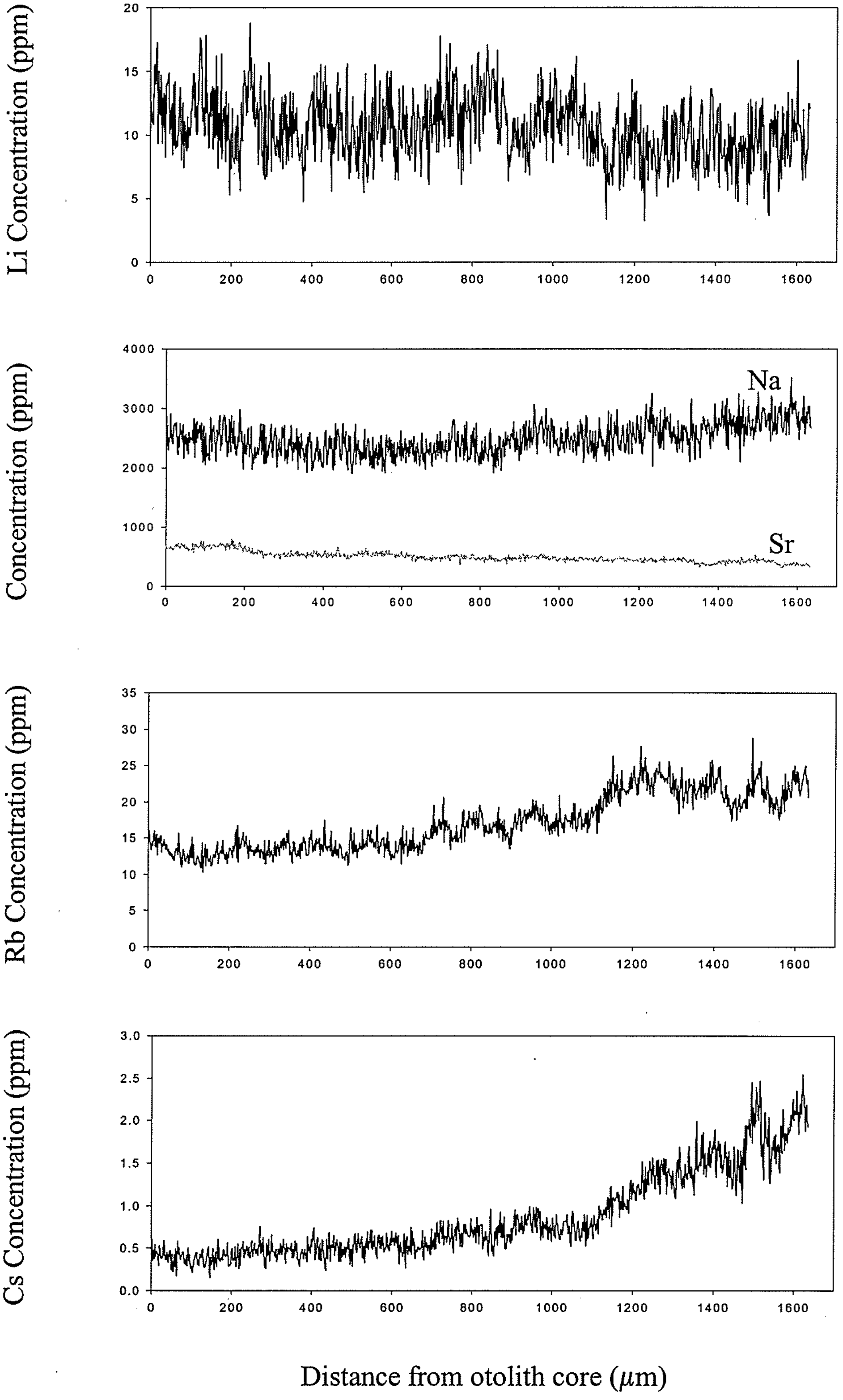


Li Concentration (ppm)
18
15
12
9
6
3
0
0
200
400
600
800
1000
1200
Concentration (ppm)
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
25
20
15
10
5
0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

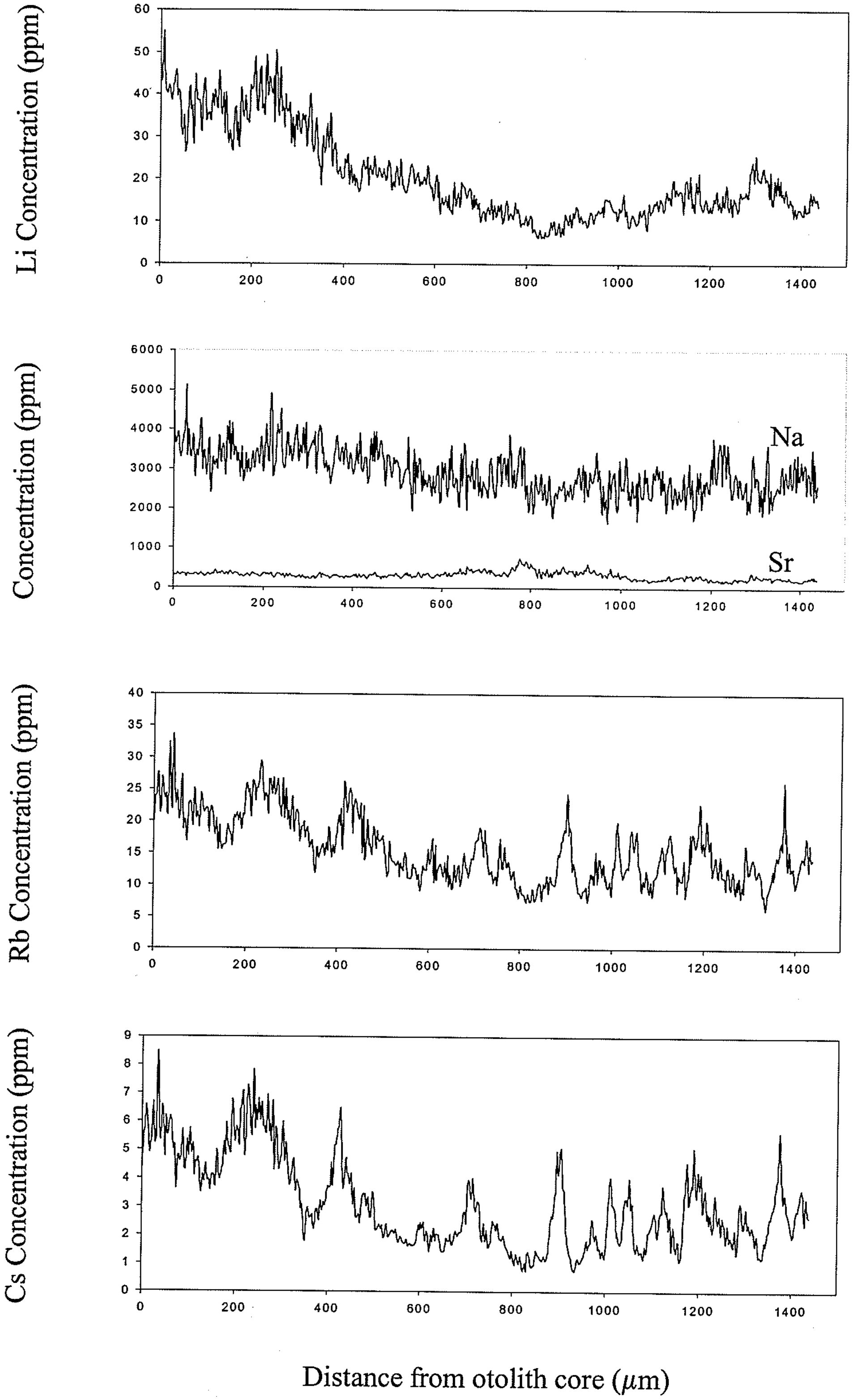
BSS08_14


Li Concentration (ppm)
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
Rb Concentration (ppm)
Cs Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
Distance from otolith core (μm)

BSS08_15

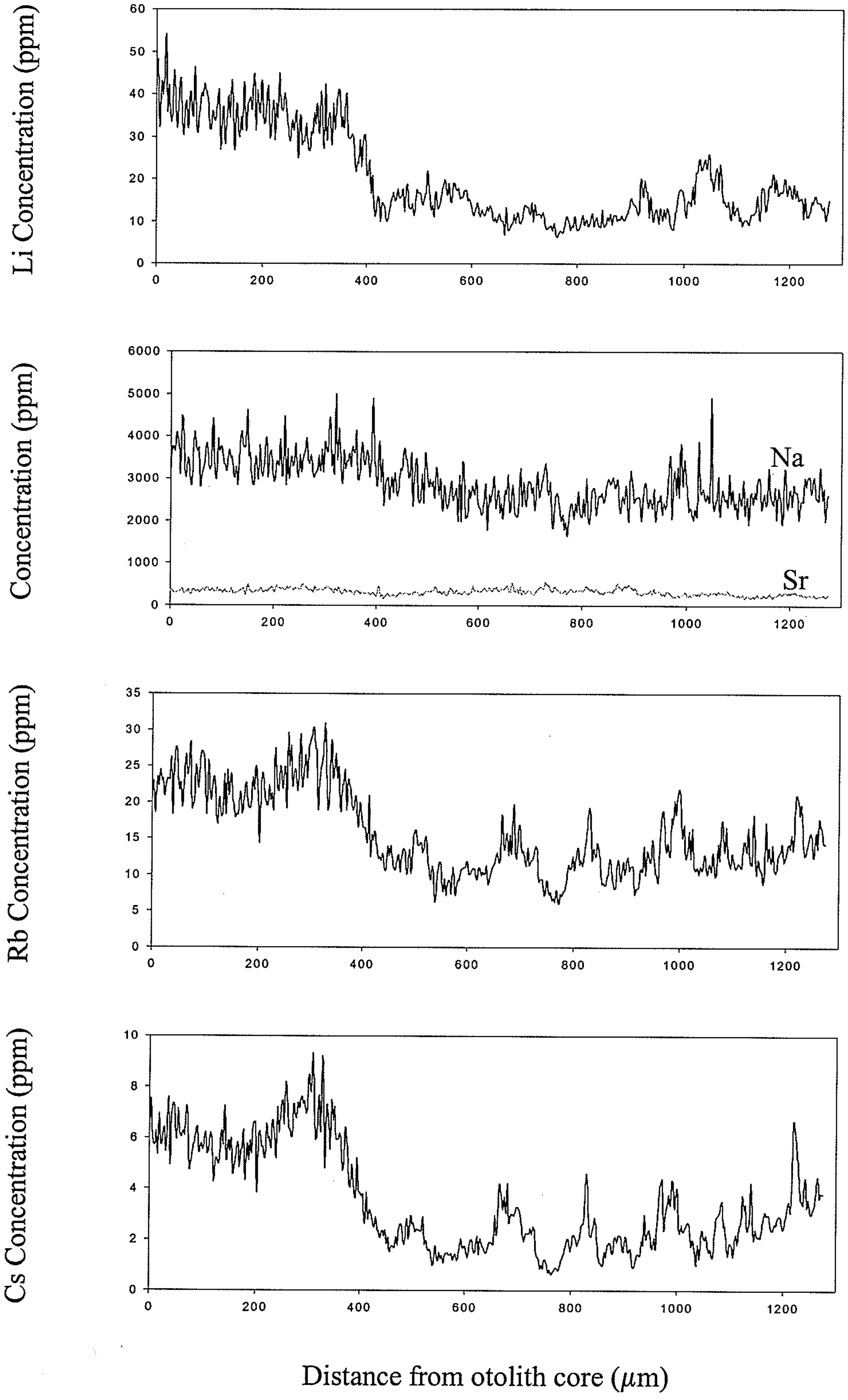

Li Concentration (ppm)
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
Rb Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
Cs Concentration (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

BSS08_16

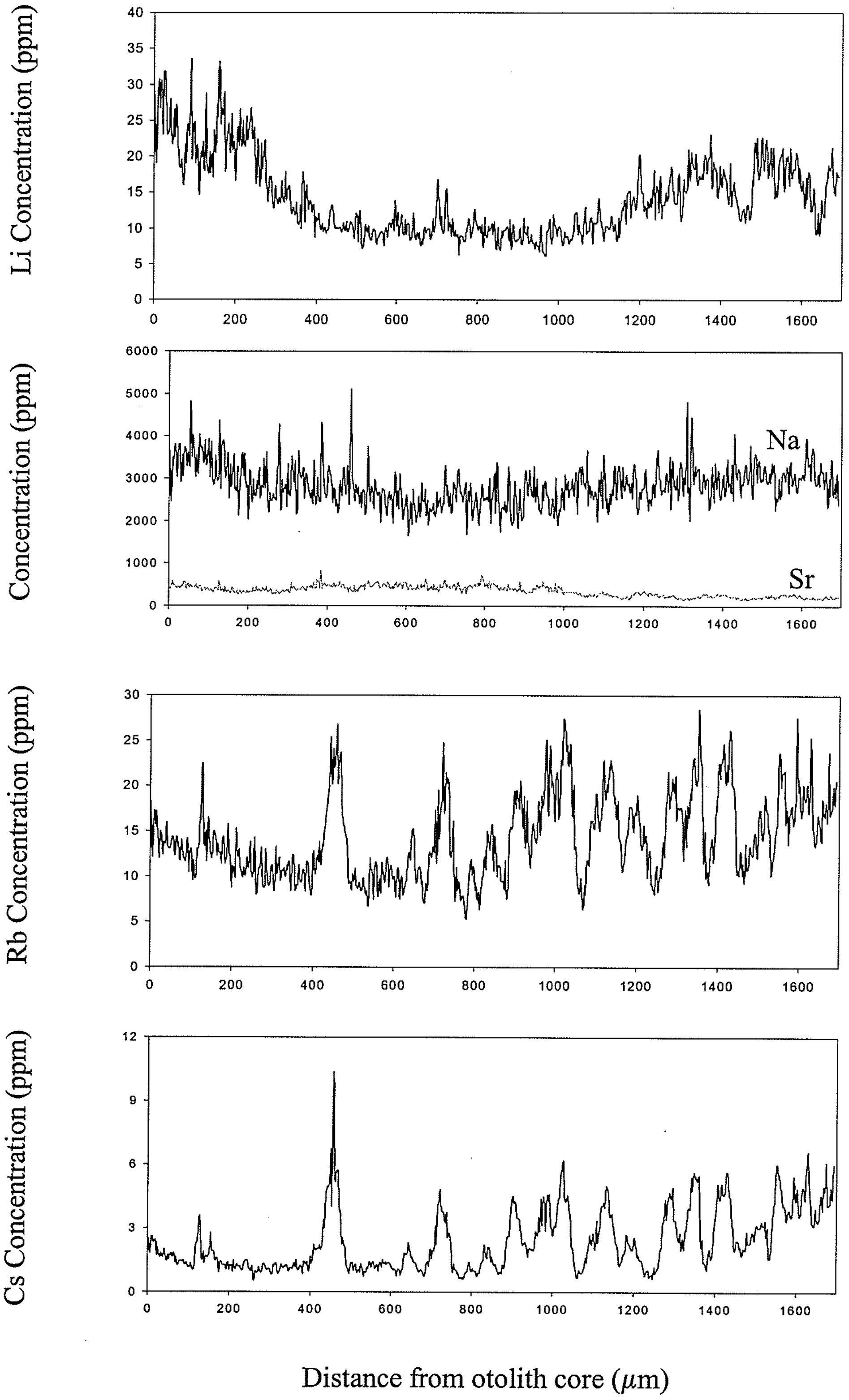


Li Concentration (ppm)
60
50
40
30
20
10
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
9
8
7
6
5
4
3
2
1
0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

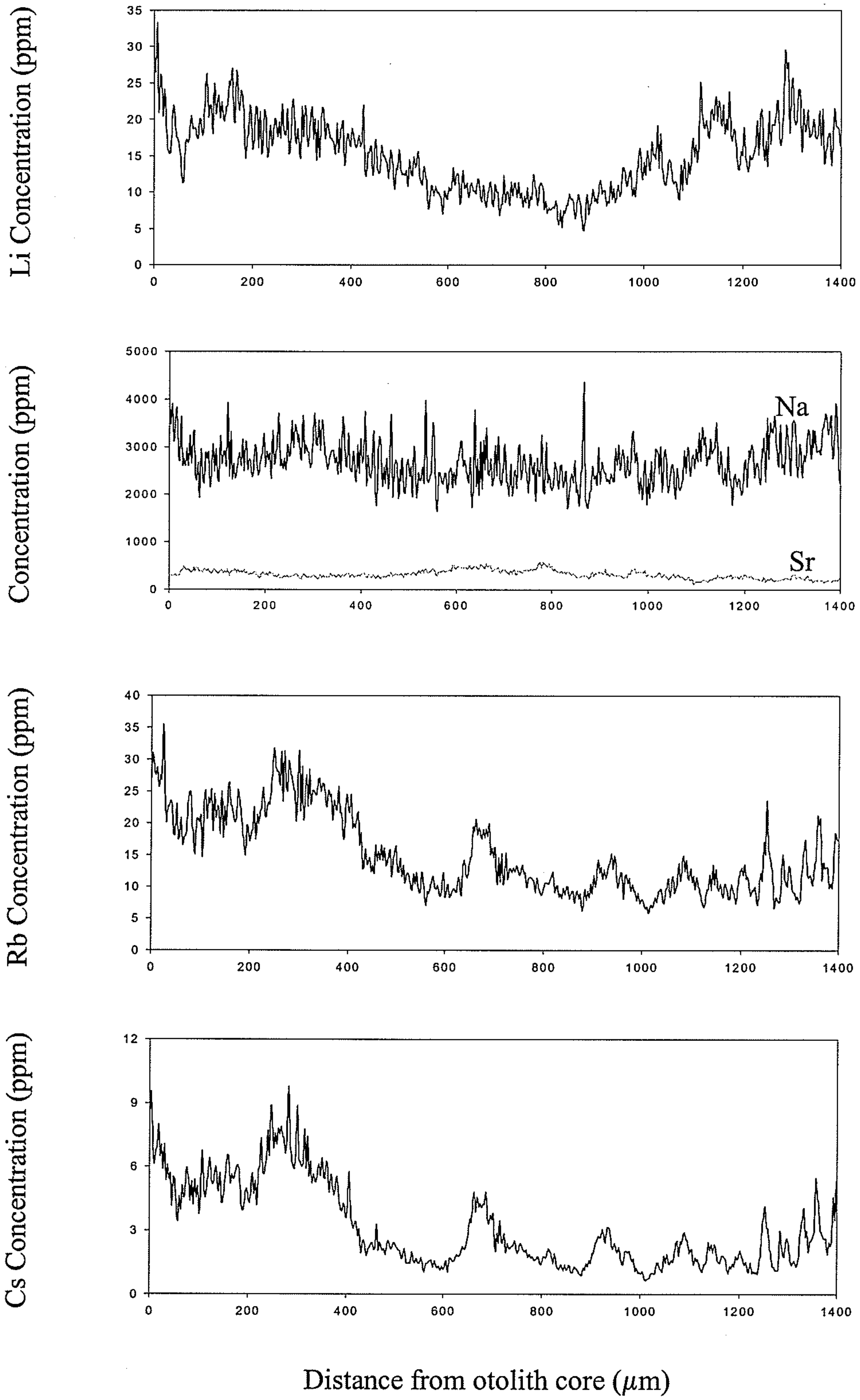
BSS08_17


Li Concentration (ppm)
60
50
40
30
20
10
0
0
200
400
600
800
1000
1200
Concentration (ppm)
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
10
8
6
4
2
0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

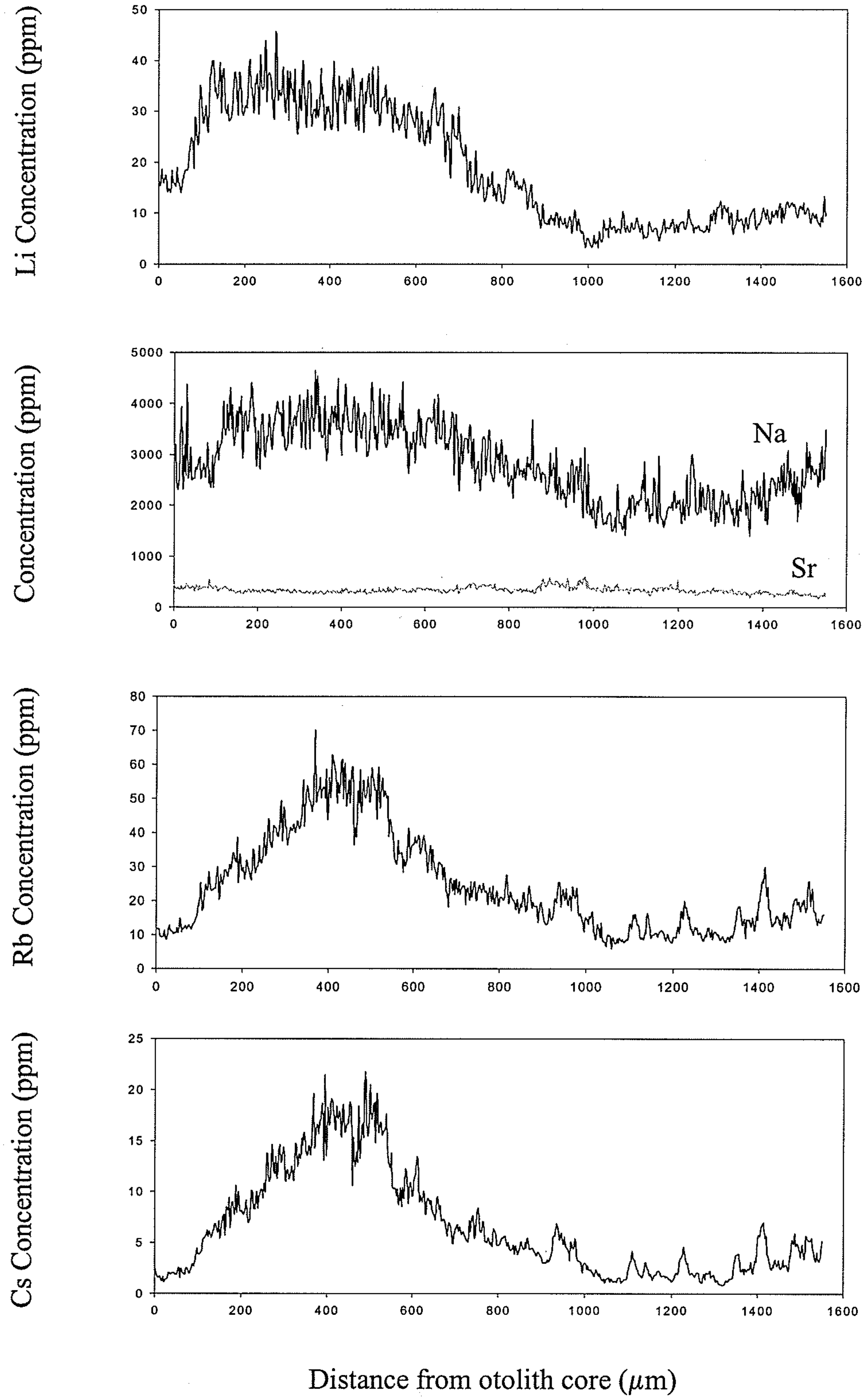
BSS08_18


Li Concentration (ppm)
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
Rb Concentration (ppm)
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
Cs Concentration (ppm)
12
9
6
3
0
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

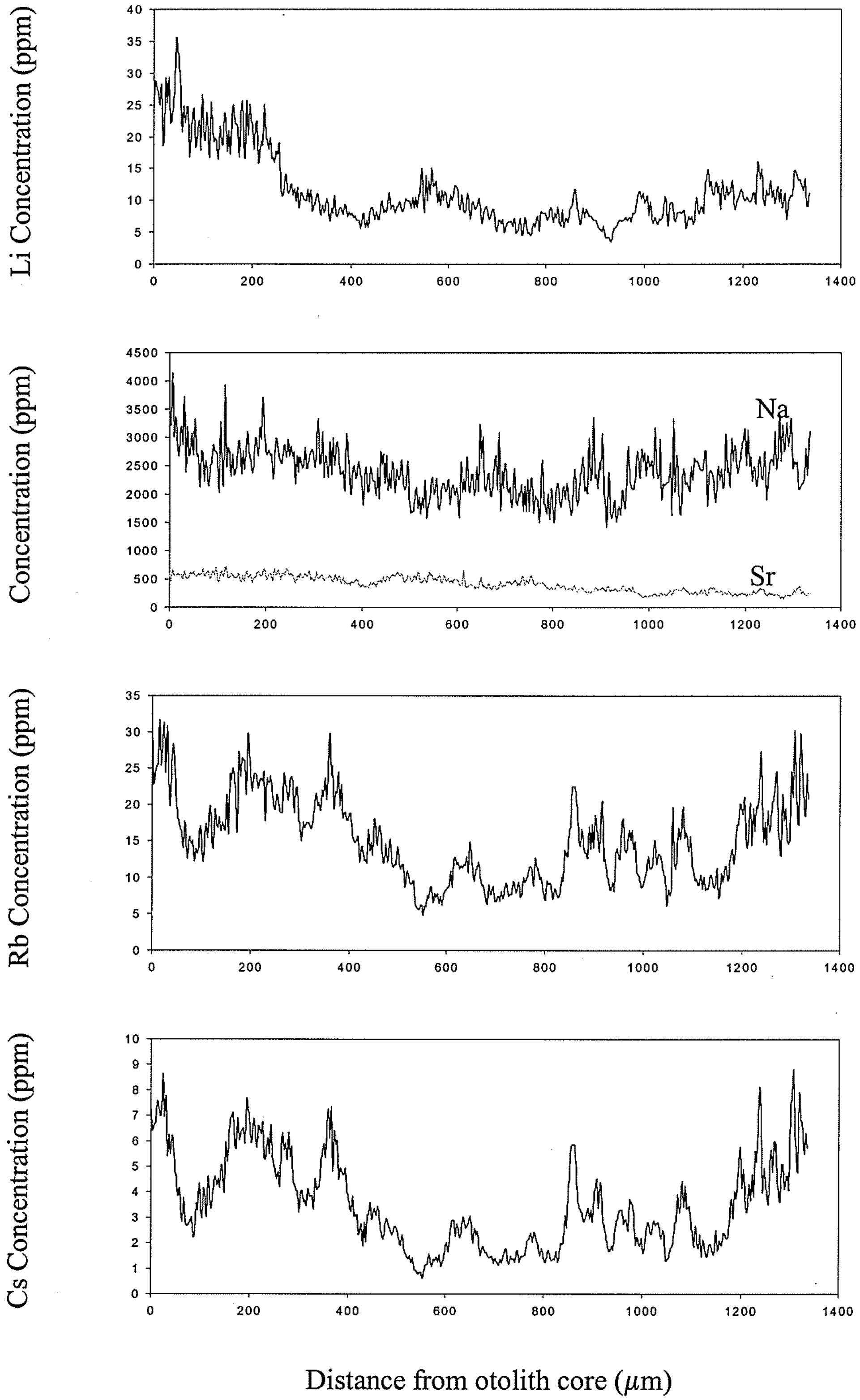
BSS08_19


Li Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
12
9
6
3
0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

BSS08_20

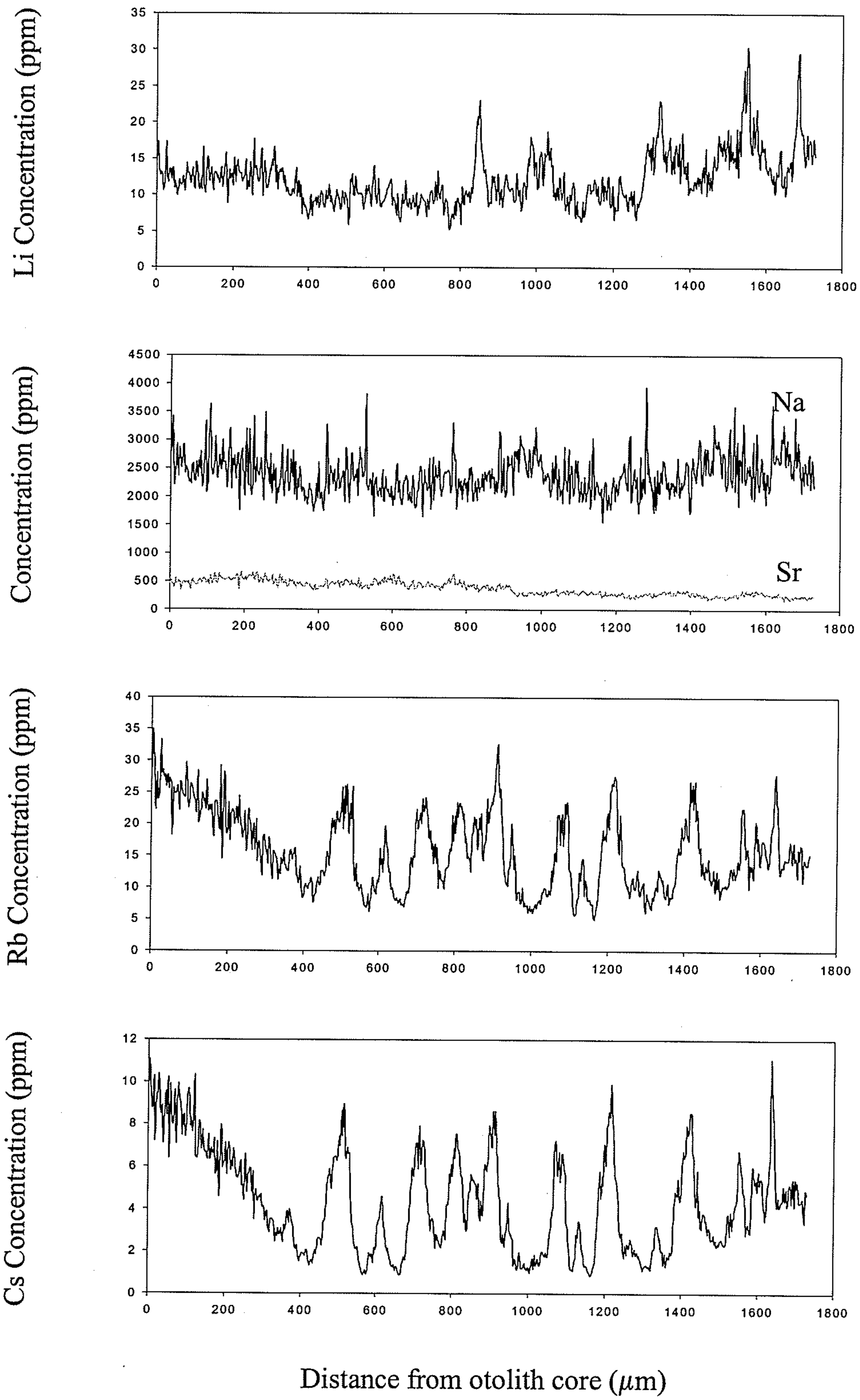

Li Concentration (ppm)
50
40
30
20
10
0
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
Rb Concentration (ppm)
80
70
60
50
40
30
20
10
0
0
200
400
600
800
1000
1200
1400
1600
Cs Concentration (ppm)
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

BSS08_21

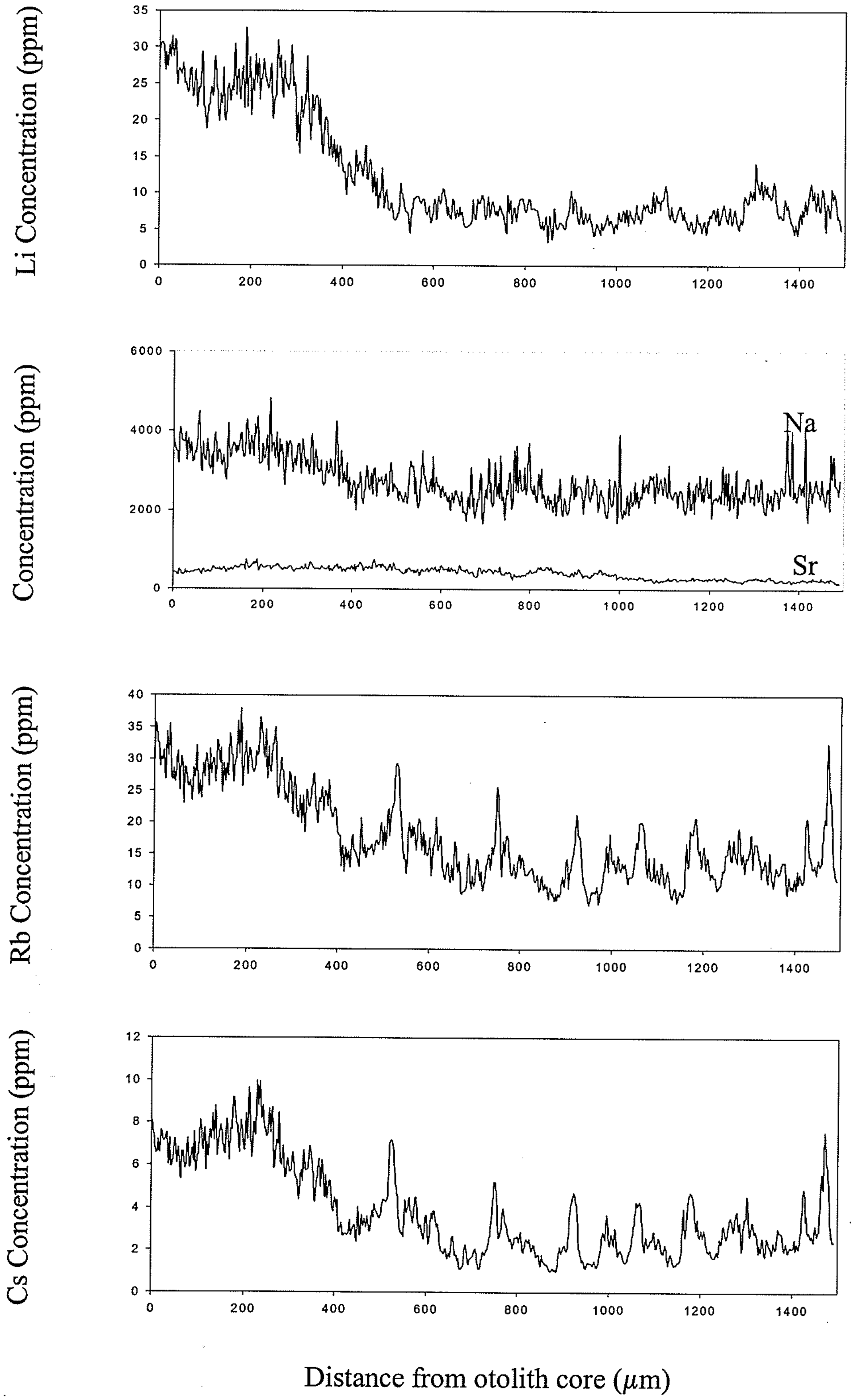


Li Concentration (ppm)
0
5
10
15
20
25
30
35
40
Concentration (ppm)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Na
Sr
Rb Concentration (ppm)
0
5
10
15
20
25
30
35
Cs Concentration (ppm)
0
1
2
3
4
5
6
7
8
9
10
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

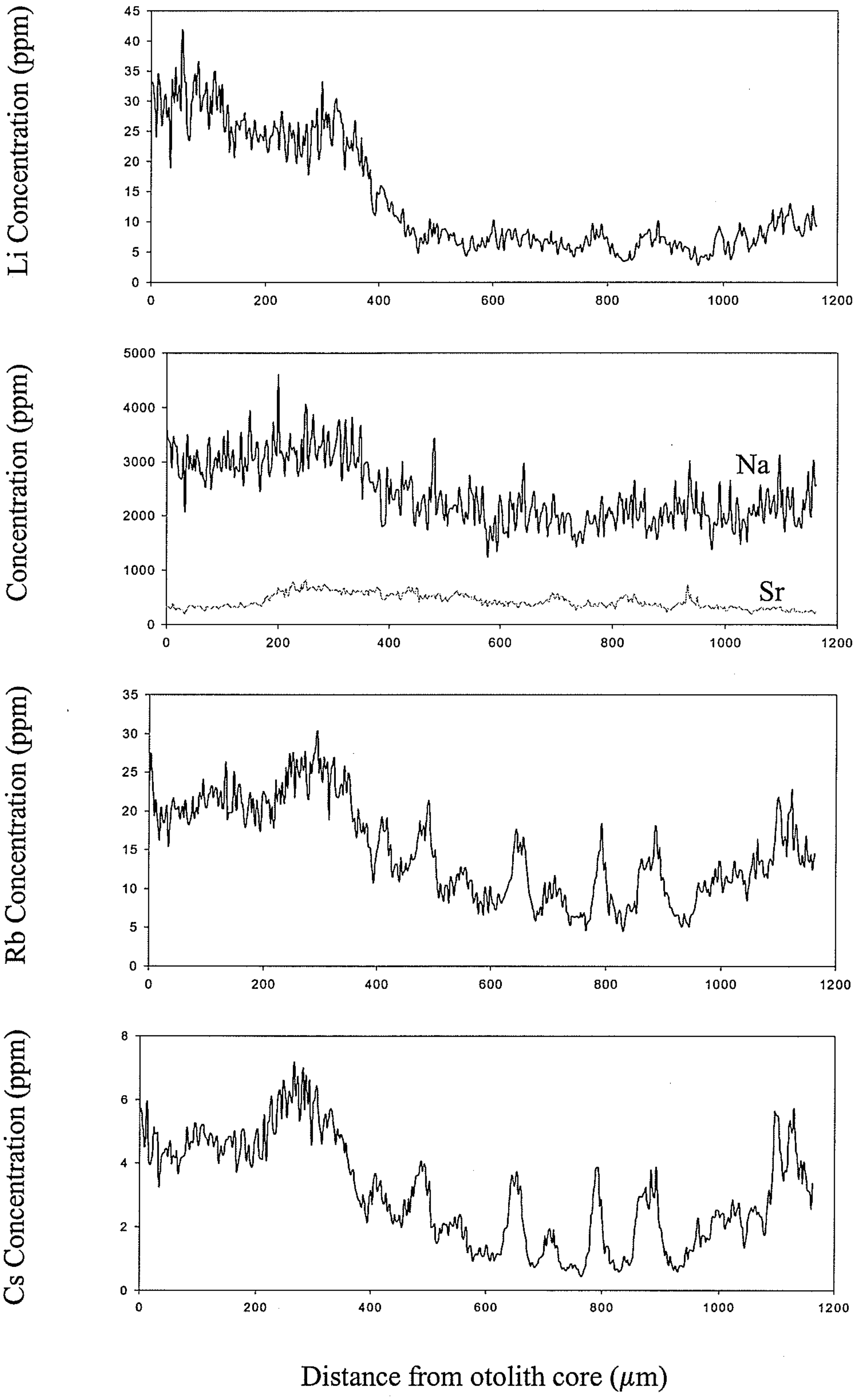
BSS08_22


Li Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
1800
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
1800
Rb Concentration (ppm)
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
1800
Cs Concentration (ppm)
12
10
8
6
4
2
0
0
200
400
600
800
1000
1200
1400
1600
1800
Distance from otolith core (μm)

BSS08_23

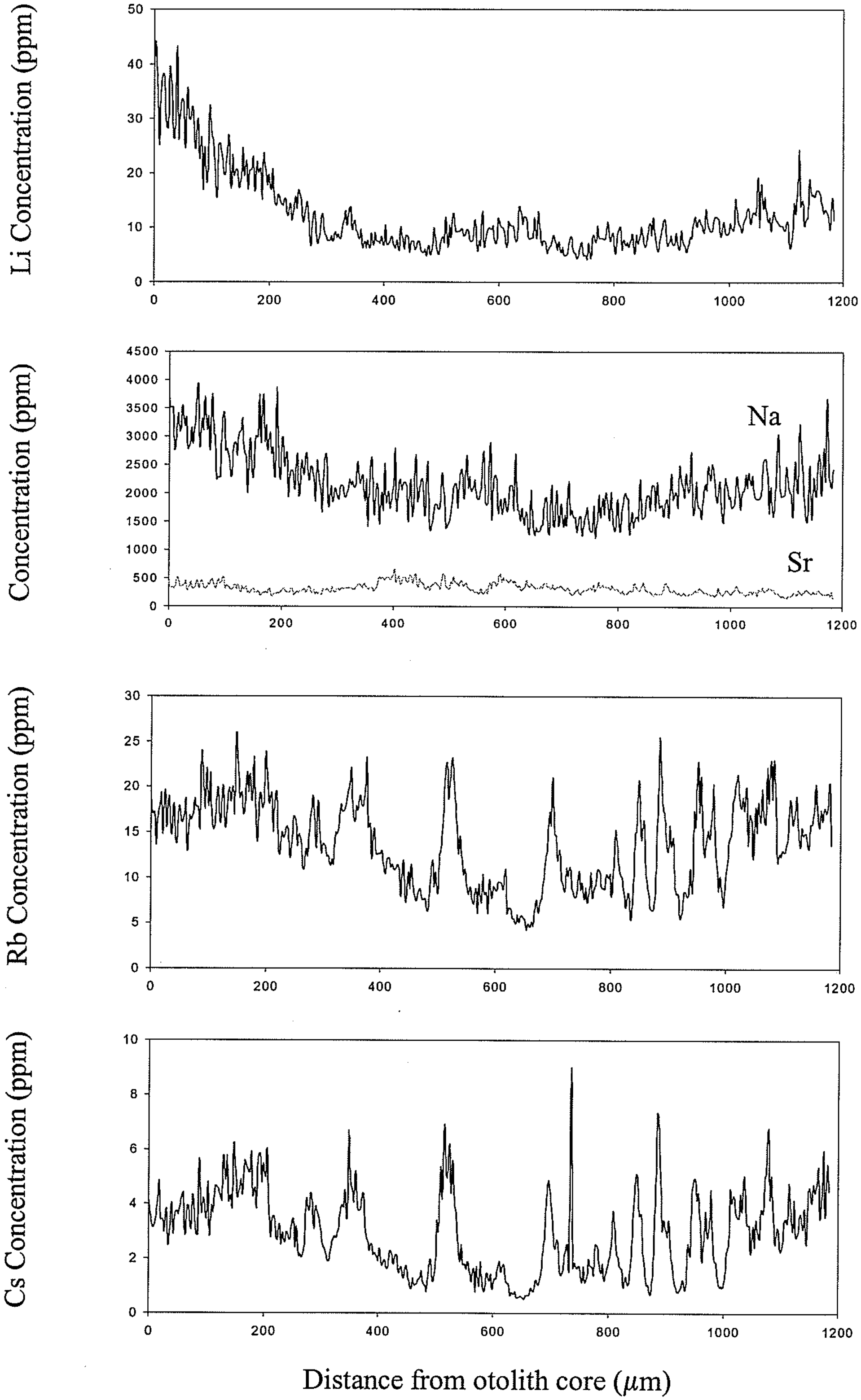

Li Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
6000
4000
2000
0
Na
Sr
Rb Concentration (ppm)
40
35
30
25
20
15
10
5
Cs Concentration (ppm)
12
10
8
6
4
2
Distance from otolith core (μm)

BSS08_24



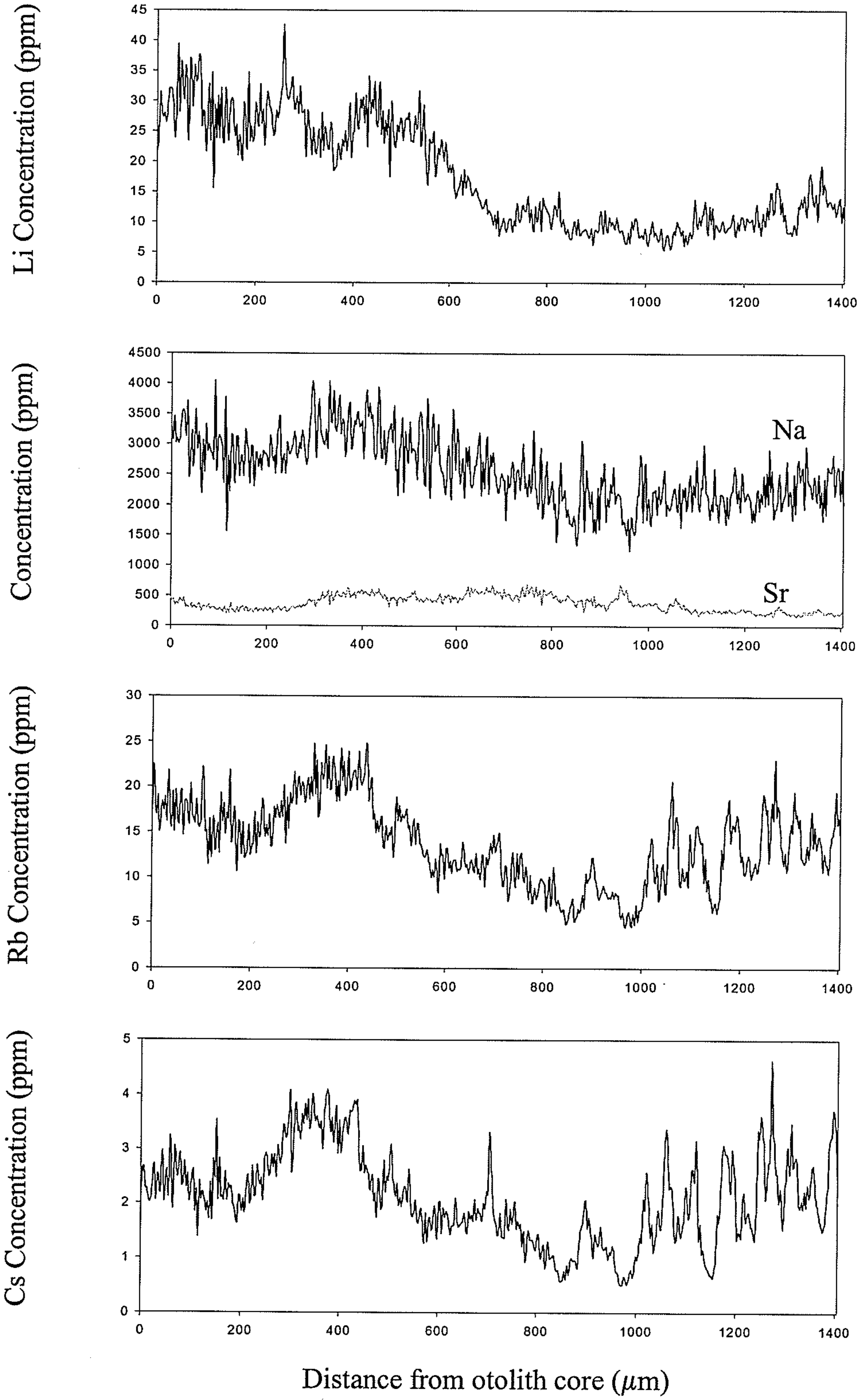
Li Concentration (ppm)
0
5
10
15
20
25
30
35
40
45
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
Rb Concentration (ppm)
0
5
10
15
20
25
30
35
Cs Concentration (ppm)
0
2
4
6
8
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

BSS08_25

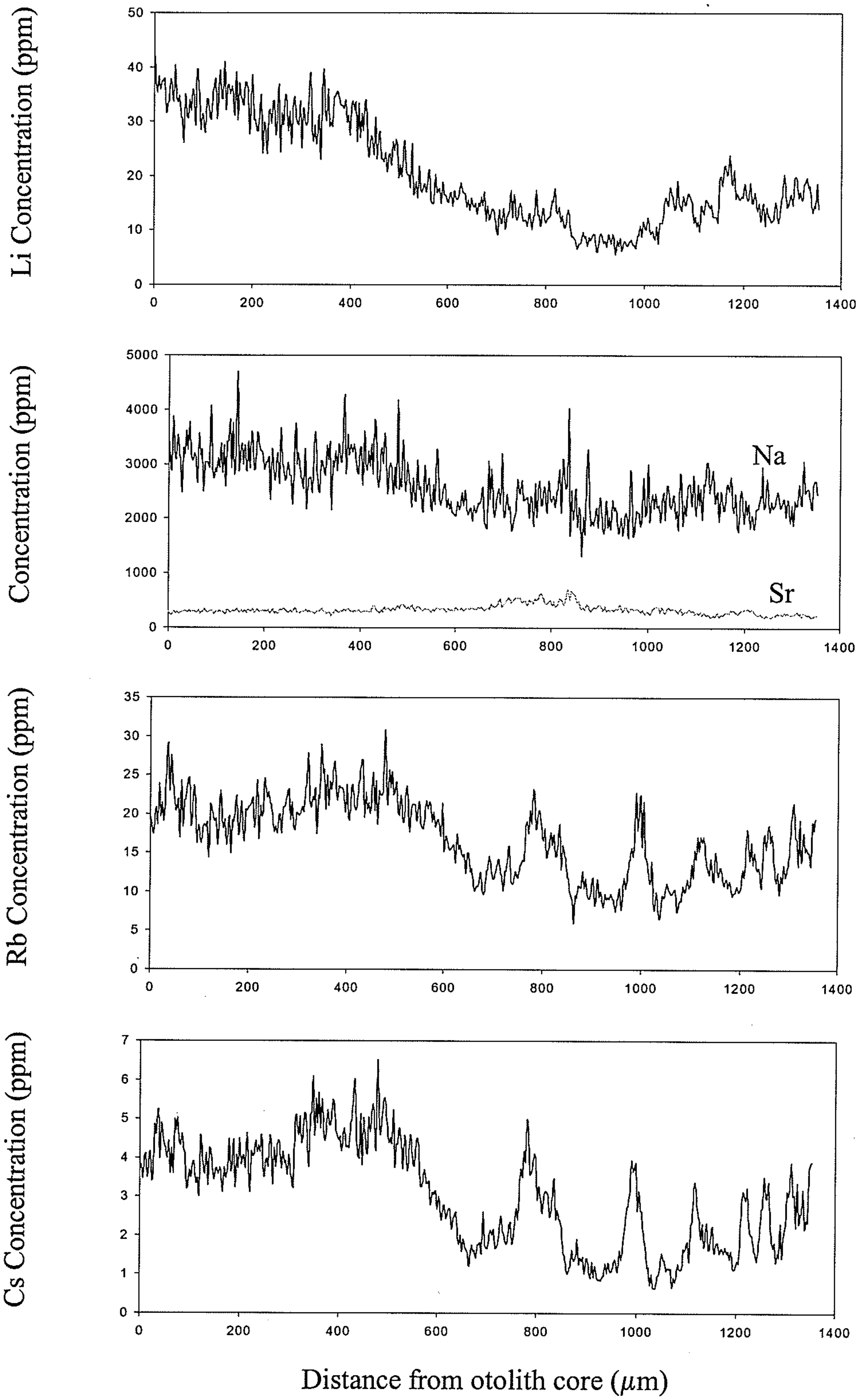


Li Concentration (ppm)
50
40
30
20
10
0
0
200
400
600
800
1000
1200
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
10
8
6
4
2
0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

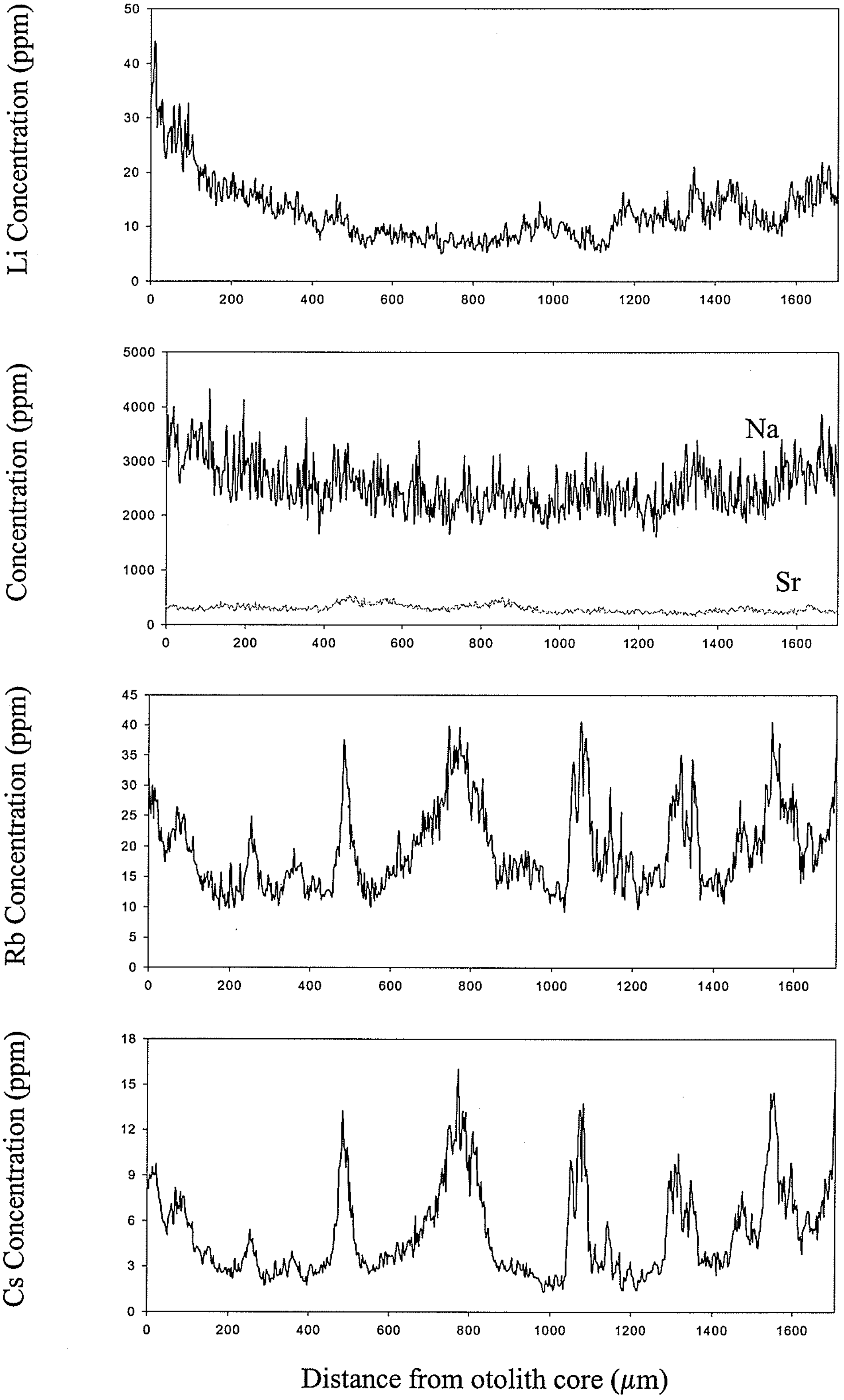
BSS08_26


Li Concentration (ppm)
45
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
5
4
3
2
1
0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

BSS08_27

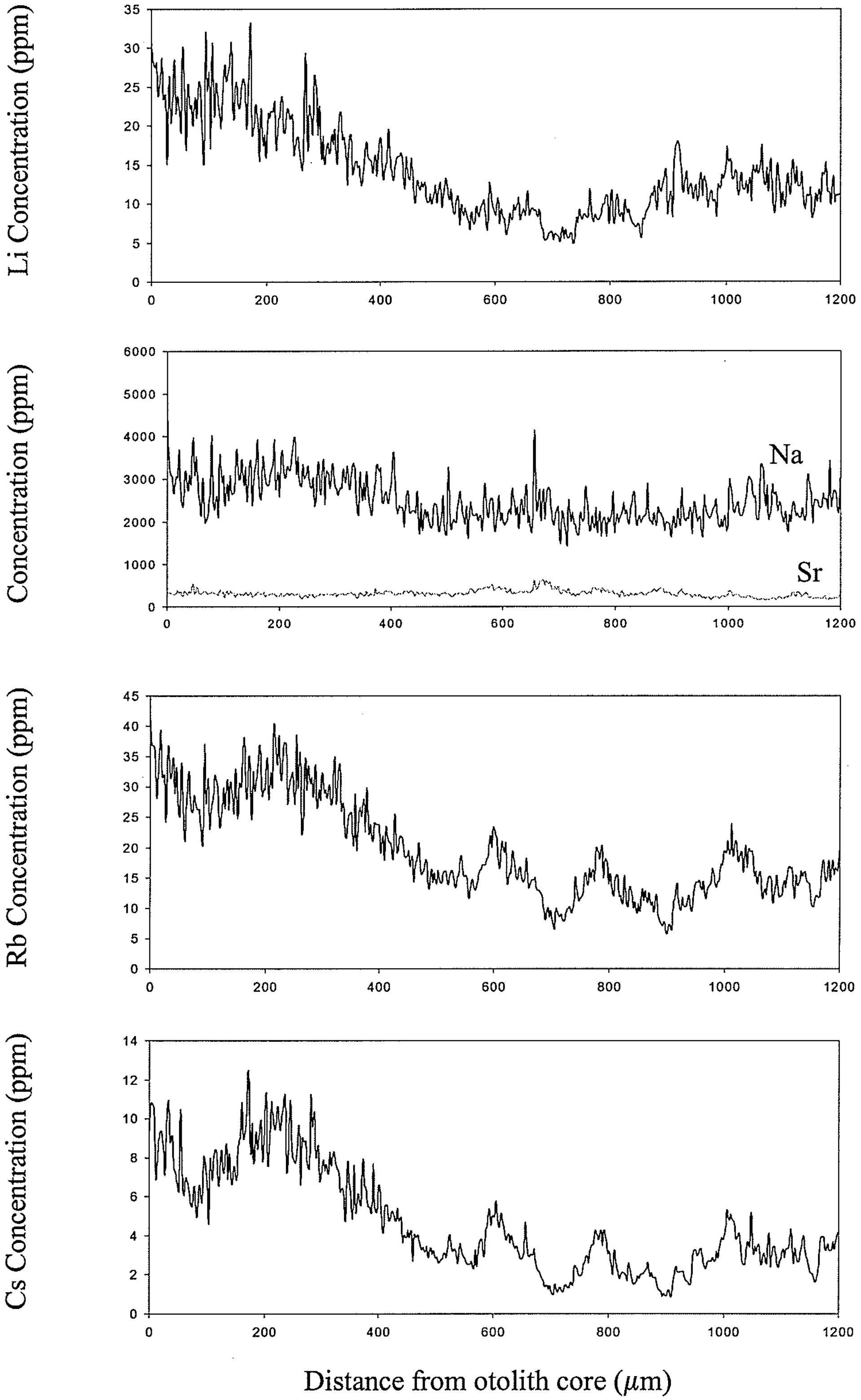

Li Concentration (ppm)
0
10
20
30
40
50
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
Rb Concentration (ppm)
0
5
10
15
20
25
30
35
Cs Concentration (ppm)
0
1
2
3
4
5
6
7
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

BSS08_28

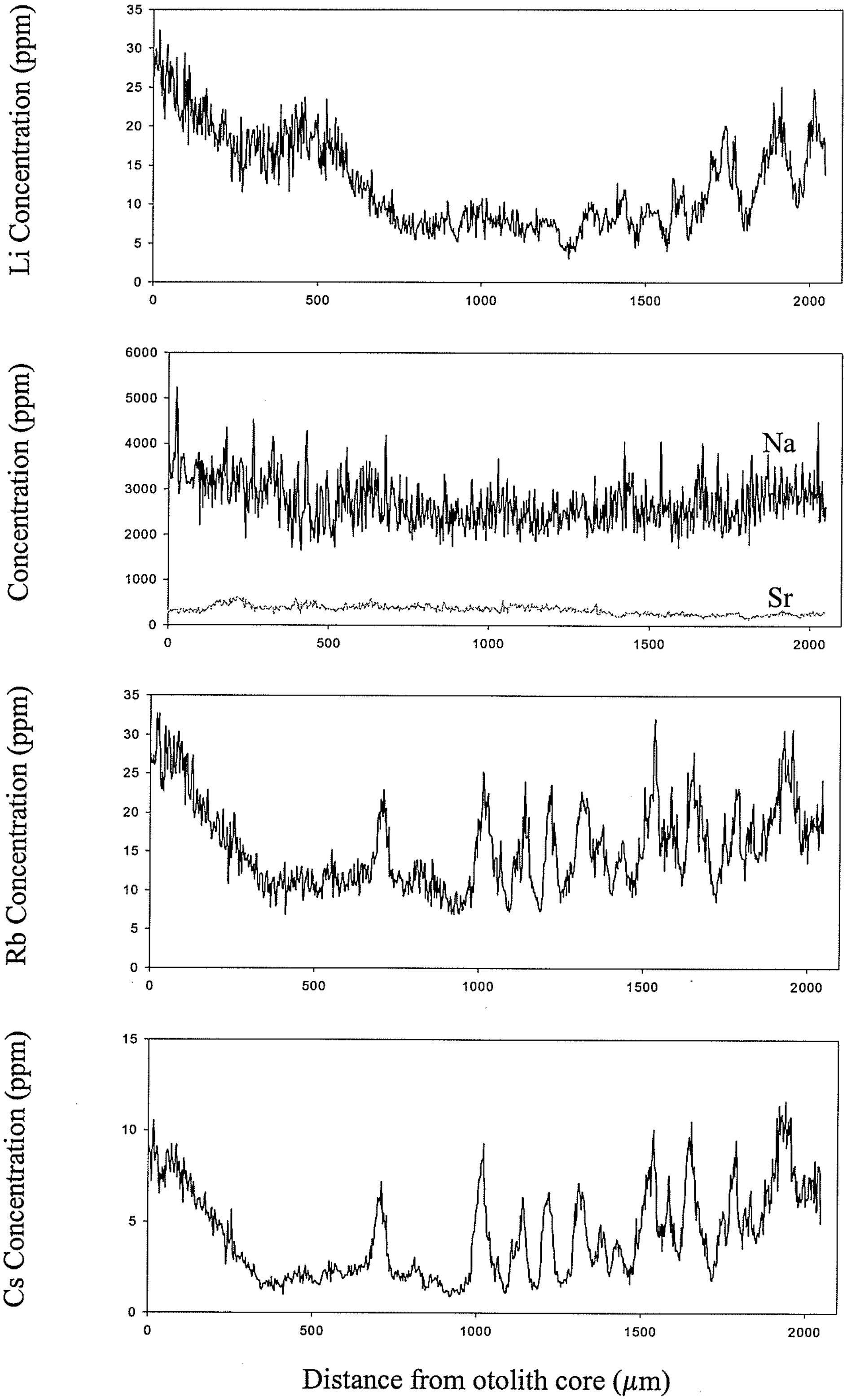


Li Concentration (ppm)
50
40
30
20
10
0
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
Rb Concentration (ppm)
45
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
Cs Concentration (ppm)
18
15
12
9
6
3
0
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

BSS08_29

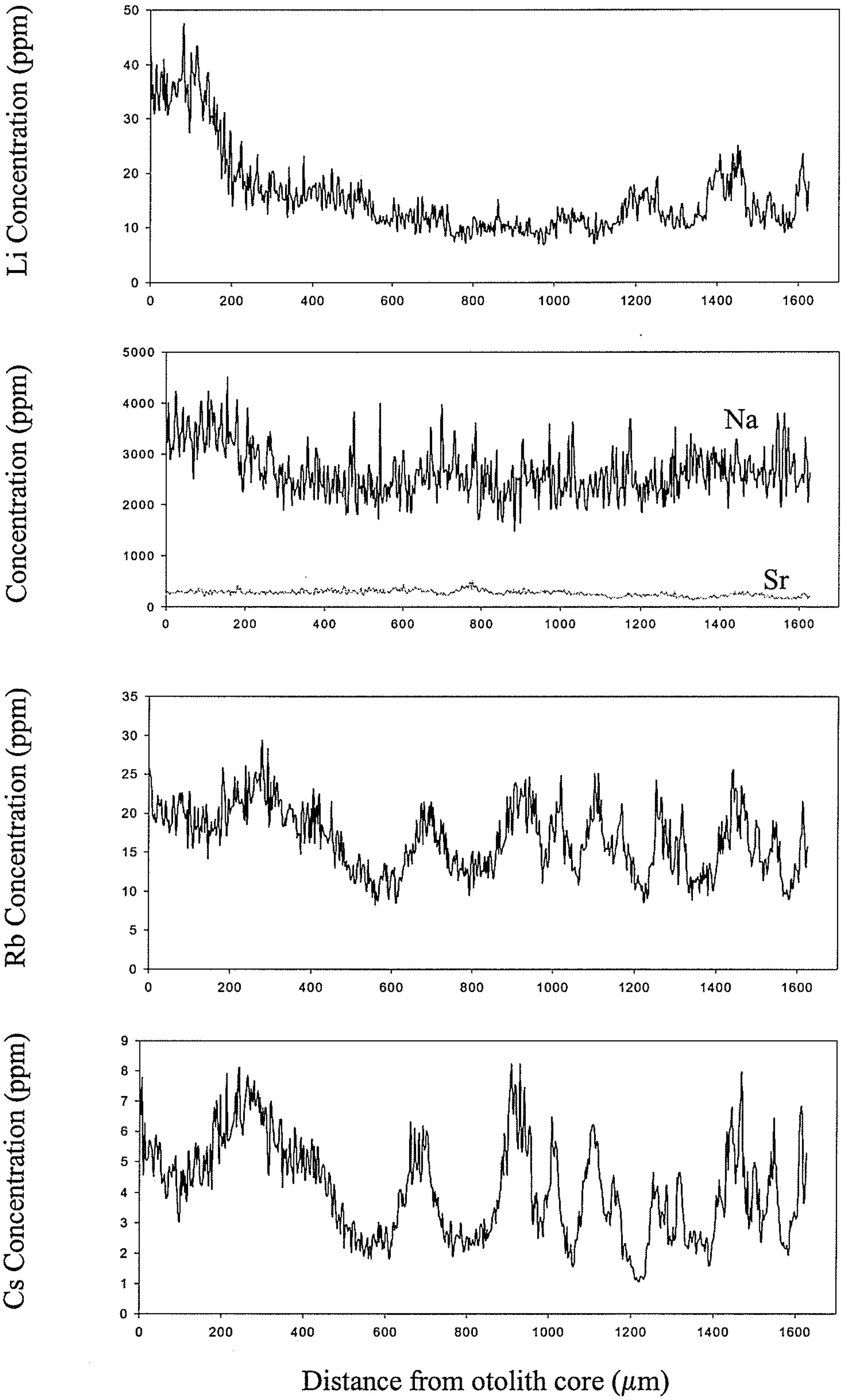

Li Concentration (ppm)
0
5
10
15
20
25
30
35
0
200
400
600
800
1000
1200
Concentration (ppm)
0
1000
2000
3000
4000
5000
6000
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
0
5
10
15
20
25
30
35
40
45
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0
2
4
6
8
10
12
14
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

BSS08_30



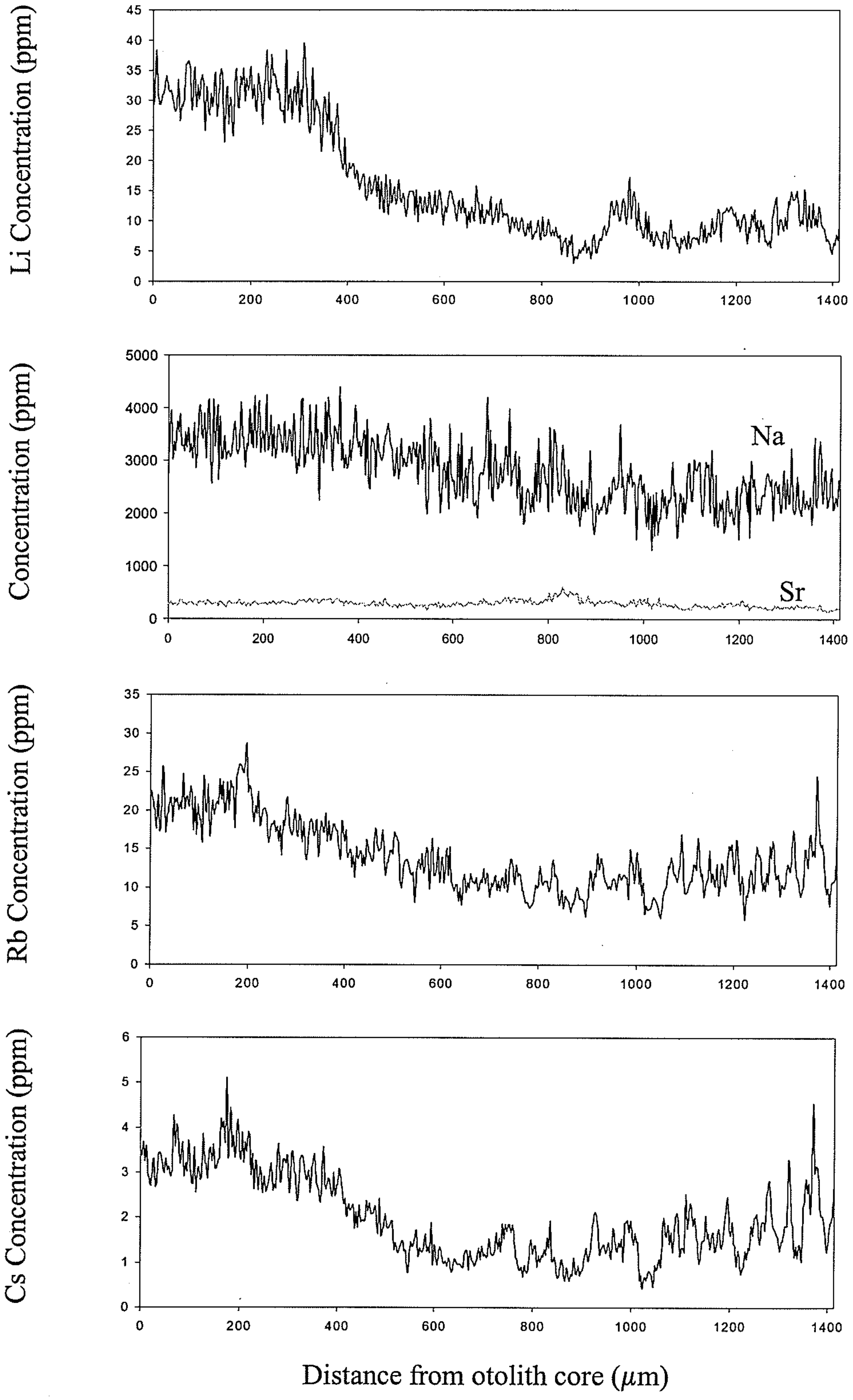
Li Concentration (ppm)
35
30
25
20
15
10
5
0
0
500
1000
1500
2000
Concentration (ppm)
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
35
30
25
20
15
10
5
0
0
500
1000
1500
2000
Cs Concentration (ppm)
15
10
5
0
0
500
1000
1500
2000
Distance from otolith core (μm)

BSS08_31

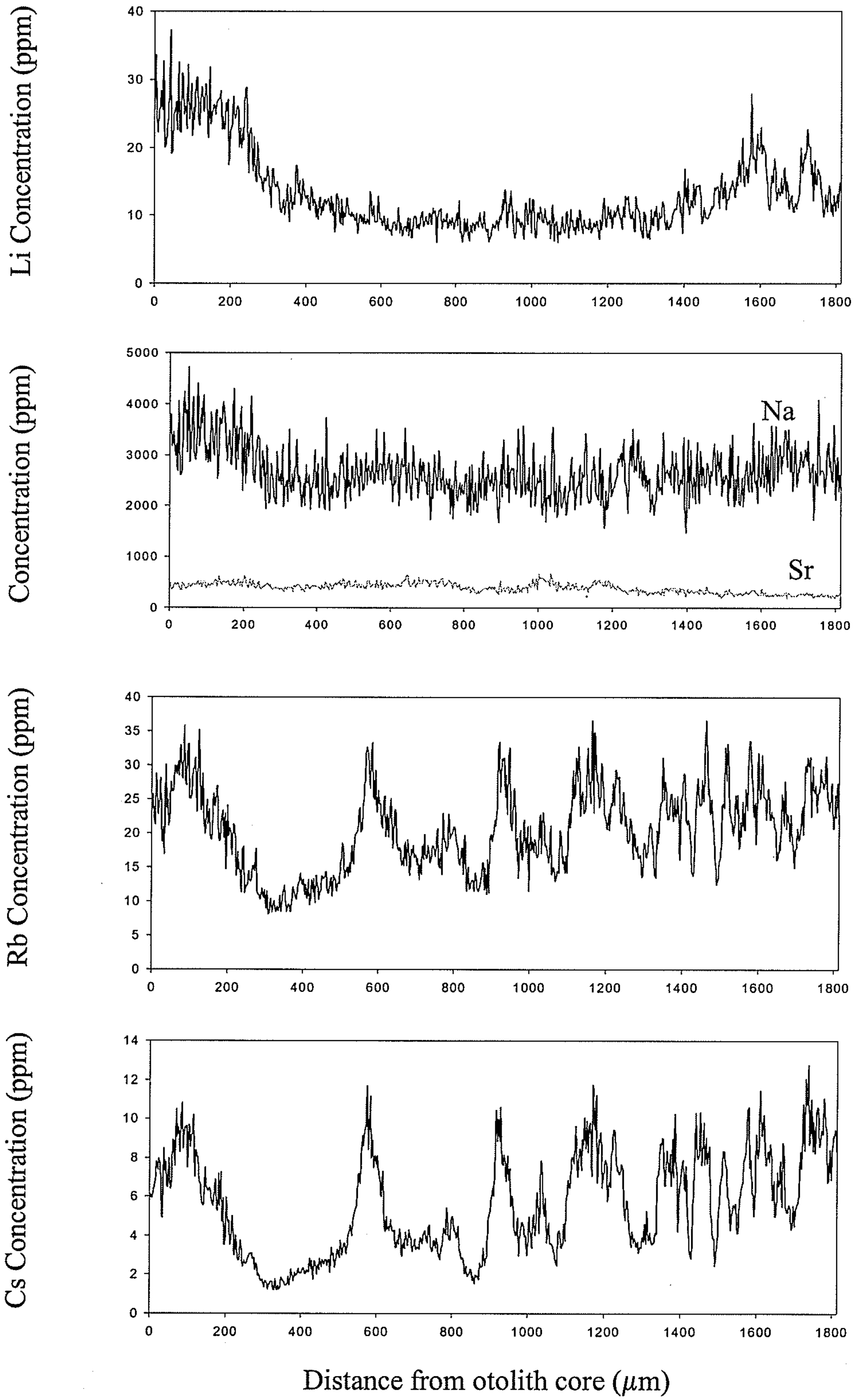


Li Concentration (ppm)
50
40
30
20
10
0
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
35
30
25
20
15
10
5
0
Cs Concentration (ppm)
9
8
7
6
5
4
3
2
1
0
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

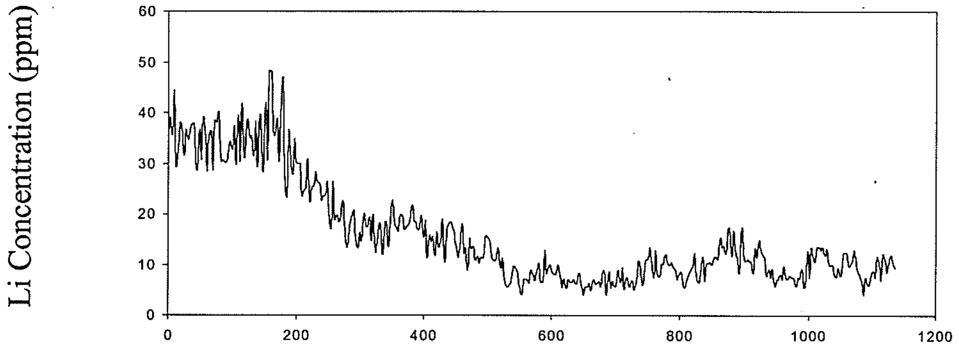
BSS08_32

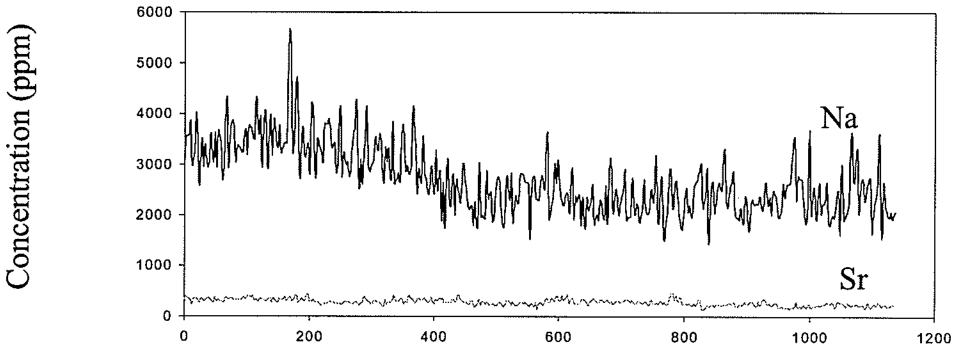

Li Concentration (ppm)
0
5
10
15
20
25
30
35
40
45
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
0
5
10
15
20
25
30
35
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
0
1
2
3
4
5
6
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

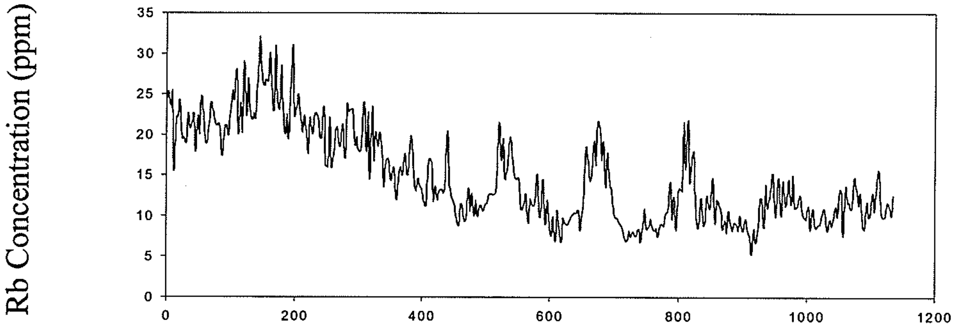
BSS08_33

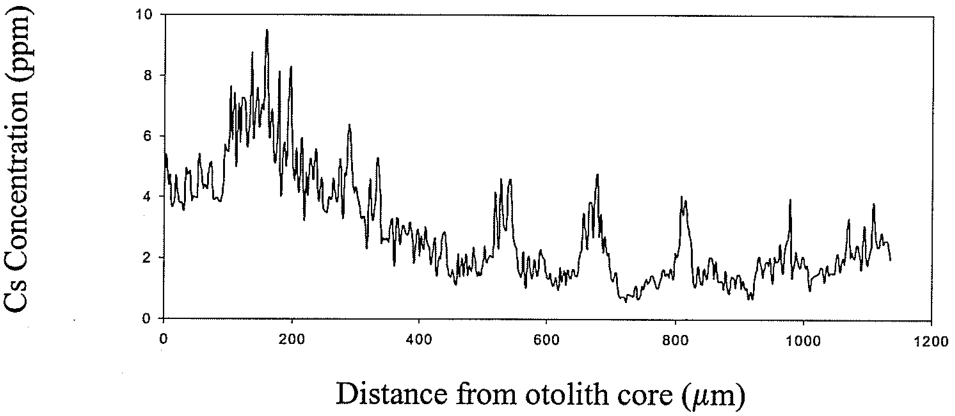

Li Concentration (ppm)
40
30
20
10
0
0
200
400
600
800
1000
1200
1400
1600
1800
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
1800
Rb Concentration (ppm)
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
1800
Cs Concentration (ppm)
14
12
10
8
6
4
2
0
0
200
400
600
800
1000
1200
1400
1600
1800
Distance from otolith core (μm)

BSS08_34

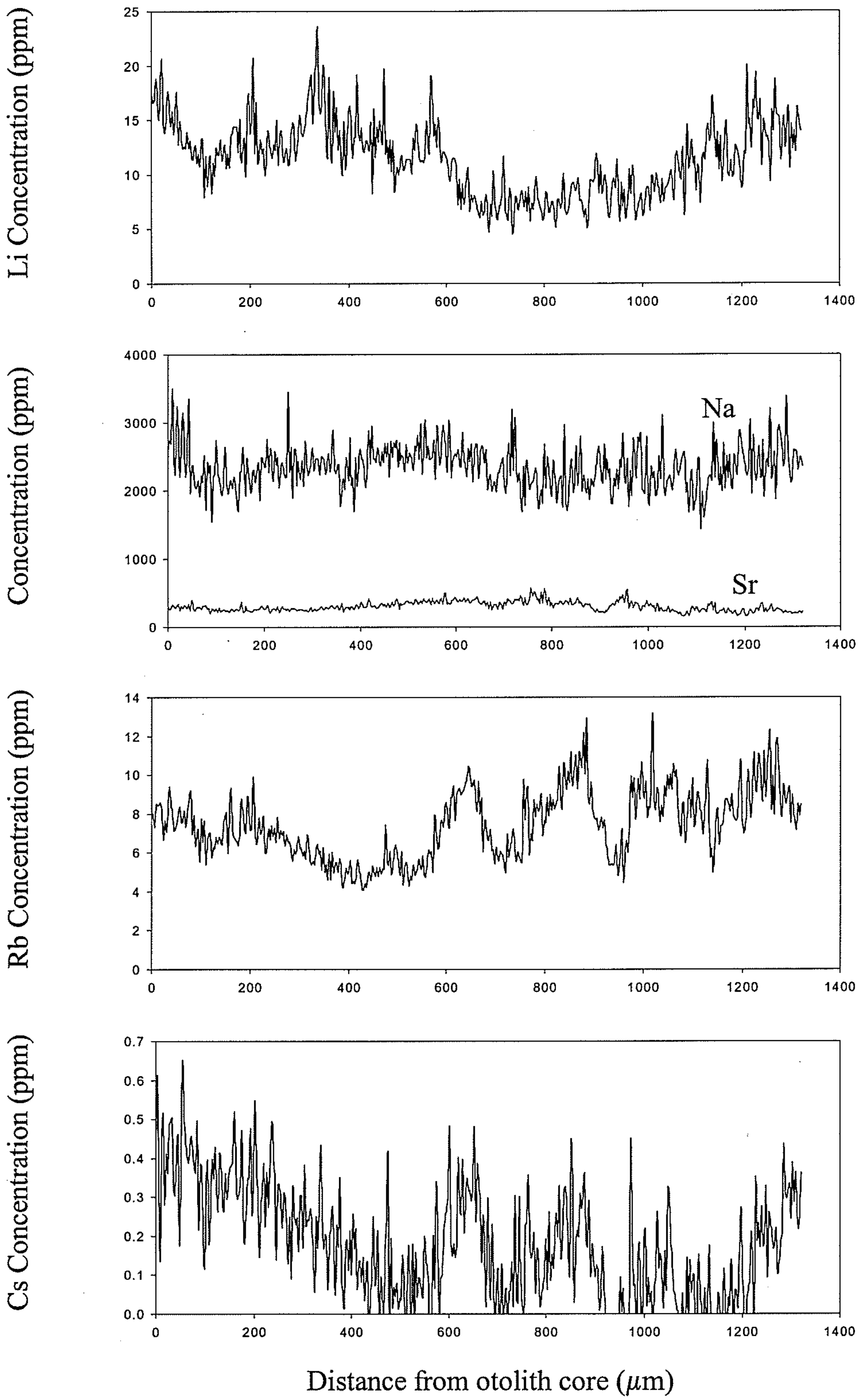

Li Concentration (ppm)
60
50
40
30
20
10
0
0
200
400
600
800
1000
1200


Concentration (ppm)
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200

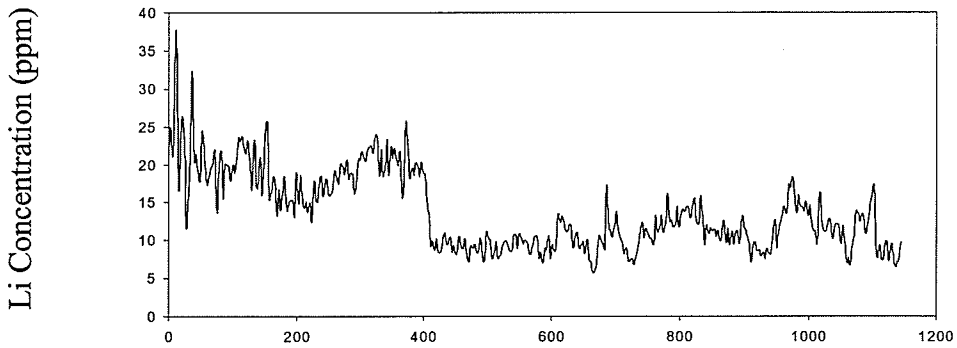

Rb Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200

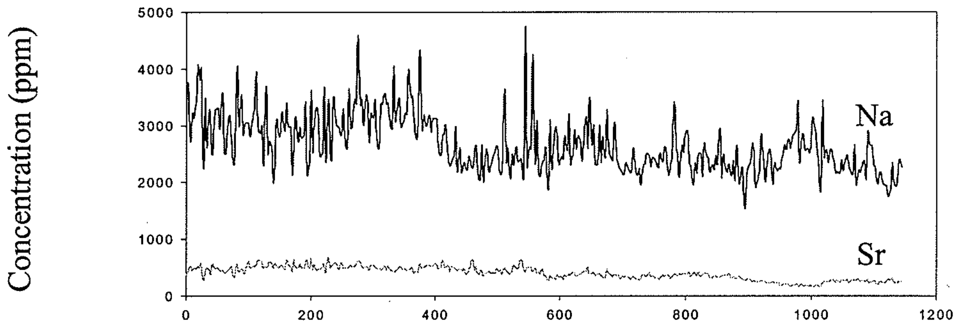

Cs Concentration (ppm)
10
8
6
4
2
0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

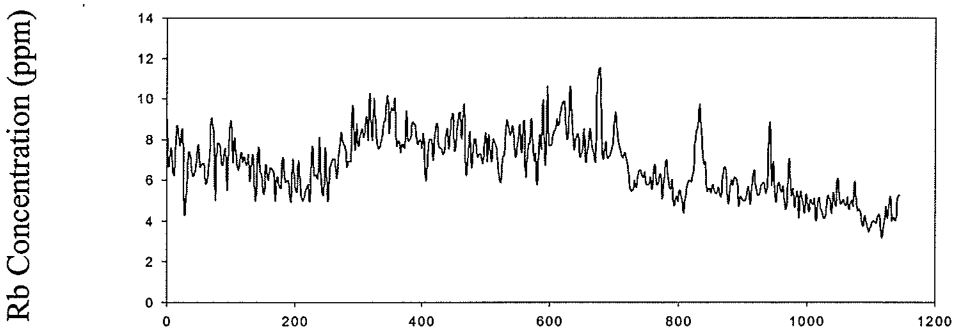
B08_01

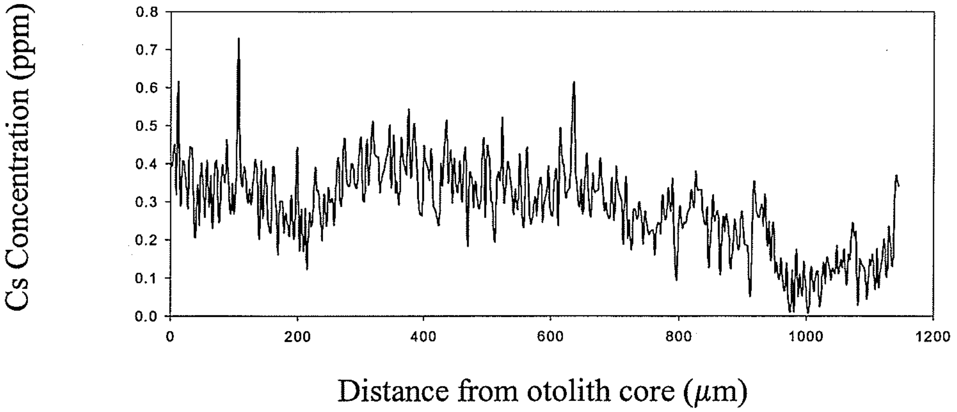

Li Concentration (ppm)
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
14
12
10
8
6
4
2
0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

B08_02

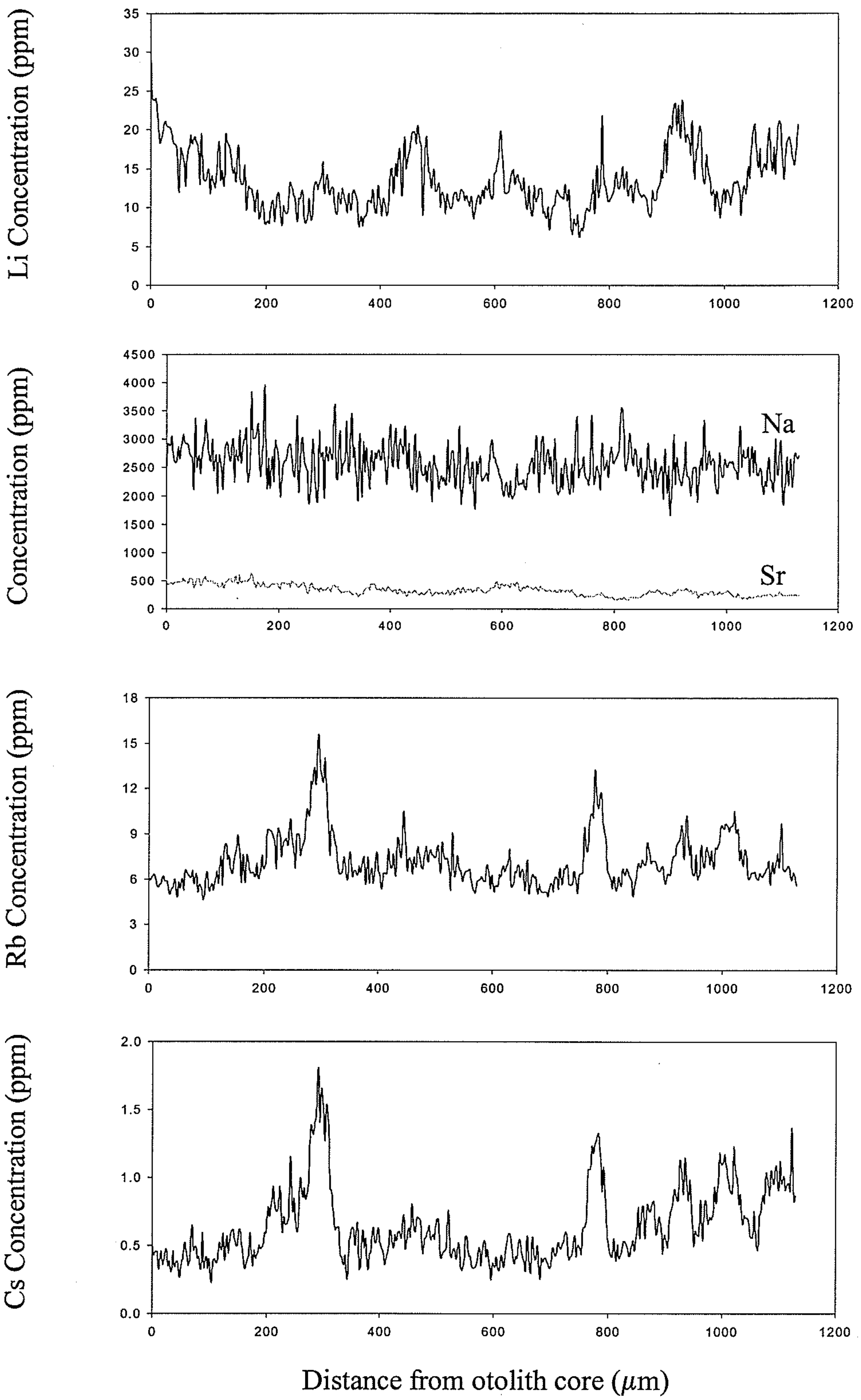

Li Concentration (ppm)
0
5
10
15
20
25
30
35
40
0
200
400
600
800
1000
1200


Concentration (ppm)
Na
Sr
0
1000
2000
3000
4000
5000
0
200
400
600
800
1000
1200

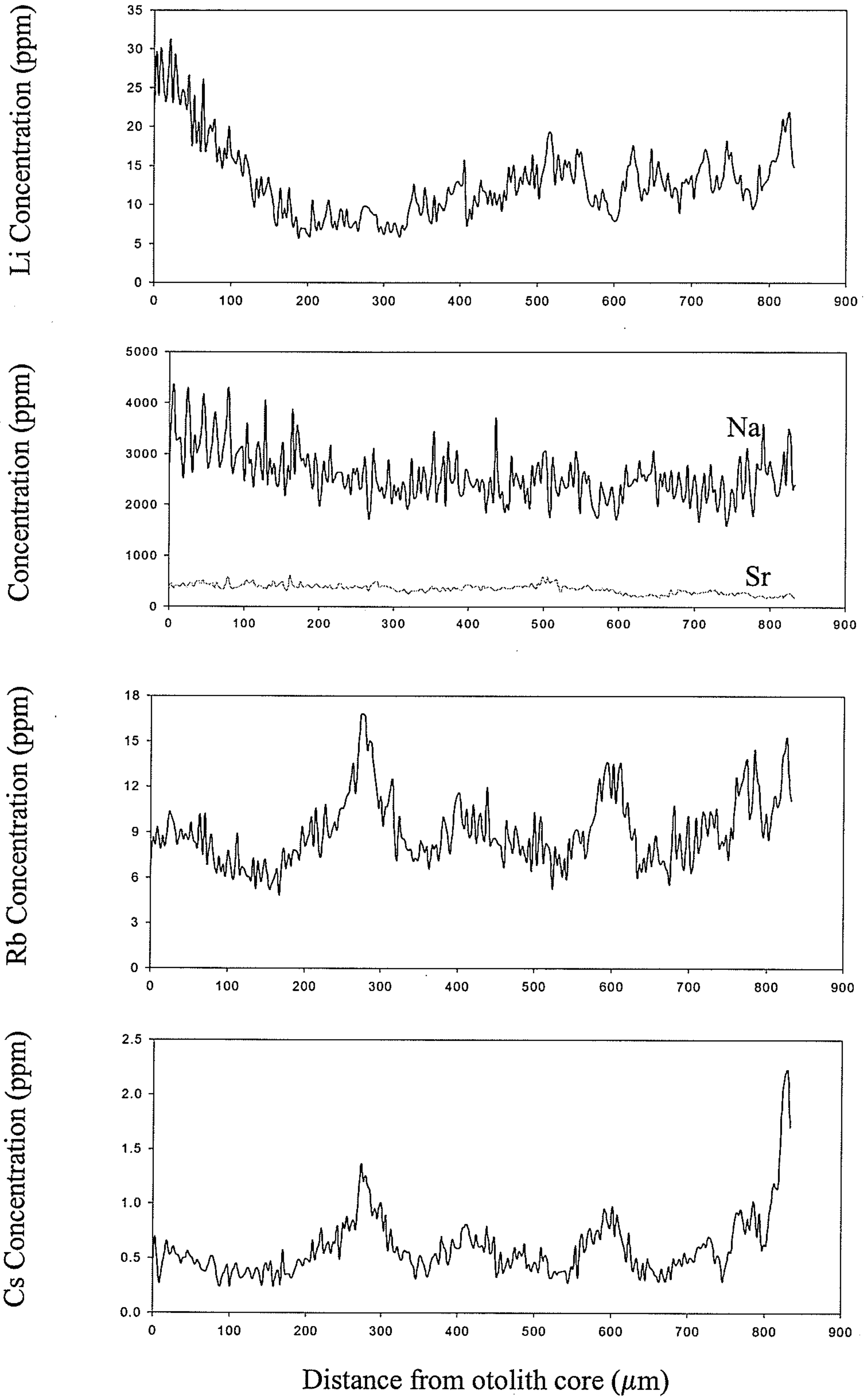

Rb Concentration (ppm)
0
2
4
6
8
10
12
14
0
200
400
600
800
1000
1200


Cs Concentration (ppm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

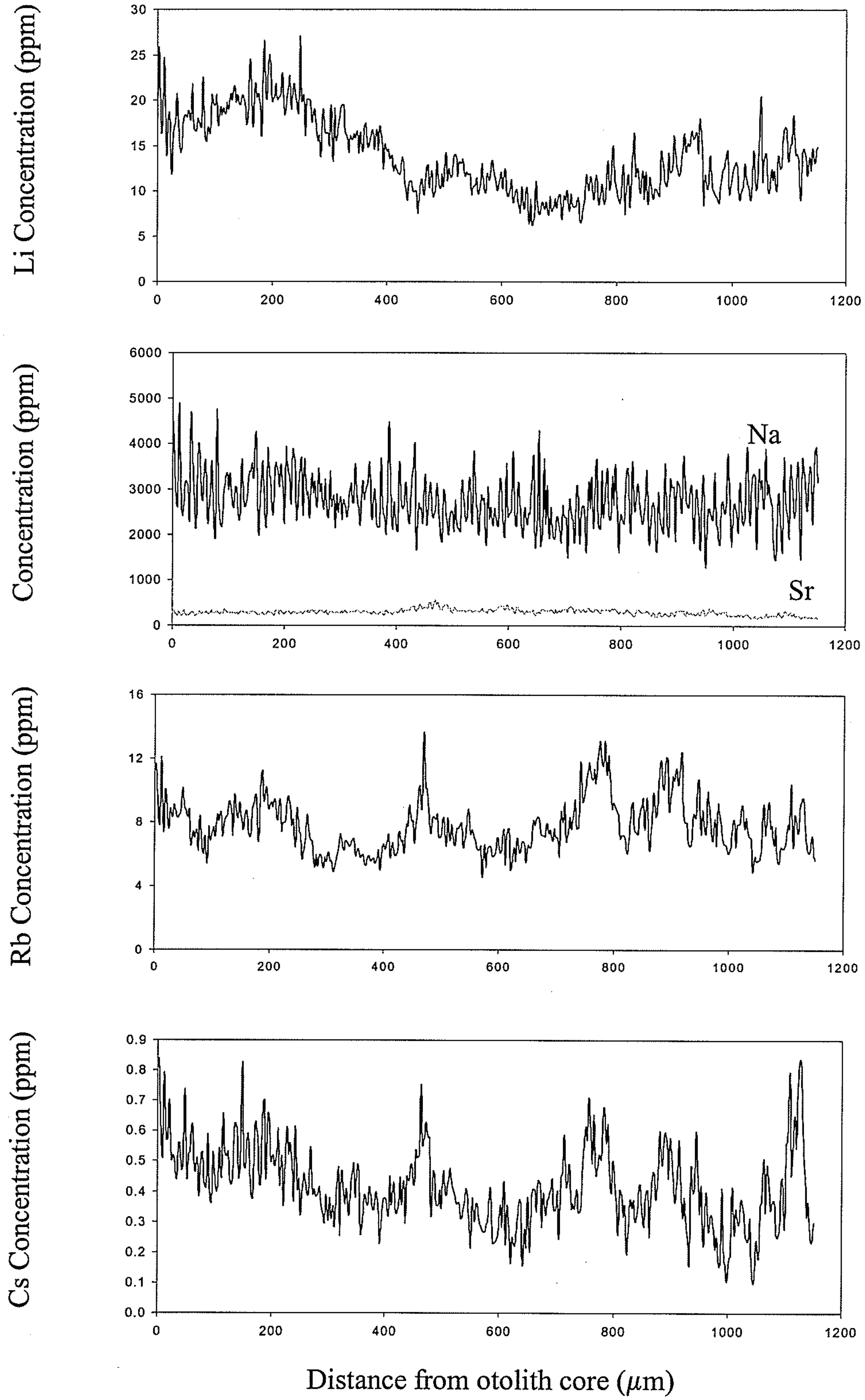
B08_03


Li Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
18
15
12
9
6
3
0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

B08_04

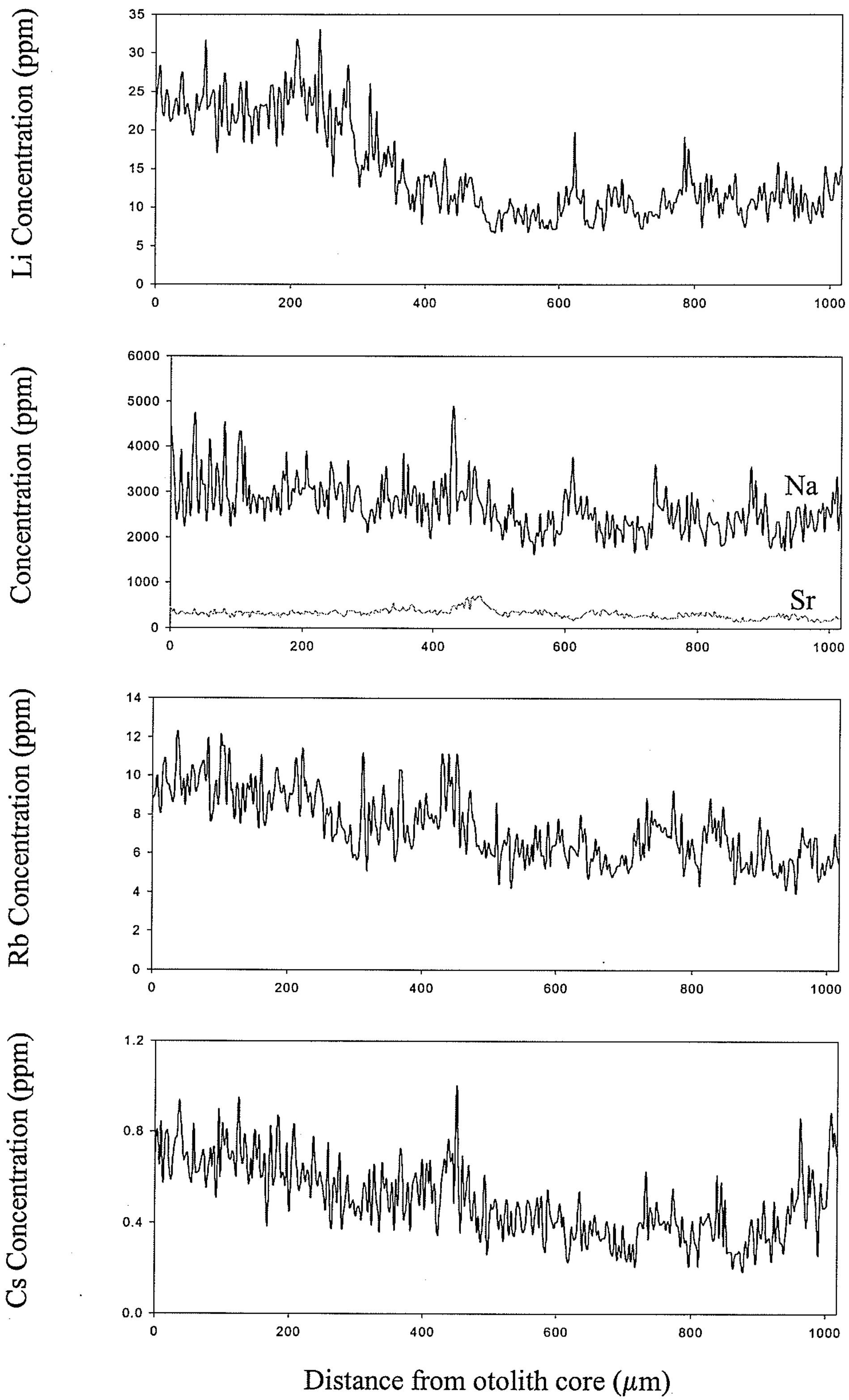

Li Concentration (ppm)
35
30
25
20
15
10
5
0
0
100
200
300
400
500
600
700
800
900
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
800
900
Rb Concentration (ppm)
18
15
12
9
6
3
0
0
100
200
300
400
500
600
700
800
900
Cs Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
900
Distance from otolith core (μm)

B08_05



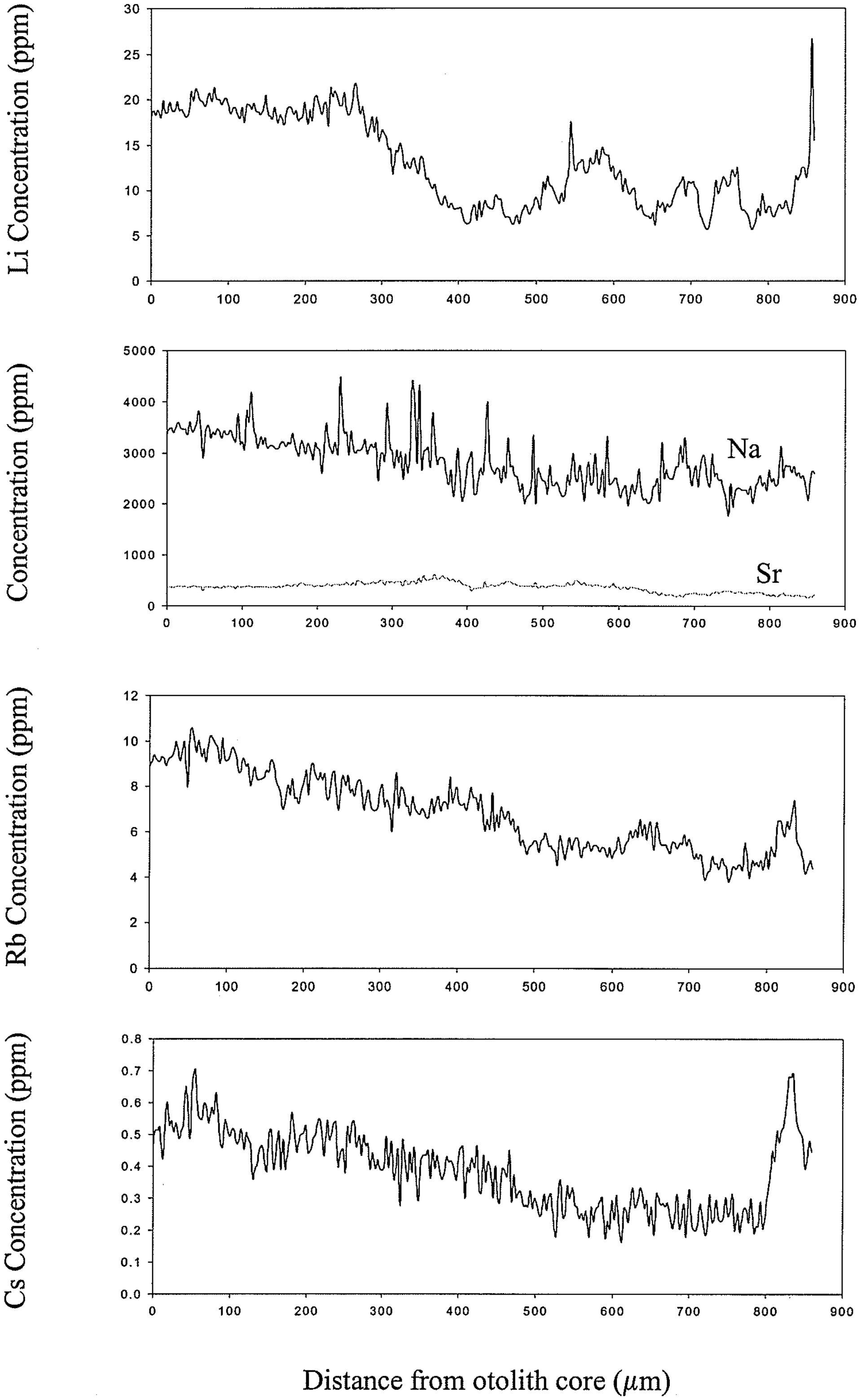
Li Concentration (ppm)
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
Concentration (ppm)
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
16
12
8
4
0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

B08_06

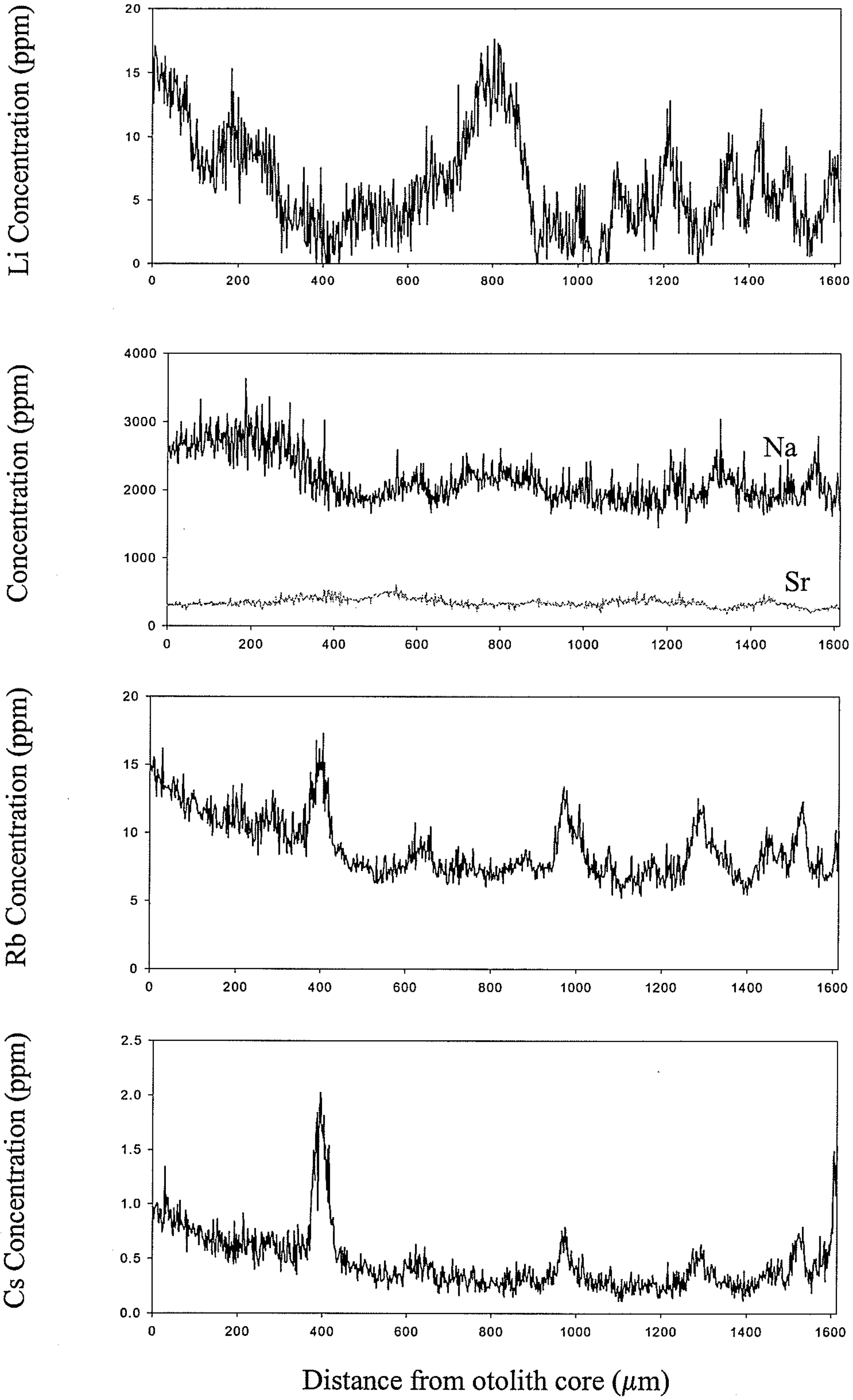


Li Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
Concentration (ppm)
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
14
12
10
8
6
4
2
0
0
200
400
600
800
1000
Cs Concentration (ppm)
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

B08_07

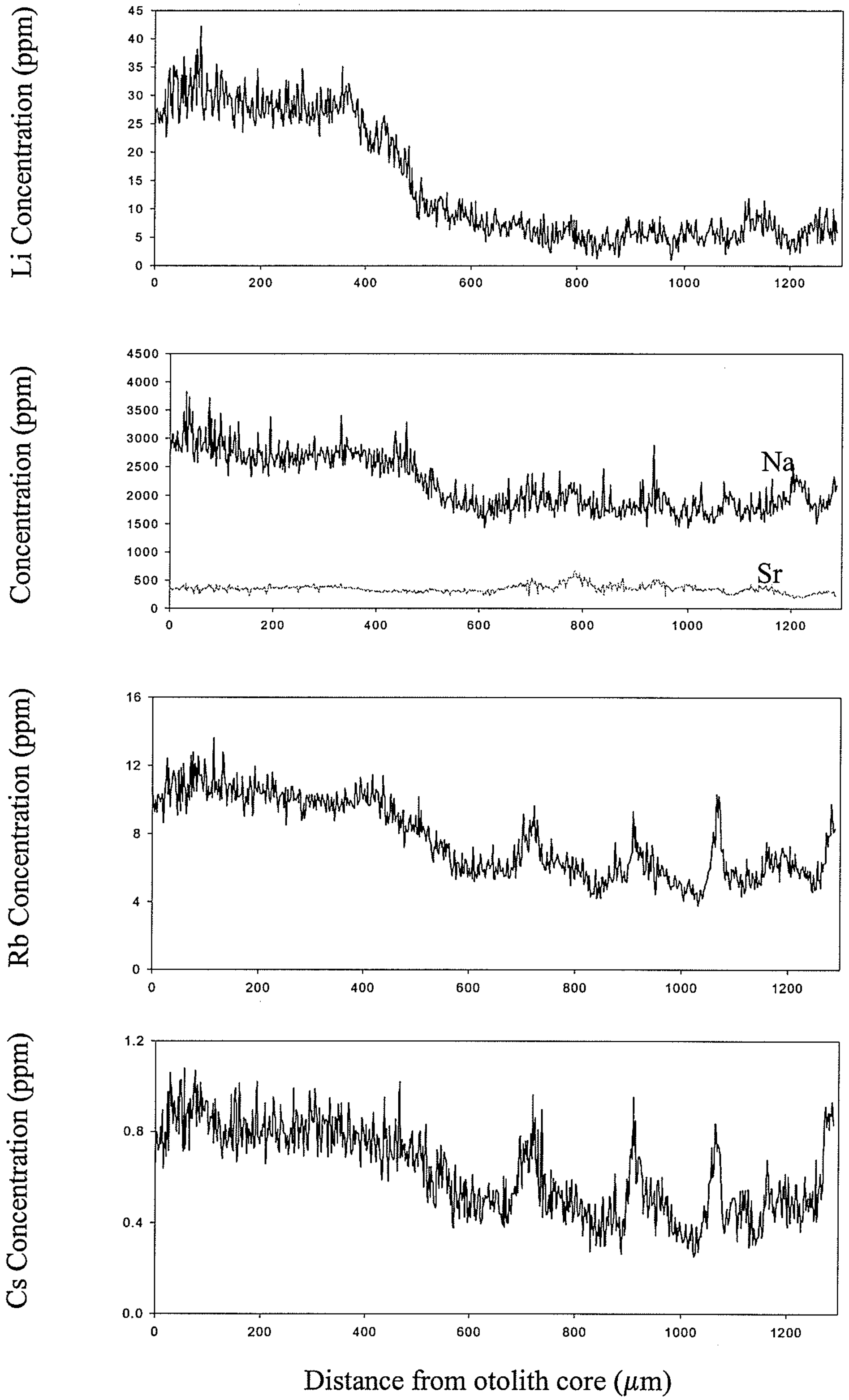

Li Concentration (ppm)
0
5
10
15
20
25
30
0
100
200
300
400
500
600
700
800
900
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
100
200
300
400
500
600
700
800
900
Rb Concentration (ppm)
0
2
4
6
8
10
12
0
100
200
300
400
500
600
700
800
900
Cs Concentration (ppm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
100
200
300
400
500
600
700
800
900
Distance from otolith core (μm)

B08_08

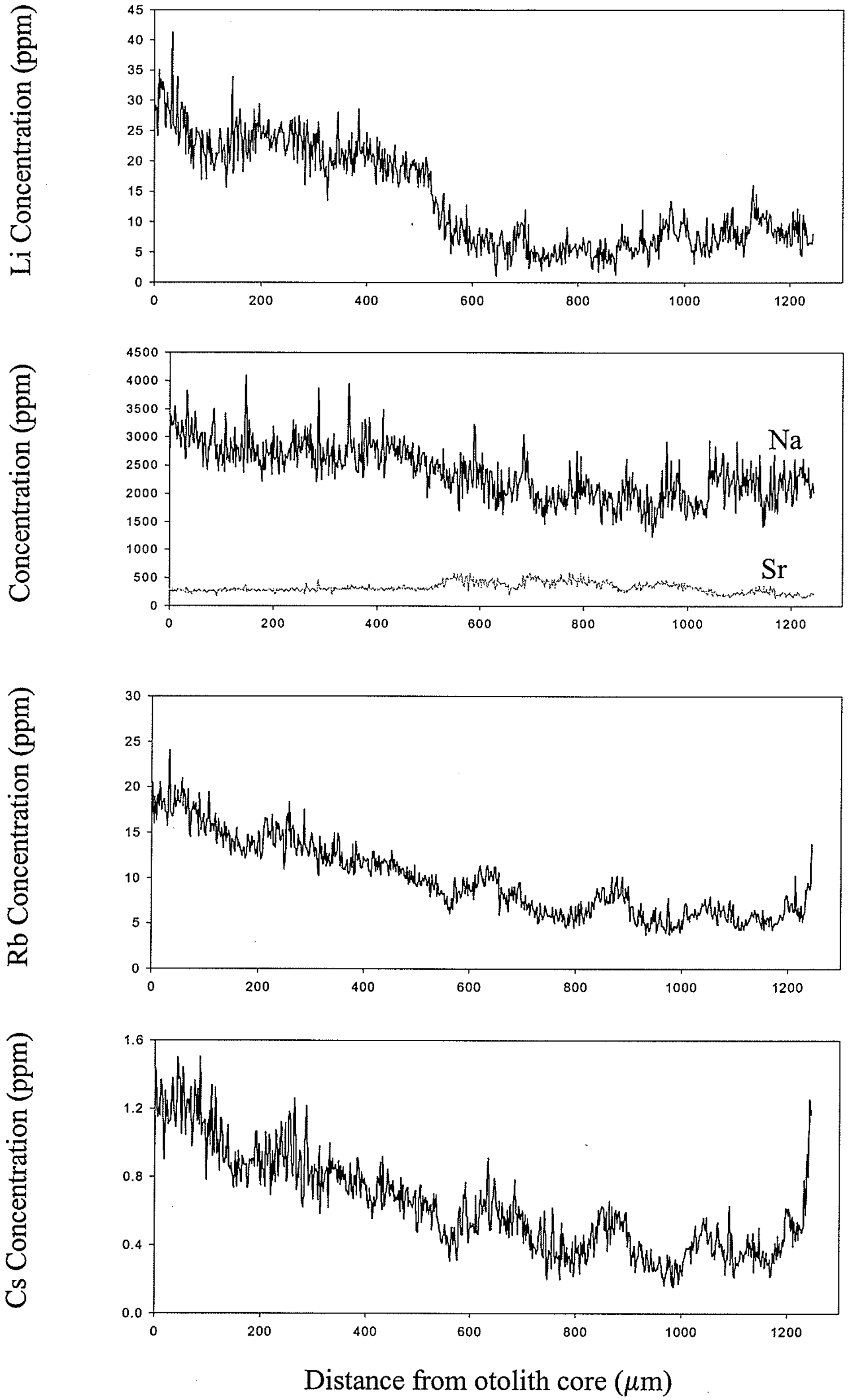


Li Concentration (ppm)
0
5
10
15
20
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
0
1000
2000
3000
4000
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
Rb Concentration (ppm)
0
5
10
15
20
0
200
400
600
800
1000
1200
1400
1600
Cs Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

B08_09

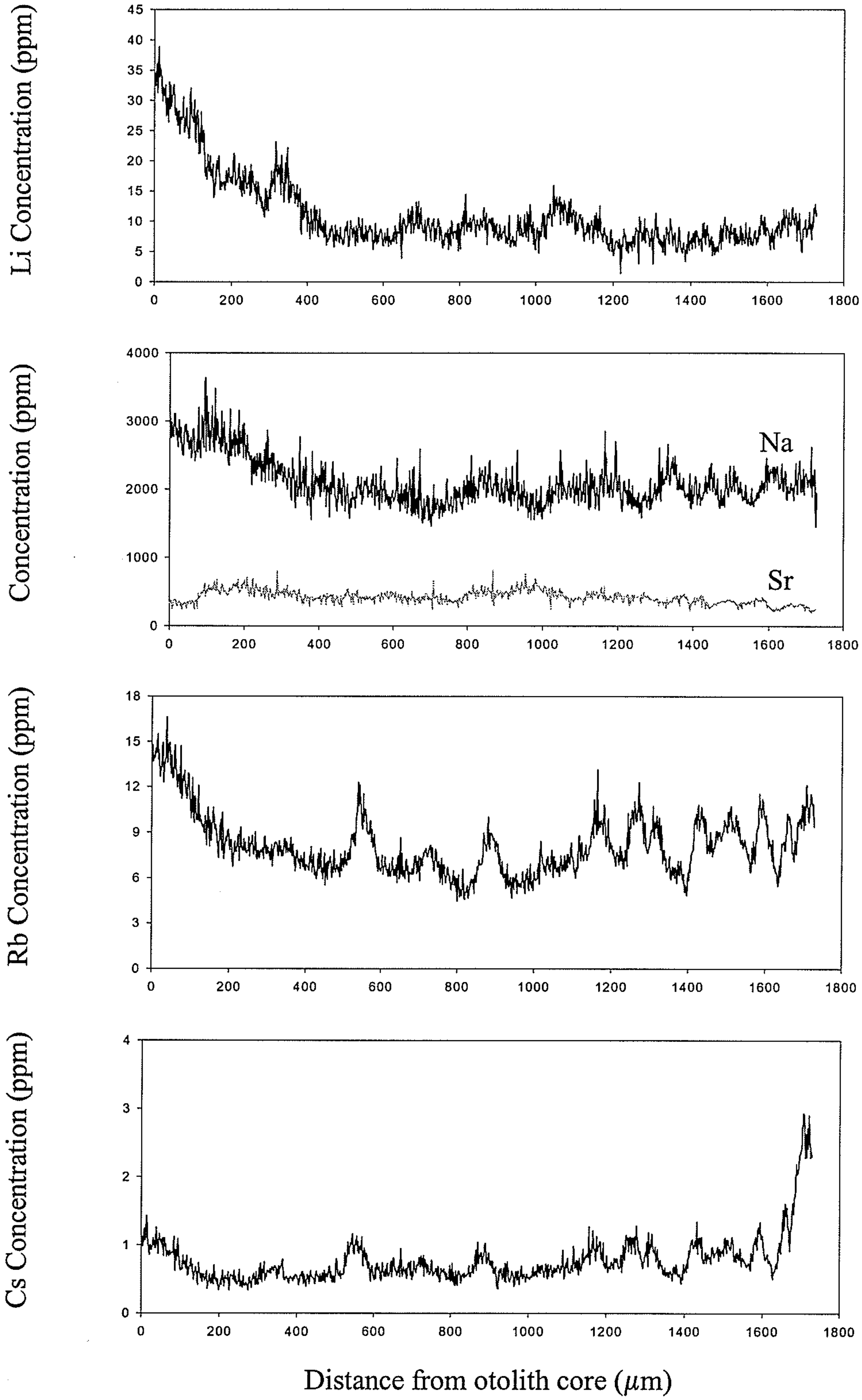

Li Concentration (ppm)
45
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
16
12
8
4
0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

B08_10

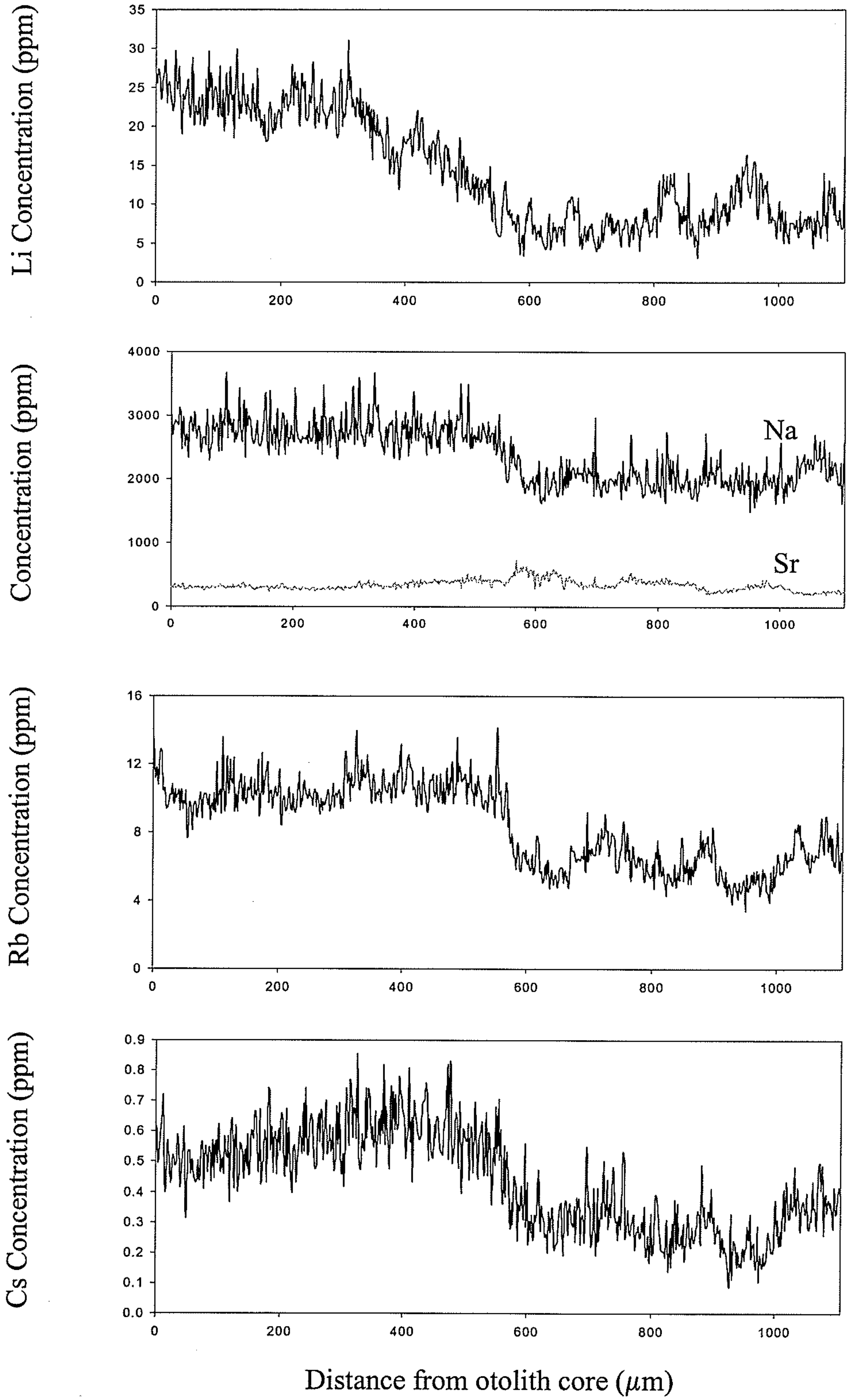


Li Concentration (ppm)
45
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

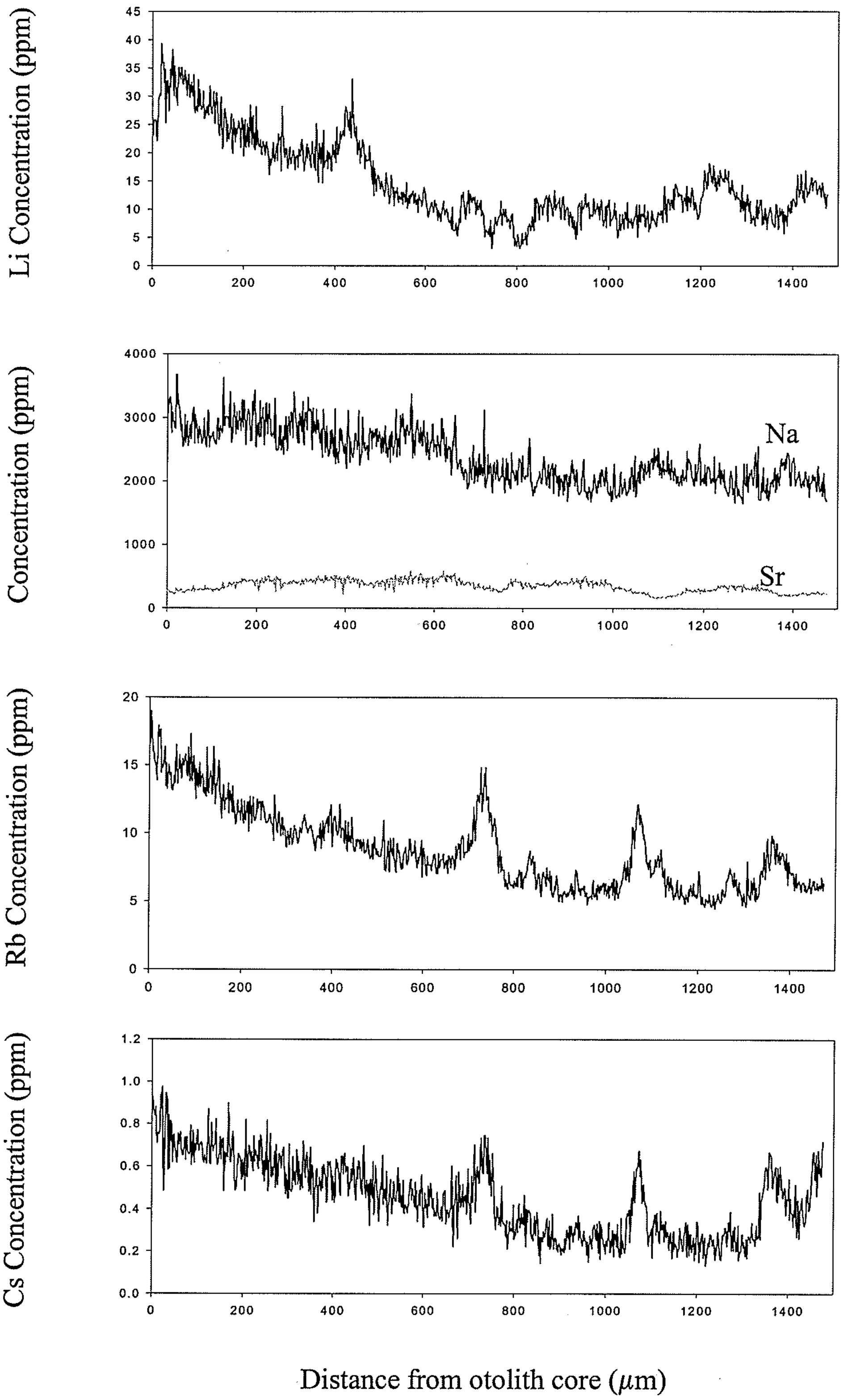
B08_11


Li Concentration (ppm)
45
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
1800
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
1800
Rb Concentration (ppm)
18
15
12
9
6
3
0
0
200
400
600
800
1000
1200
1400
1600
1800
Cs Concentration (ppm)
4
3
2
1
0
0
200
400
600
800
1000
1200
1400
1600
1800
Distance from otolith core (μm)

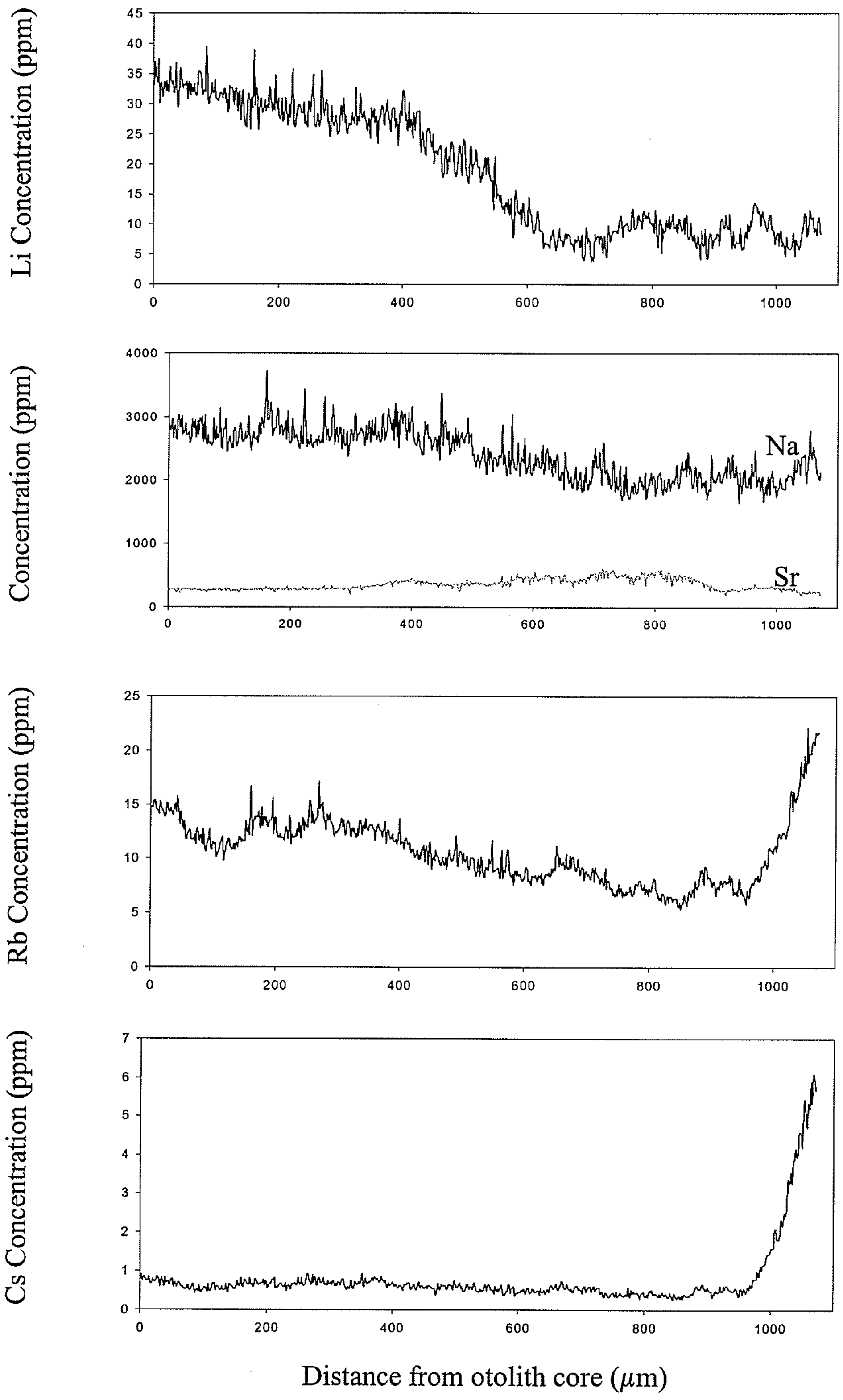
B08_12


Li Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
16
12
8
4
0
Cs Concentration (ppm)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Distance from otolith core (μm)

B08_13

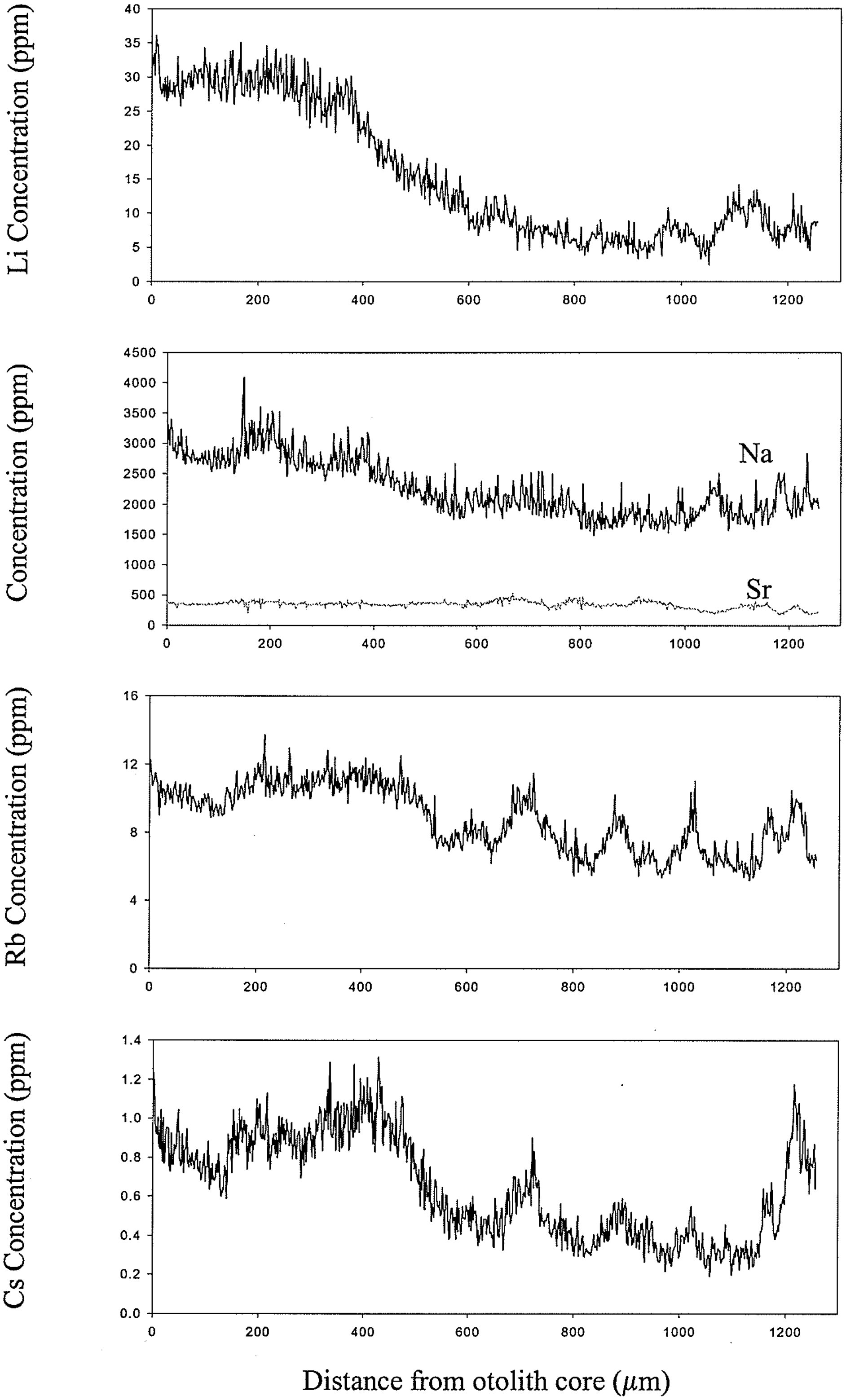

Li Concentration (ppm)
0
5
10
15
20
25
30
35
40
45
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
0
1000
2000
3000
4000
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
0
5
10
15
20
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

B08_14

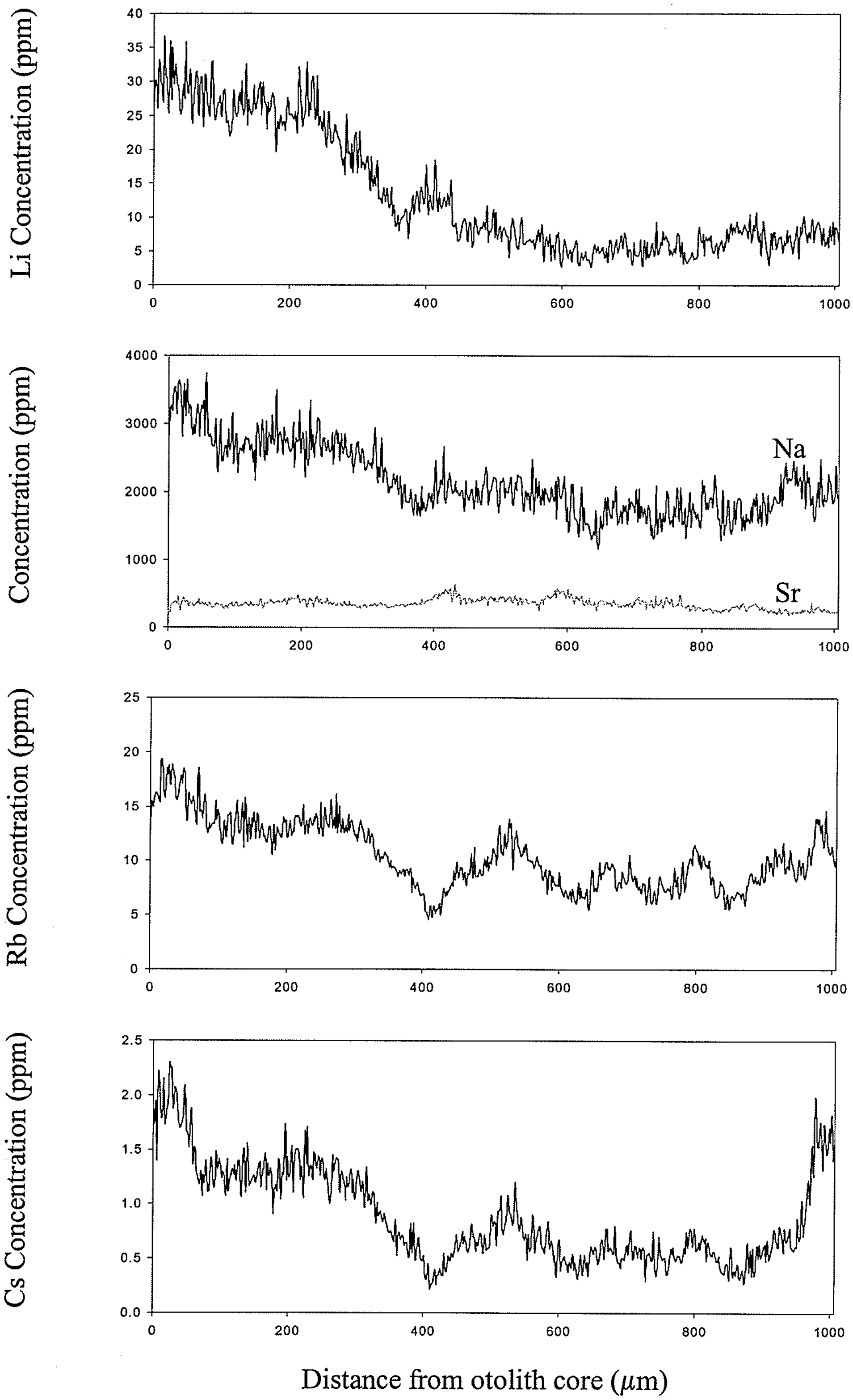


Li Concentration (ppm)
45
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
25
20
15
10
5
0
0
200
400
600
800
1000
Cs Concentration (ppm)
7
6
5
4
3
2
1
0
0
200
400
600
800
1000
Distance from otolith core (μm)

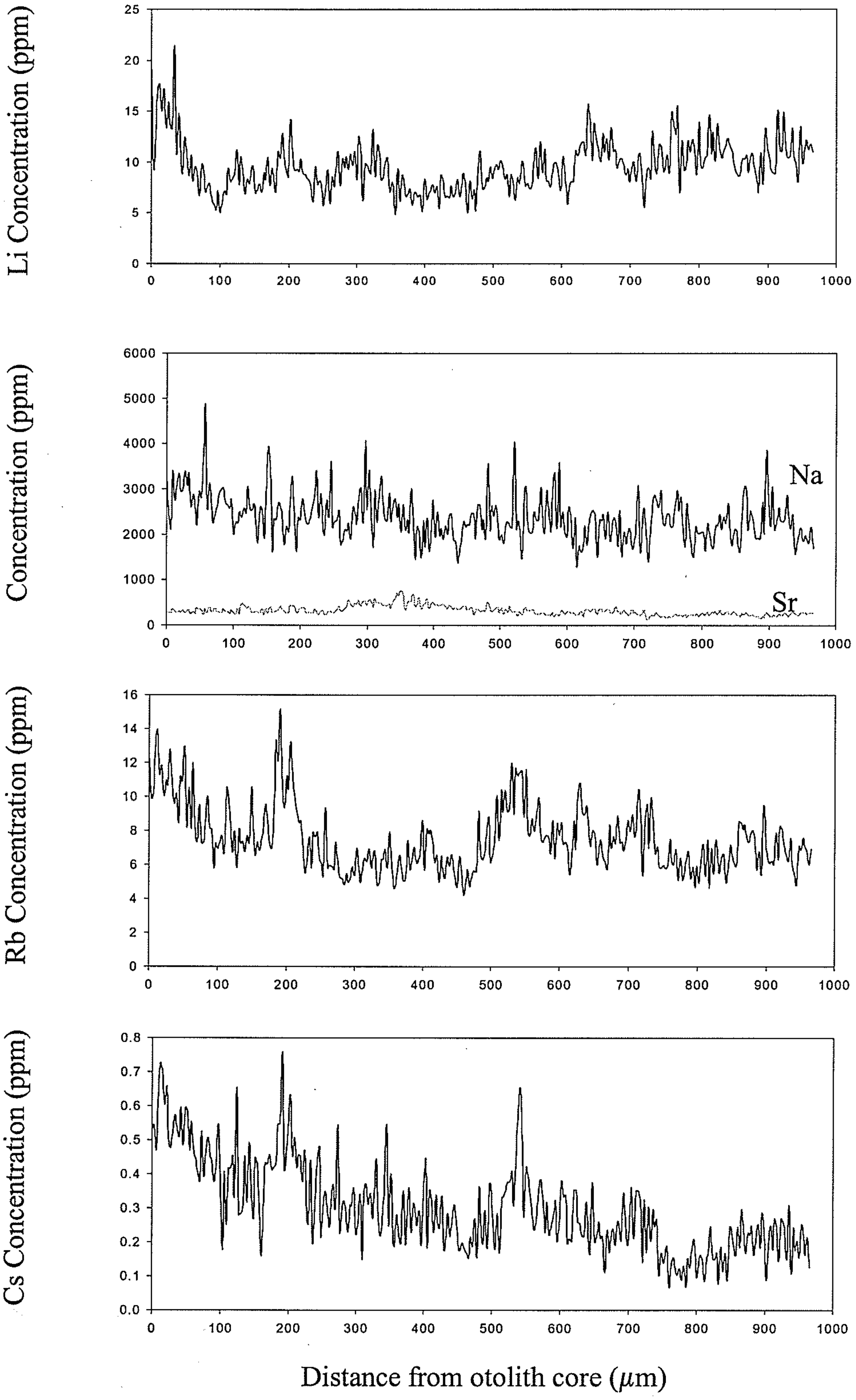
B08_15


Li Concentration (ppm)
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
16
12
8
4
0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

B08_16

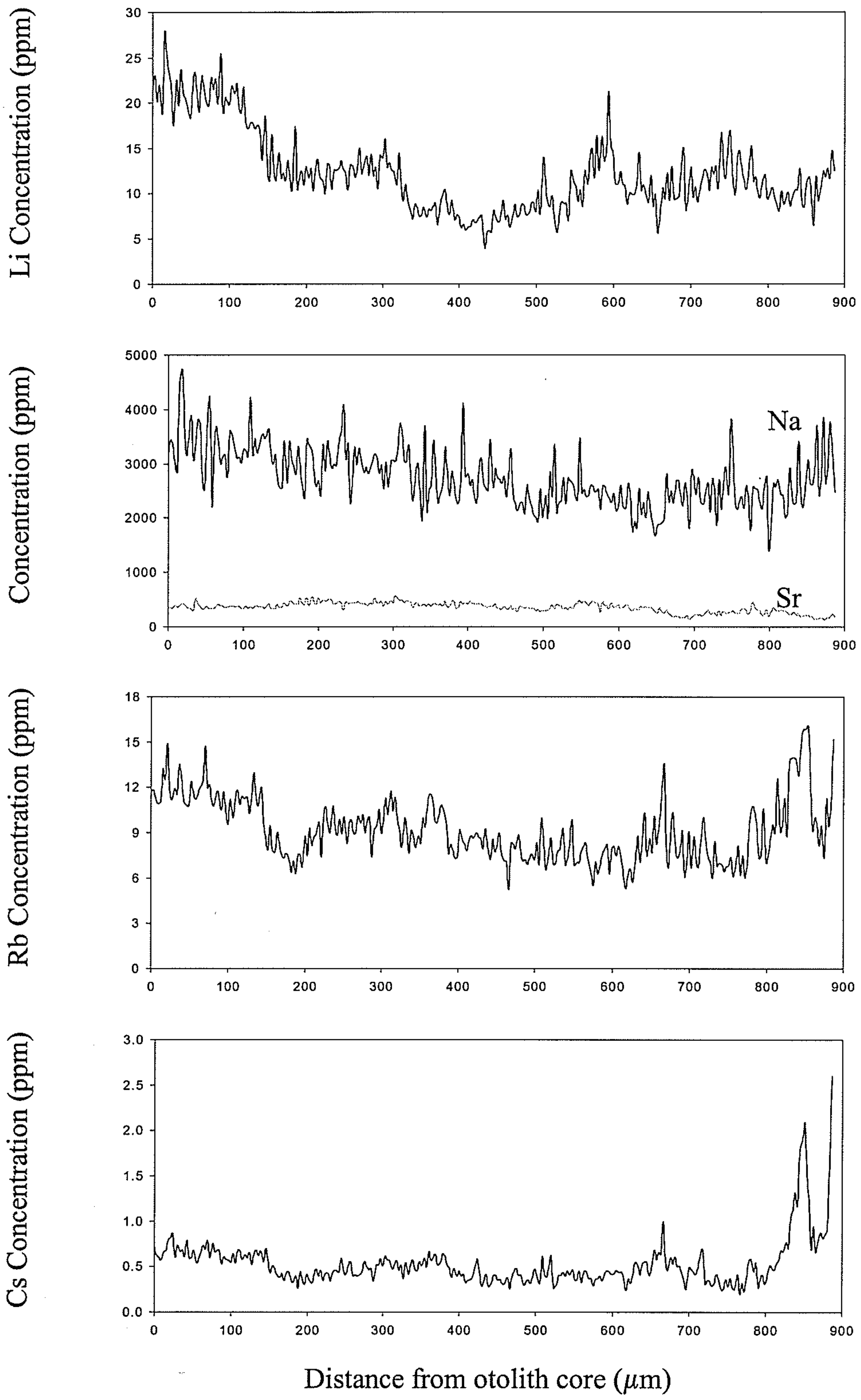

Li Concentration (ppm)
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
25
20
15
10
5
0
0
200
400
600
800
1000
Cs Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

B08_17

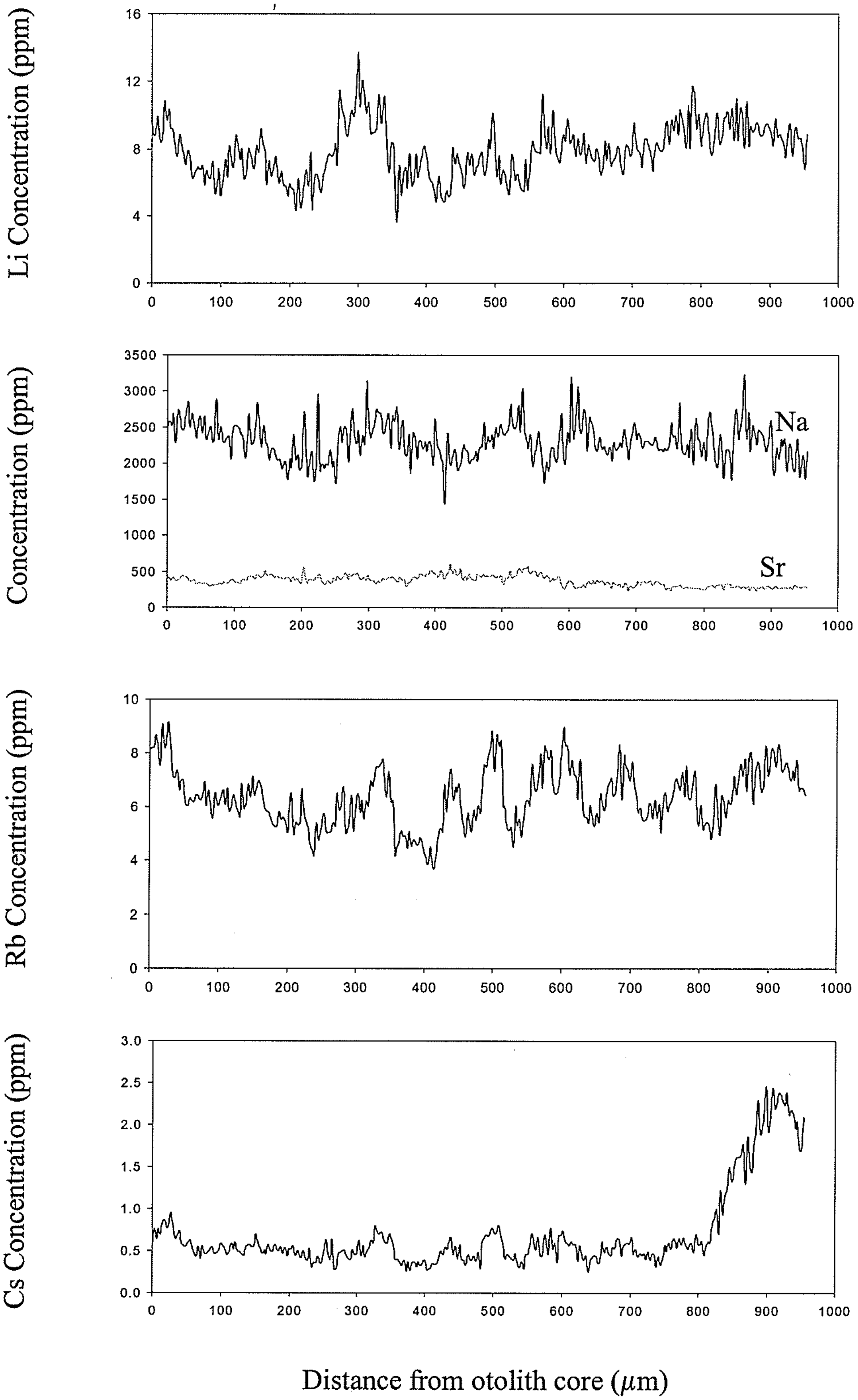


Li Concentration (ppm)
25
20
15
10
5
0
0
100
200
300
400
500
600
700
800
900
1000
Concentration (ppm)
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
800
900
1000
Rb Concentration (ppm)
16
14
12
10
8
6
4
2
0
0
100
200
300
400
500
600
700
800
900
1000
Cs Concentration (ppm)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
100
200
300
400
500
600
700
800
900
1000
Distance from otolith core (μm)

B08_18

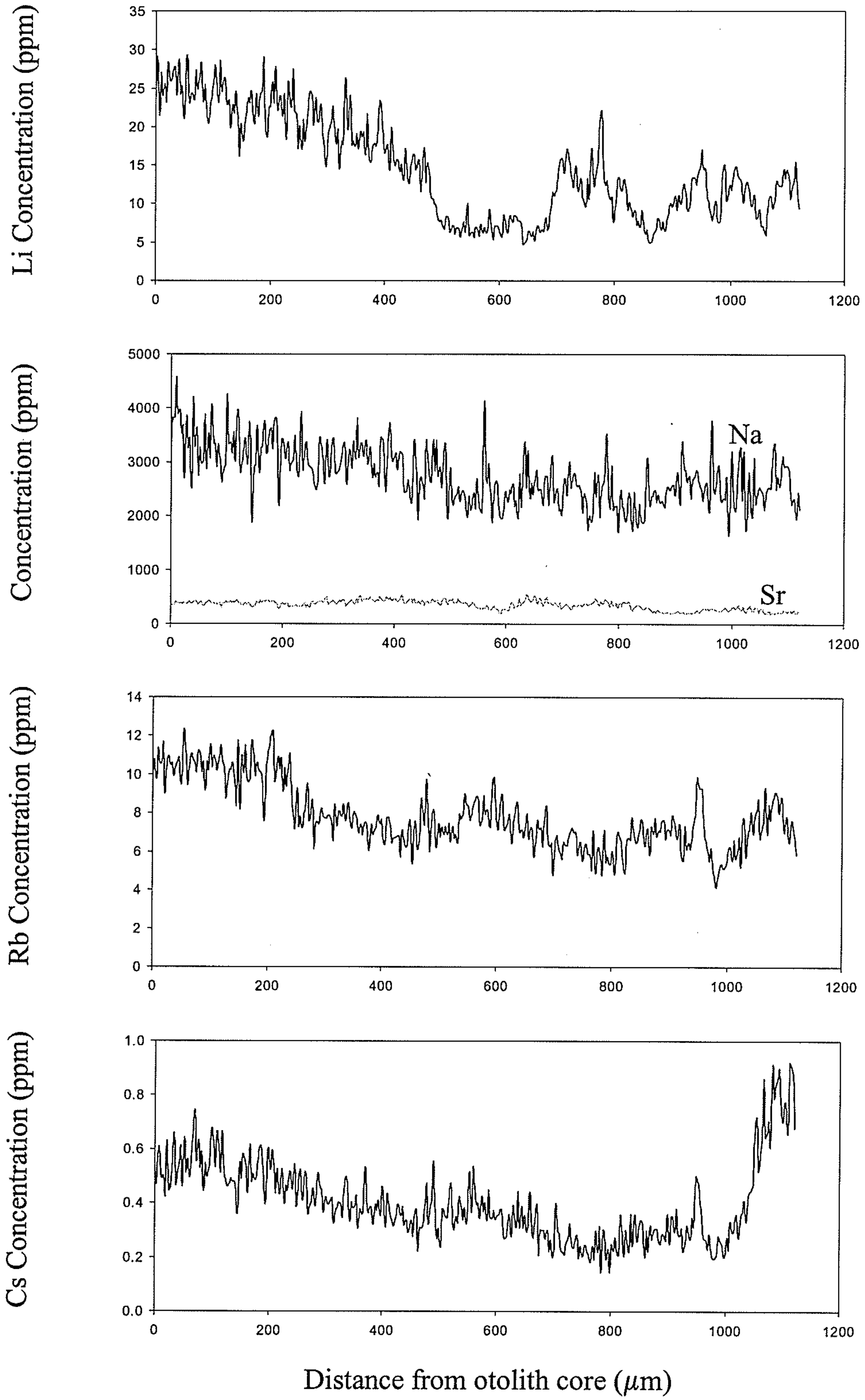

Li Concentration (ppm)
30
25
20
15
10
5
0
0
100
200
300
400
500
600
700
800
900
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
800
900
Rb Concentration (ppm)
18
15
12
9
6
3
0
0
100
200
300
400
500
600
700
800
900
Cs Concentration (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
100
200
300
400
500
600
700
800
900
Distance from otolith core (μm)

B08_19

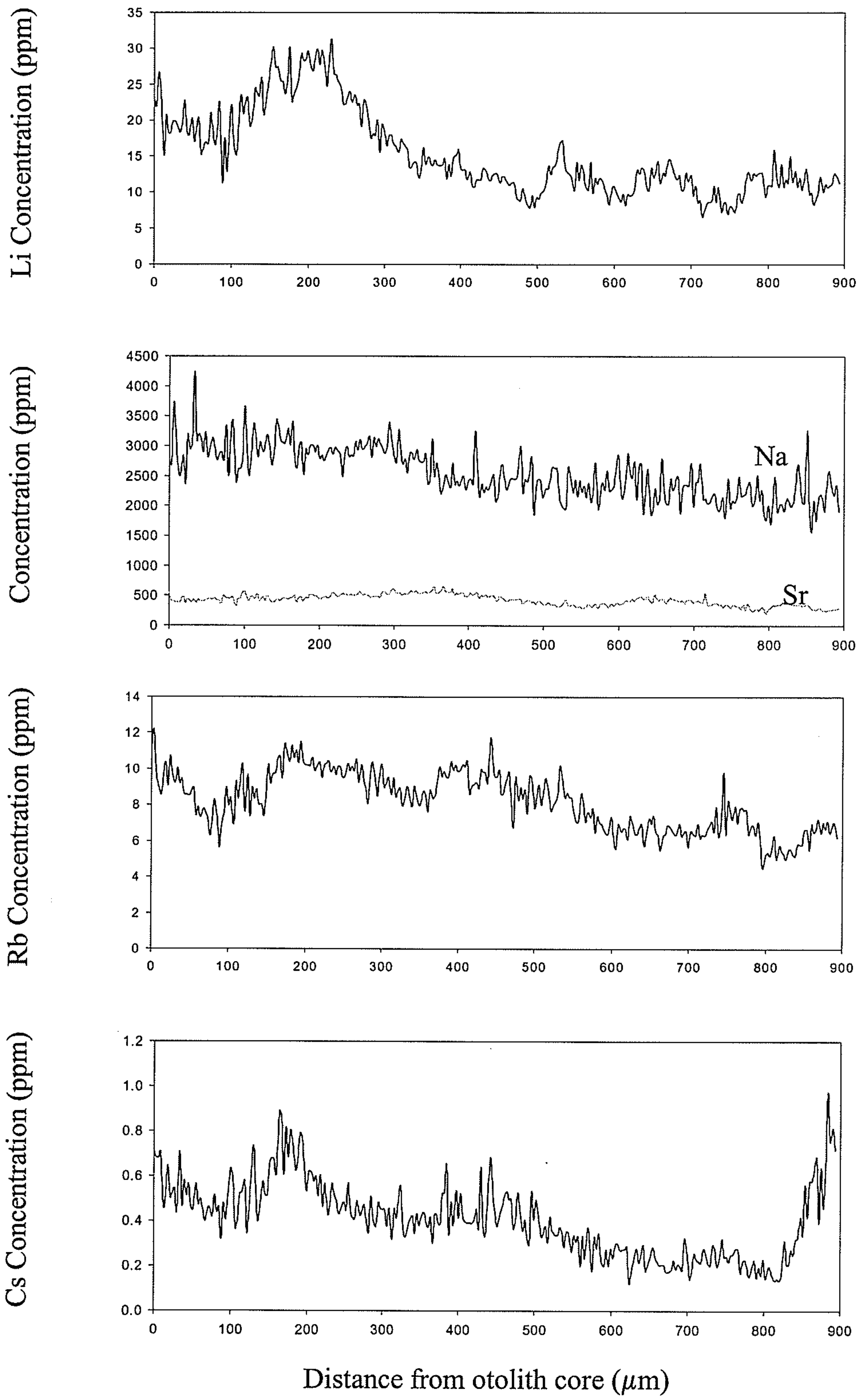


Li Concentration (ppm)
0
4
8
12
16
Concentration (ppm)
0
500
1000
1500
2000
2500
3000
3500
Na
Sr
Rb Concentration (ppm)
0
2
4
6
8
10
Cs Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
100
200
300
400
500
600
700
800
900
1000
Distance from otolith core (μm)

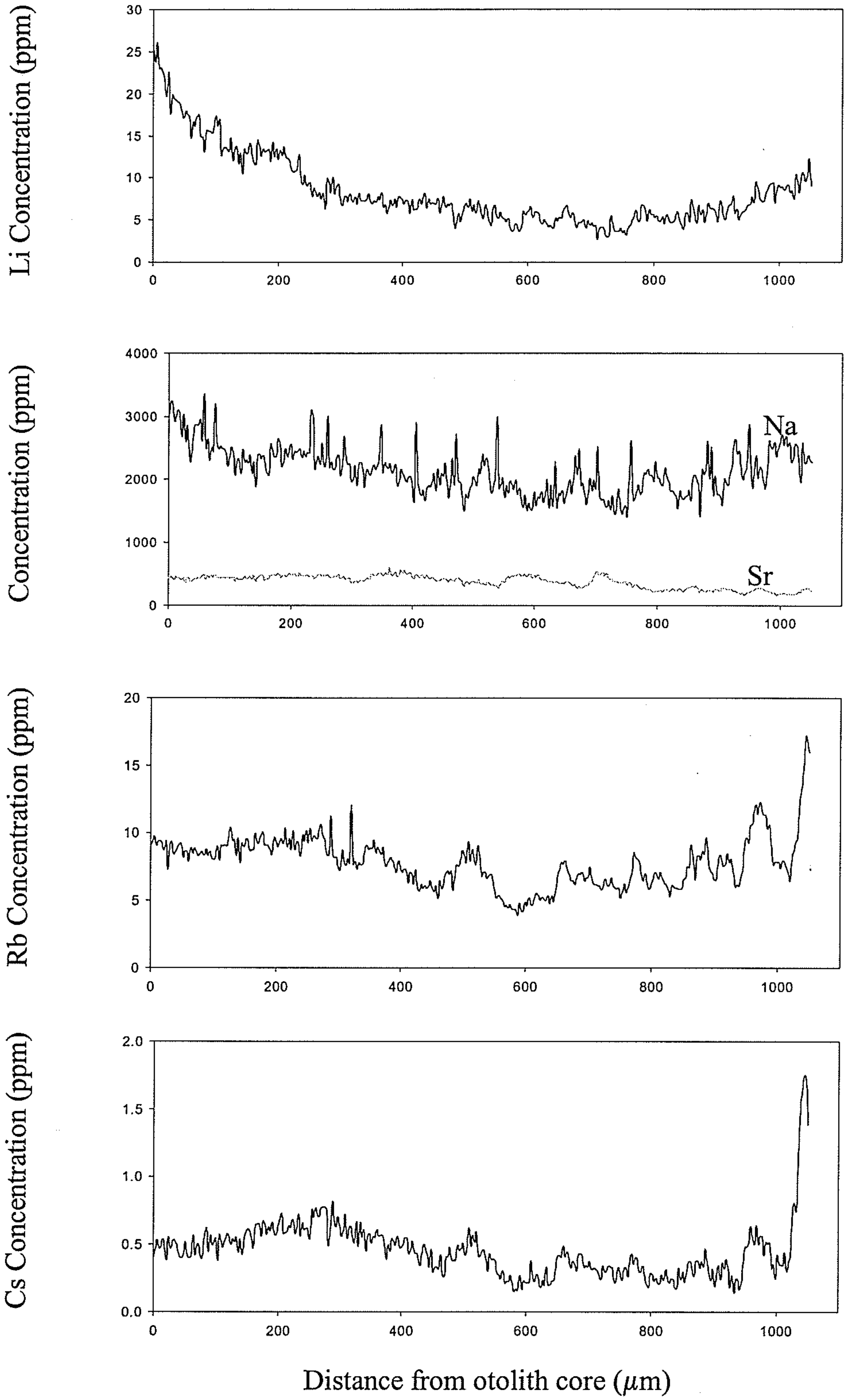
B08_20


Li Concentration (ppm)
35
30
25
20
15
10
5
0
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
14
12
10
8
6
4
2
0
Cs Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

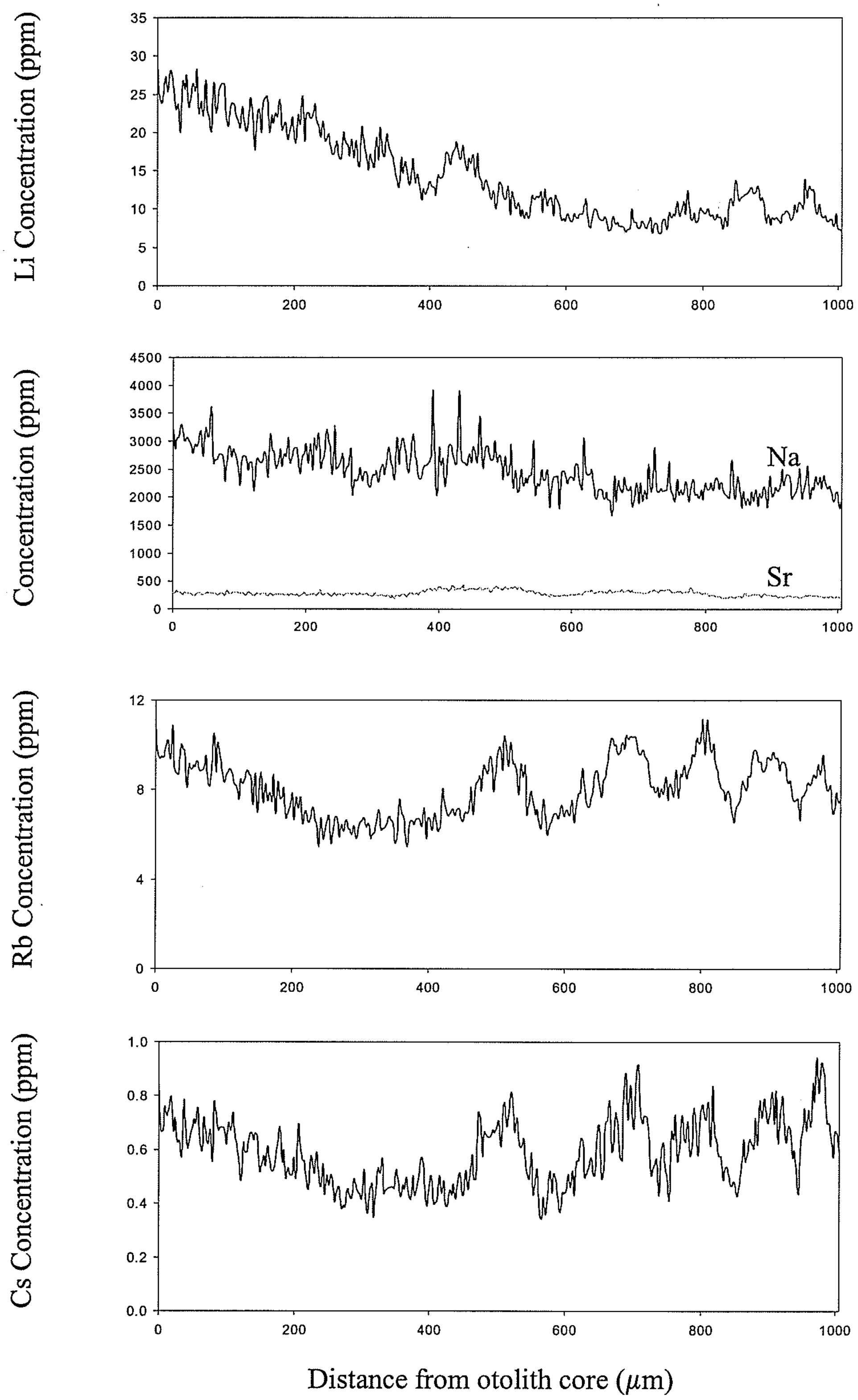
B08_21


Li Concentration (ppm)
35
30
25
20
15
10
5
0
0
100
200
300
400
500
600
700
800
900
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
100
200
300
400
500
600
700
800
900
Rb Concentration (ppm)
14
12
10
8
6
4
2
0
0
100
200
300
400
500
600
700
800
900
Cs Concentration (ppm)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
100
200
300
400
500
600
700
800
900
Distance from otolith core (μm)

B08_22

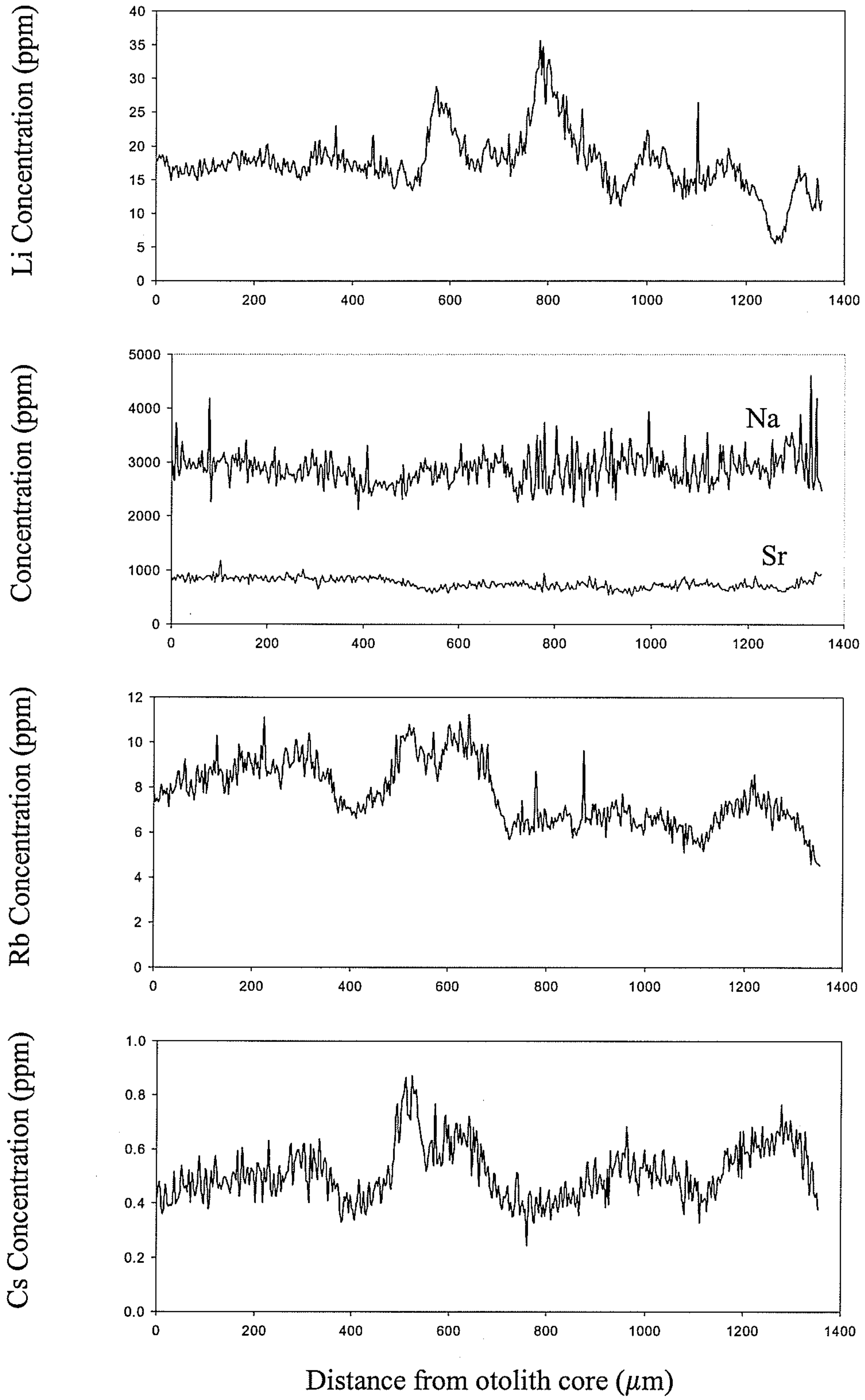

Li Concentration (ppm)
30
25
20
15
10
5
0
0
200
400
600
800
1000
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
20
15
10
5
0
0
200
400
600
800
1000
Cs Concentration (ppm)
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

B08_23

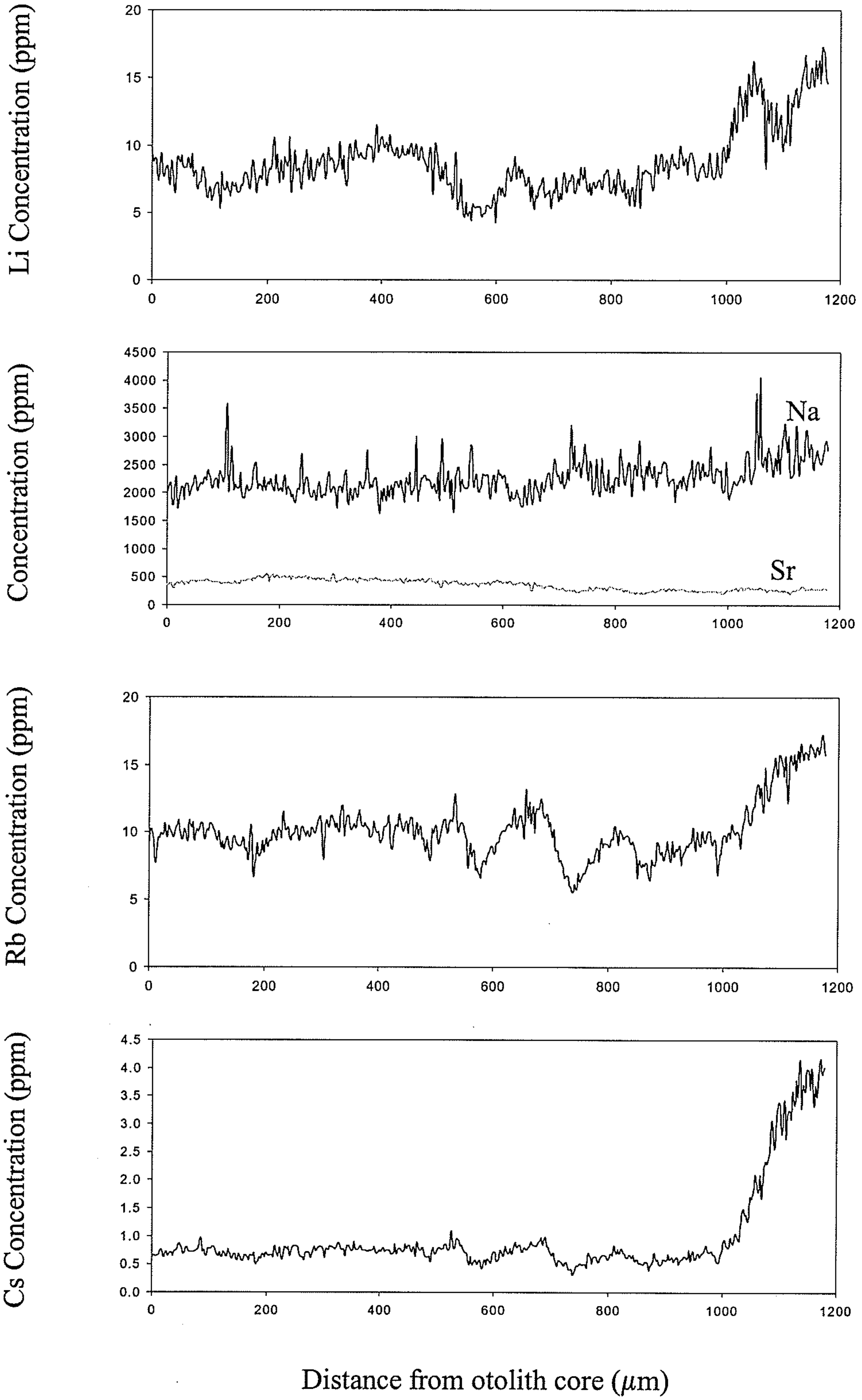


Li Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
12
8
4
0
0
200
400
600
800
1000
Cs Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

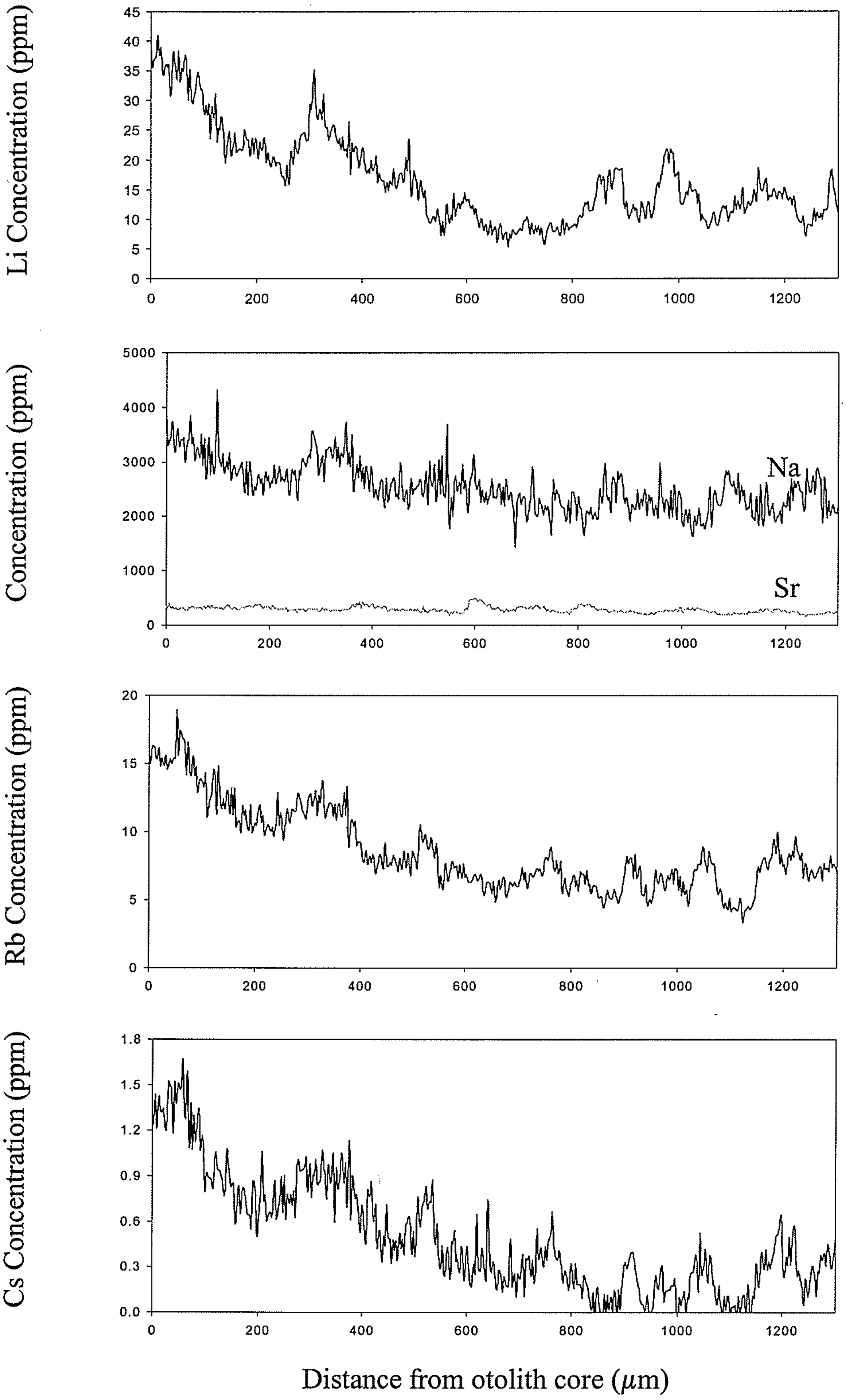
B08_24


Li Concentration (ppm)
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
12
10
8
6
4
2
0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

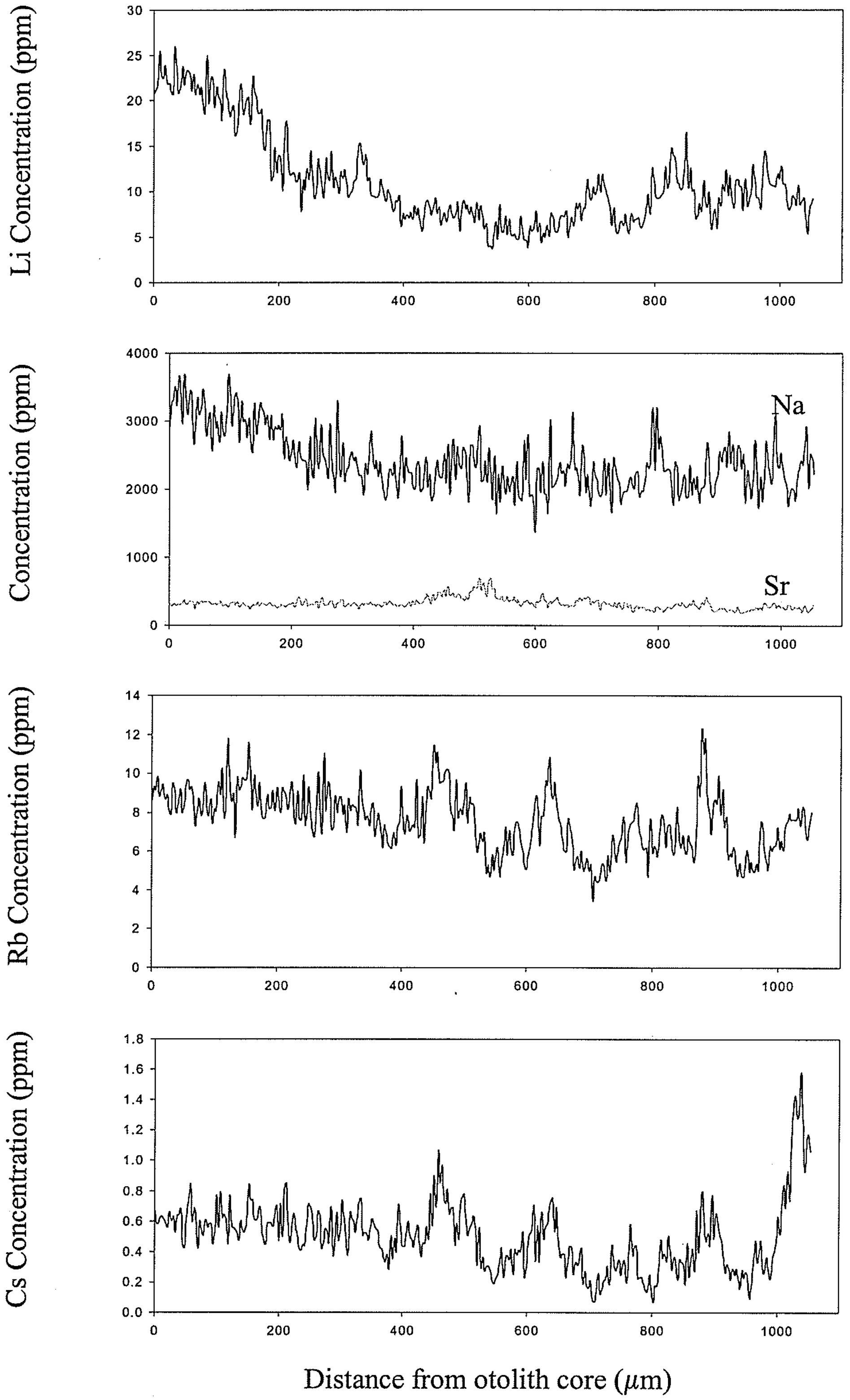
B08_25


Li Concentration (ppm)
20
15
10
5
0
0
200
400
600
800
1000
1200
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
20
15
10
5
0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

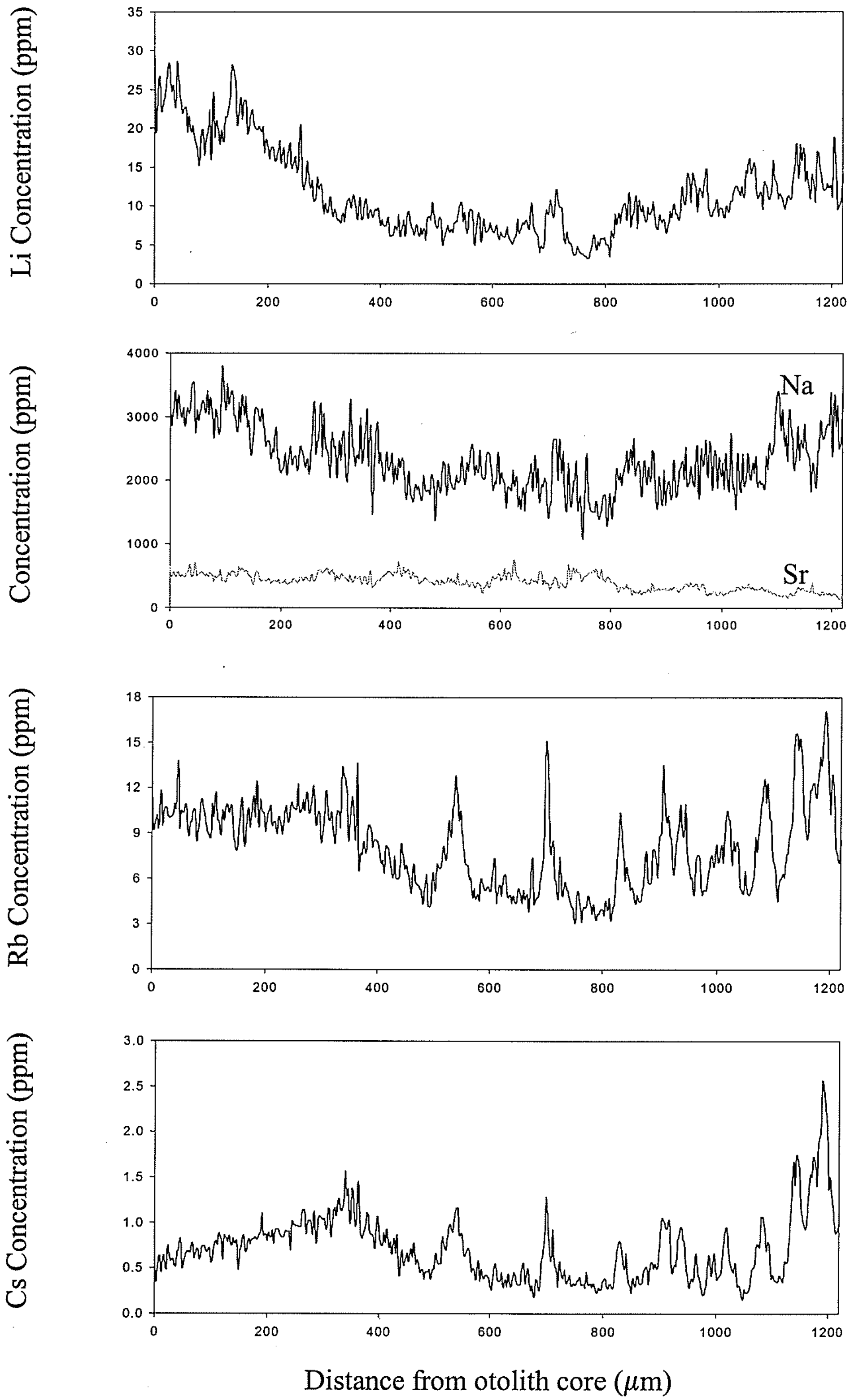
B08_26


Li Concentration (ppm)
45
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
20
15
10
5
0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

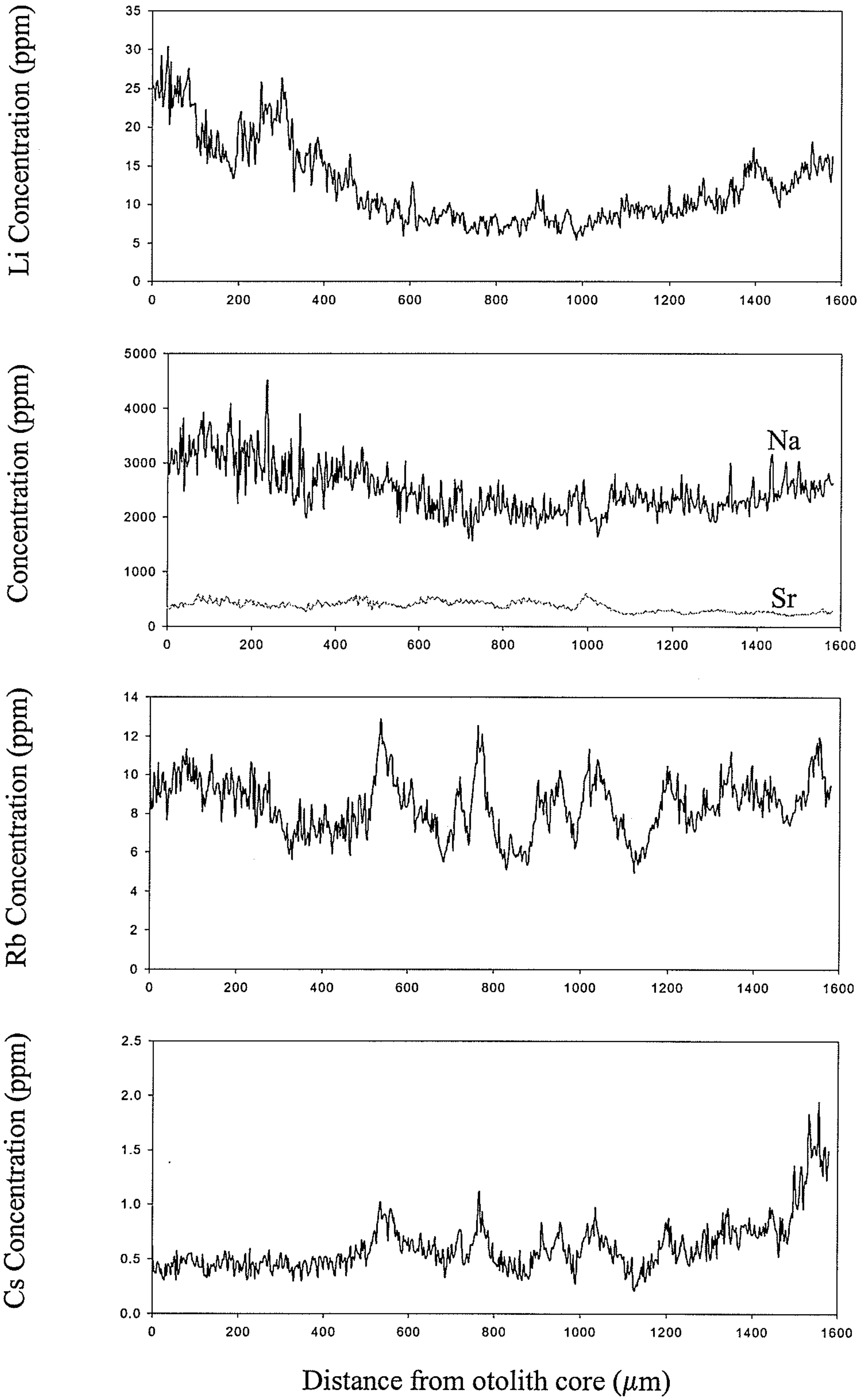
B08_27


Li Concentration (ppm)
30
25
20
15
10
5
0
0
200
400
600
800
1000
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
14
12
10
8
6
4
2
0
0
200
400
600
800
1000
Cs Concentration (ppm)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

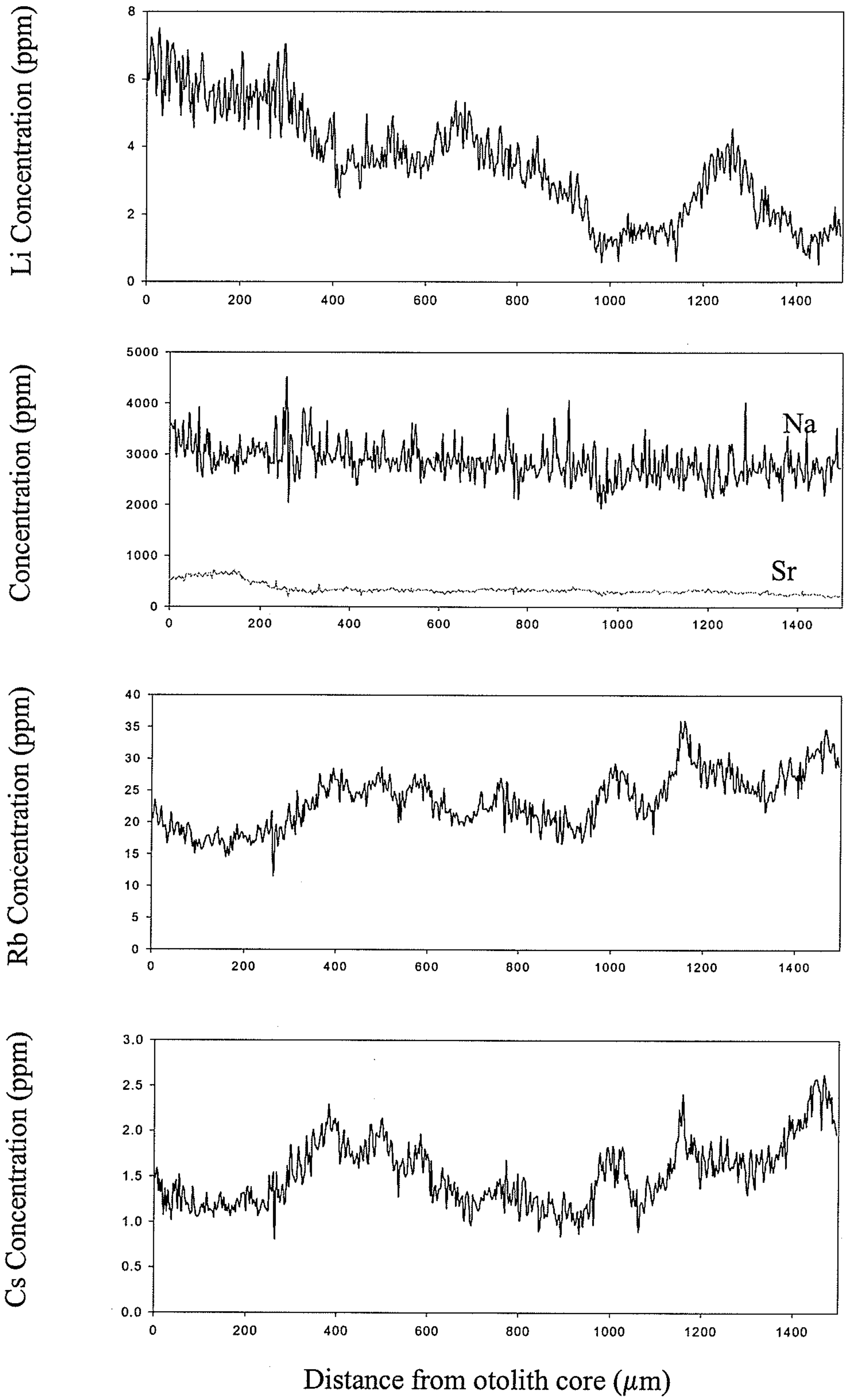
B08_28


Li Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
18
15
12
9
6
3
0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

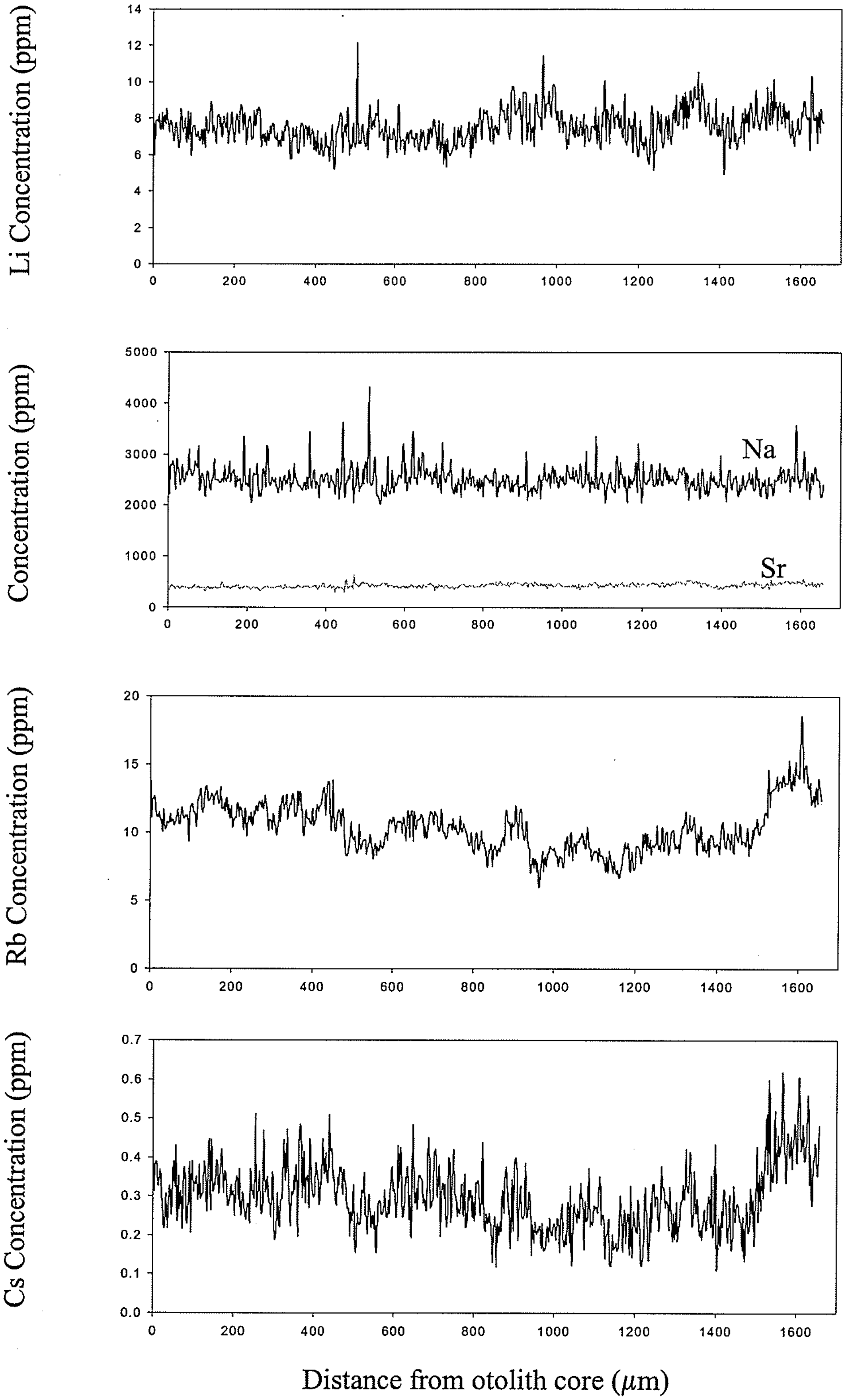
B08_29


Li Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
Rb Concentration (ppm)
14
12
10
8
6
4
2
0
0
200
400
600
800
1000
1200
1400
1600
Cs Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

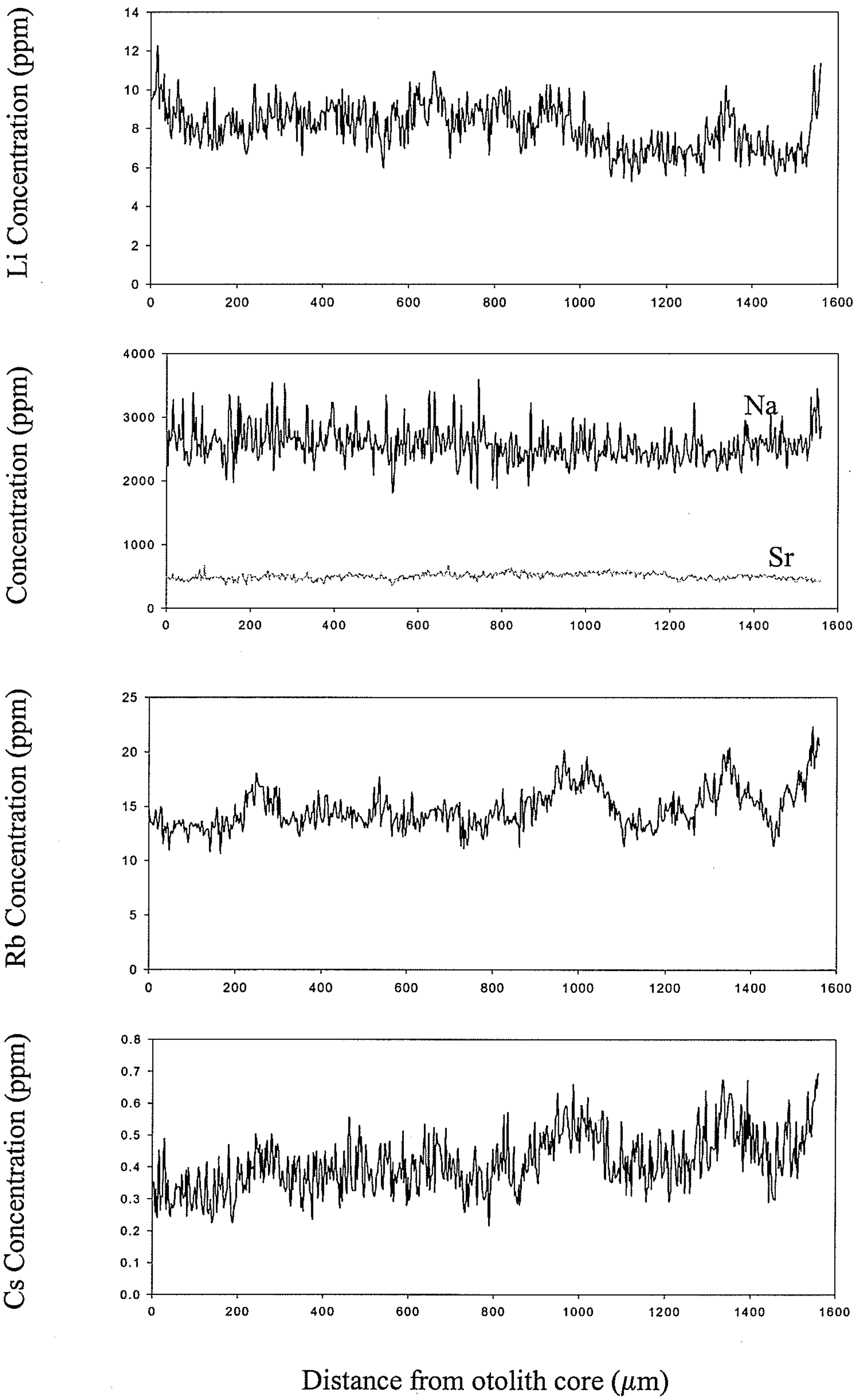
B08_30


Li Concentration (ppm)
8
6
4
2
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

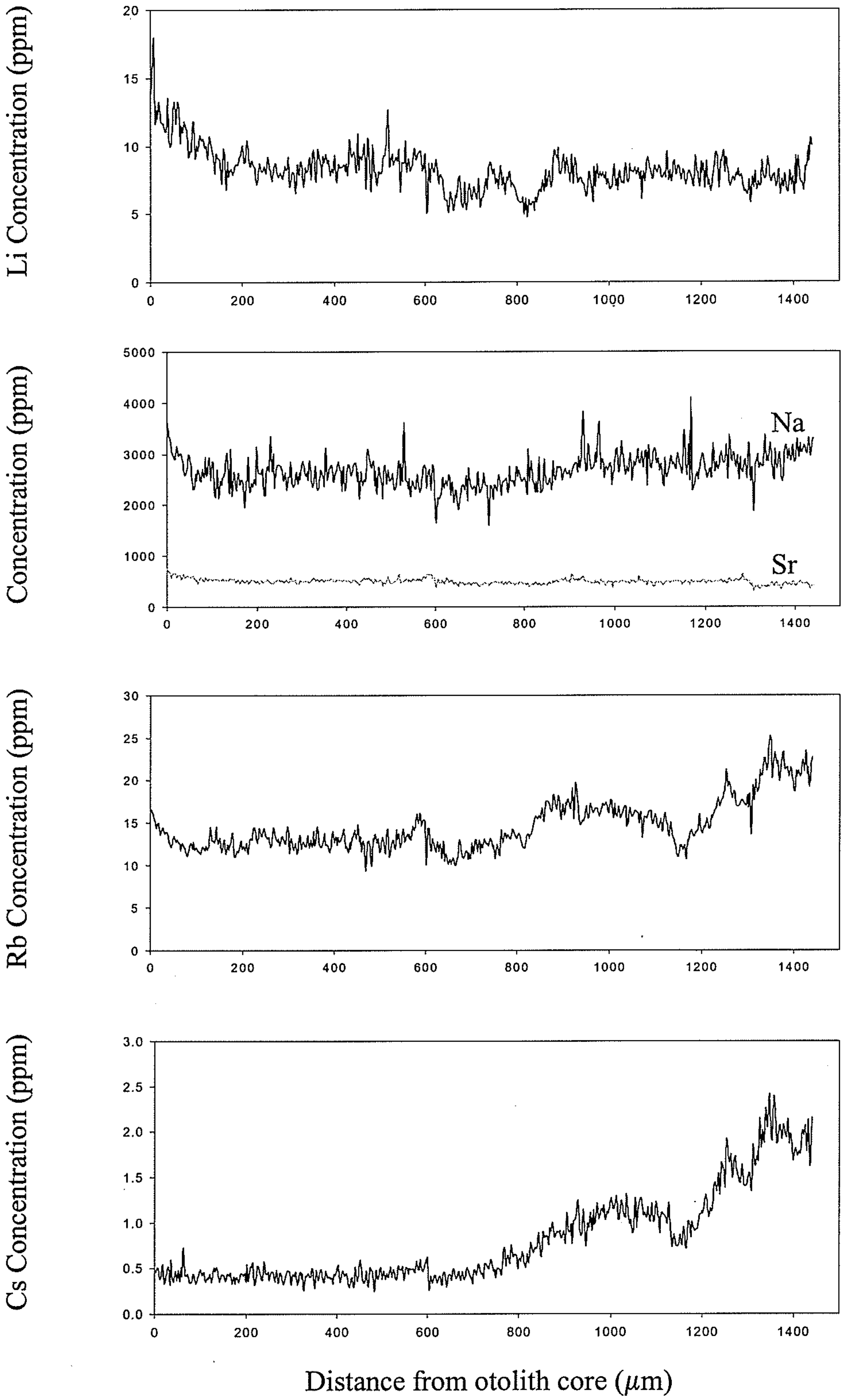
B08_31


Li Concentration (ppm)
14
12
10
8
6
4
2
0
0
200
400
600
800
1000
1200
1400
1600
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
Rb Concentration (ppm)
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
Cs Concentration (ppm)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

B08_32

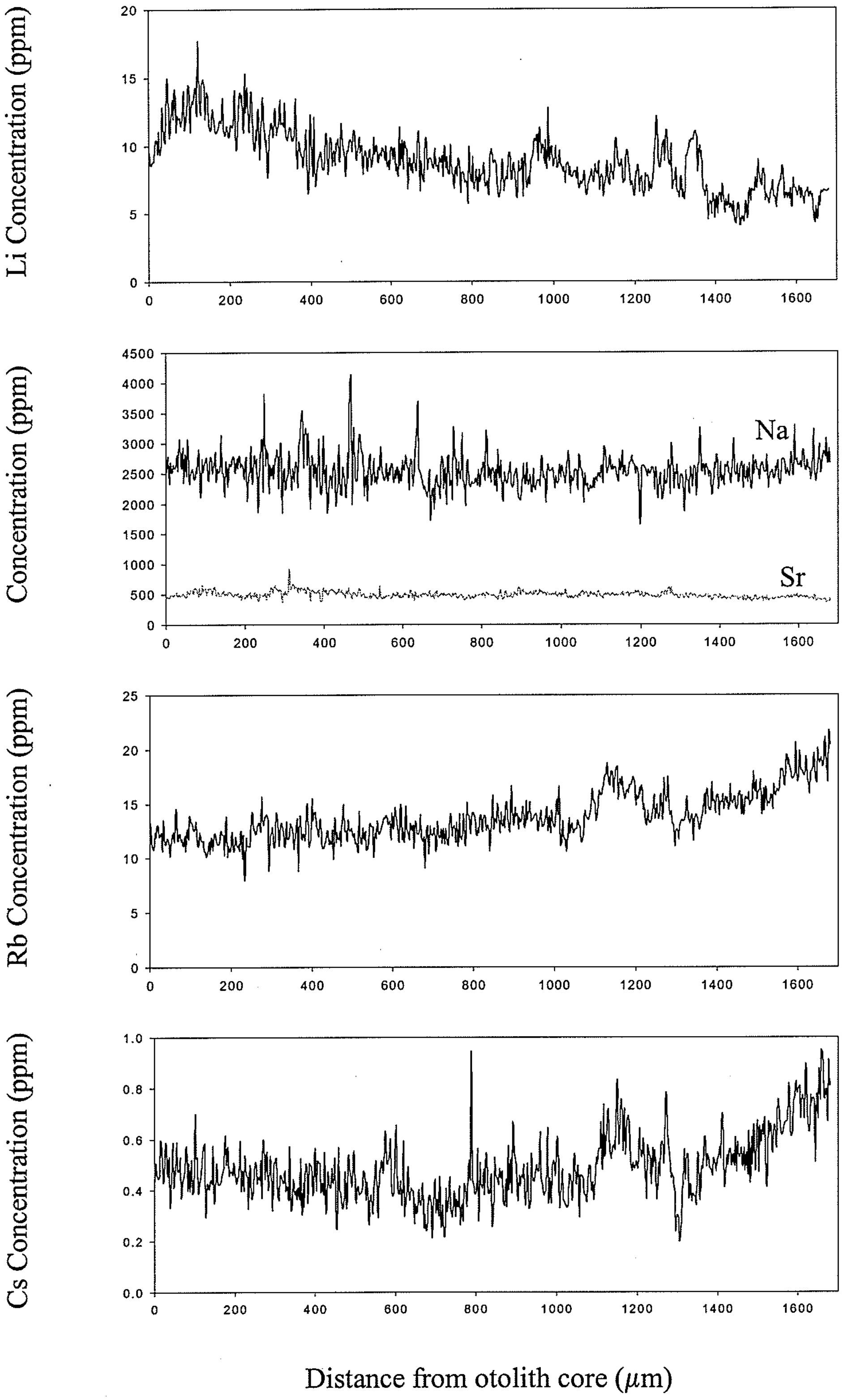

Li Concentration (ppm)
0
2
4
6
8
10
12
14
Concentration (ppm)
Na
Sr
0
1000
2000
3000
4000
Rb Concentration (ppm)
0
5
10
15
20
25
Cs Concentration (ppm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

B08_33

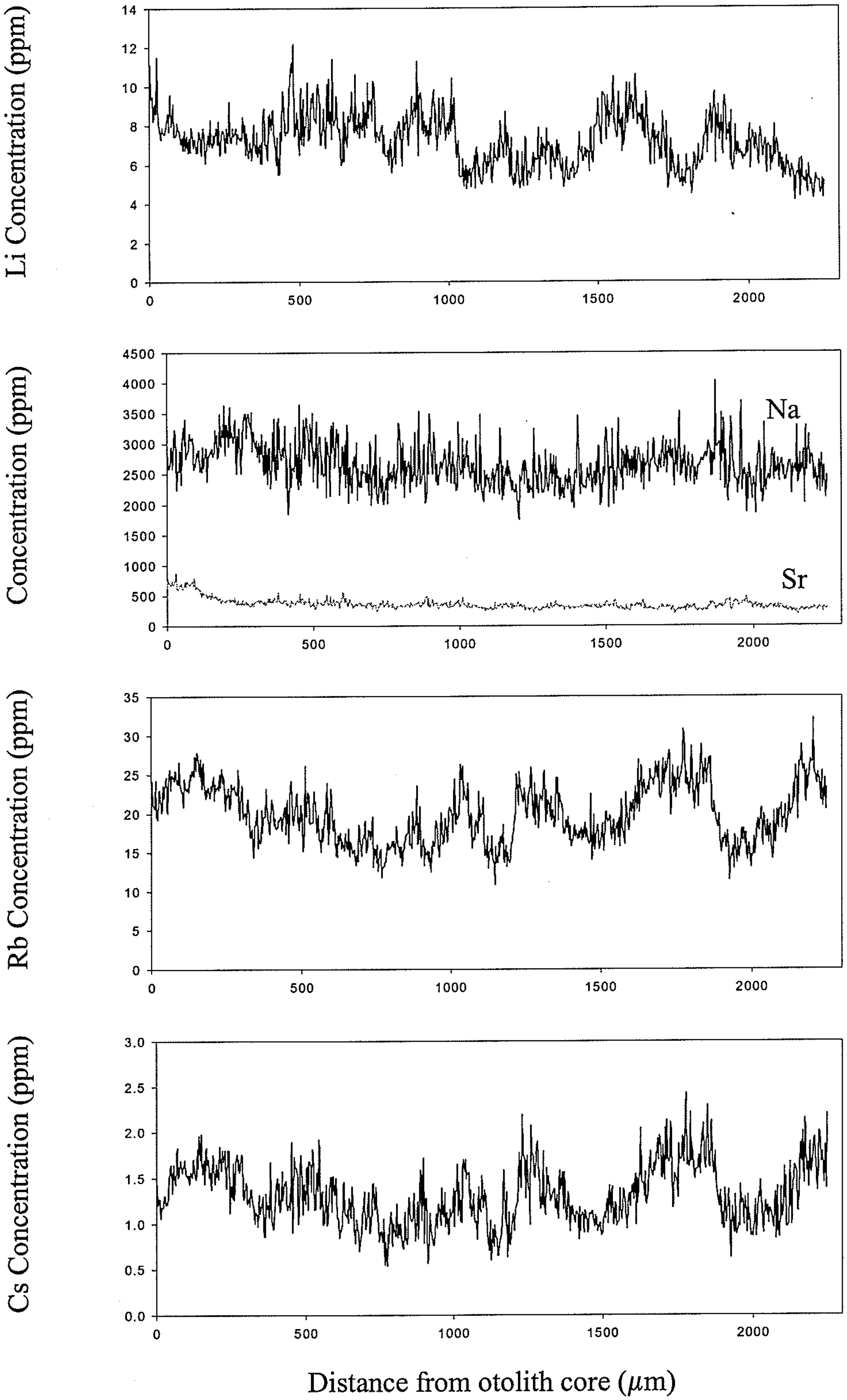


Li Concentration (ppm)
20
15
10
5
0
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
30
25
20
15
10
5
0
Cs Concentration (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

B08_34

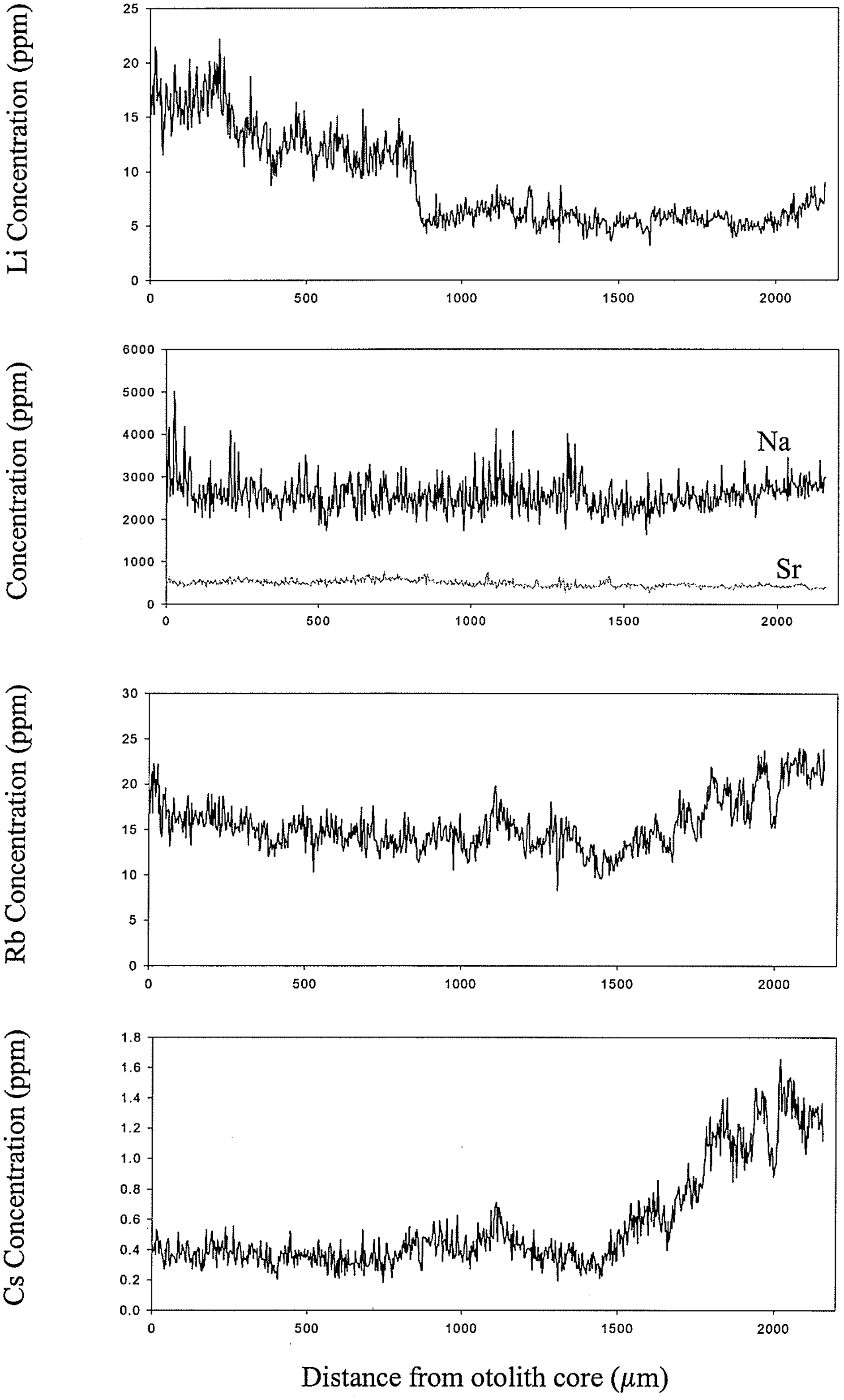

Li Concentration (ppm)
0
5
10
15
20
Concentration (ppm)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Na
Sr
Rb Concentration (ppm)
0
5
10
15
20
25
Cs Concentration (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

B08_35

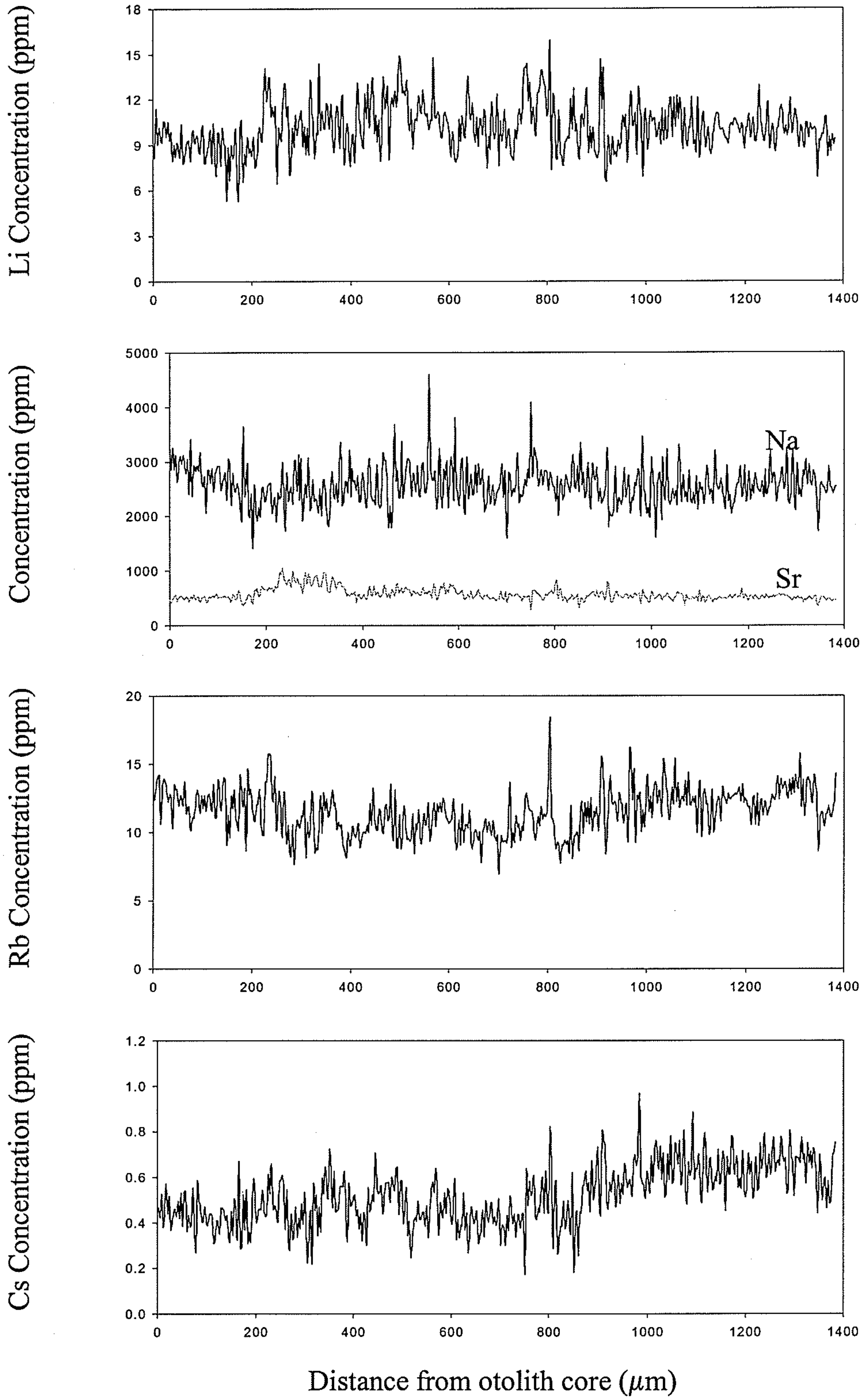


Li Concentration (ppm)
14
12
10
8
6
4
2
0
0
500
1000
1500
2000
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
35
30
25
20
15
10
5
0
0
500
1000
1500
2000
Cs Concentration (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
Distance from otolith core (μm)

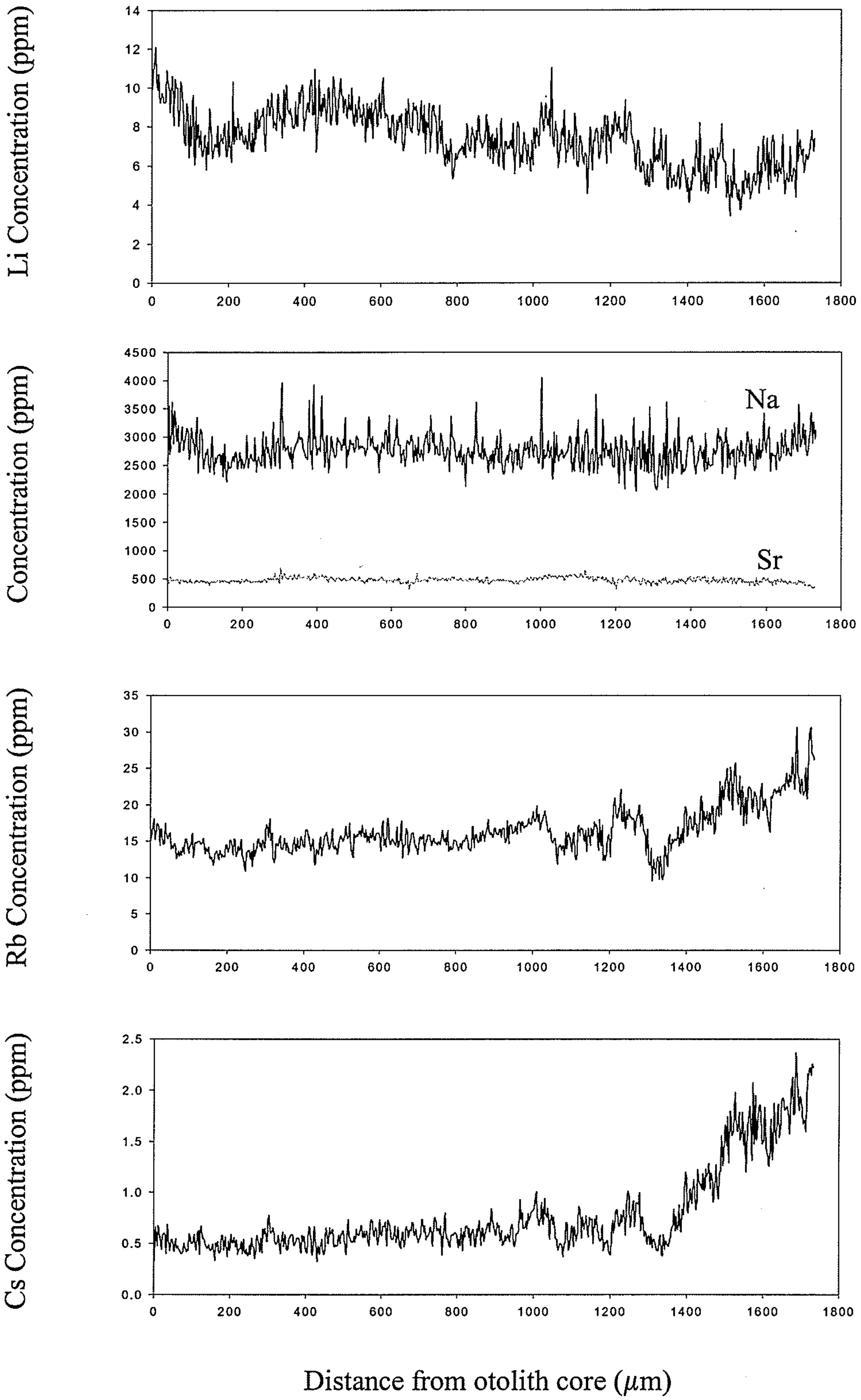
B08_36


Li Concentration (ppm)
25
20
15
10
5
0
0
500
1000
1500
2000
Concentration (ppm)
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
Rb Concentration (ppm)
30
25
20
15
10
5
0
0
500
1000
1500
2000
Cs Concentration (ppm)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500
2000
Distance from otolith core (μm)

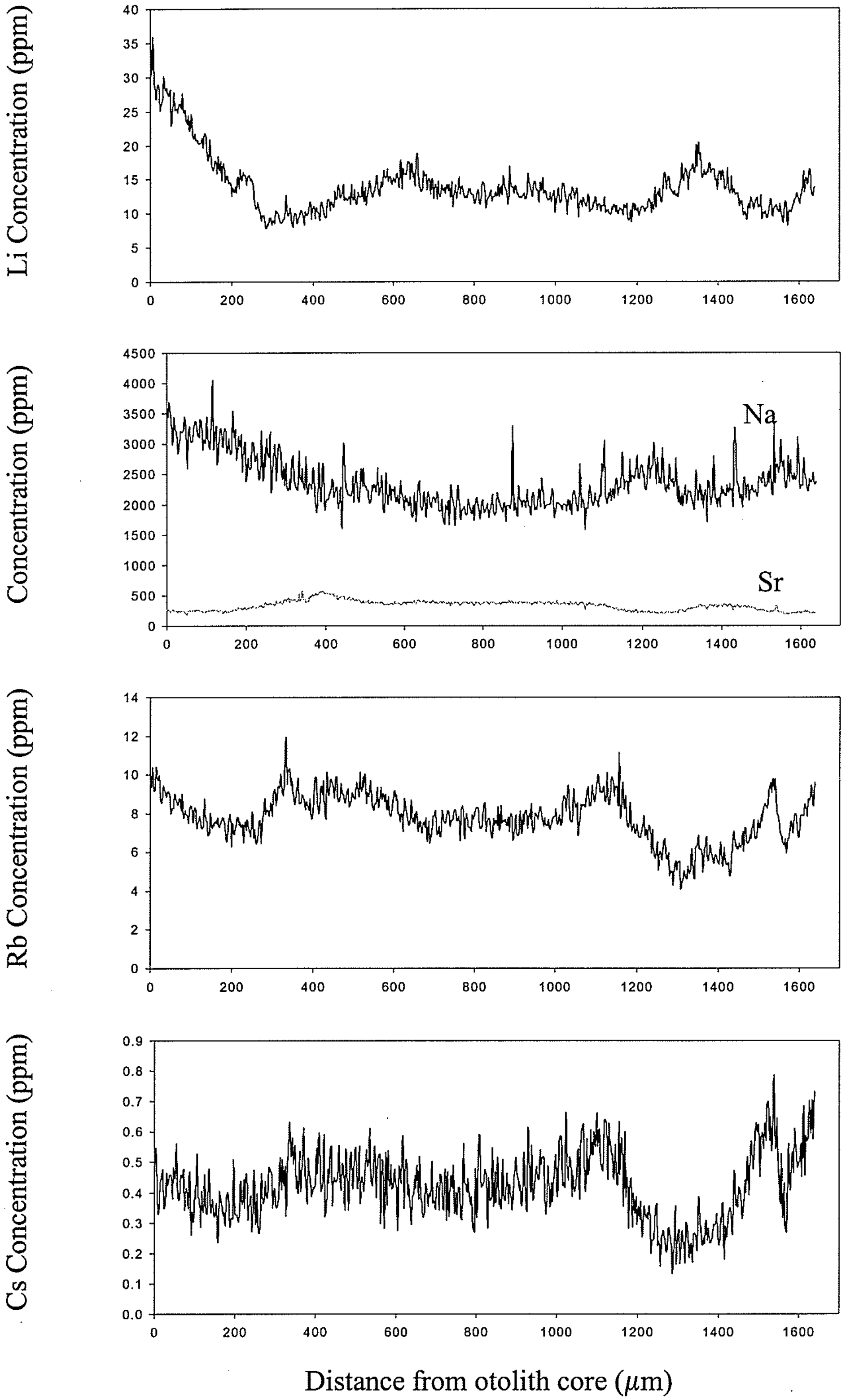
B08_37


Li Concentration (ppm)
18
15
12
9
6
3
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

B08_38

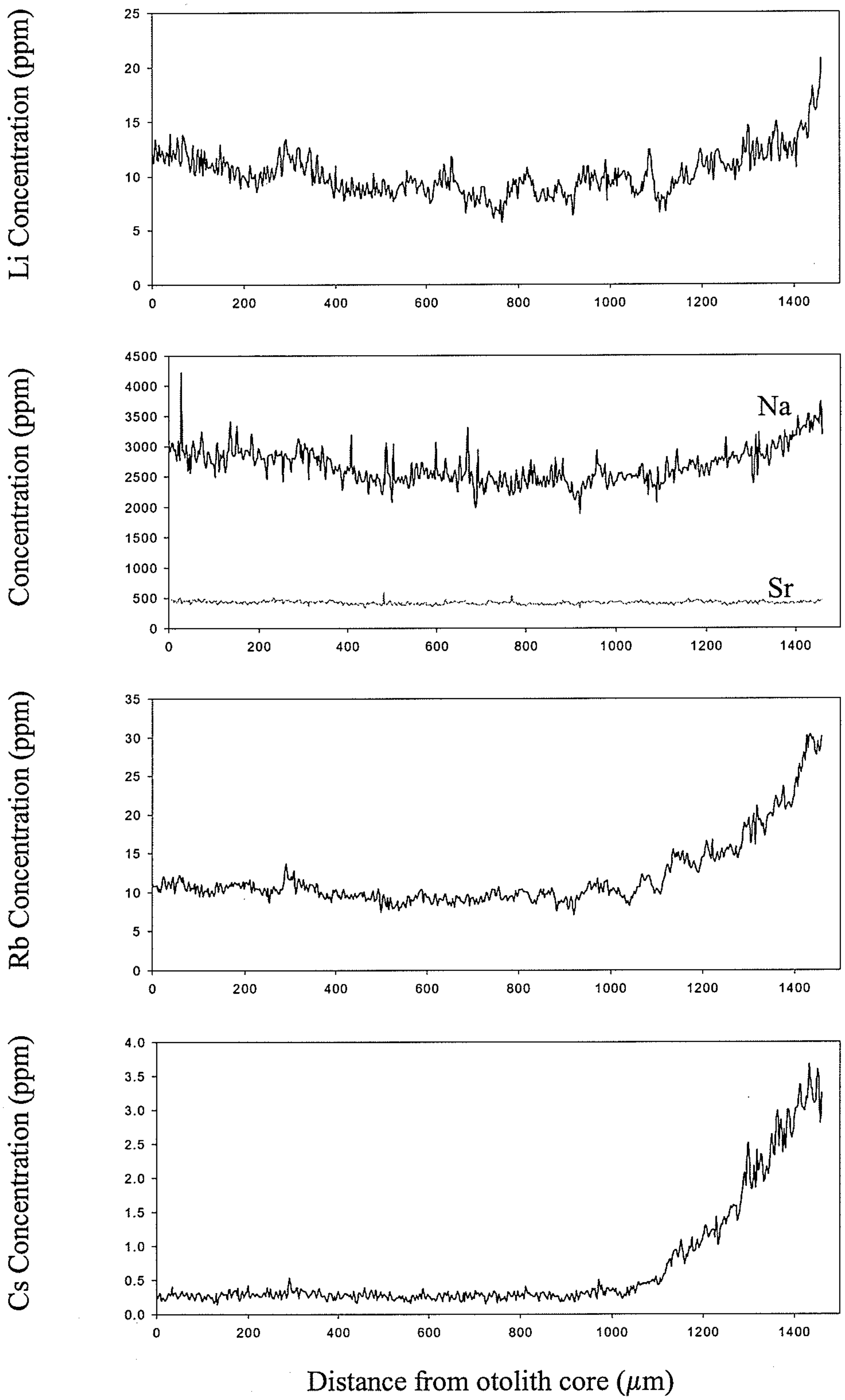

Li Concentration (ppm)
14
12
10
8
6
4
2
0
0
200
400
600
800
1000
1200
1400
1600
1800
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
1200
1400
1600
1800
Rb Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
1800
Cs Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
1600
1800
Distance from otolith core (μm)

B08_39

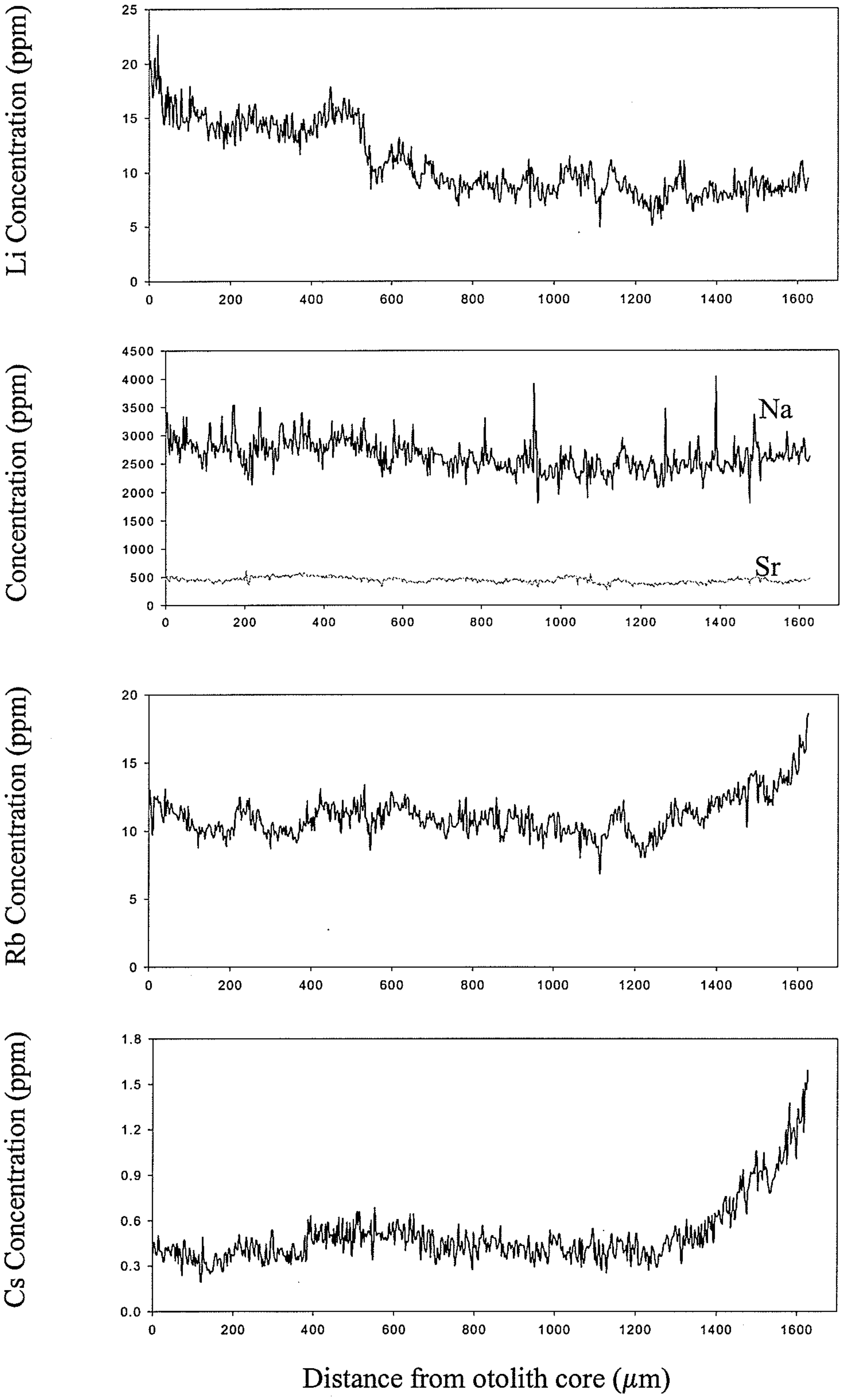


Li Concentration (ppm)
0
5
10
15
20
25
30
35
40
Concentration (ppm)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Na
Sr
Rb Concentration (ppm)
0
2
4
6
8
10
12
14
Cs Concentration (ppm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

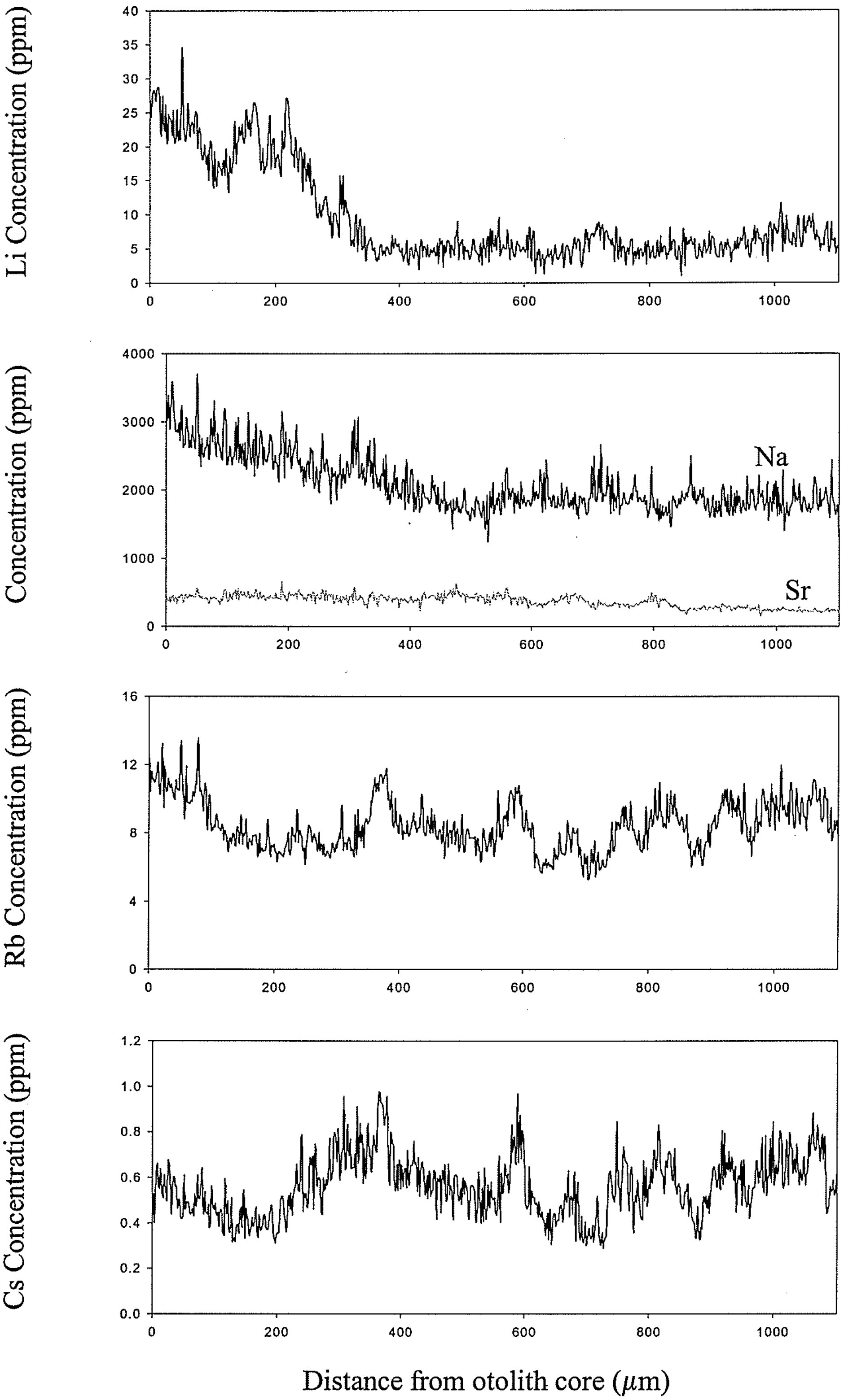
B08_40


Li Concentration (ppm)
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

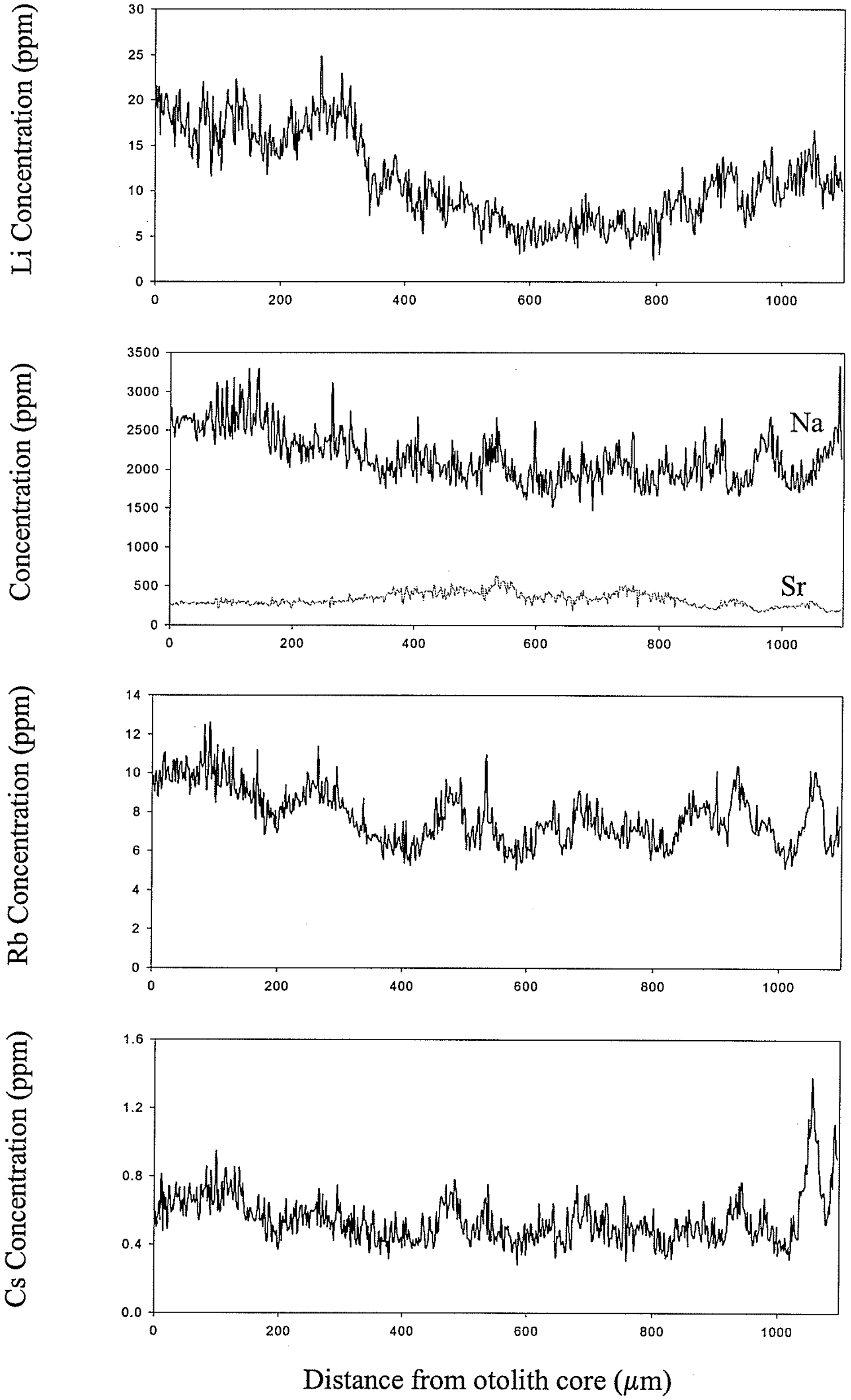
B08_41


Li Concentration (ppm)
0
5
10
15
20
25
Concentration (ppm)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Na
Sr
Rb Concentration (ppm)
0
5
10
15
20
Cs Concentration (ppm)
0.0
0.3
0.6
0.9
1.2
1.5
1.8
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

BM08_01

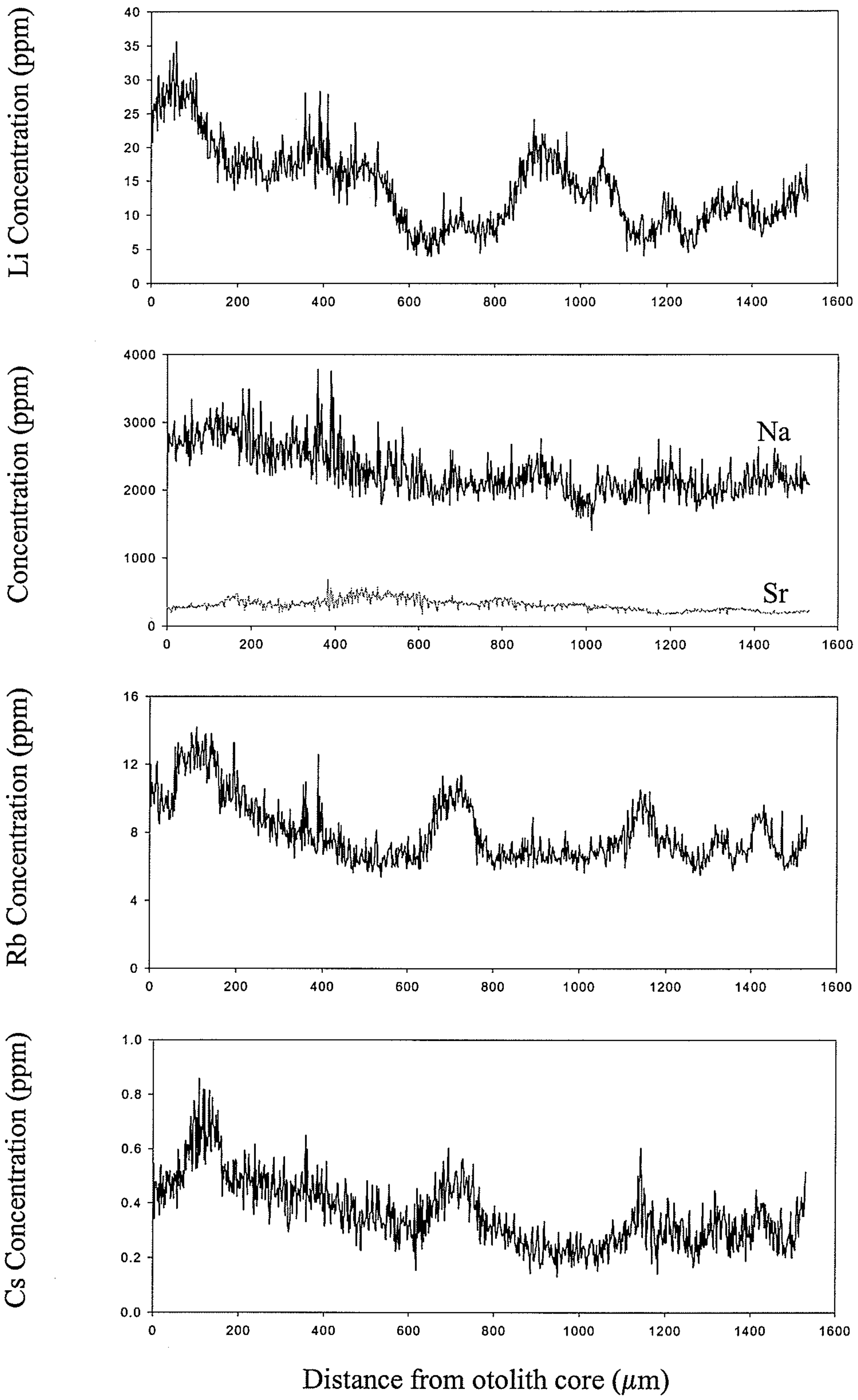

Li Concentration (ppm)
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
16
12
8
4
0
0
200
400
600
800
1000
Cs Concentration (ppm)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

BM08_02

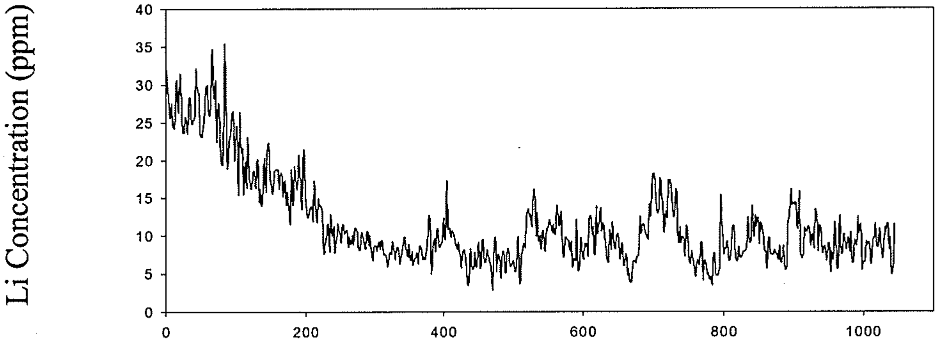


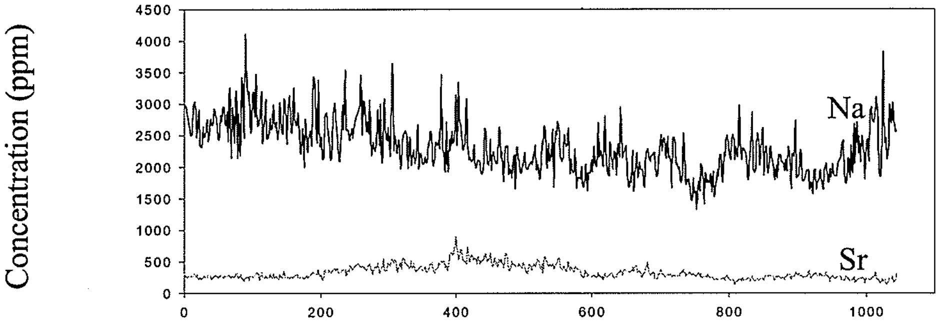
Li Concentration (ppm)
30
25
20
15
10
5
0
0
200
400
600
800
1000
Concentration (ppm)
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
14
12
10
8
6
4
2
0
0
200
400
600
800
1000
Cs Concentration (ppm)
1.6
1.2
0.8
0.4
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

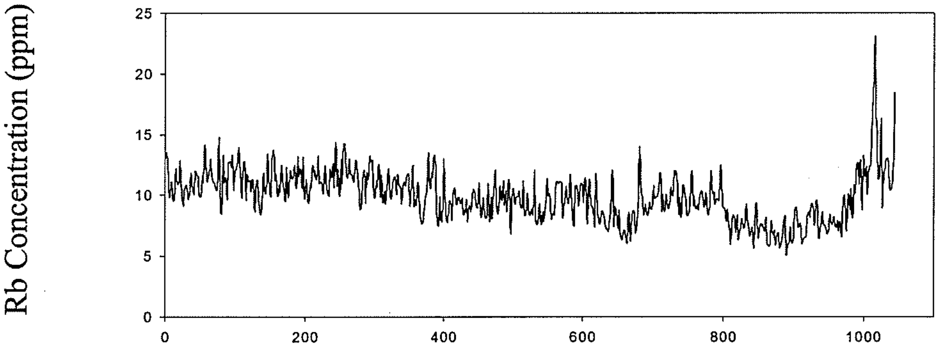
BM08_03

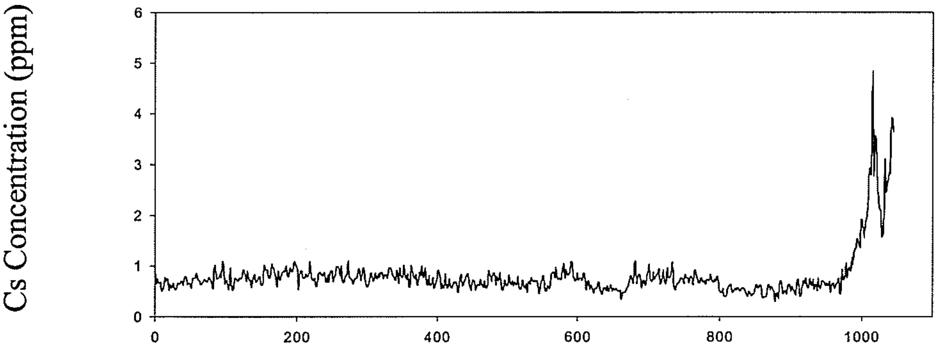

Li Concentration (ppm)
40
35
30
25
20
15
10
5
0
Concentration (ppm)
4000
3000
2000
1000
Na
Sr
Rb Concentration (ppm)
16
12
8
4
Cs Concentration (ppm)
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

BM08_04



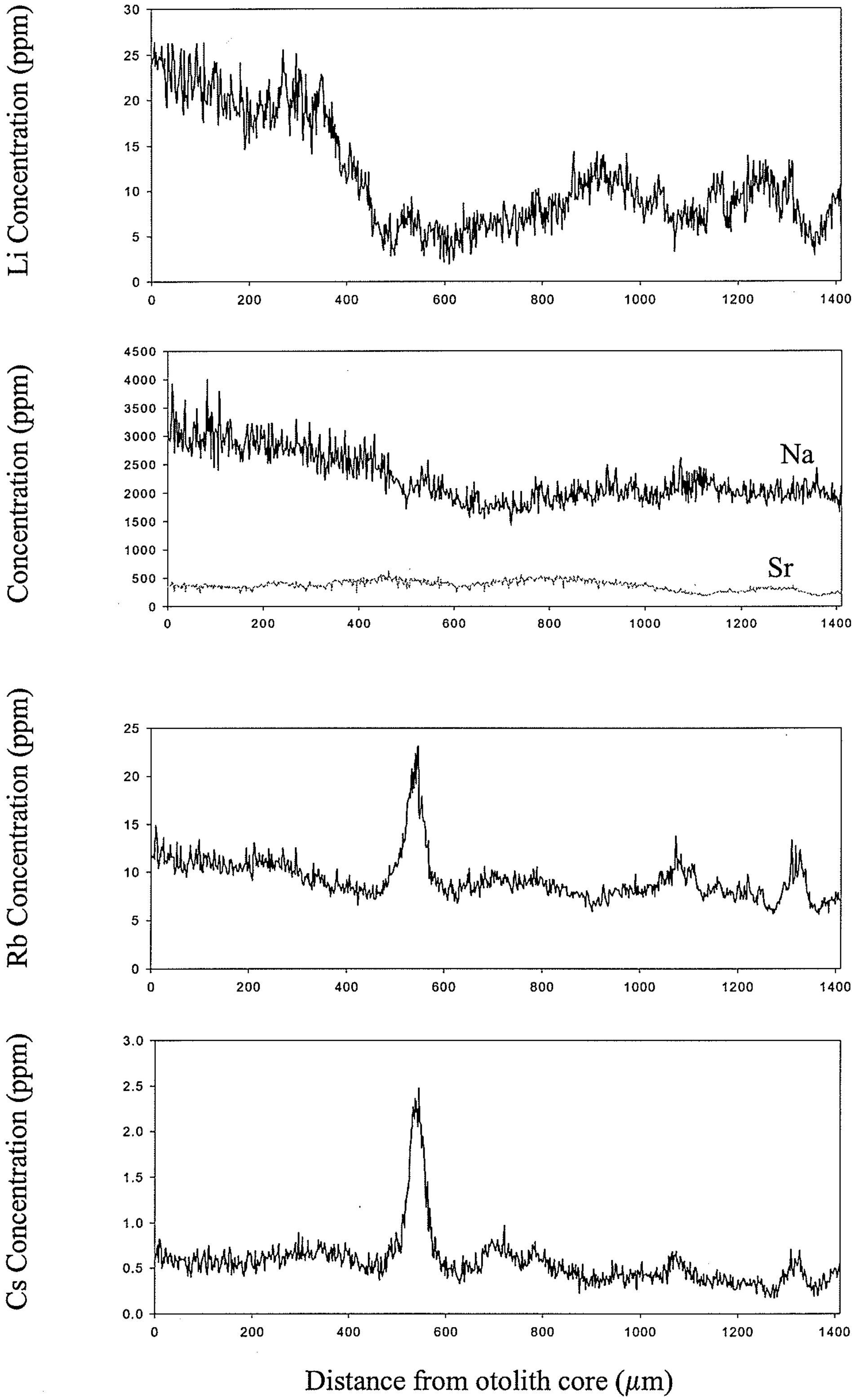




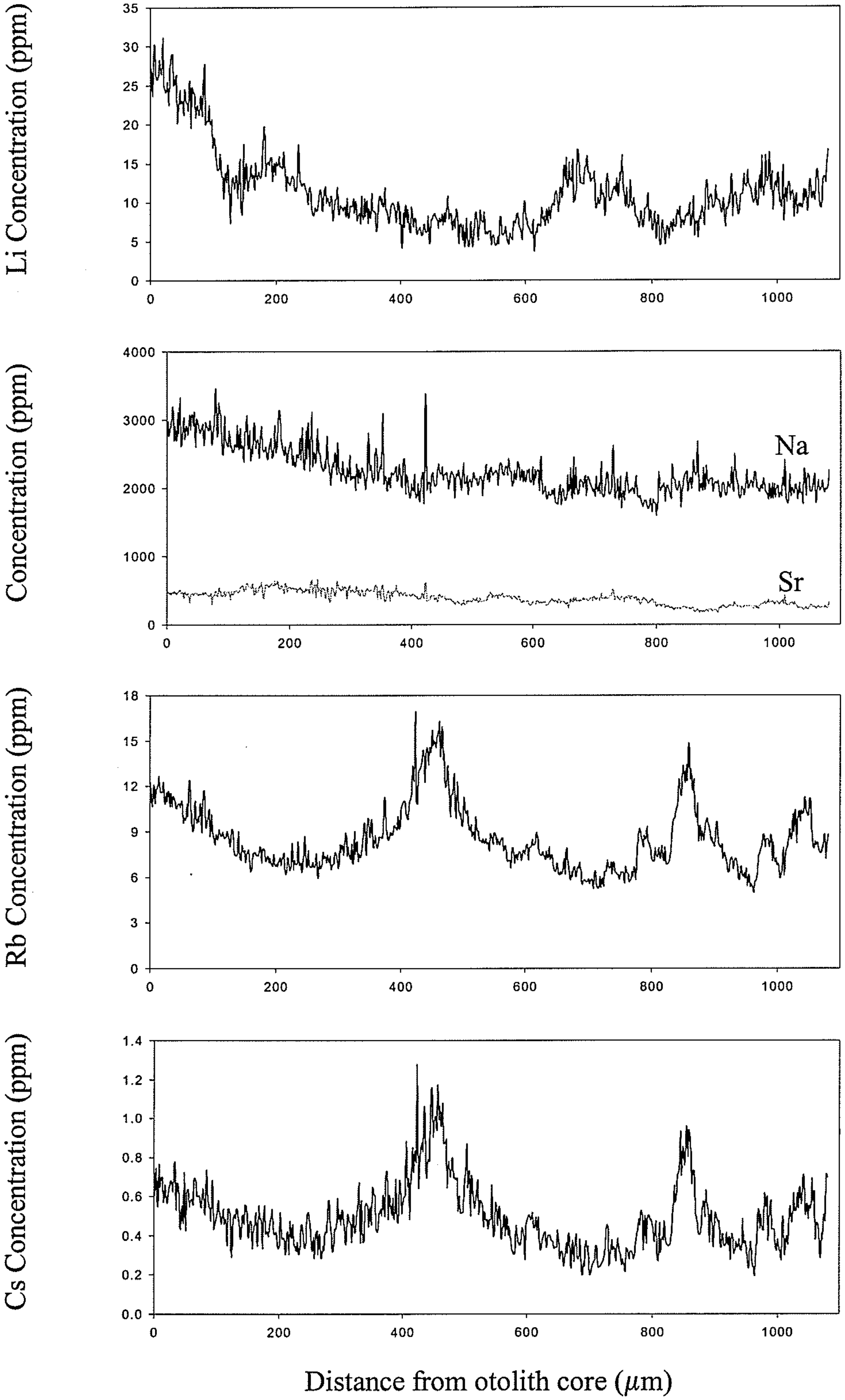


Distance from otolith core (μm)

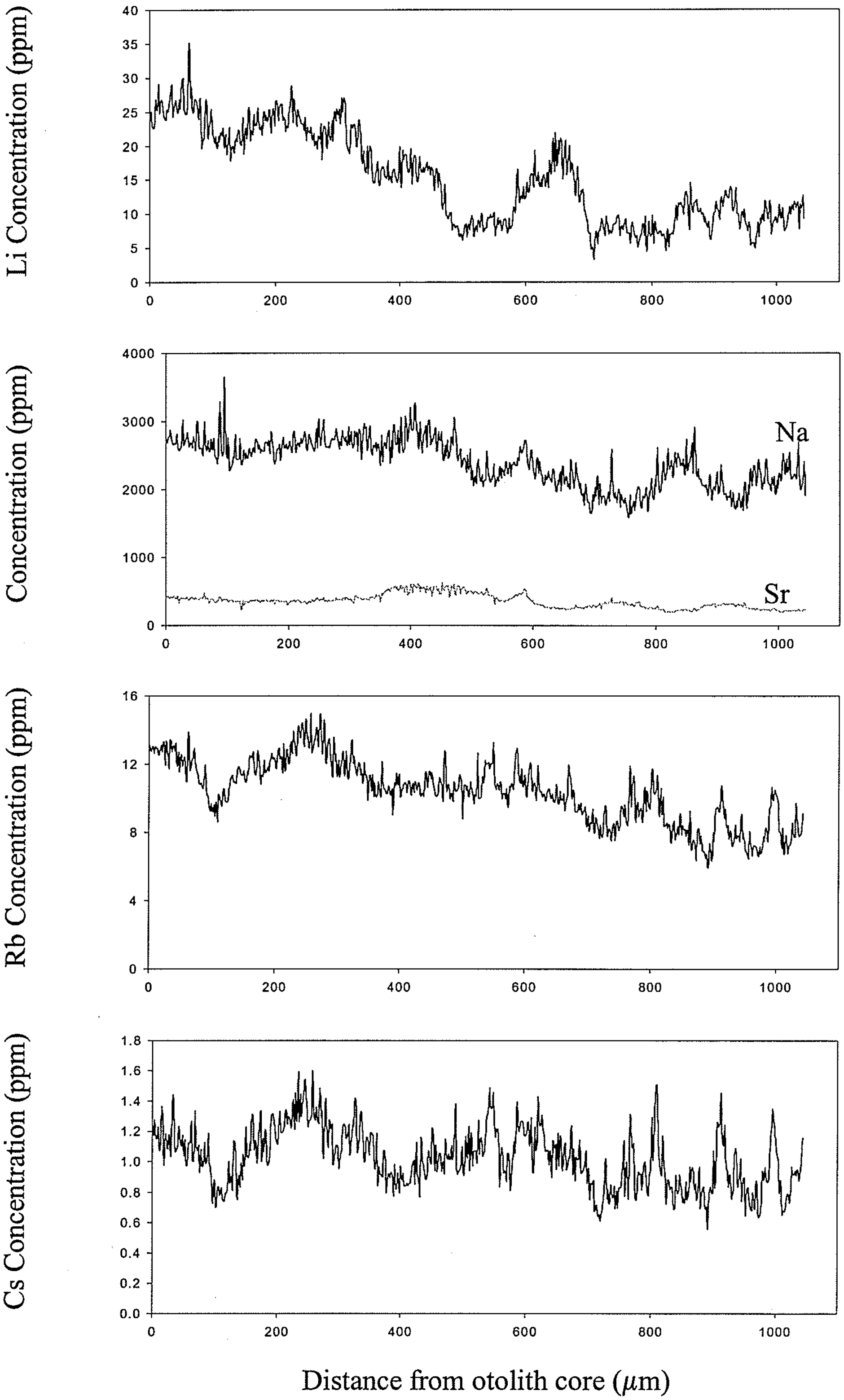
BM08_05


Li Concentration (ppm)
0
5
10
15
20
25
30
Concentration (ppm)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Na
Sr
Rb Concentration (ppm)
0
5
10
15
20
25
Cs Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

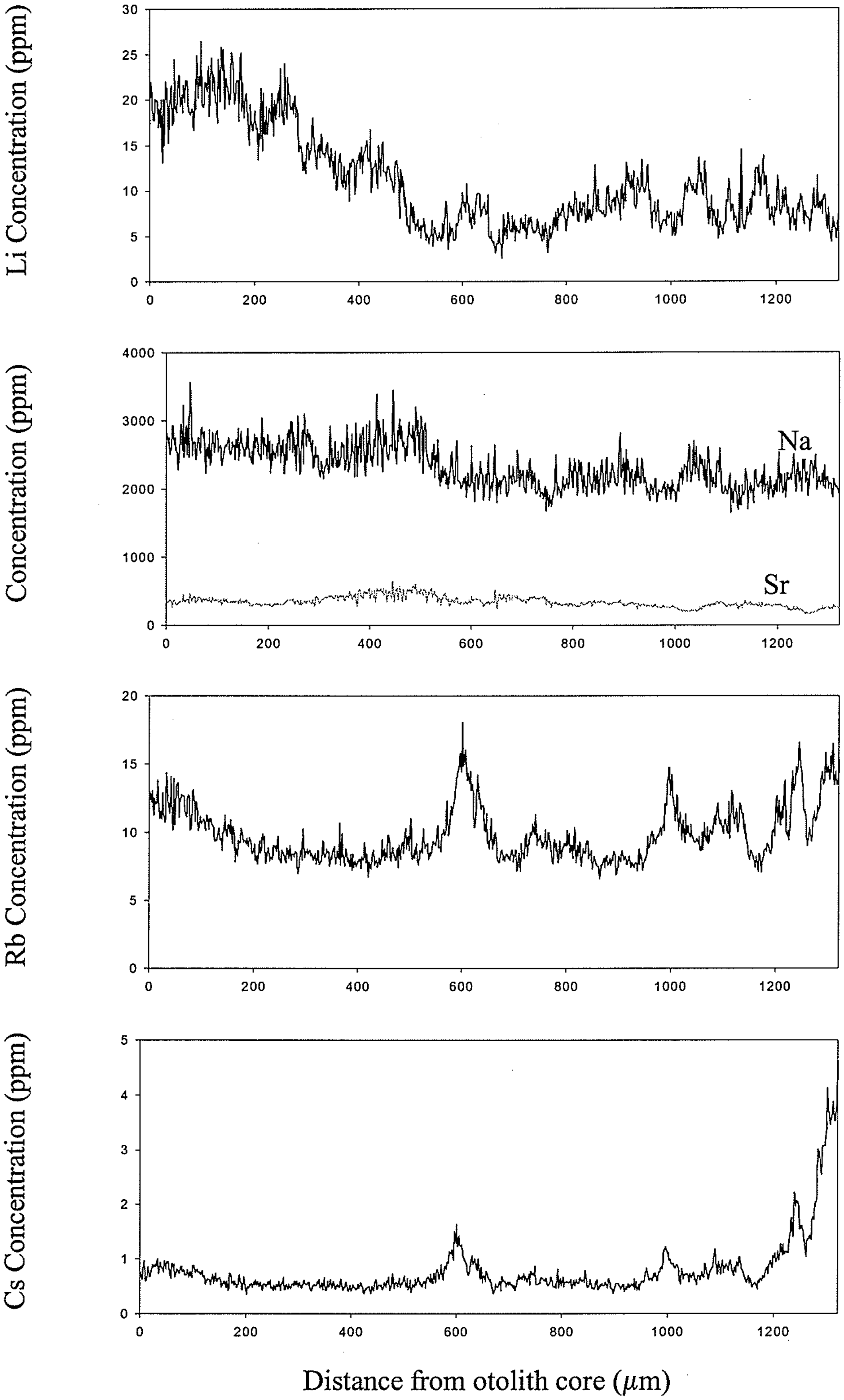
BM08_06


Li Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
18
15
12
9
6
3
0
0
200
400
600
800
1000
Cs Concentration (ppm)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

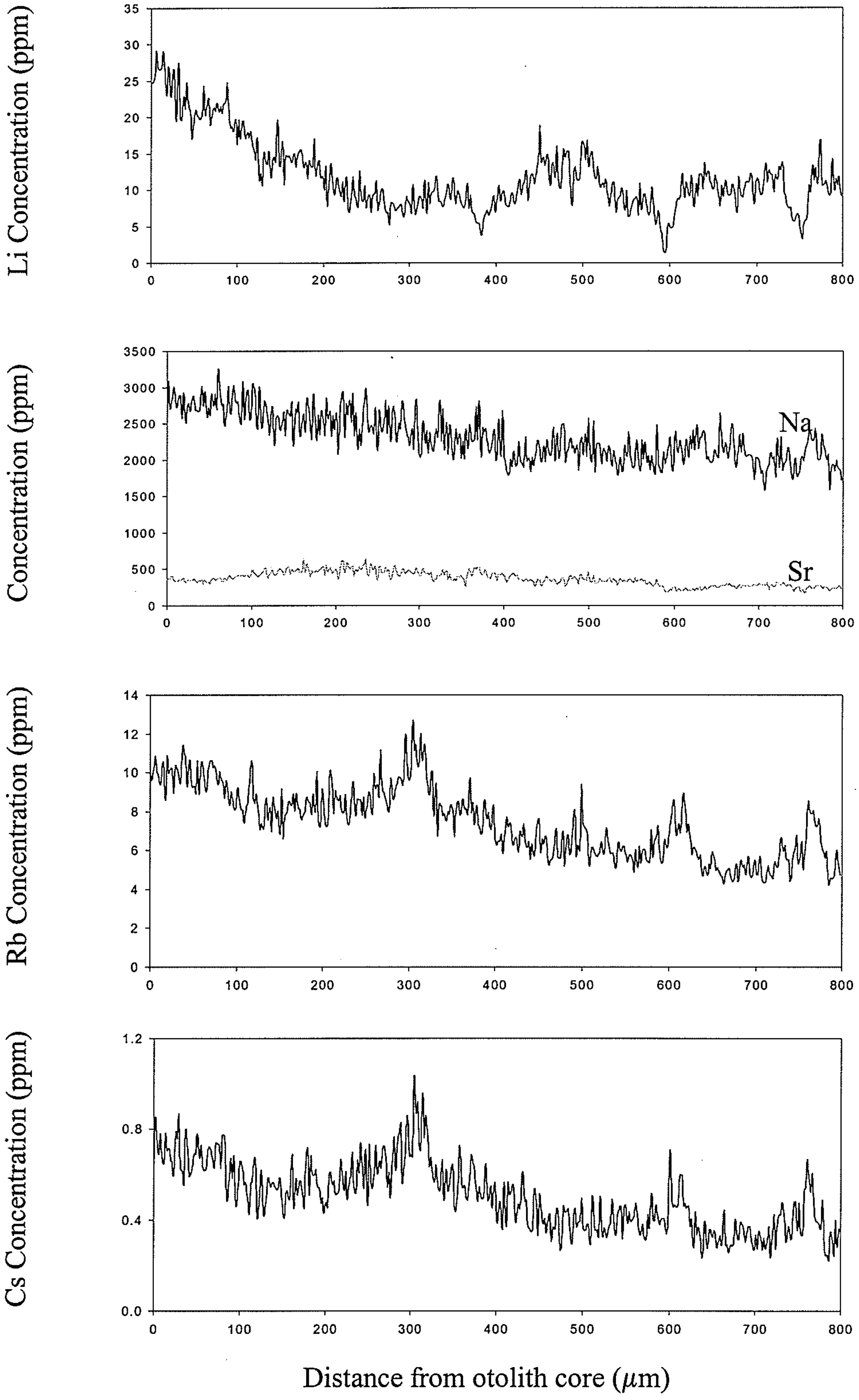
BM08_07


Li Concentration (ppm)
0
5
10
15
20
25
30
35
40
Concentration (ppm)
0
1000
2000
3000
4000
Na
Sr
Rb Concentration (ppm)
0
4
8
12
16
Cs Concentration (ppm)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
0
200
400
600
800
1000
Distance from otolith core (μm)

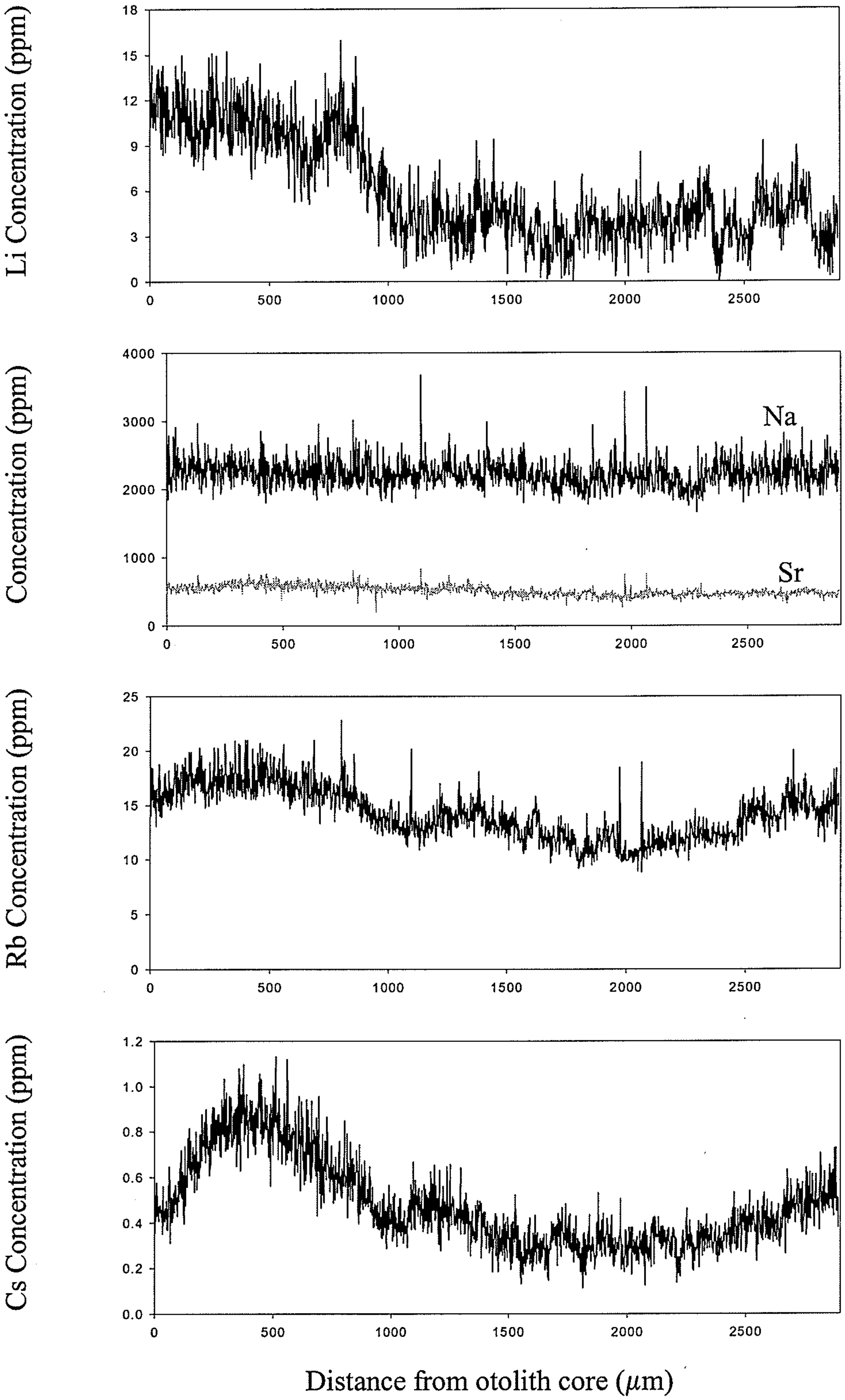
BM08_08


Li Concentration (ppm)
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
20
15
10
5
0
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
5
4
3
2
1
0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

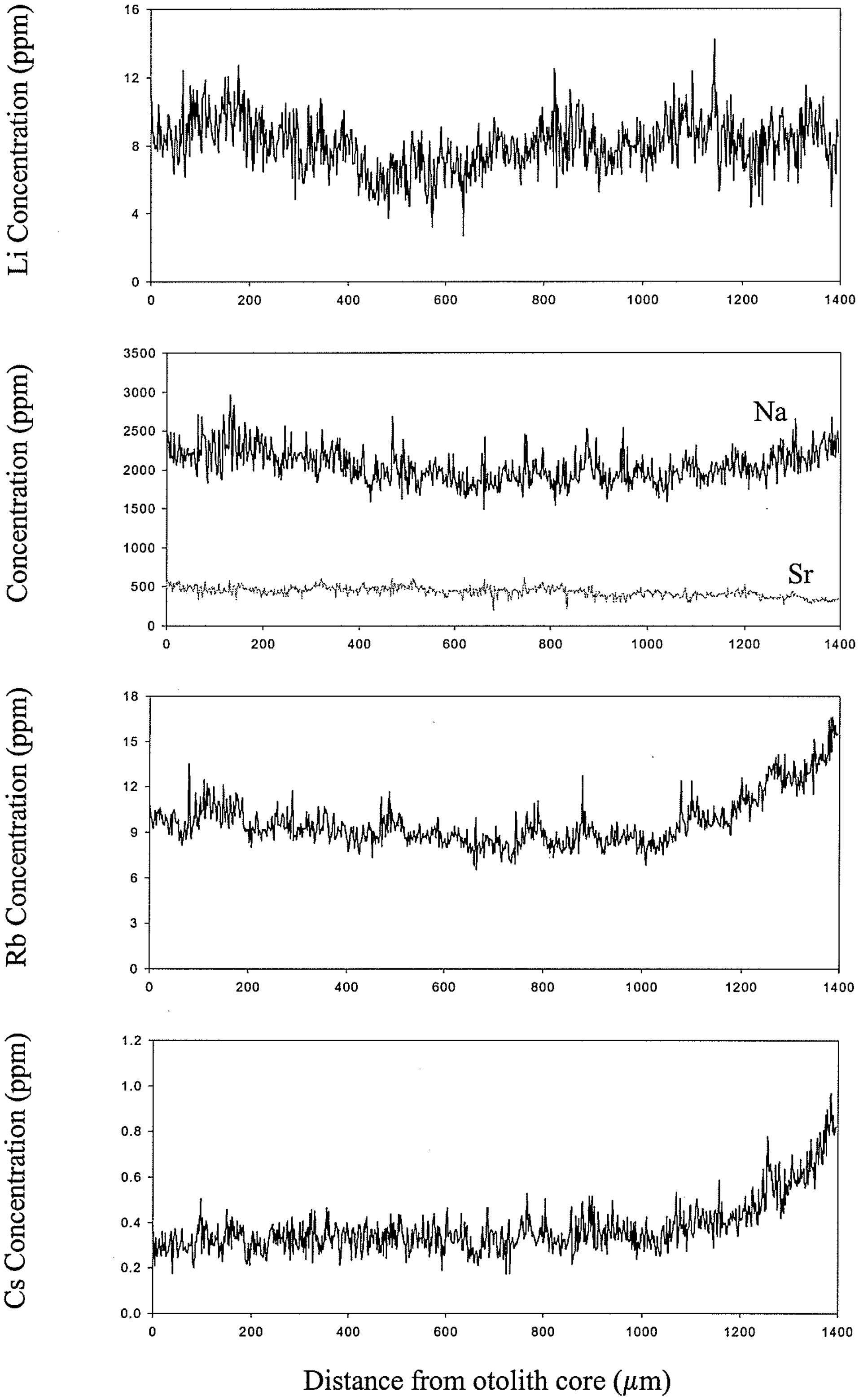
BM08_09


Li Concentration (ppm)
0
5
10
15
20
25
30
35
Concentration (ppm)
0
500
1000
1500
2000
2500
3000
3500
Na
Sr
Rb Concentration (ppm)
0
2
4
6
8
10
12
14
Cs Concentration (ppm)
0.0
0.4
0.8
1.2
0
100
200
300
400
500
600
700
800
Distance from otolith core (μm)

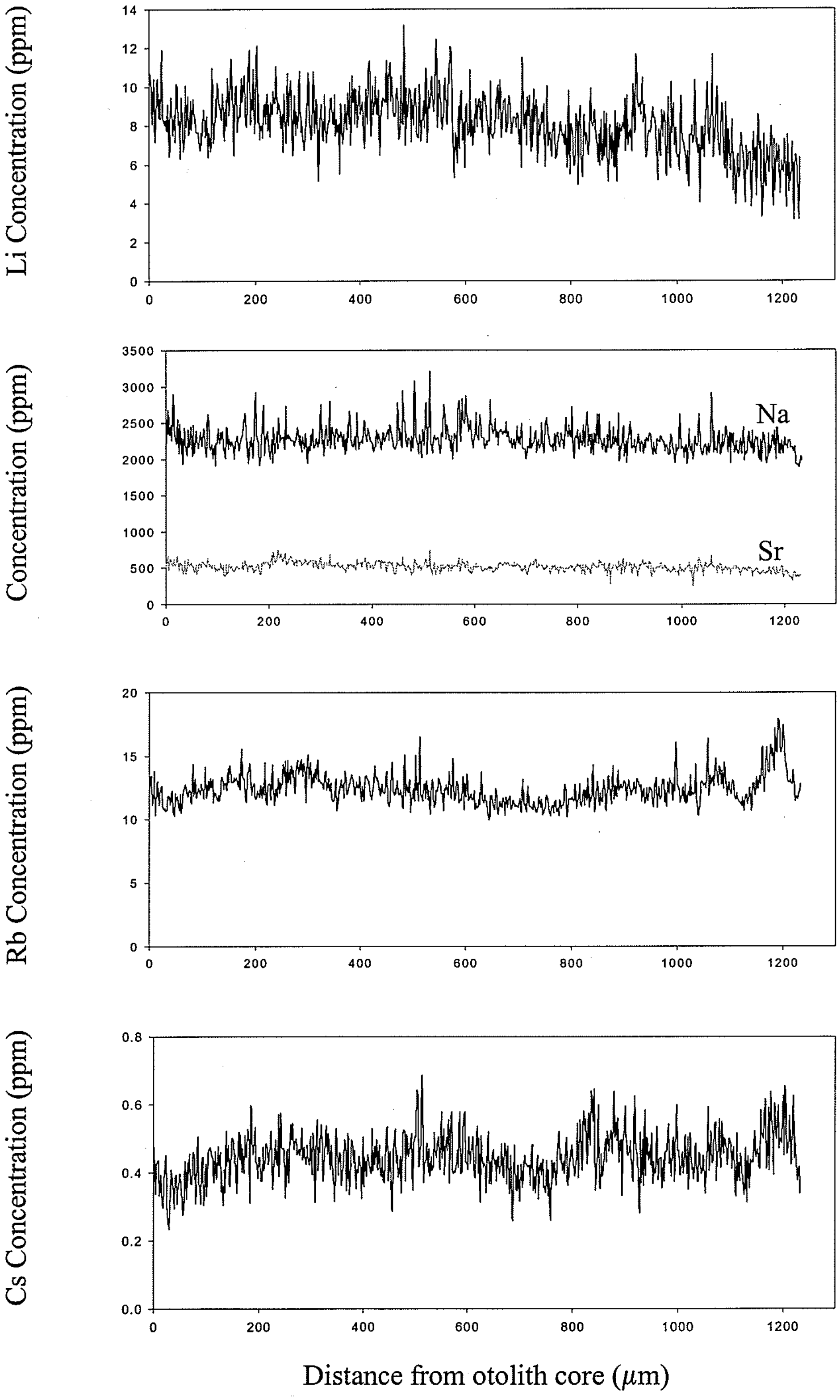
BL08_01


Li Concentration (ppm)
18
15
12
9
6
3
0
0
500
1000
1500
2000
2500
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
2500
Rb Concentration (ppm)
25
20
15
10
5
0
0
500
1000
1500
2000
2500
Cs Concentration (ppm)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
500
1000
1500
2000
2500
Distance from otolith core (μm)

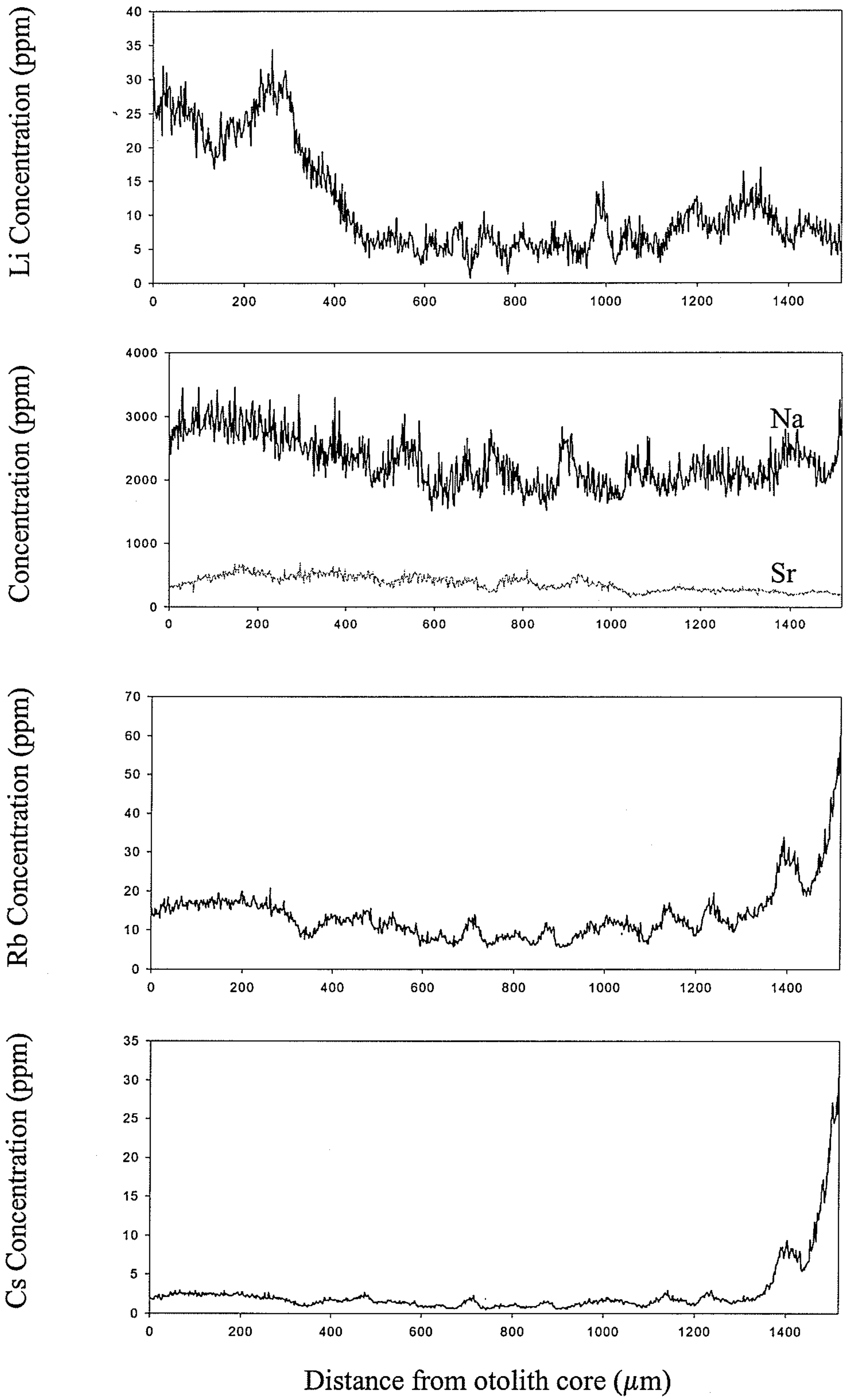
BL08_02


Li Concentration (ppm)
16
12
8
4
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
18
15
12
9
6
3
0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

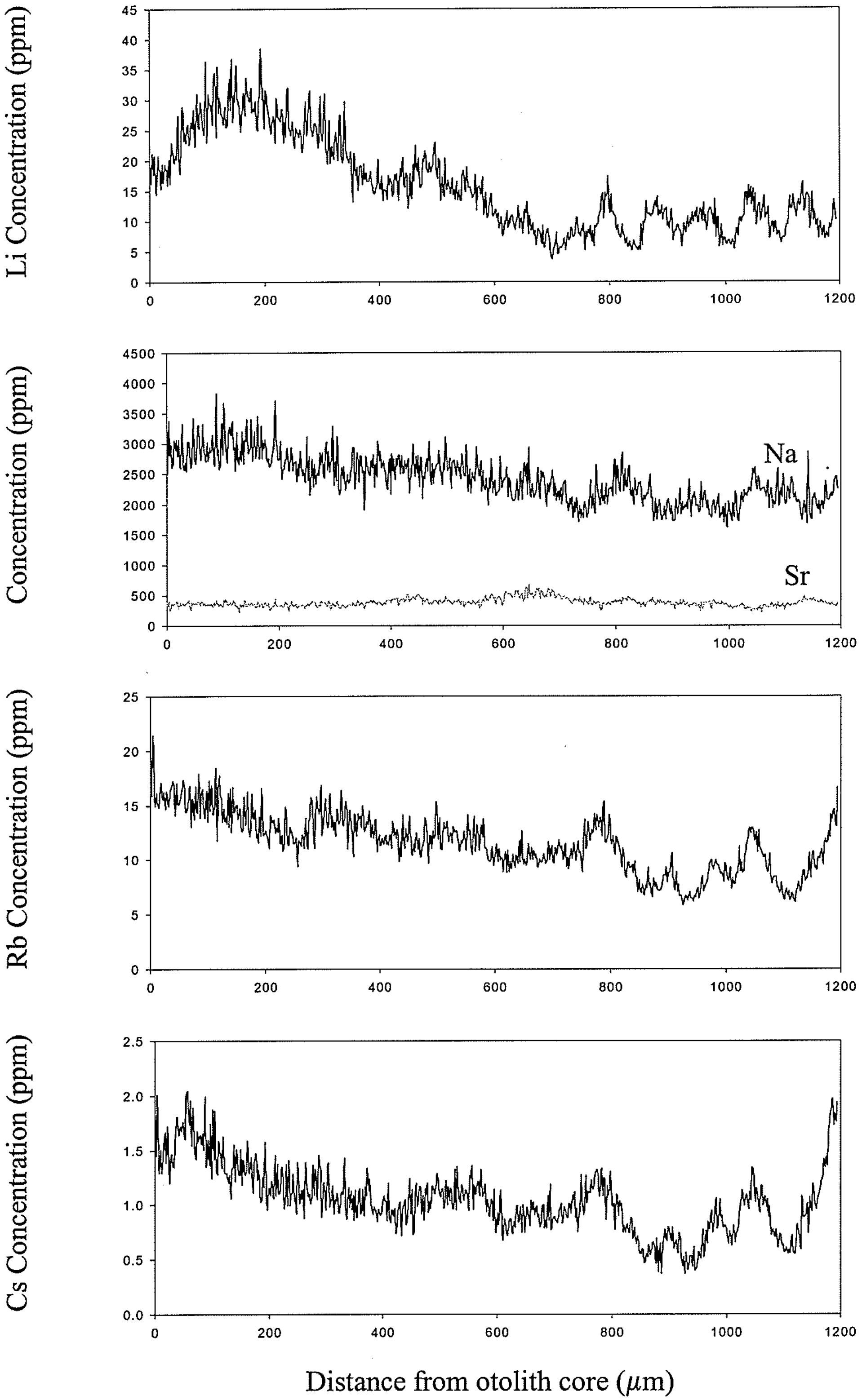
BL08_03


Li Concentration (ppm)
0
2
4
6
8
10
12
14
0
200
400
600
800
1000
1200
Concentration (ppm)
Na
Sr
0
500
1000
1500
2000
2500
3000
3500
0
200
400
600
800
1000
1200
Rb Concentration (ppm)
0
5
10
15
20
0
200
400
600
800
1000
1200
Cs Concentration (ppm)
0.0
0.2
0.4
0.6
0.8
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

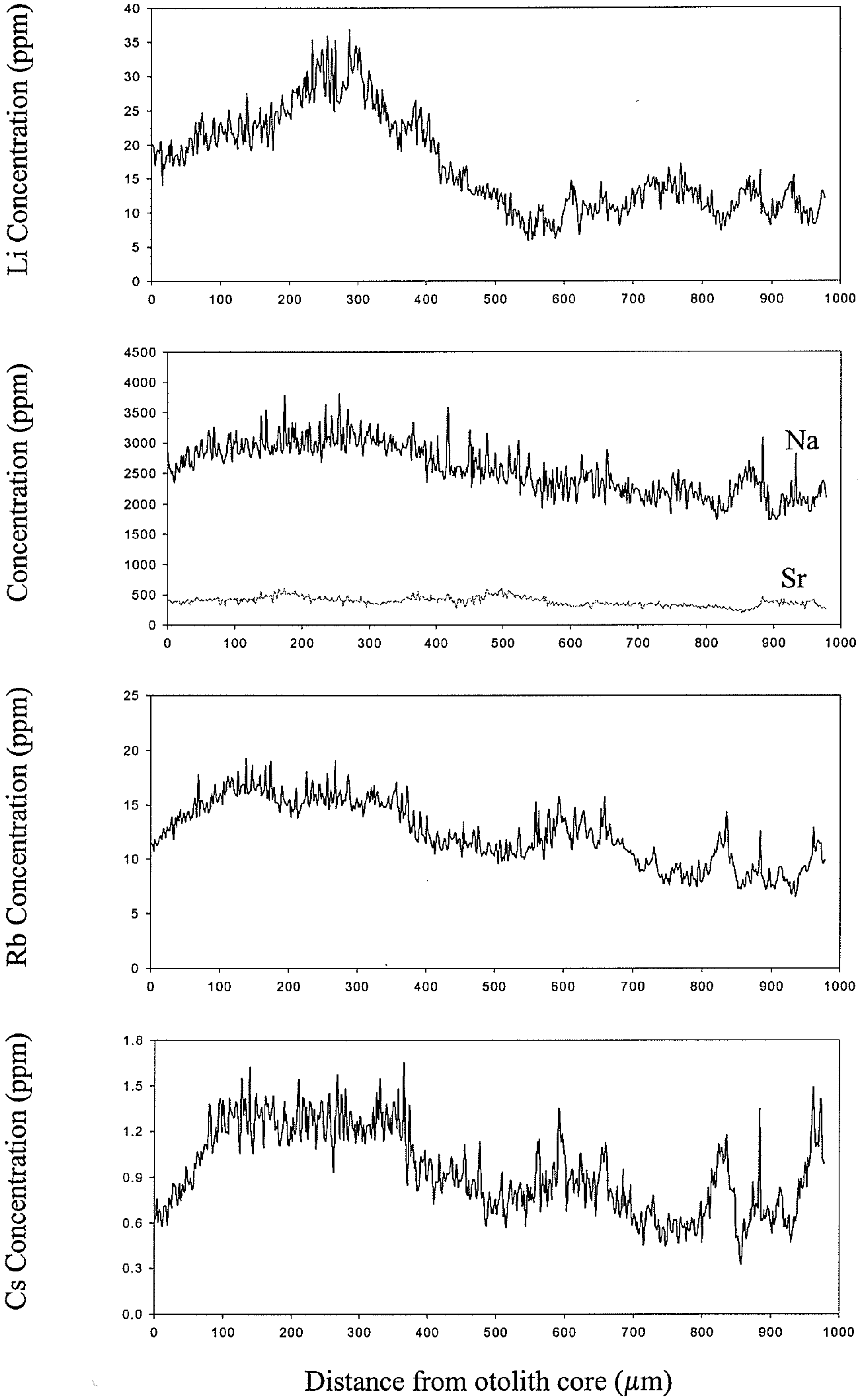
BL08_04


Li Concentration (ppm)
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
70
60
50
40
30
20
10
0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

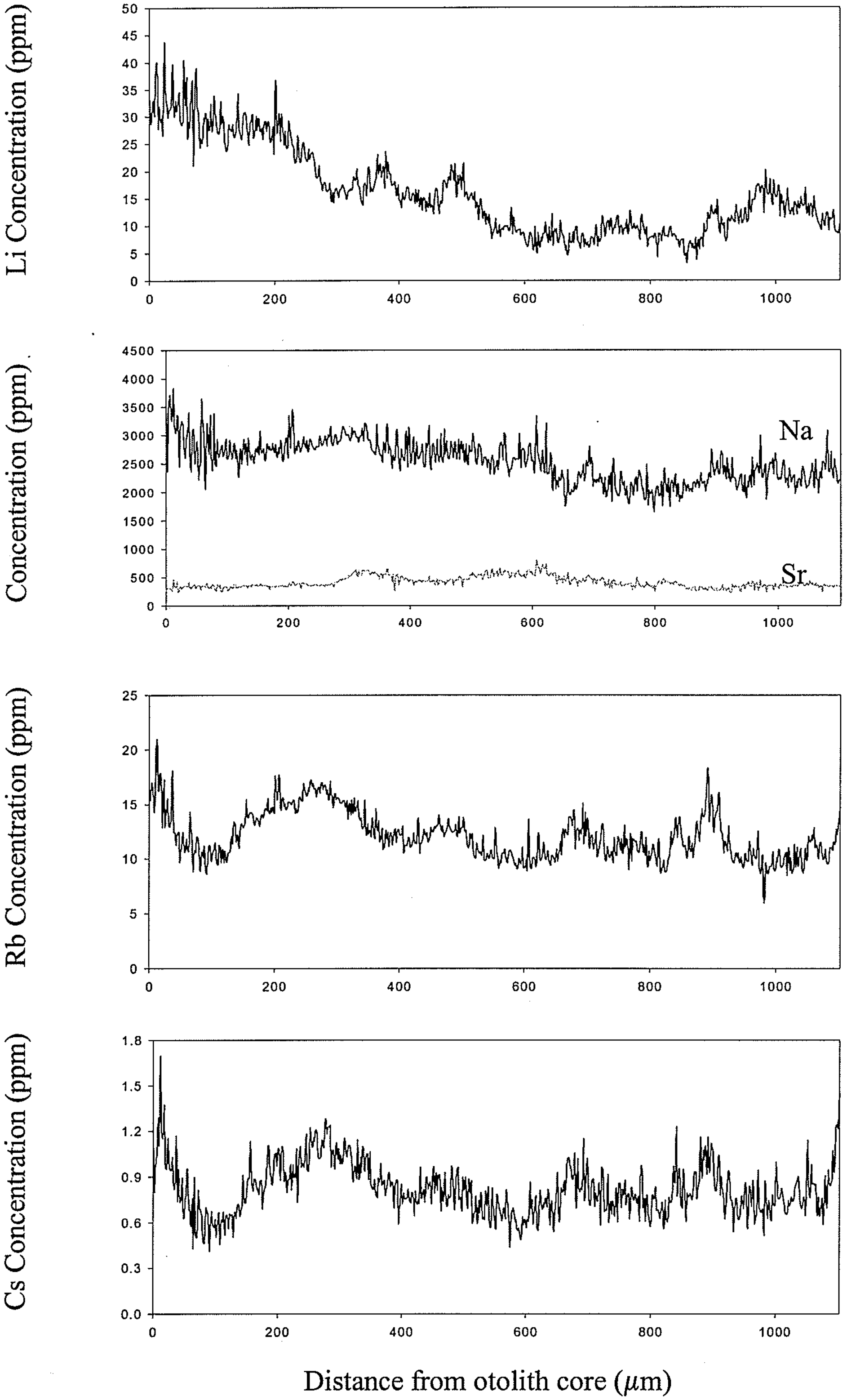
BL08_05


Li Concentration (ppm)
45
40
35
30
25
20
15
10
5
0
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
Rb Concentration (ppm)
25
20
15
10
5
0
Cs Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
1200
Distance from otolith core (μm)

BL08_06


Li Concentration (ppm)
0
5
10
15
20
25
30
35
40
Concentration (ppm)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Na
Sr
Rb Concentration (ppm)
0
5
10
15
20
25
Cs Concentration (ppm)
0.0
0.3
0.6
0.9
1.2
1.5
1.8
0
100
200
300
400
500
600
700
800
900
1000
Distance from otolith core (μm)

BL08_07



Li Concentration (ppm)
50
45
40
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
25
20
15
10
5
0
0
200
400
600
800
1000
Cs Concentration (ppm)
1.8
1.5
1.2
0.9
0.6
0.3
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

Appendix I LA-ICP-MS data for Bernic Lake otoliths *continued*

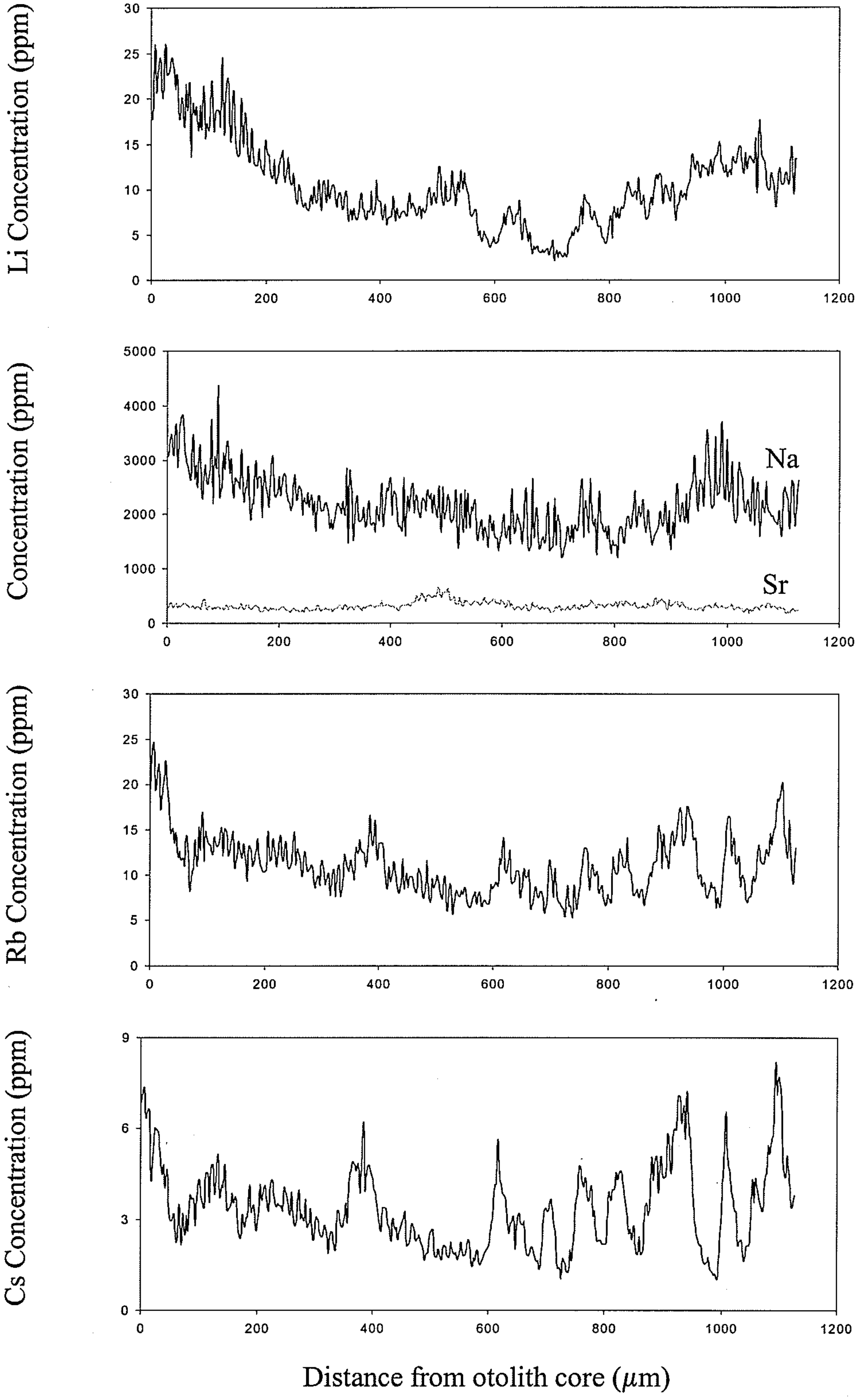
Species: Yellow Perch (*Perca flavescens*)

Captured: 2006

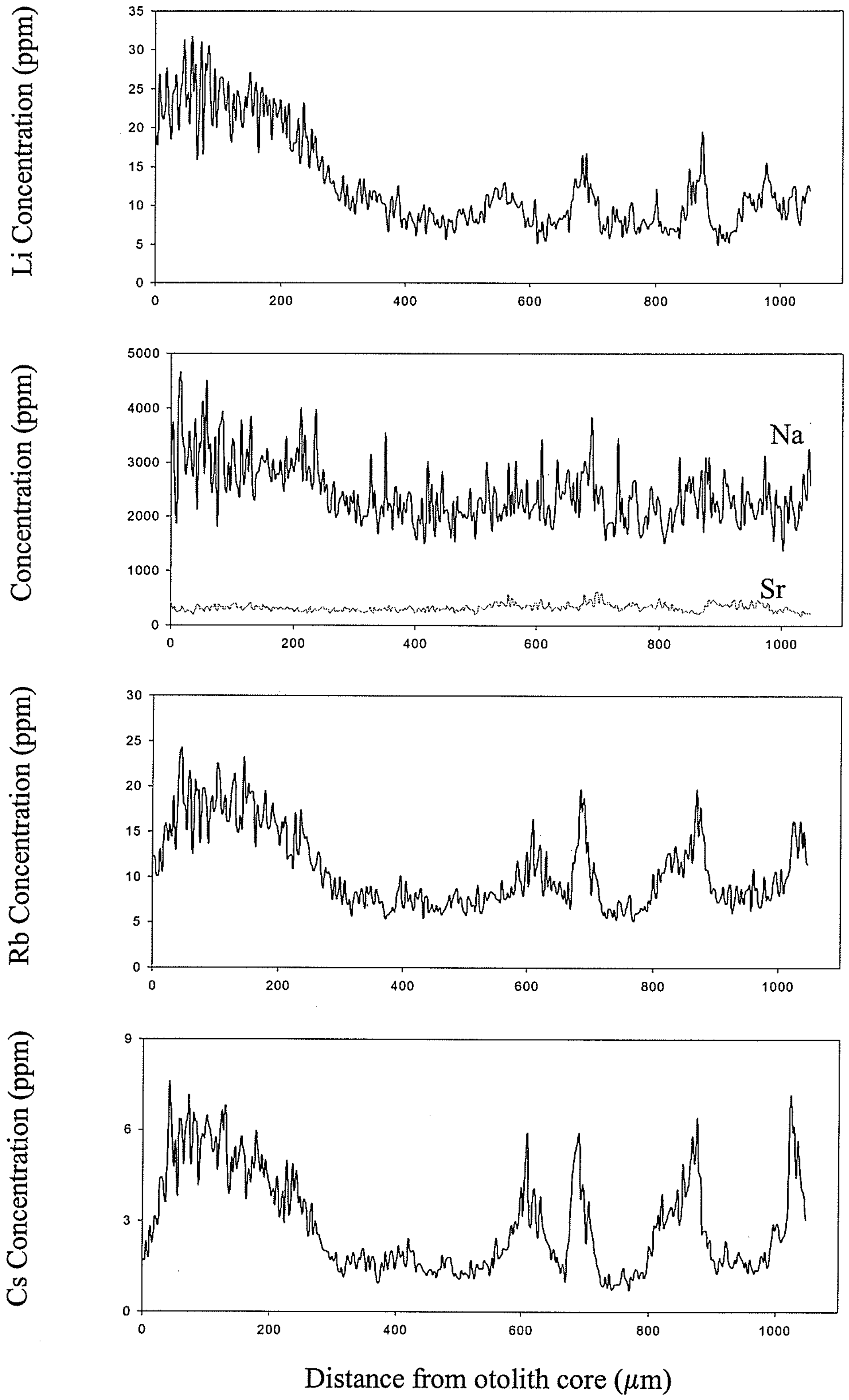
Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
Bernic06_01	Yellow Perch	6
Bernic06_02	Yellow Perch	3
Bernic06_03	Yellow Perch	4

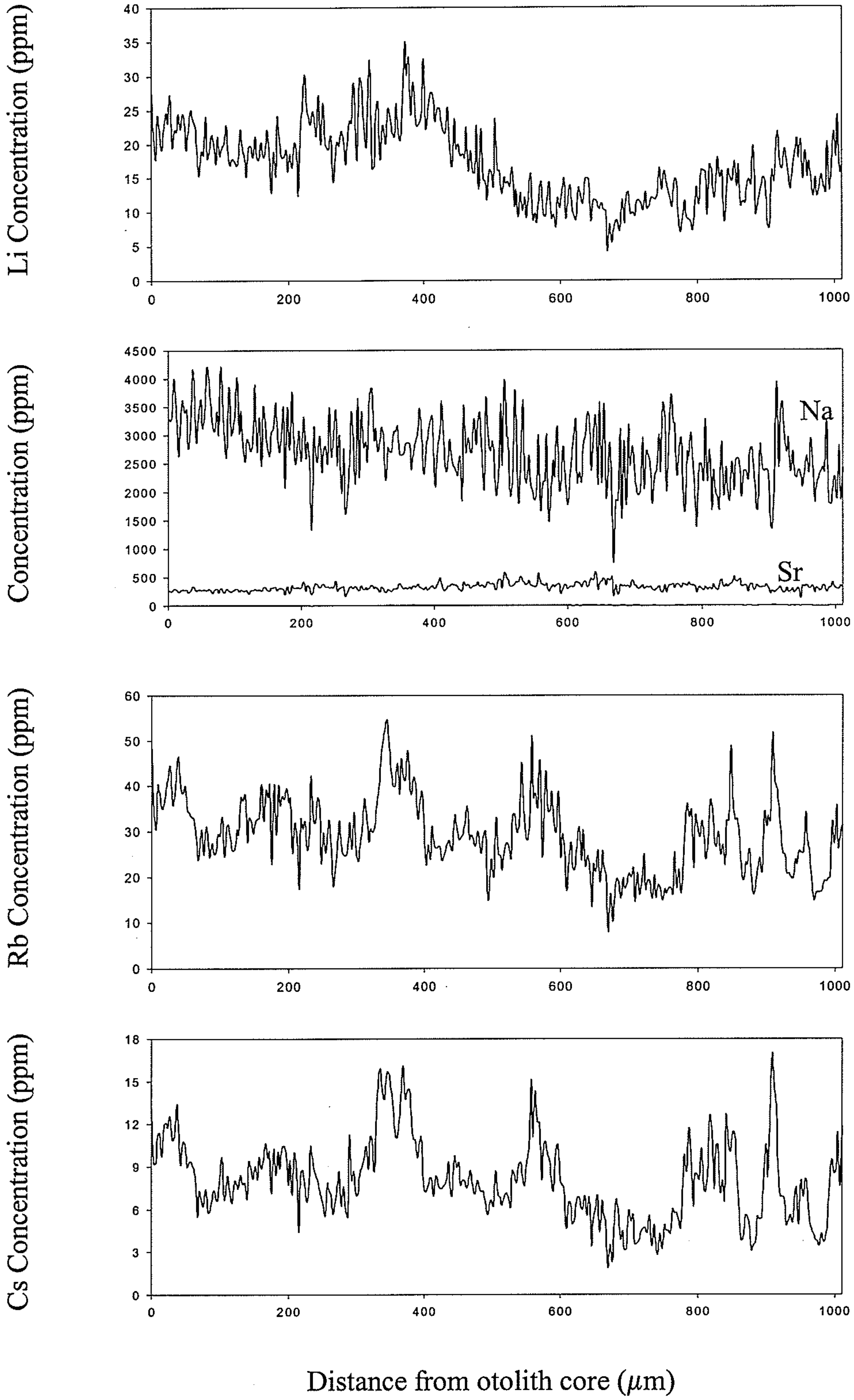
Bernic06_01


Li Concentration (ppm)
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
Cs Concentration (ppm)
9
6
3
Distance from otolith core (μm)

Bernic06_02


Li Concentration (ppm)
0
5
10
15
20
25
30
35
0
200
400
600
800
1000
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
0
5
10
15
20
25
30
0
200
400
600
800
1000
Cs Concentration (ppm)
0
3
6
9
0
200
400
600
800
1000
Distance from otolith core (μm)

Bernic06_03



Li Concentration (ppm)
0
5
10
15
20
25
30
35
40
0
200
400
600
800
1000
Concentration (ppm)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
0
10
20
30
40
50
60
0
200
400
600
800
1000
Cs Concentration (ppm)
0
3
6
9
12
15
18
0
200
400
600
800
1000
Distance from otolith core (μm)

Appendix I LA-ICP-MS data for Bernic Lake otoliths *continued*

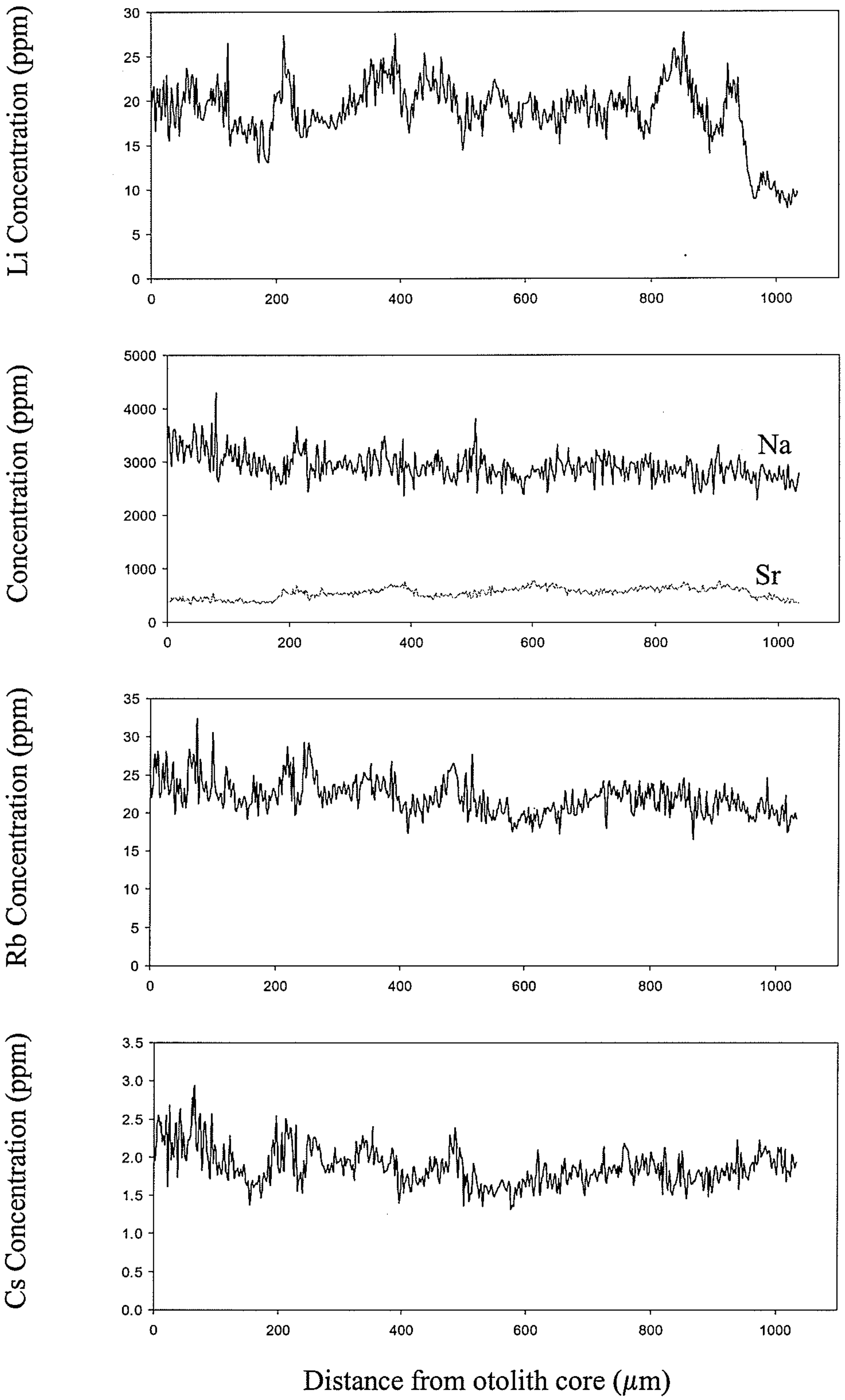
Species: Cisco (*Coregonus artedii*), White Sucker (*Catostomus commersoni*)

Captured: 1998 (TetrES Consultants, Inc.)

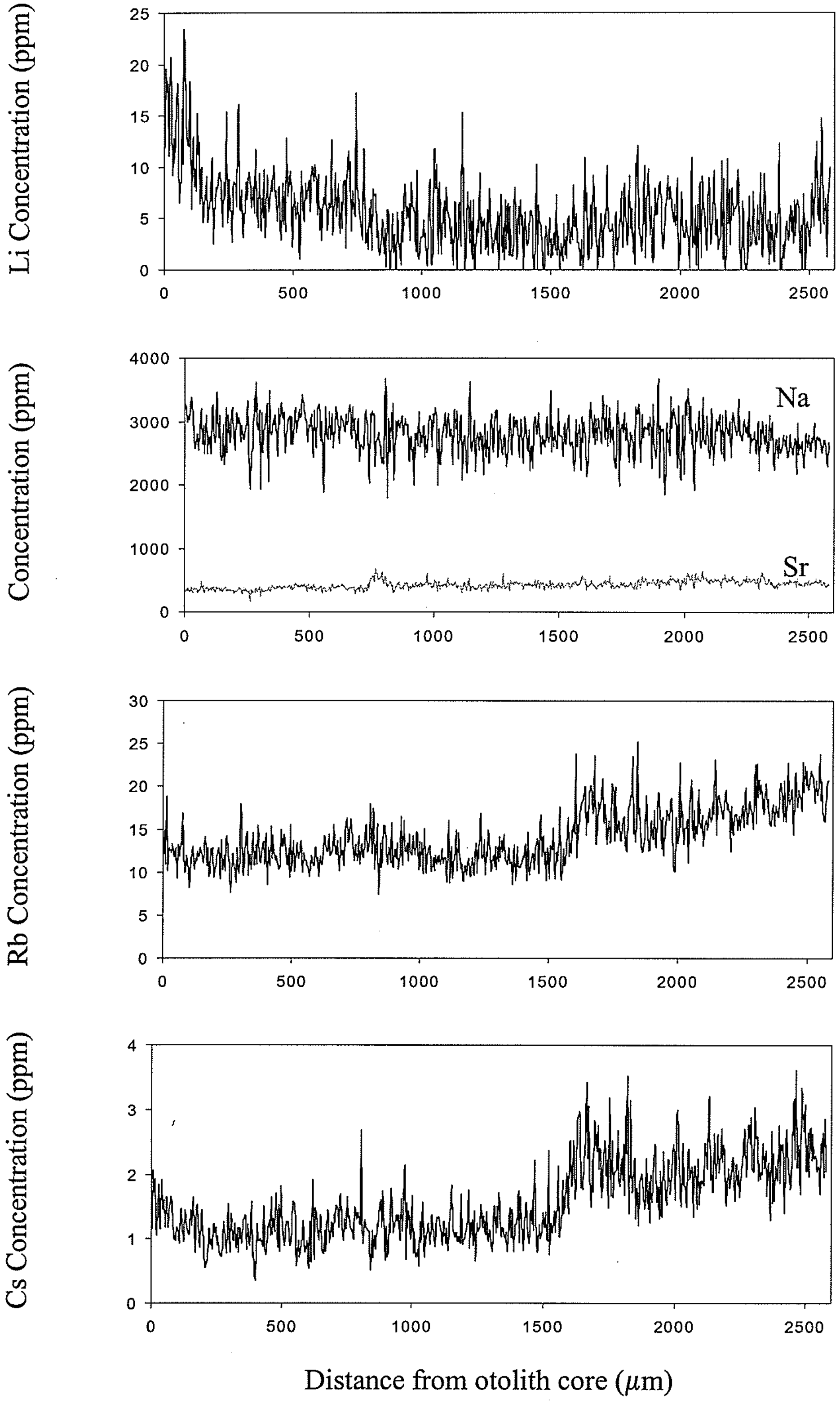
Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

Sample Number	***Species***	***Age***
77	White Sucker	9
81	White Sucker	
83	White Sucker	
84	White Sucker	18
85	White Sucker	
86	White Sucker	
87	White Sucker	18
88	White Sucker	9
90	White Sucker	10
92	White Sucker	7
93	White Sucker	11
98	Cisco	
99	Cisco	
100	Cisco	6
101	Cisco	8
102	Cisco	7
103	Cisco	7
104	Cisco	7
105	Cisco	
108	Cisco	
109	Cisco	8

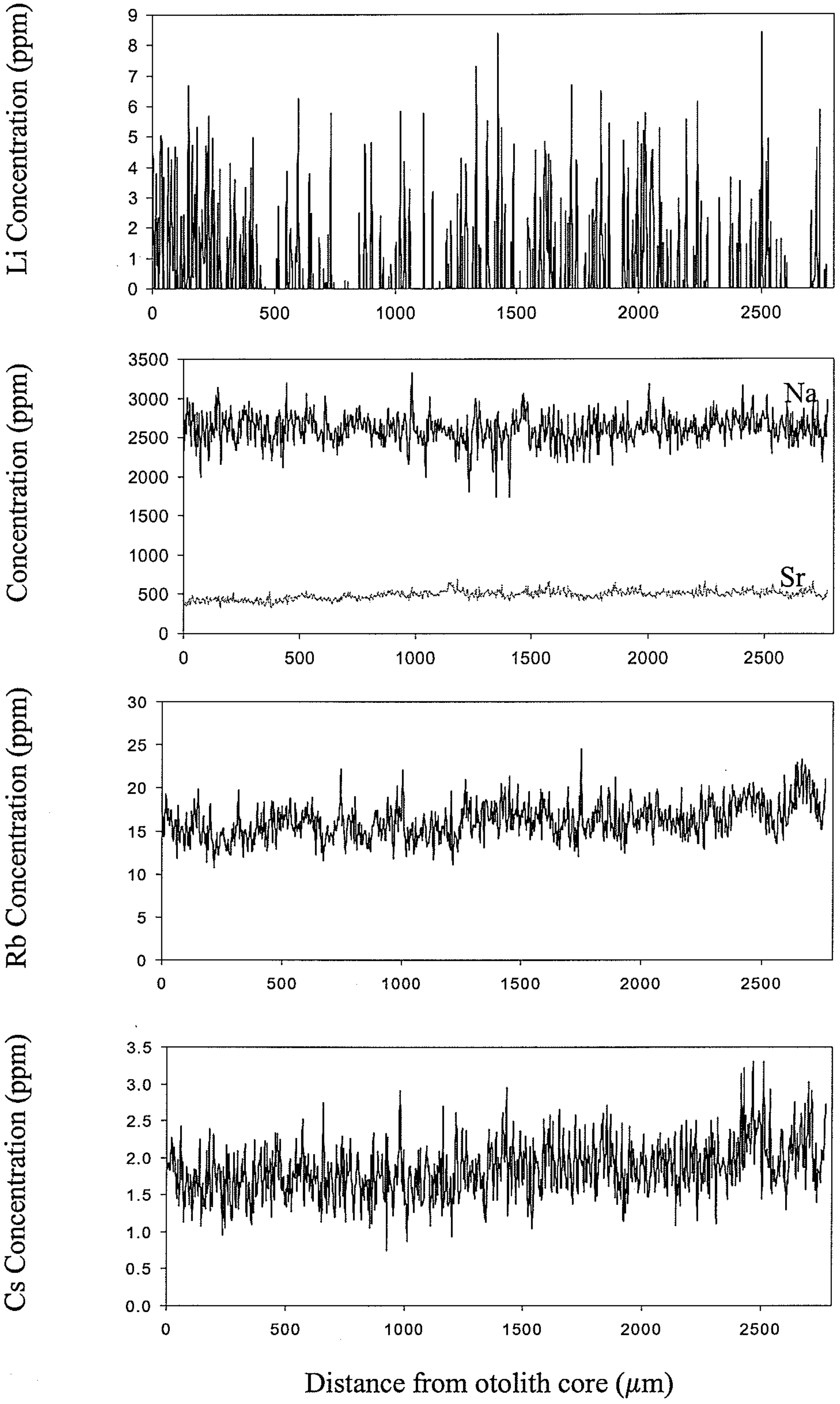
Bernic98_77


Li Concentration (ppm)
30
25
20
15
10
5
0
0
200
400
600
800
1000
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
Cs Concentration (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Distance from otolith core (µm)

Bernic98_81

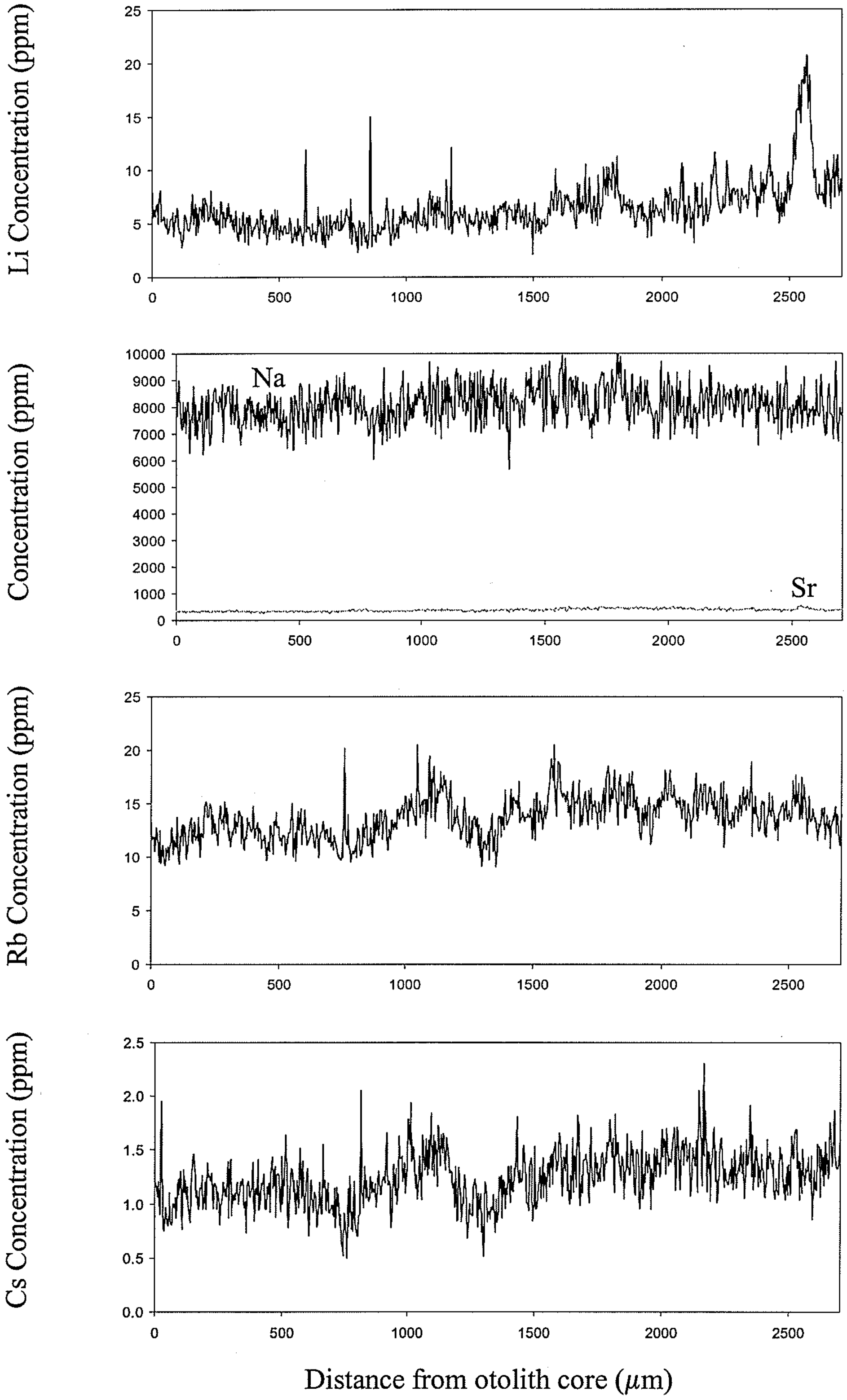

Li Concentration (ppm)
25
20
15
10
5
0
0
500
1000
1500
2000
2500
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
2500
Rb Concentration (ppm)
30
25
20
15
10
5
0
0
500
1000
1500
2000
2500
Cs Concentration (ppm)
4
3
2
1
0
0
500
1000
1500
2000
2500
Distance from otolith core (μm)

Bernic98_83

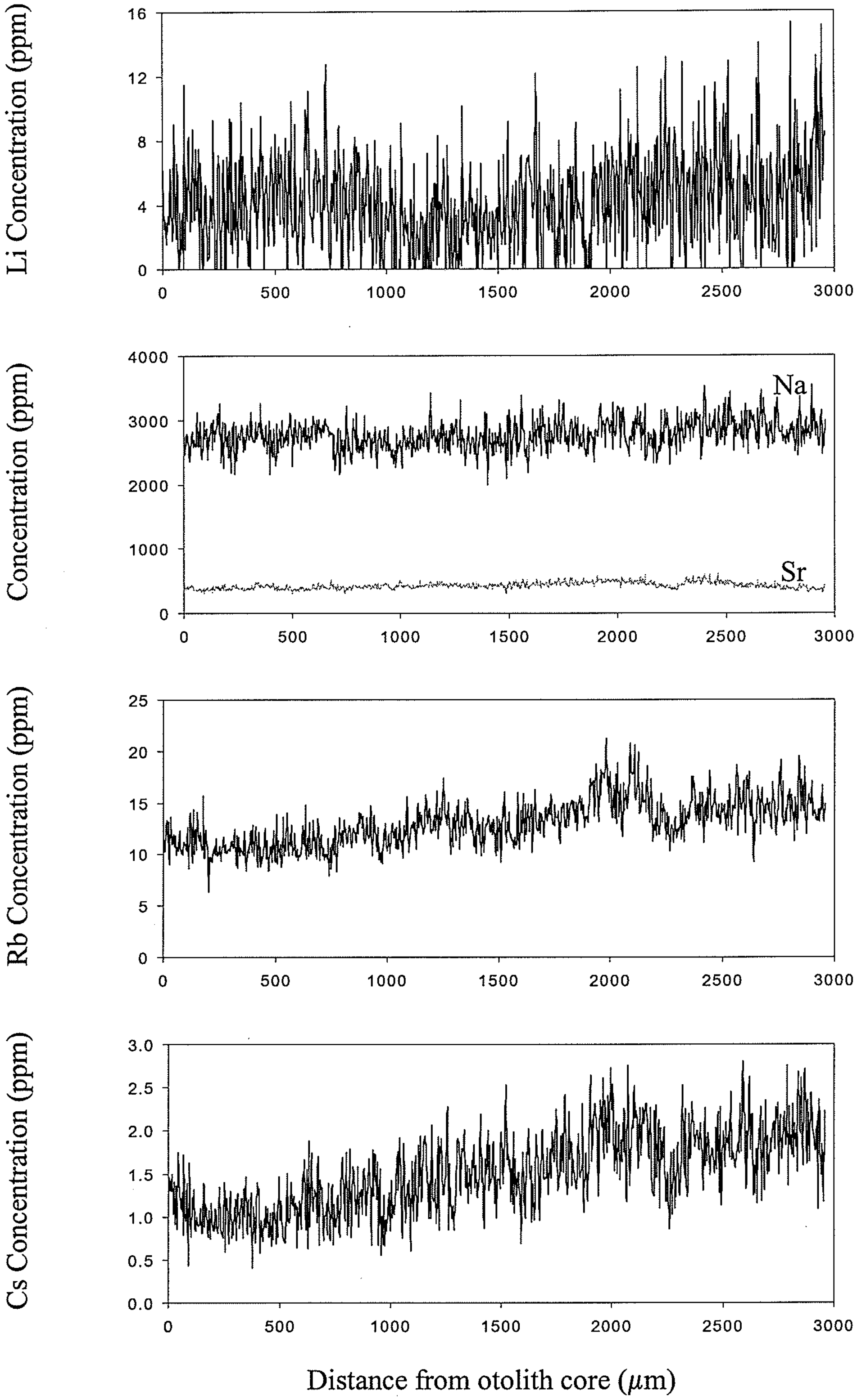


Li Concentration (ppm)
9
8
7
6
5
4
3
2
1
0
0
500
1000
1500
2000
2500
Concentration (ppm)
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
500
1000
1500
2000
2500
Rb Concentration (ppm)
30
25
20
15
10
5
0
0
500
1000
1500
2000
2500
Cs Concentration (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
2500
Distance from otolith core (μm)

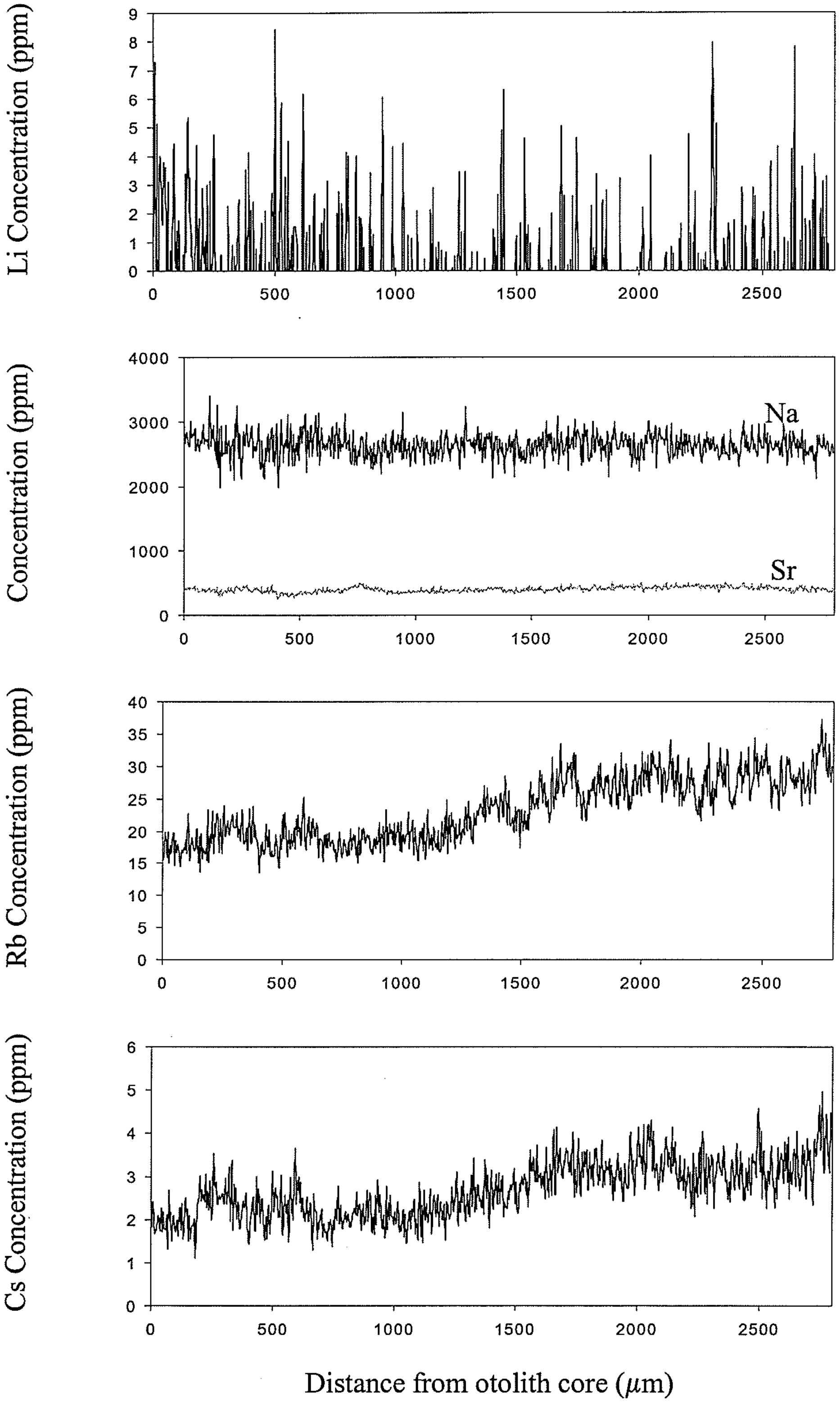
Bernic98_84


Li Concentration (ppm)
25
20
15
10
5
0
0
500
1000
1500
2000
2500
Concentration (ppm)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
2500
Rb Concentration (ppm)
25
20
15
10
5
0
0
500
1000
1500
2000
2500
Cs Concentration (ppm)
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
2500
Distance from otolith core (μm)

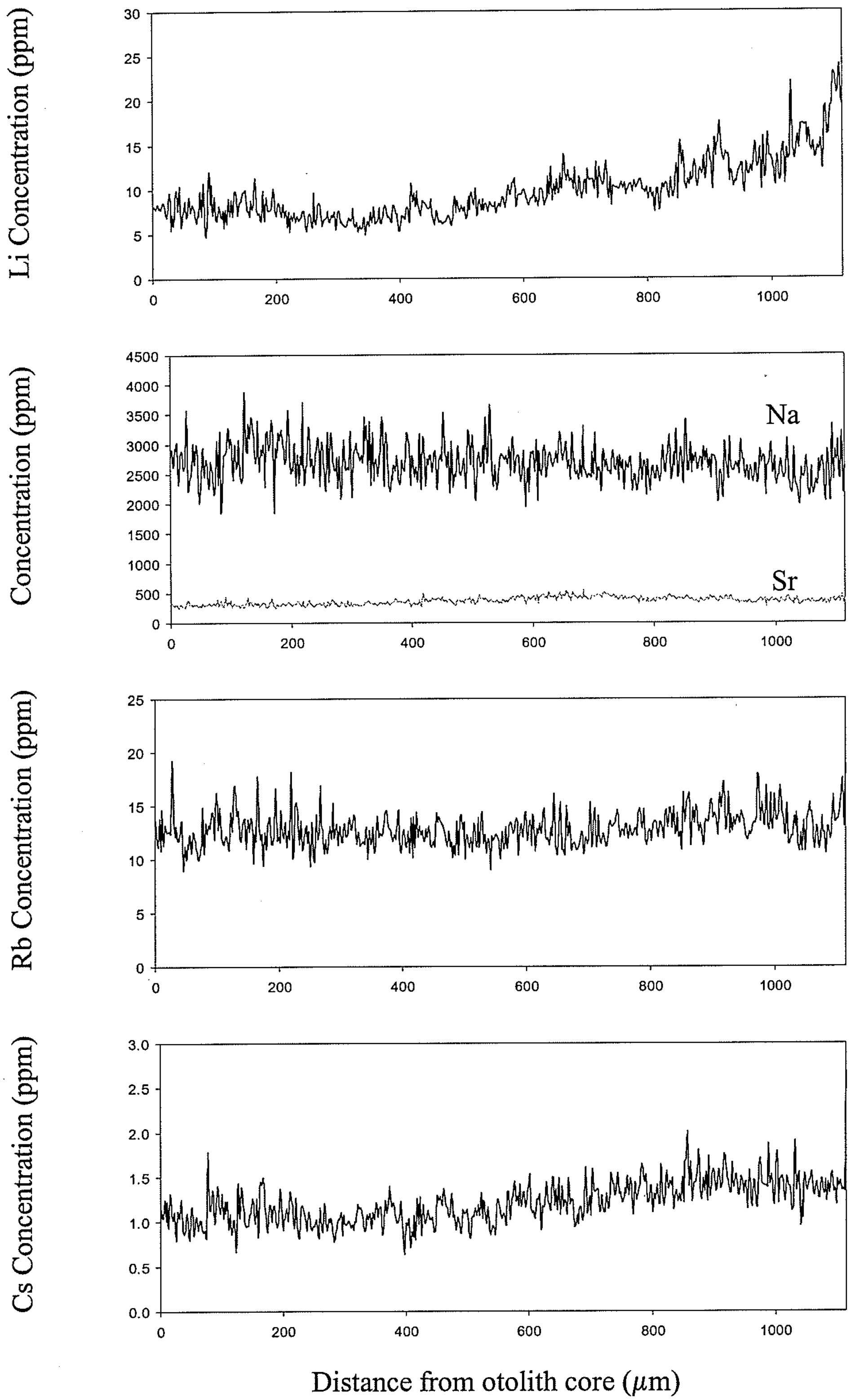
Bernic98_85


Li Concentration (ppm)
16
12
8
4
0
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
25
20
15
10
5
0
Cs Concentration (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
500
1000
1500
2000
2500
3000
Distance from otolith core (µm)

Bernic98_86

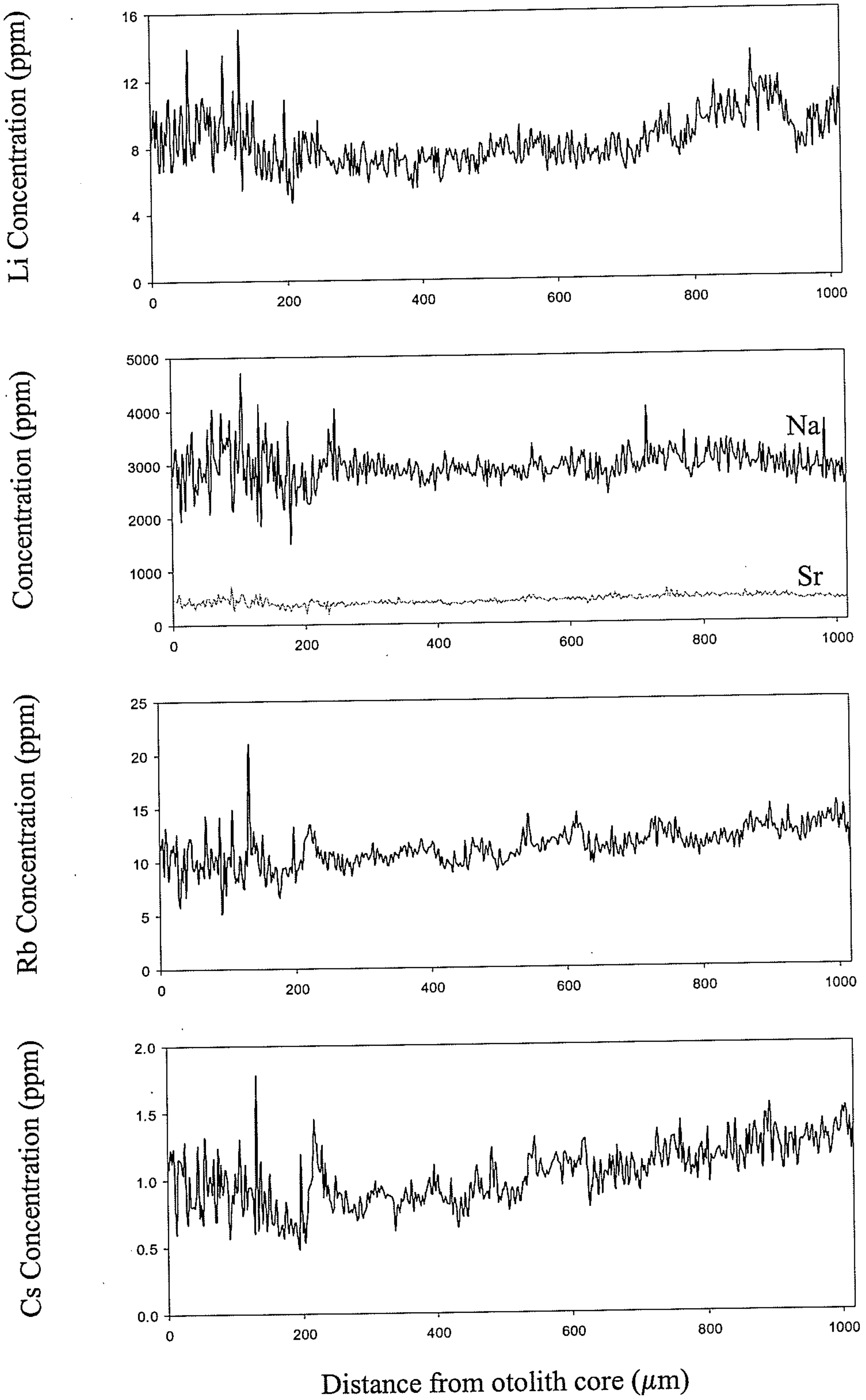

Li Concentration (ppm)
0
1
2
3
4
5
6
7
8
9
0
500
1000
1500
2000
2500
Concentration (ppm)
0
1000
2000
3000
4000
Na
Sr
0
500
1000
1500
2000
2500
Rb Concentration (ppm)
0
5
10
15
20
25
30
35
40
0
500
1000
1500
2000
2500
Cs Concentration (ppm)
0
1
2
3
4
5
6
0
500
1000
1500
2000
2500
Distance from otolith core (μm)

Bernic98_87

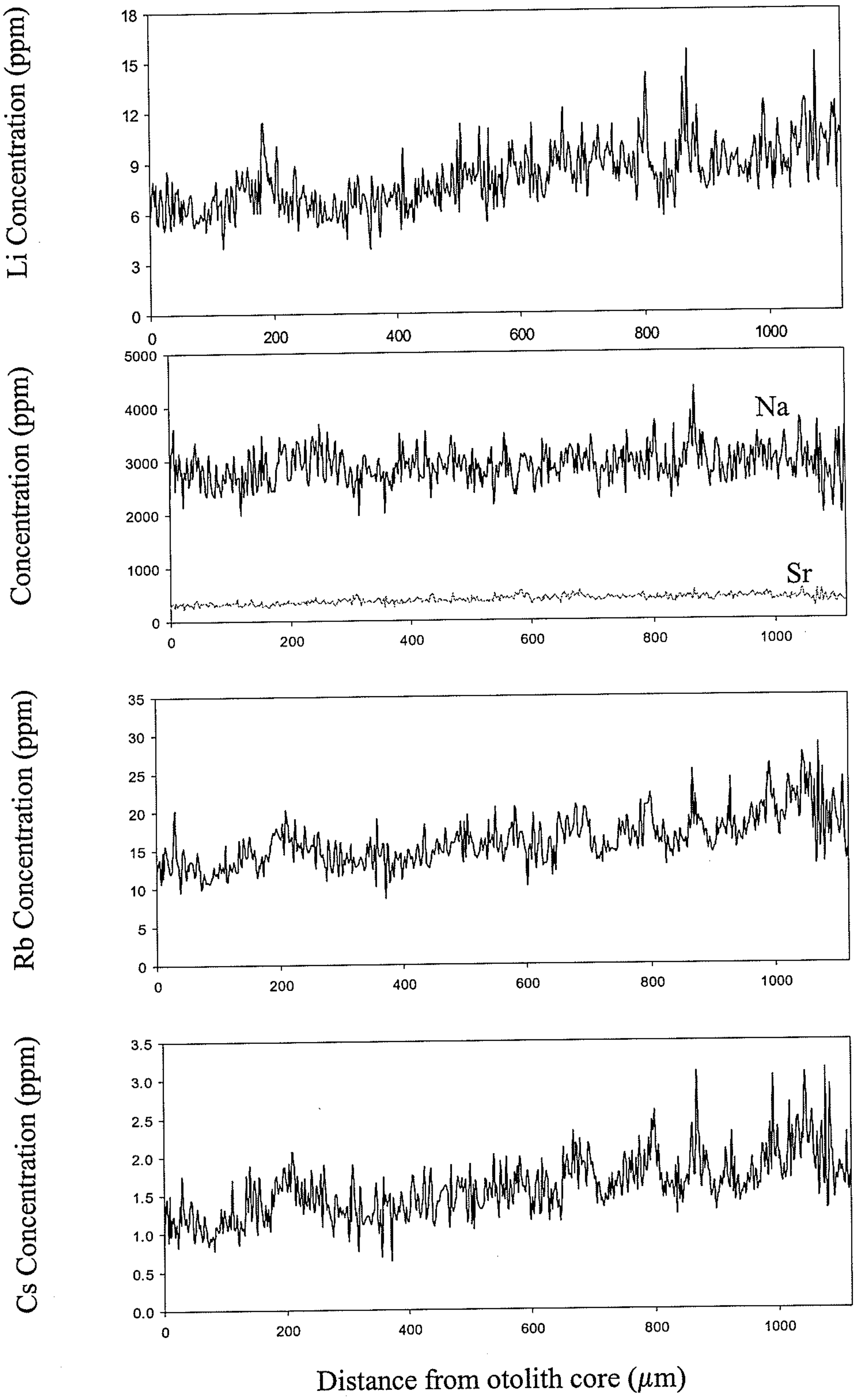


Li Concentration (ppm)
30
25
20
15
10
5
0
0
200
400
600
800
1000
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
25
20
15
10
5
0
0
200
400
600
800
1000
Cs Concentration (ppm)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

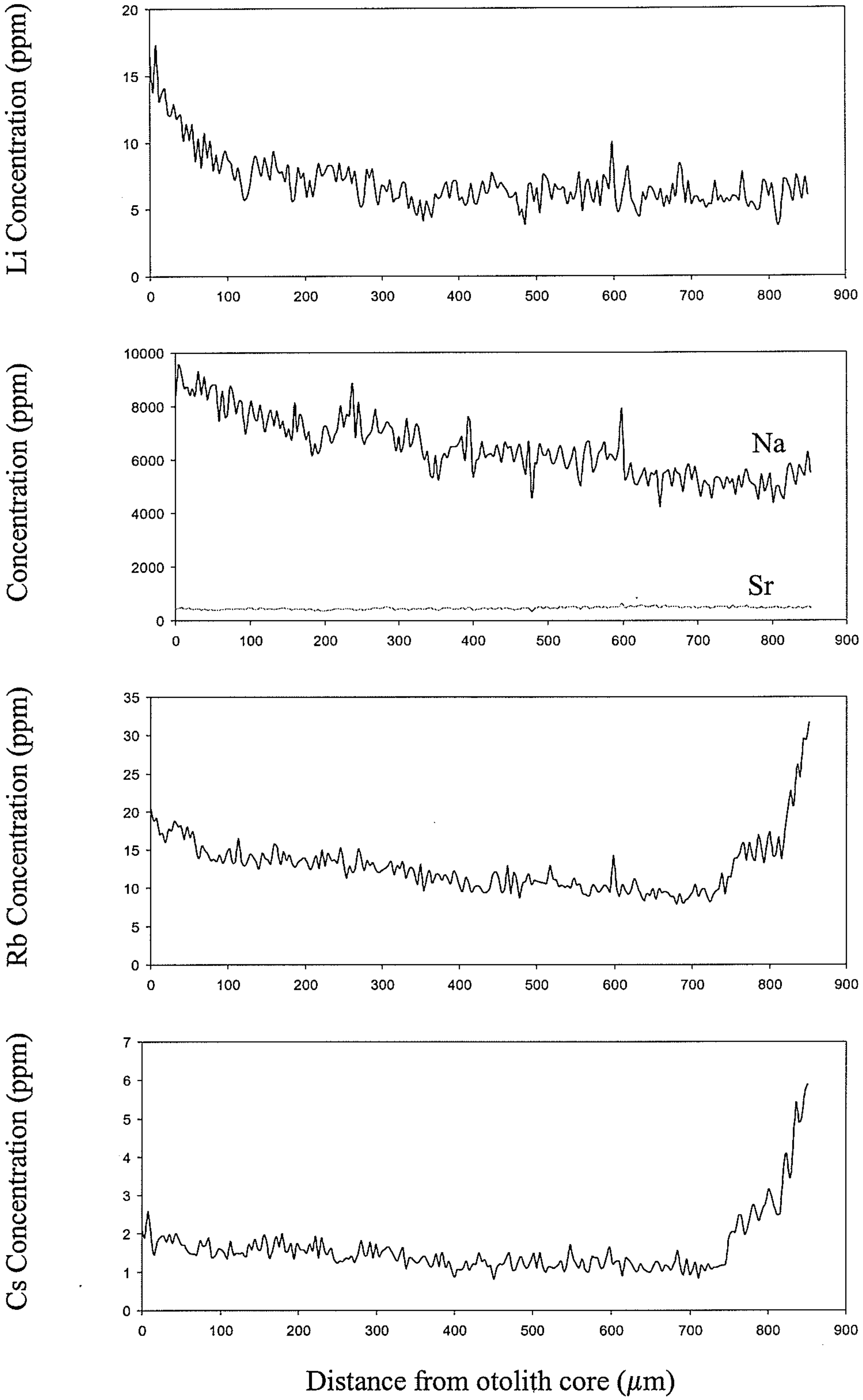
Bernic98_88


Li Concentration (ppm)
0
4
8
12
16
0
200
400
600
800
1000
Concentration (ppm)
0
1000
2000
3000
4000
5000
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
0
5
10
15
20
25
0
200
400
600
800
1000
Cs Concentration (ppm)
0.0
0.5
1.0
1.5
2.0
0
200
400
600
800
1000
Distance from otolith core (μm)

Bernic98_90

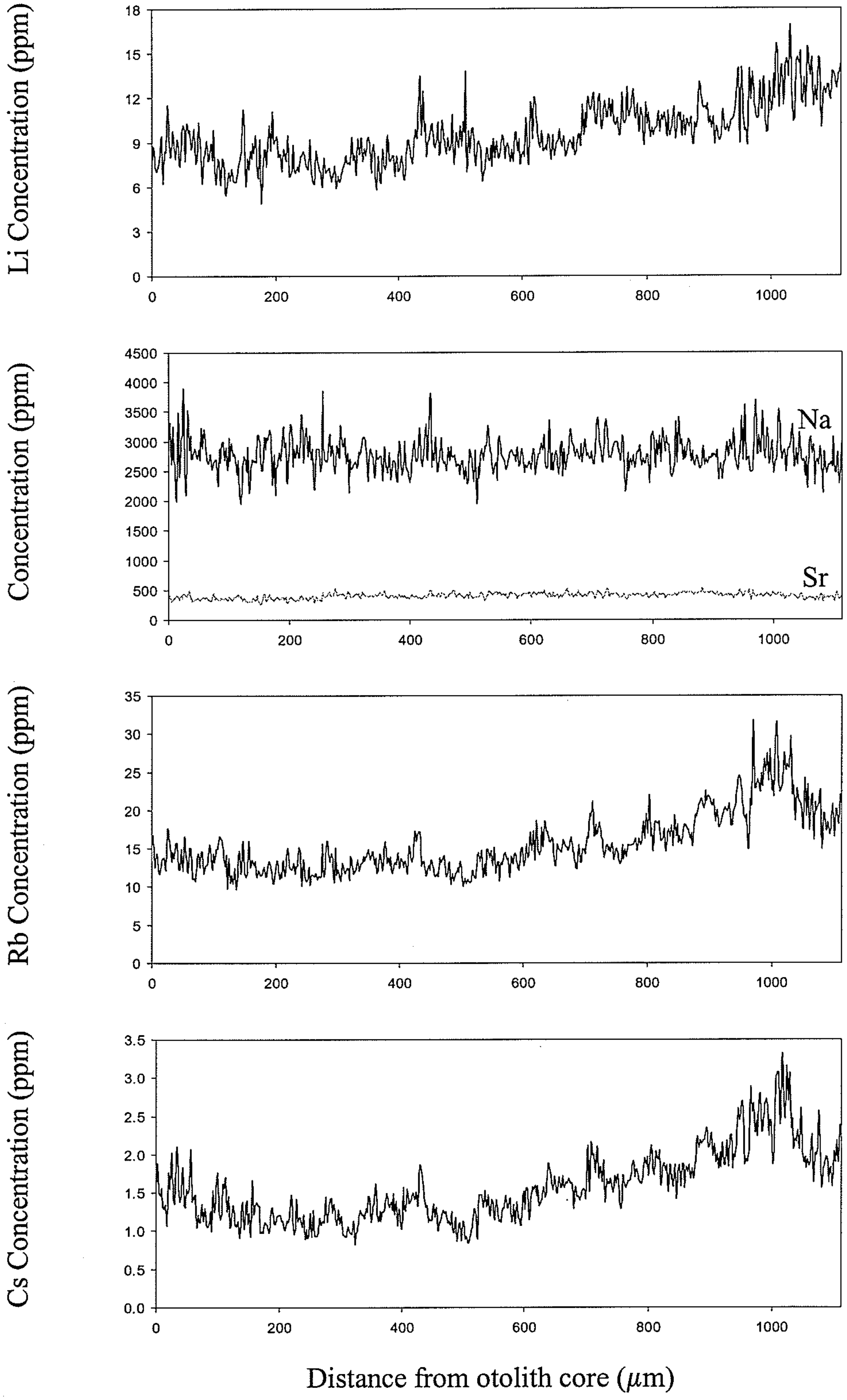

Li Concentration (ppm)
18
15
12
9
6
3
0
0
200
400
600
800
1000
Concentration (ppm)
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
Cs Concentration (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

Bernic98_92

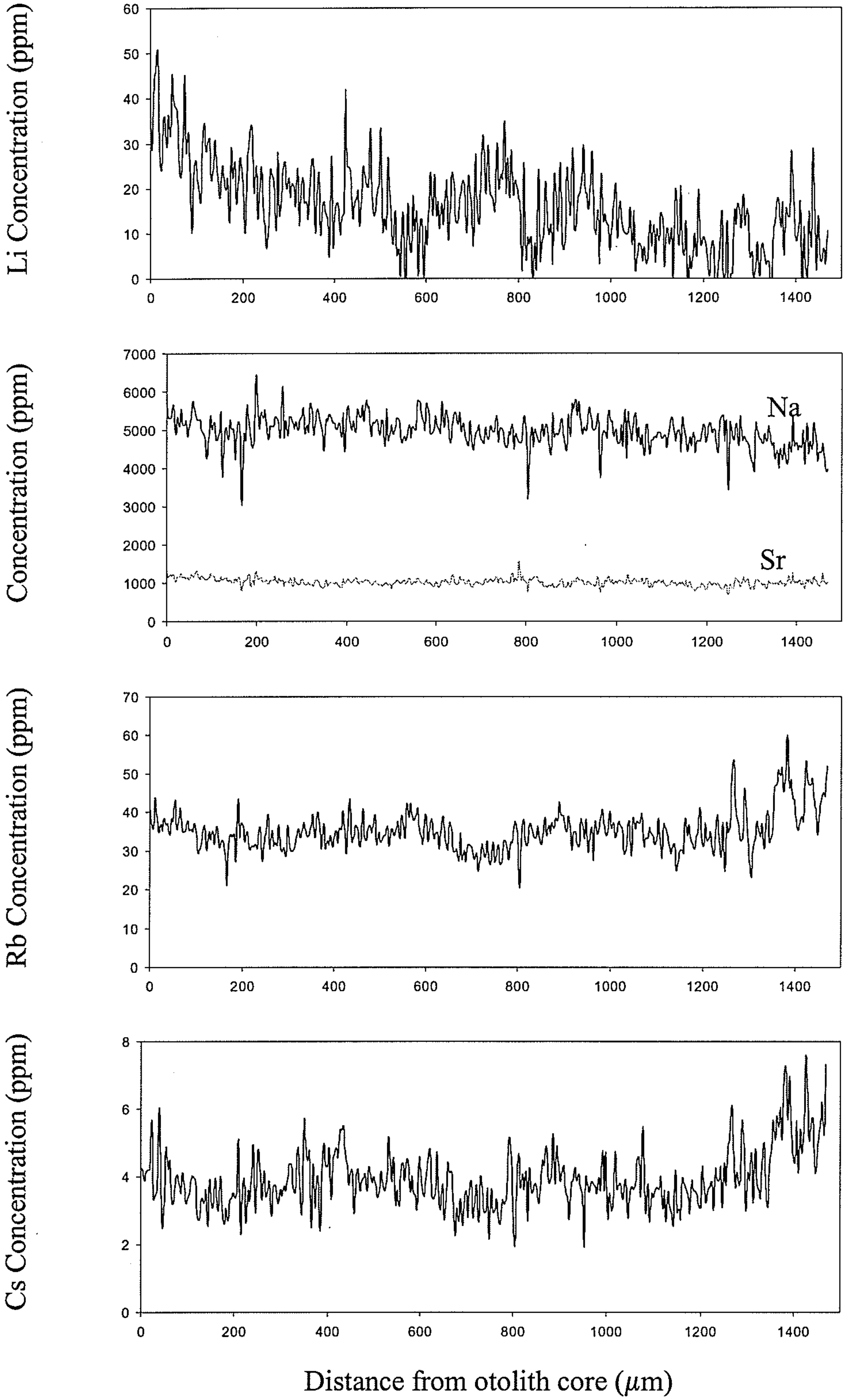


Li Concentration (ppm)
20
15
10
5
0
Concentration (ppm)
10000
8000
6000
4000
2000
0
Na
Sr
Rb Concentration (ppm)
35
30
25
20
15
10
5
0
Cs Concentration (ppm)
7
6
5
4
3
2
1
0
0
100
200
300
400
500
600
700
800
900
Distance from otolith core (μm)

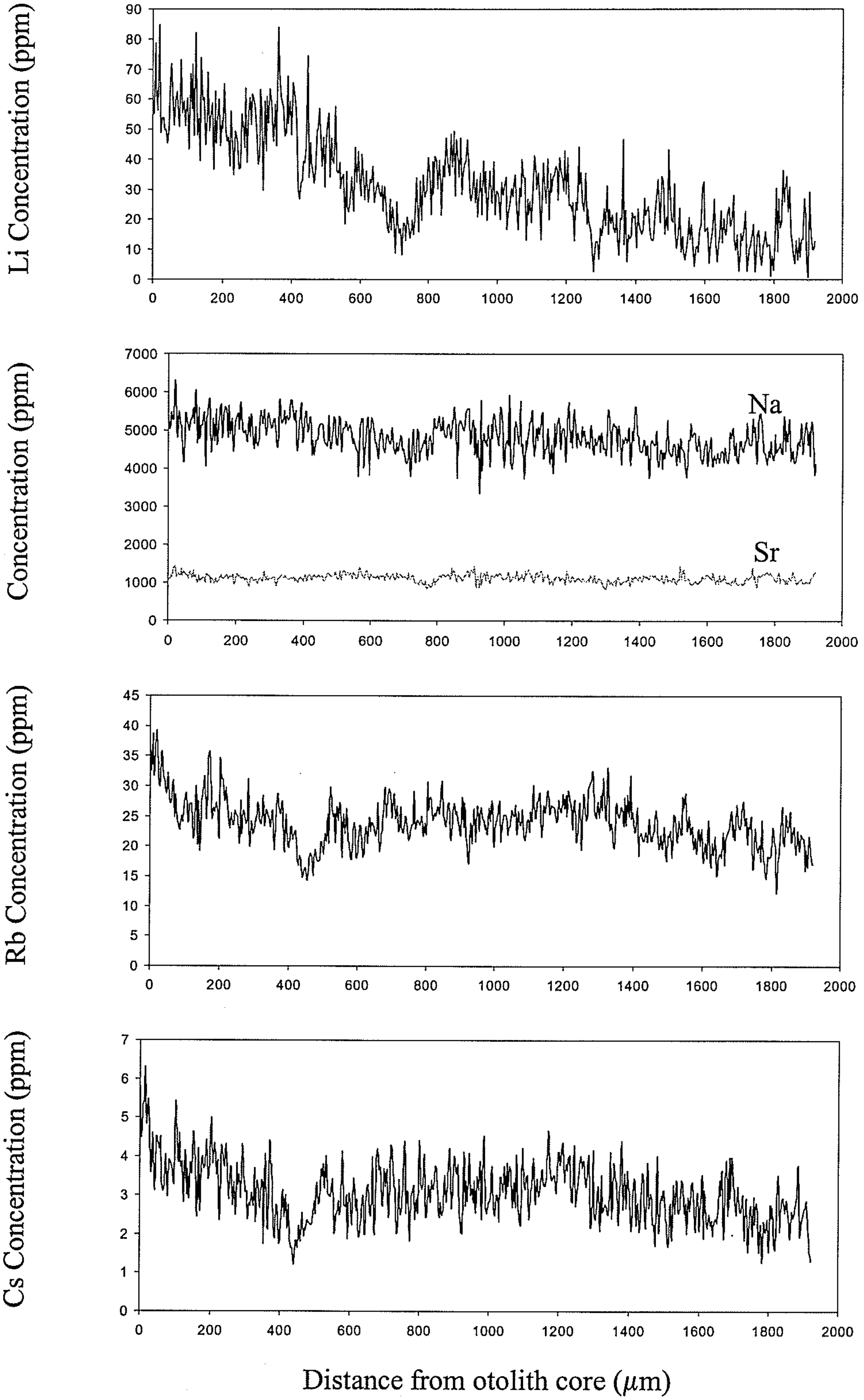
Bernic98_93


Li Concentration (ppm)
18
15
12
9
6
3
0
0
200
400
600
800
1000
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
200
400
600
800
1000
Rb Concentration (ppm)
35
30
25
20
15
10
5
0
0
200
400
600
800
1000
Cs Concentration (ppm)
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Distance from otolith core (μm)

Bernic98_98

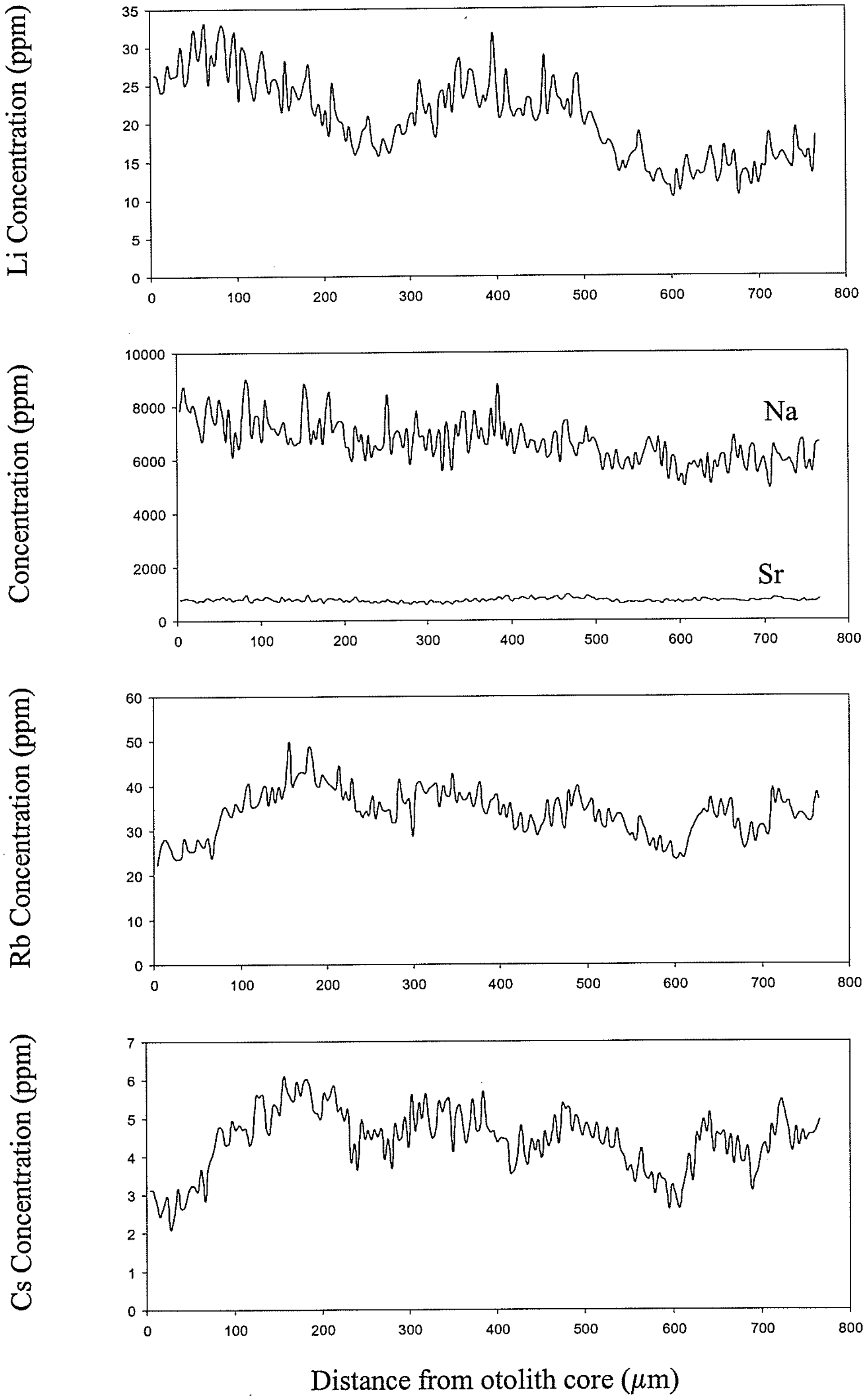

Li Concentration (ppm)
60
50
40
30
20
10
0
0
200
400
600
800
1000
1200
1400
Concentration (ppm)
7000
6000
5000
4000
3000
2000
1000
0
Na
Sr
0
200
400
600
800
1000
1200
1400
Rb Concentration (ppm)
70
60
50
40
30
20
10
0
0
200
400
600
800
1000
1200
1400
Cs Concentration (ppm)
8
6
4
2
0
0
200
400
600
800
1000
1200
1400
Distance from otolith core (μm)

Bernic98_99

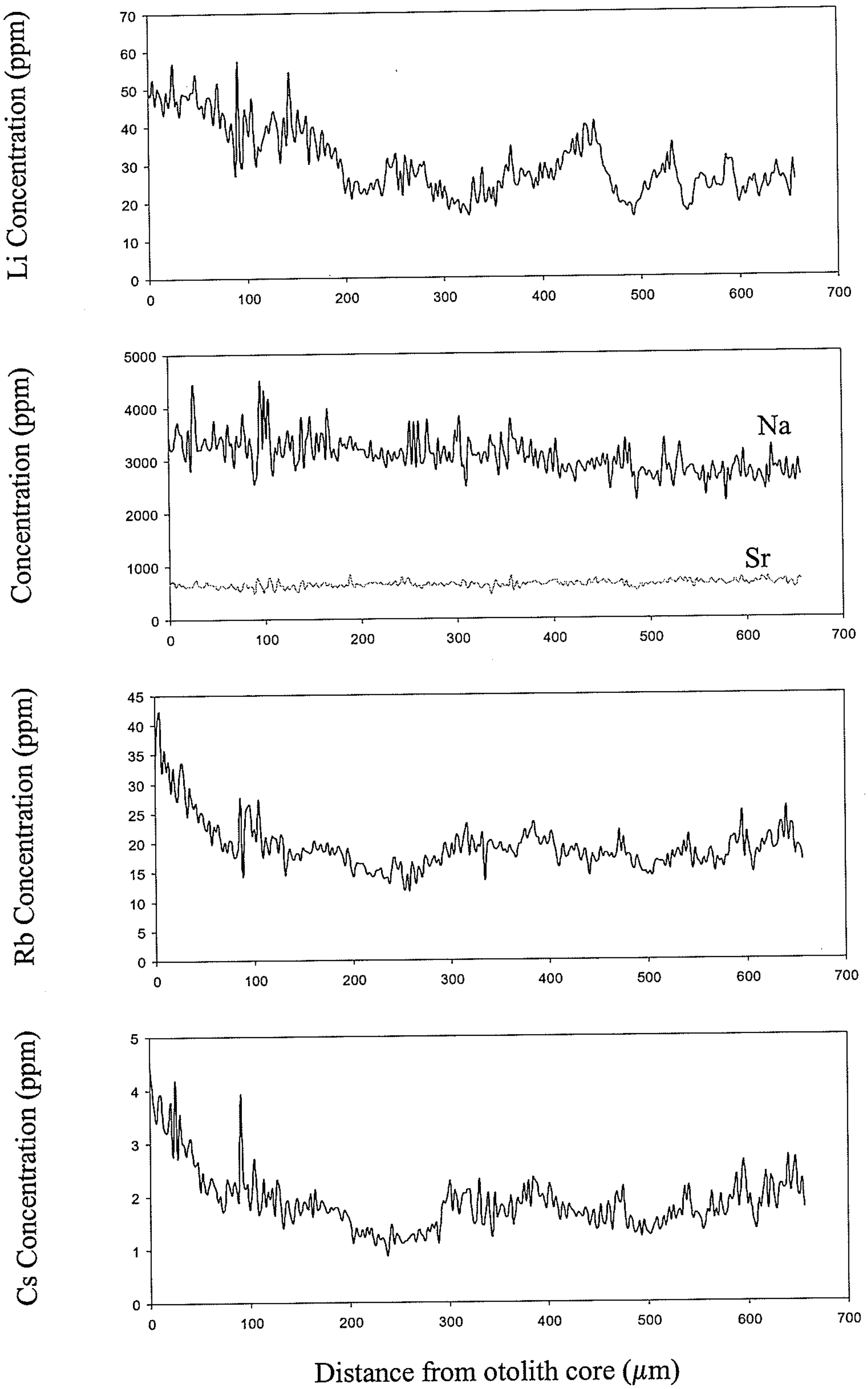


Li Concentration (ppm)
0
10
20
30
40
50
60
70
80
90
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Concentration (ppm)
Na
Sr
0
1000
2000
3000
4000
5000
6000
7000
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Rb Concentration (ppm)
0
5
10
15
20
25
30
35
40
45
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Cs Concentration (ppm)
0
1
2
3
4
5
6
7
0
200
400
600
800
1000
1200
1400
1600
1800
2000
Distance from otolith core (μm)

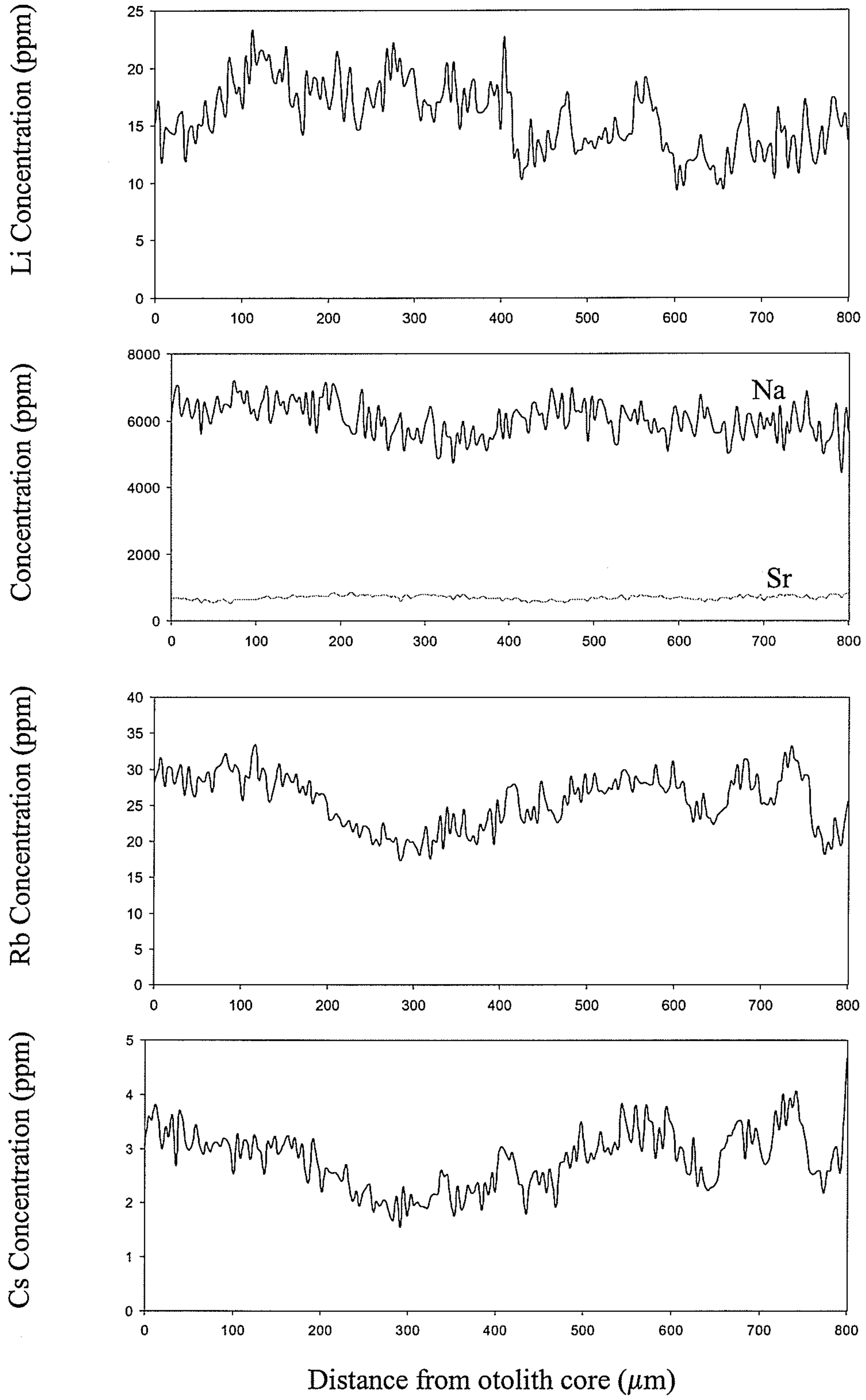
Bernic98_100



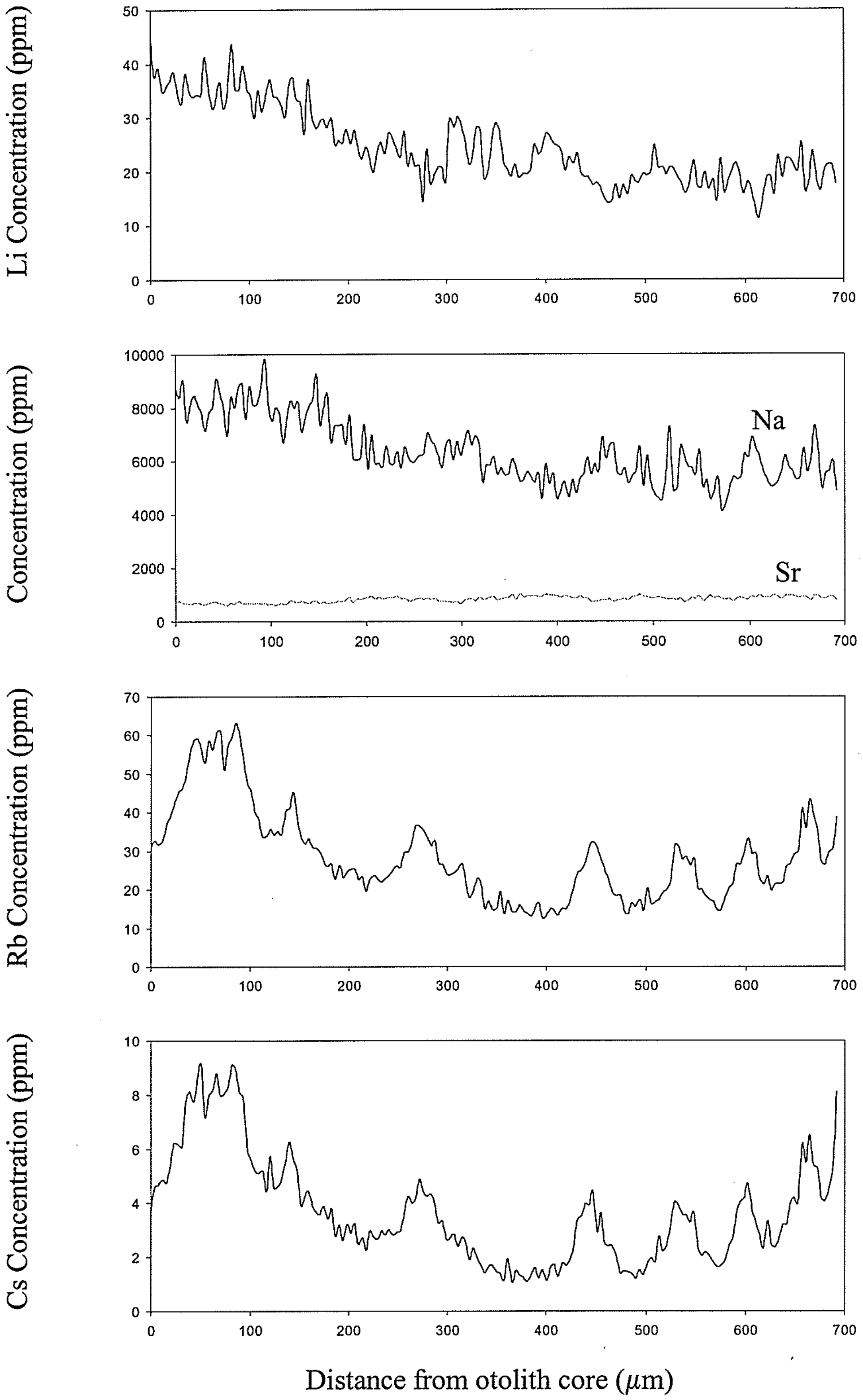
Bernic98_101



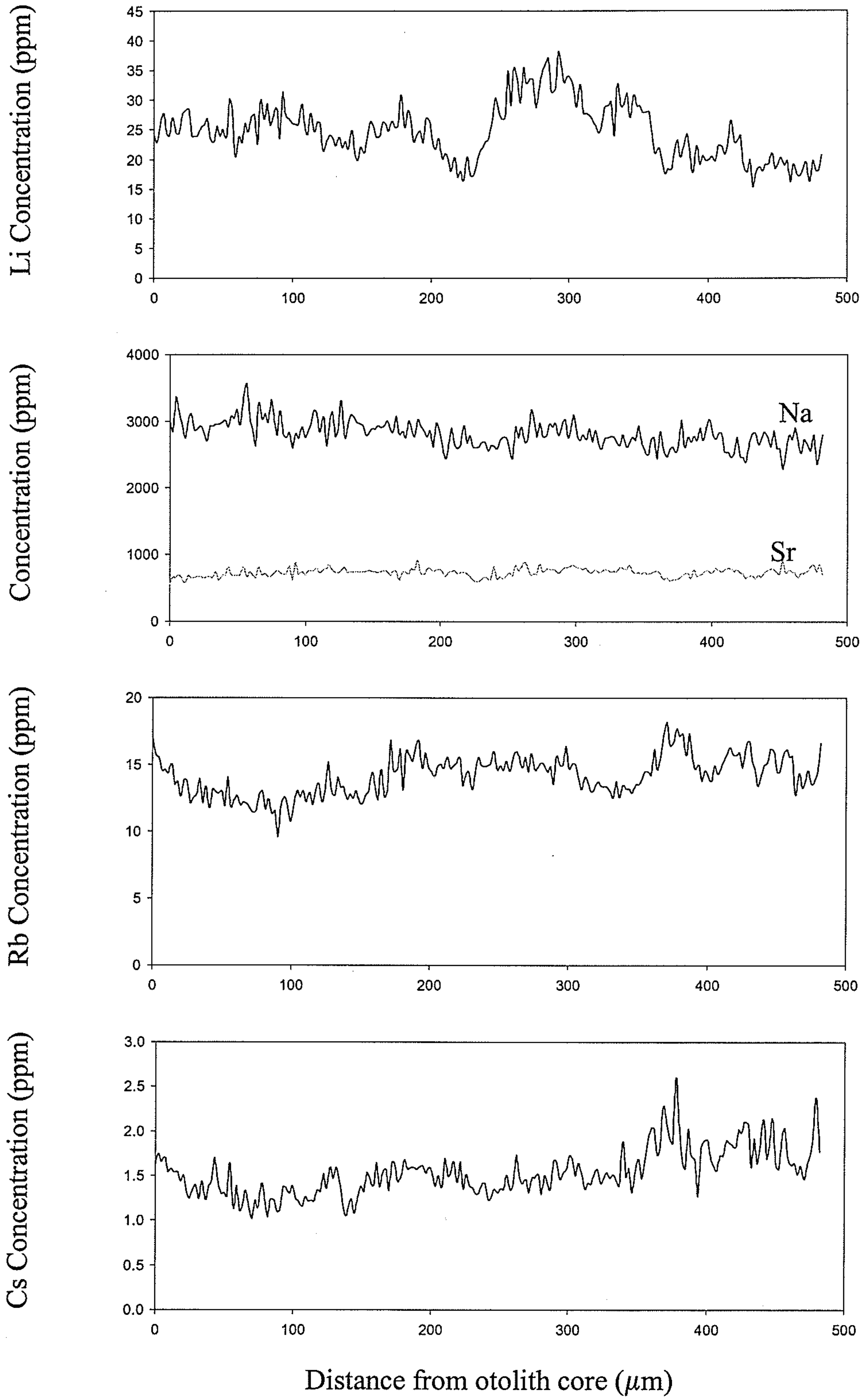
Bernic98_102



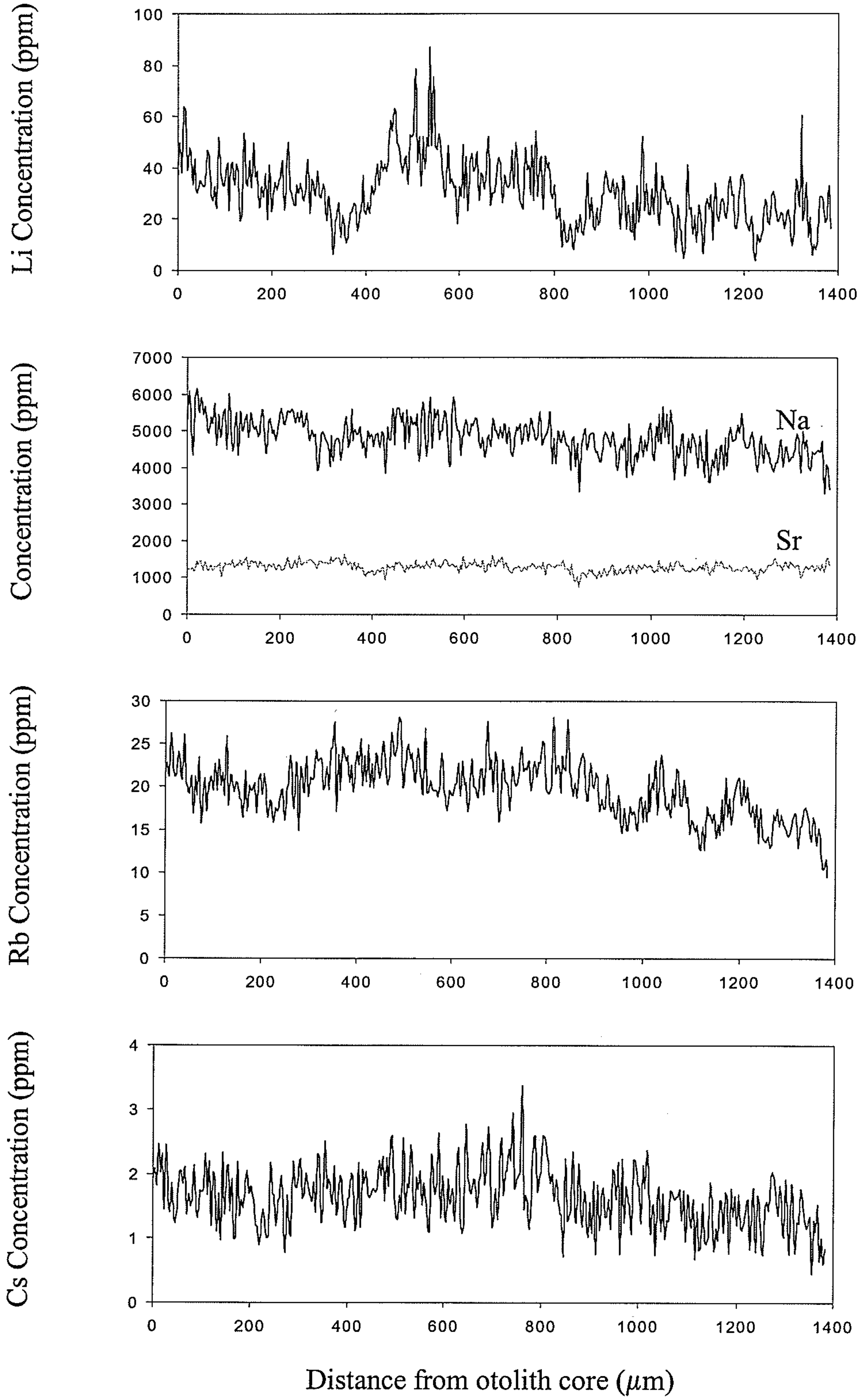
Bernic98_103



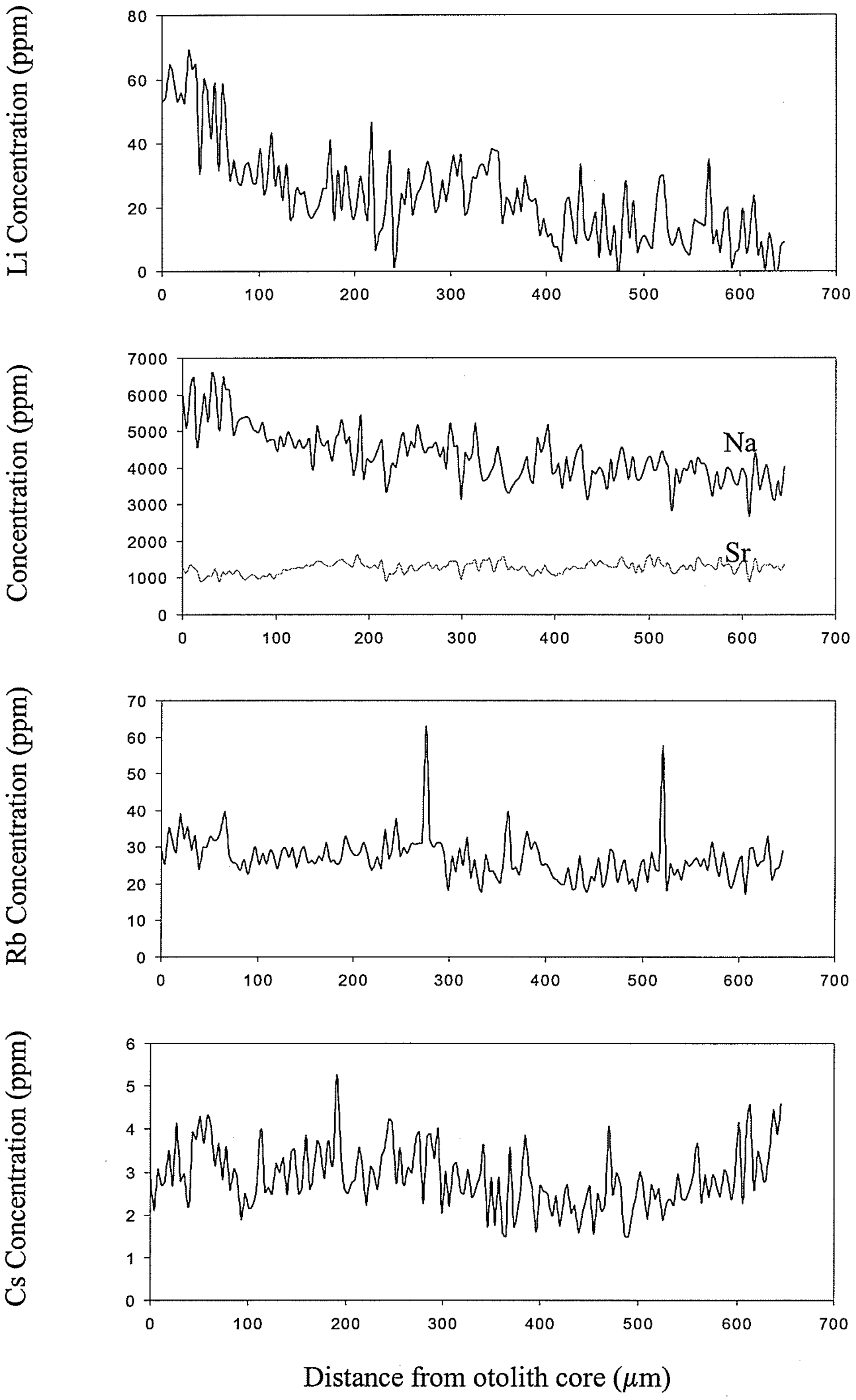
Bernic98_104



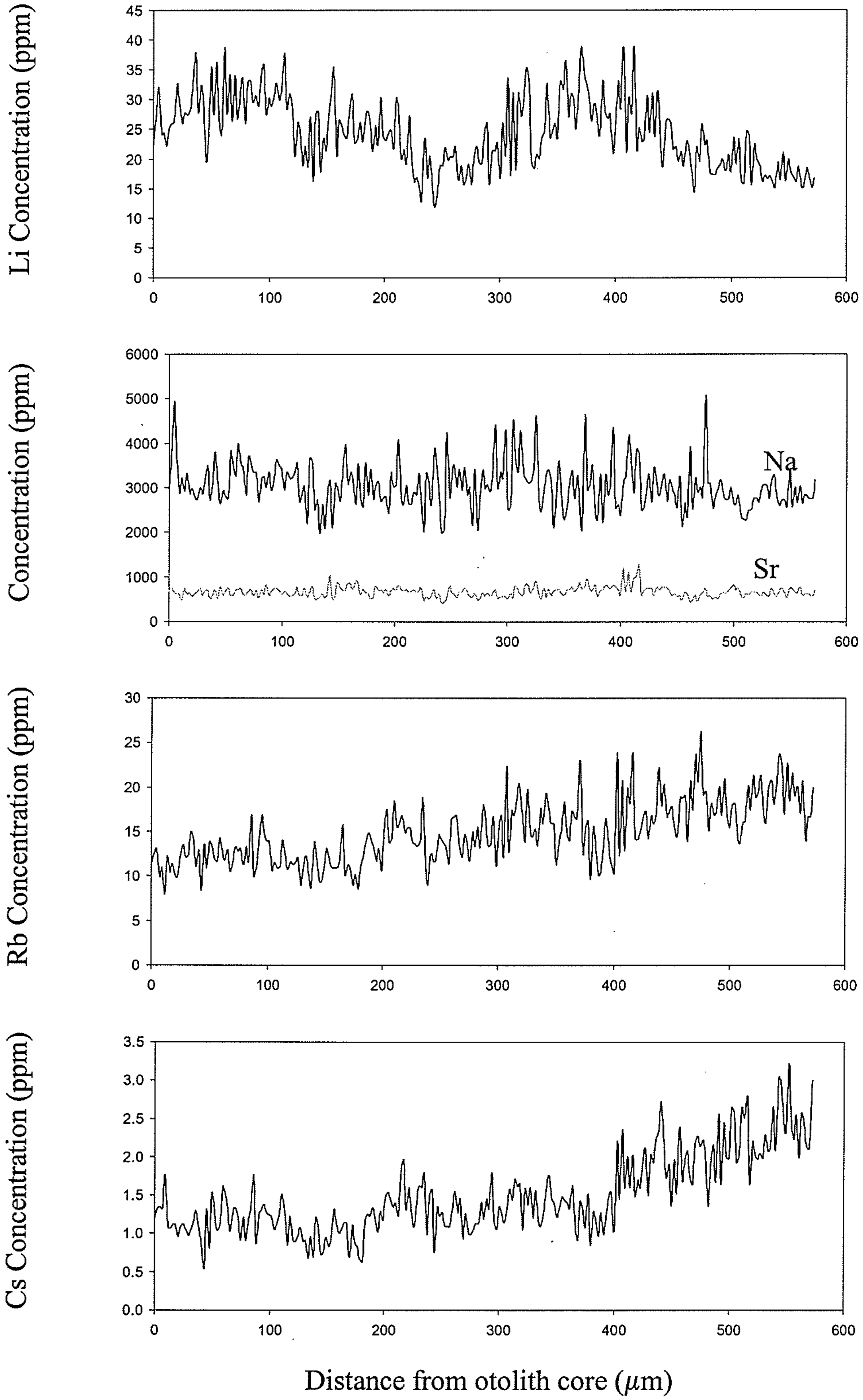
Bernic98_105



Bernic98_108



Bernic98_109



Appendix J LA-ICP-MS data for Tailings Management Area otoliths at Tanco mine

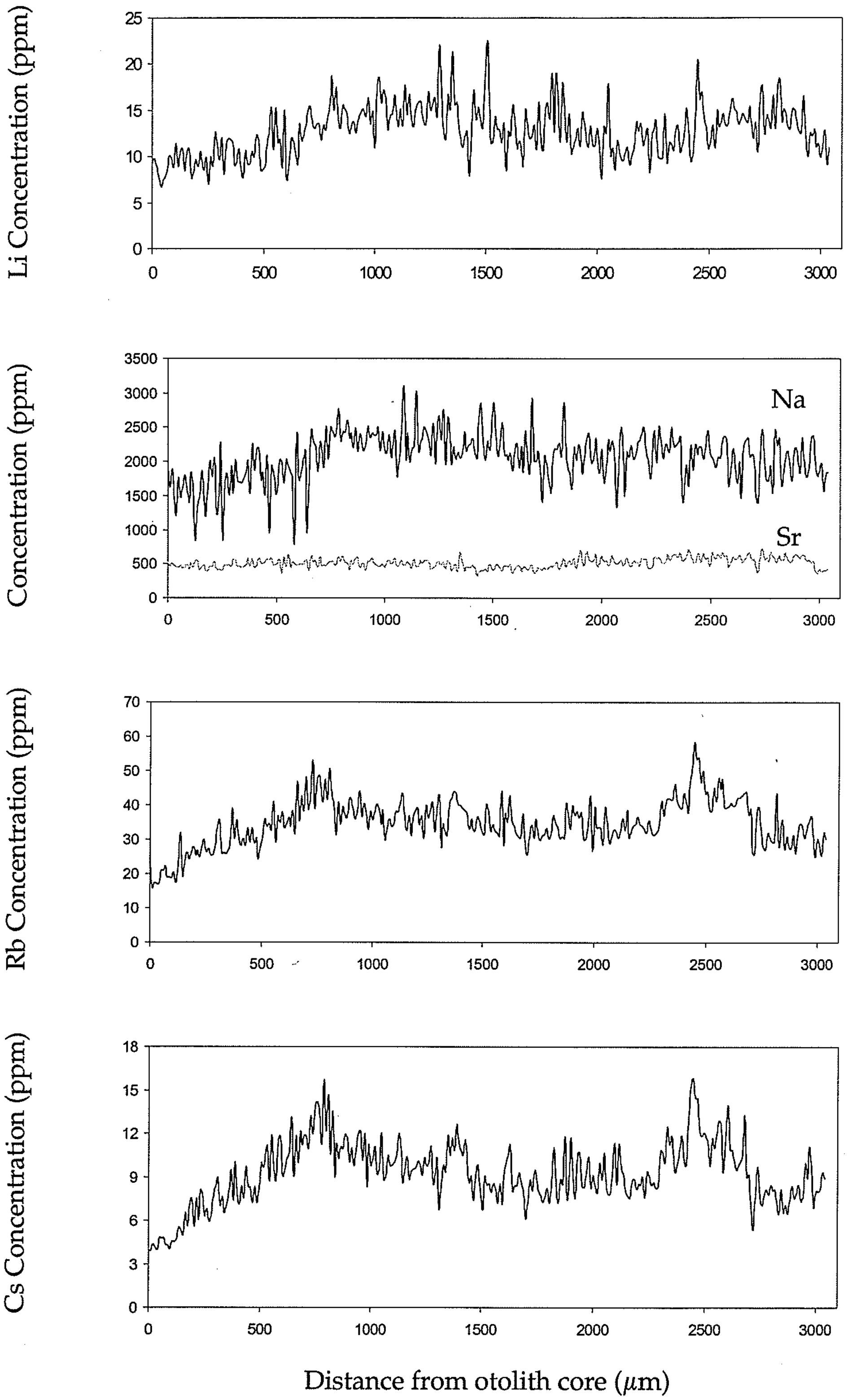
Species: White Sucker (*Catostomus commersoni*)

Captured: 1998 (TetrES Consultants, Inc.)

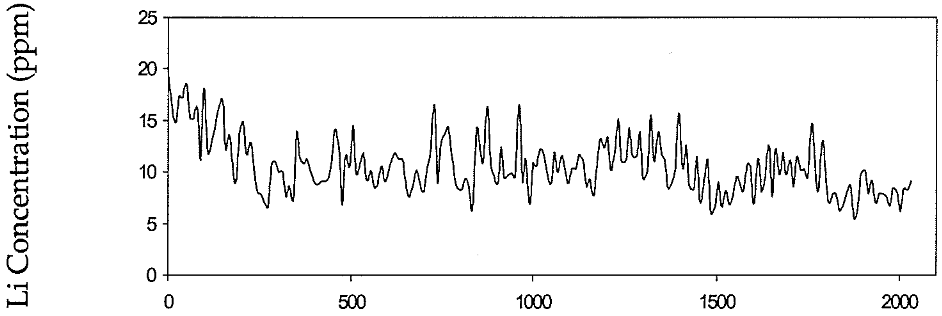
Isotopes	**Li^7**	**Na^{23}**	**Rb^{85}**	**Sr^{88}**	**Cs^{133}**
Typical Detection Limit	2.9	5.2	0.15	0.25	0.1
Typical 1 σ Error	2	200	1	30	0.1

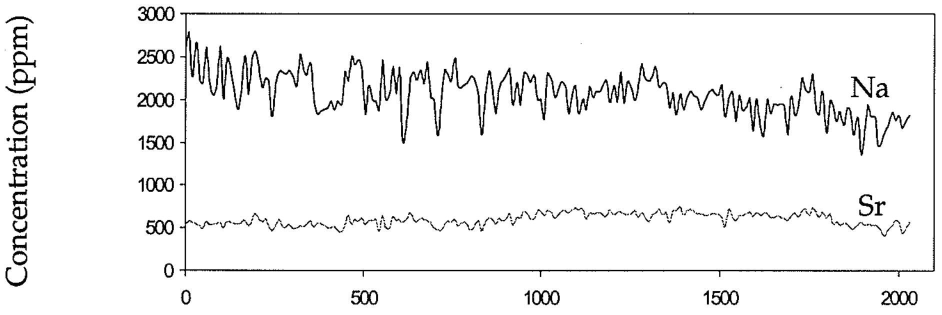
Sample Number	***Species***	***Age***
52	White Sucker	8
53	White Sucker	9
54	White Sucker	8
55	White Sucker	5
56	White Sucker	9
57	White Sucker	7
58	White Sucker	7
59	White Sucker	6

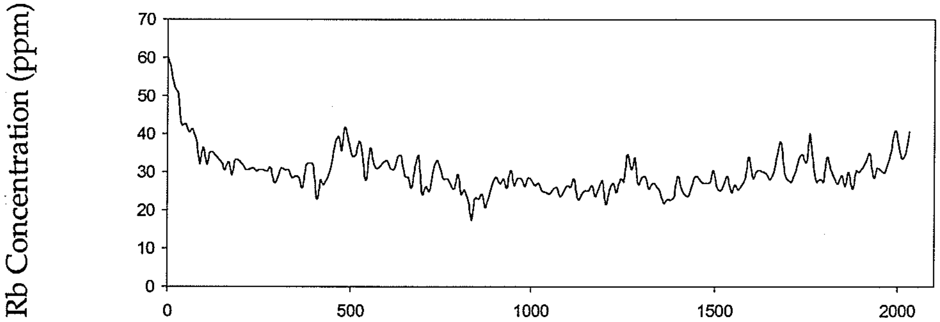
TMA98_52

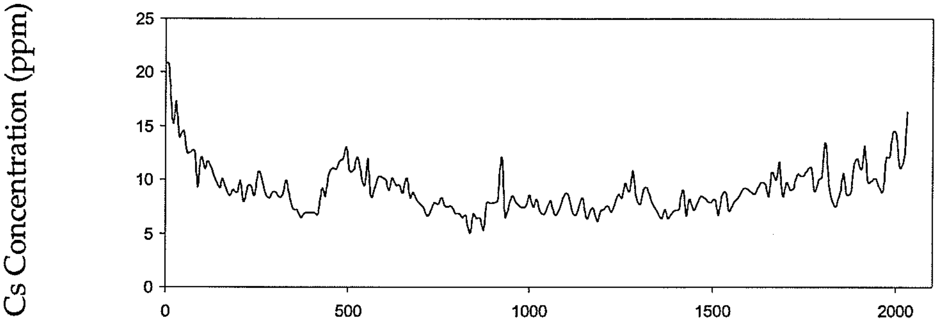

Li Concentration (ppm)
25
20
15
10
5
0
0
500
1000
1500
2000
2500
3000
Concentration (ppm)
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
500
1000
1500
2000
2500
3000
Rb Concentration (ppm)
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
3000
Cs Concentration (ppm)
18
15
12
9
6
3
0
0
500
1000
1500
2000
2500
3000
Distance from otolith core (μm)

TMA98_53



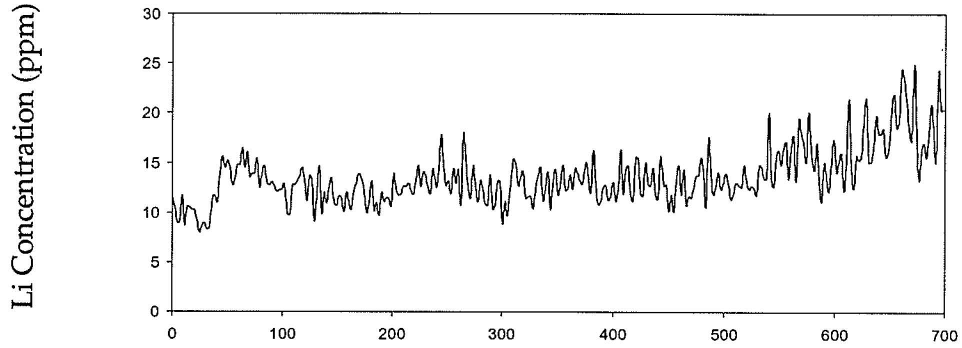


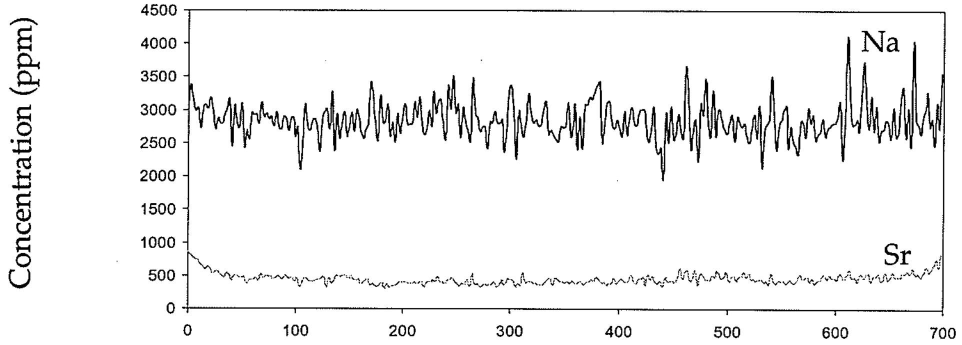


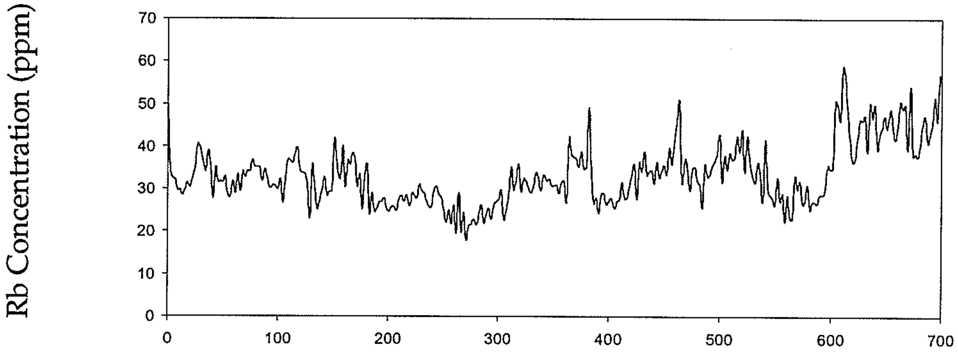


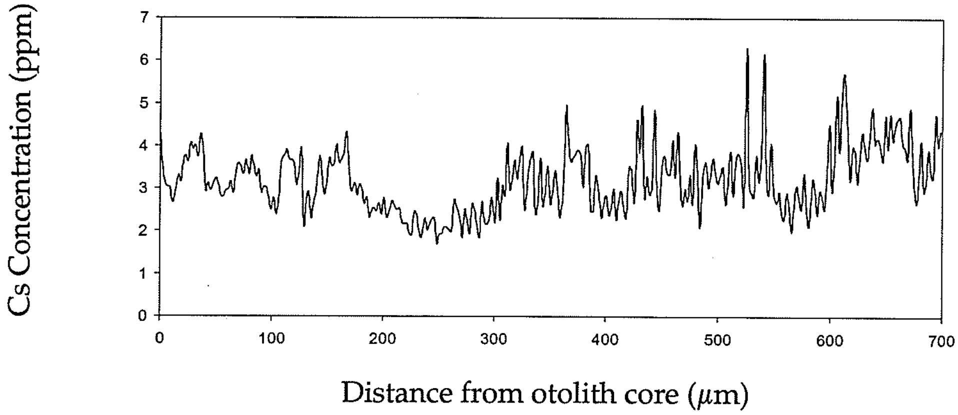
Distance from otolith core (μm)

TMA98_54

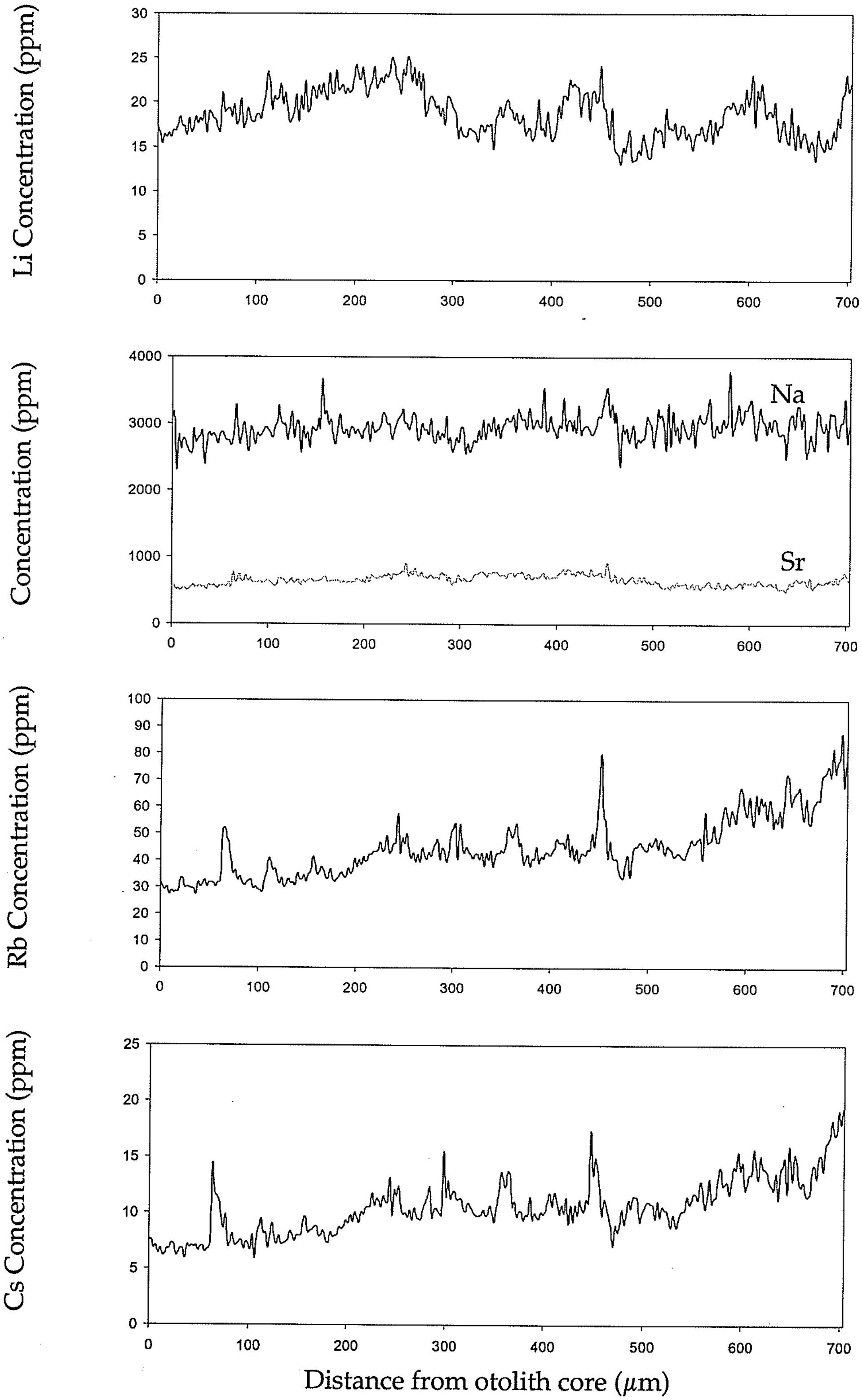

Li Concentration (ppm)
30
25
20
15
10
5
0
0
100
200
300
400
500
600
700


Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
100
200
300
400
500
600
700

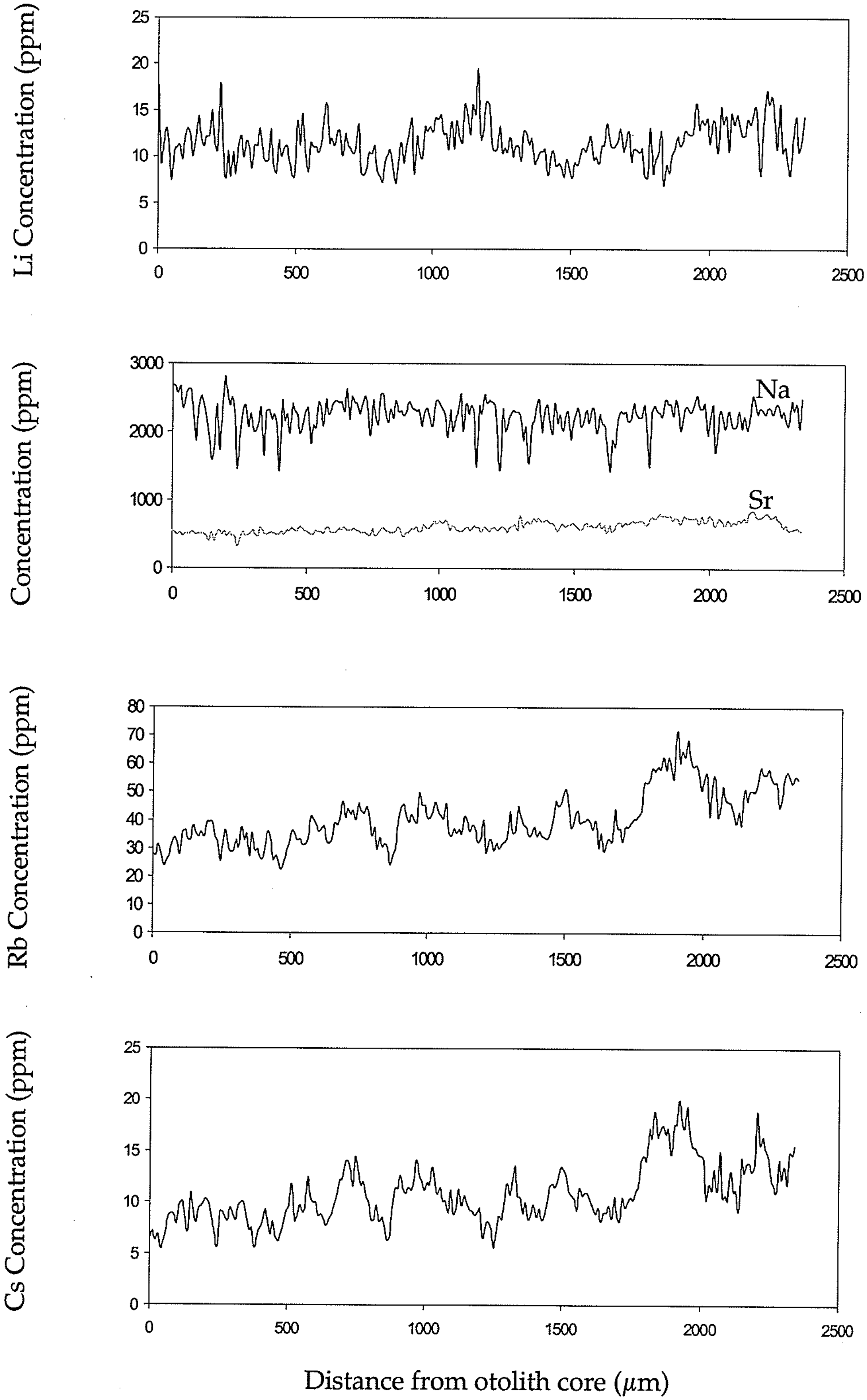

Rb Concentration (ppm)
70
60
50
40
30
20
10
0
0
100
200
300
400
500
600
700


Cs Concentration (ppm)
7
6
5
4
3
2
1
0
0
100
200
300
400
500
600
700
Distance from otolith core (μm)

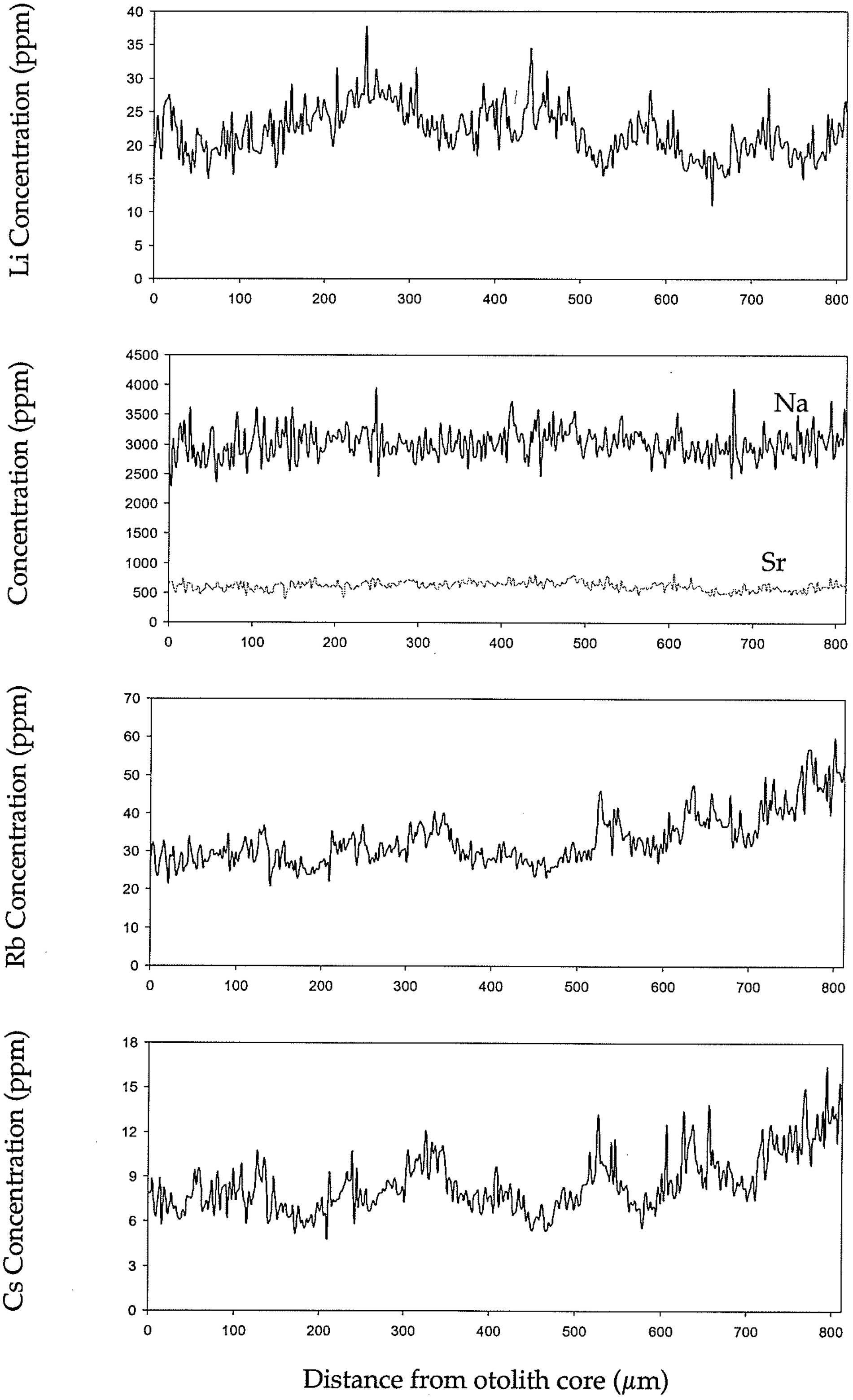
TMA98_55


Li Concentration (ppm)
30
25
20
15
10
5
0
0
100
200
300
400
500
600
700
Concentration (ppm)
4000
3000
2000
1000
0
Na
Sr
0
100
200
300
400
500
600
700
Rb Concentration (ppm)
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
500
600
700
Cs Concentration (ppm)
25
20
15
10
5
0
0
100
200
300
400
500
600
700
Distance from otolith core (μm)

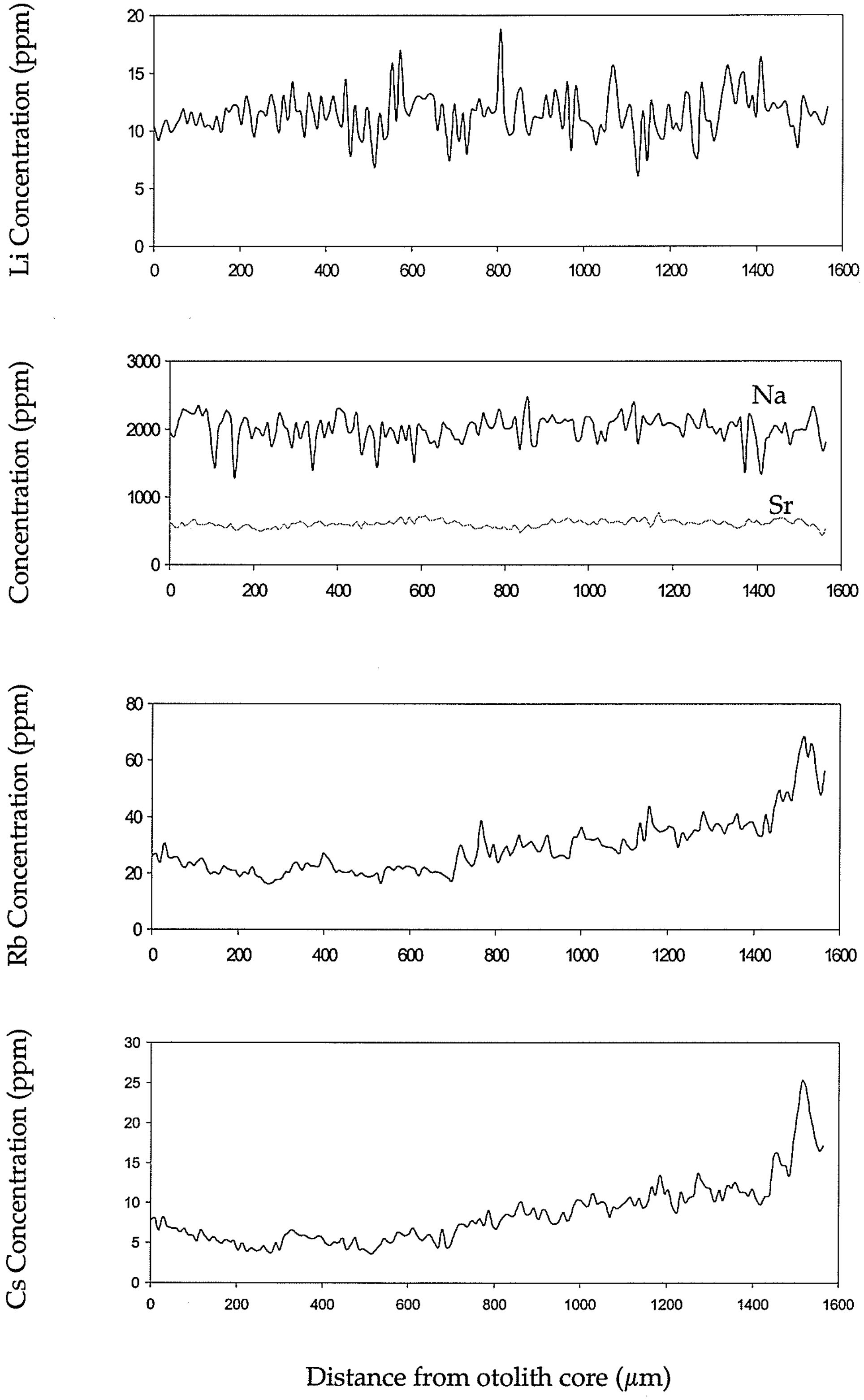
TMA98_56


Li Concentration (ppm)
25
20
15
10
5
0
0
500
1000
1500
2000
2500
Concentration (ppm)
3000
2000
1000
0
Na
Sr
0
500
1000
1500
2000
2500
Rb Concentration (ppm)
80
70
60
50
40
30
20
10
0
0
500
1000
1500
2000
2500
Cs Concentration (ppm)
25
20
15
10
5
0
0
500
1000
1500
2000
2500
Distance from otolith core (µm)

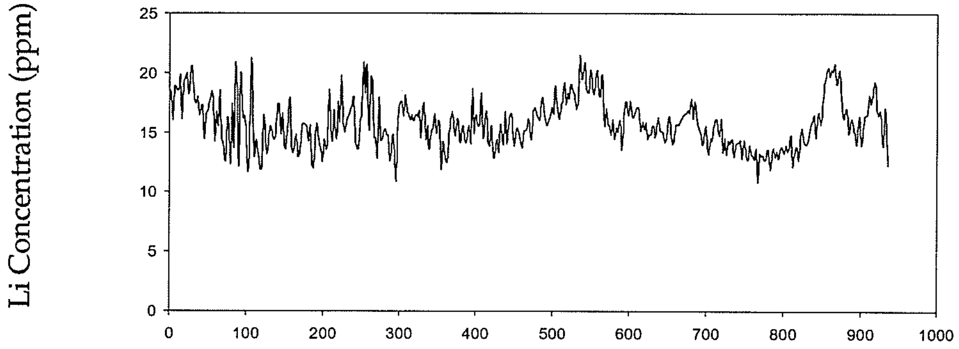
TMA98_57

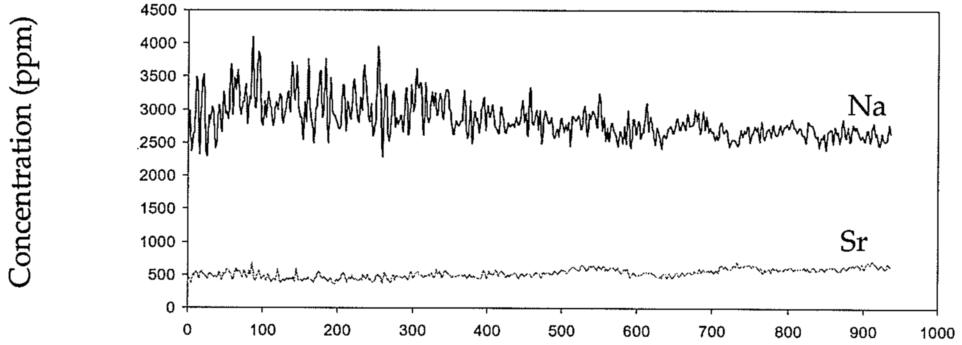

Li Concentration (ppm)
40
35
30
25
20
15
10
5
0
0
100
200
300
400
500
600
700
800
Concentration (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
Na
Sr
0
100
200
300
400
500
600
700
800
Rb Concentration (ppm)
70
60
50
40
30
20
10
0
0
100
200
300
400
500
600
700
800
Cs Concentration (ppm)
18
15
12
9
6
3
0
0
100
200
300
400
500
600
700
800
Distance from otolith core (µm)

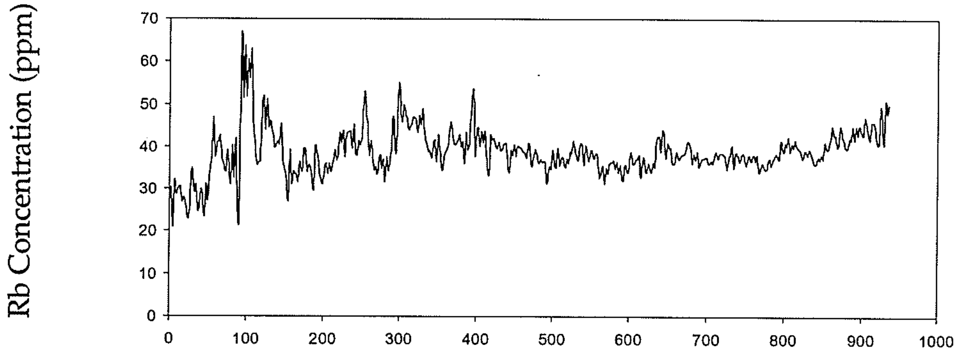
TMA98_58

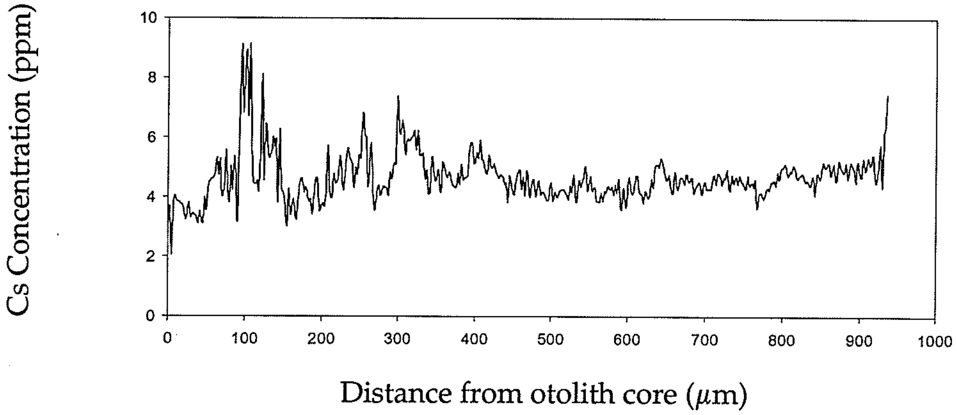

Li Concentration (ppm)
20
15
10
5
0
Concentration (ppm)
3000
2000
1000
0
Na
Sr
Rb Concentration (ppm)
80
60
40
20
0
Cs Concentration (ppm)
30
25
20
15
10
5
0
0
200
400
600
800
1000
1200
1400
1600
Distance from otolith core (μm)

TMA98_59


Li Concentration (ppm)
0
5
10
15
20
25
0
100
200
300
400
500
600
700
800
900
1000


Concentration (ppm)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
Na
Sr
0
100
200
300
400
500
600
700
800
900
1000


Rb Concentration (ppm)
0
10
20
30
40
50
60
70
0
100
200
300
400
500
600
700
800
900
1000


Cs Concentration (ppm)
0
2
4
6
8
10
0
100
200
300
400
500
600
700
800
900
1000
Distance from otolith core (μm)

Appendix K Maskwa Pit Water Quality Data 2006

Collected by Wardrop Engineering, Inc. October 18, 2006 at 1 m depth.

	Units	Maskwa Pit (1m)
Physicochemical Properties		
Alkalinity (Total as CaCO3)	mg/L	152
Alkalinity (PP as CaCO3)	mg/L	<0.5
Ammonia (N)	mg/L	<0.005
Chloride (Cl)	mg/L	25.4
Conductivity	uS/cm	626
Dissolved Hardness (CaCO3)	mg/L	304
Dissolved Inorganic Carbon (C)	mg/L	34.8
Dissolved Organic Carbon (C)	mg/L	5.1
Dissolved Phosphorus (P)	mg/L	0.003
Dissolved Sulphate (SO4)	mg/L	135 (1)
Fluoride (F)	mg/L	n/a
Nitrate (N)	mg/L	<0.02
Nitrate plus Nitrite (N)	mg/L	<0.02
Nitrite (N)	mg/L	<0.005
pH	pH	8.2
Total Dissolved Solids	mg/L	430
Total Hardness (CaCO3)	mg/L	305
Total Inorganic Carbon (C)	mg/L	37.0
Total Kjeldahl Nitrogen (Calc)	mg/L	0.26
Total Nitrogen (N)	mg/L	0.26
Total Organic Carbon (C)	mg/L	4.8
Total Phosphorus (P)	mg/L	0.025
Total Suspended Solids	mg/L	1
True Colour	Col.	<5
Turbidity	NTU	0.7
Radiological		
Radium 226	Bq/l	<0.01
Note (1) Detection limits increased due to matrix interference		

Dissolved Metals	**Units**	**Maskwa Pit (1m)**
Dissolved Aluminum (Al)	mg/L	0.0033
Dissolved Antimony (Sb)	mg/L	0.00010
Dissolved Arsenic (As)	mg/L	0.0013
Dissolved Barium (Ba)	mg/L	0.0348
Dissolved Beryllium (Be)	mg/L	<0.00005
Dissolved Bismuth (Bi)	mg/L	<0.00005
Dissolved Boron (B)	mg/L	0.162
Dissolved Cadmium (Cd)	mg/L	<0.00001
Dissolved Calcium (Ca)	mg/L	56.6
Dissolved Chromium (Cr)	mg/L	<0.0002
Dissolved Cobalt (Co)	mg/L	0.00004
Dissolved Copper (Cu)	mg/L	0.0037
Dissolved Iron (Fe)	mg/L	<0.005
Dissolved Lead (Pb)	mg/L	0.00004
Dissolved Lithium (Li)	mg/L	0.0090
Dissolved Magnesium (Mg)	mg/L	39.6
Dissolved Manganese (Mn)	mg/L	0.00059
Dissolved Mercury (Hg)	mg/L	<0.00005
Dissolved Molybdenum (Mo)	mg/L	0.00049
Dissolved Nickel (Ni)	mg/L	0.0807
Dissolved Phosphorus (P)	mg/L	<0.1
Dissolved Potassium (K)	mg/L	4.310
Dissolved Selenium (Se)	mg/L	0.0006
Dissolved Silicon (Si)	mg/L	0.84
Dissolved Silver (Ag)	mg/L	0.00001
Dissolved Sodium (Na)	mg/L	20.0
Dissolved Strontium (Sr)	mg/L	0.164
Dissolved Sulphur (S)	mg/L	n/a
Dissolved Thallium (Tl)	mg/L	<0.00005
Dissolved Tin (Sn)	mg/L	0.00046
Dissolved Titanium (Ti)	mg/L	<0.0005
Dissolved Uranium (U)	mg/L	0.00037
Dissolved Vanadium (V)	mg/L	0.00026
Dissolved Zinc (Zn)	mg/L	<0.0005
Dissolved Zirconium (Zr)	mg/L	<0.005

Total Metals	Units	Maskwa Pit (1m)
Total Aluminum (Al)	mg/L	0.0236
Total Antimony (Sb)	mg/L	0.00012
Total Arsenic (As)	mg/L	0.0010
Total Barium (Ba)	mg/L	0.0382
Total Beryllium (Be)	mg/L	<0.00005
Total Bismuth (Bi)	mg/L	<0.00005
Total Boron (B)	mg/L	0.164
Total Cadmium (Cd)	mg/L	0.00001
Total Calcium (Ca)	mg/L	57.0
Total Chromium (Cr)	mg/L	0.0007
Total Cobalt (Co)	mg/L	0.00017
Total Copper (Cu)	mg/L	0.0040
Total Iron (Fe)	mg/L	0.040
Total Lead (Pb)	mg/L	0.00011
Total Lithium (Li)	mg/L	0.0094
Total Magnesium (Mg)	mg/L	39.5
Total Manganese (Mn)	mg/L	0.00468
Total Mercury (Hg)	mg/L	<0.00005
Total Molybdenum (Mo)	mg/L	0.00055
Total Nickel (Ni)	mg/L	0.0909
Total Phosphorus (P)	mg/L	<0.1
Total Potassium (K)	mg/L	4.840
Total Selenium (Se)	mg/L	<0.0005
Total Silicon (Si)	mg/L	0.84
Total Silver (Ag)	mg/L	0.00001
Total Sodium (Na)	mg/L	19.3
Total Strontium (Sr)	mg/L	0.174
Total Sulphur (S)		n/a
Total Thallium (Tl)	mg/L	<0.00005
Total Tin (Sn)	mg/L	0.00048
Total Titanium (Ti)	mg/L	0.0010
Total Uranium (U)	mg/L	0.00039
Total Vanadium (V)	mg/L	0.00039
Total Zinc (Zn)	mg/L	0.0013
Total Zirconium (Zr)	mg/L	<0.005