

AGE DETERMINATION OF ACCESSORY  
ZIRCON FROM GRANITIC ROCKS OF  
THE KENORA AREA, ONTARIO

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ABSTRACT

A method of recovering accessory zircon from large granite samples is described. The major equipment includes a disc-pulverizer, Haultain Superpanner, and Franz isodynamic separator.

The zircon ages were determined by the lead:alpha method. A description of scintillation alpha counting of zircon samples is given along with a brief outline of the method of colorimetric trace lead analysis. Results are given for an X-ray:alpha method of age determination of zircon which proved unsuccessful.

The lead:alpha ages of three accessory zircons were found to be 771 million years, 869 million years, and 1707 million years, indicating at least two widely separated periods of granite intrusion in the area.

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## INTRODUCTION

Age determination of radioactive minerals has achieved a position of some respect and promises to provide solutions to many geological problems, particularly problems of the Precambrian.

The lead:alpha method has been used with success to date zircon. The purpose of the present work was to improve methods of recovering accessory zircon from granitic rocks and to determine the lead:alpha ages of the zircons collected.

A Haultain Superpanner was used to concentrate the heavy accessory minerals. Following this, a Franz isodynamic separator, heavy liquids, and acid treatment were used to recover the zircon.

A scintillation counter was used to determine the alpha activity of the zircon samples. Lead analyses were done by a chemical colorimetric method. Ages were also determined by an X-ray:alpha method to find how they compared to the lead:alpha ages.

### Acknowledgements

Assistance and advice on various aspects of the work given by Dr. H.D.B. Wilson, Dr. G.M. Brownell, and Dr. R.B. Ferguson of the Geology department, are gratefully acknowledged. Dr. K.I. Roulston was helpful in correcting electronic difficulties. The Assay Laboratory of the Manitoba Mines Branch kindly permitted the use of their grinding equipment.

## DATING IGNEOUS ROCKS FROM THEIR ACCESSORY MINERALS

According to Larsen and Phair (1954) the minerals of moderate to high radioactivity in order of decreasing abundance in igneous rocks are: zircon, allanite, monazite, xenotime, thorite, pyrochlore, and uraninite. Zircon, sphene, and apatite have been used by Larsen, Keevil, and Harrison, (1952) to date granitic rocks with the lead:alpha method. Zircon gave the most consistently good results. Sphene and apatite gave erratic values with sphene ages tending to be very high, probably due to primary lead content. Apatite has very low radioactivity.

Zircon averages less than 100 ppm. in most igneous rocks but occasionally it is much more abundant. It is more common in granites than in basic rocks and also contains proportionately more radioactive elements. The average zircon contains about equal amounts by weight of uranium and thorium, but in some specimens either uranium or thorium is abnormally high.

The lead method is one of the earliest to be applied to age determination of minerals. It is based on the natural disintegration of  $U^{238}$ ,  $U^{235}$ , and  $Th^{232}$ , into the stable lead isotopes  $Pb^{206}$ ,  $Pb^{207}$ , and  $Pb^{208}$ . If nothing has been added or removed from a system in equilibrium and the amount of parent and daughter elements is known together with the rate of decay of the parent, the age of the system can be calculated.

Innumerable age determinations have been made with the

lead method but many of them have been shown to be valueless due to selective leaching by ground waters or primary lead content in the mineral. Zircon is highly resistant to chemical change unless badly metamict. Measurements on young, inactive zircons have indicated that primary lead is negligible. Abnormally high ages have not been obtained from zircon, which is further evidence of low primary lead content. Apparently the closely-packed zircon structure prohibits the entrance of lead ions during crystallization. Thus the basic requirements of the method seem to be satisfied by the properties of zircon.

The lead:alpha method used by Larsen et al (1952) is a variation of the lead method. It is rapid and relatively simple, requiring only an alpha count and a lead analysis on the zircon. The age is given by:

$$t = \frac{c \text{ Pb}}{\alpha}$$

where  $t$  = age in millions of years  
 $c$  = a constant varying from  
 2660 (U only) to 1990(Th only)  
 $\text{Pb}$  = lead content in ppm.  
 $\alpha$  = alpha activity in  
 alphas / mg. / hr.

Most zircons have been found to have their radioactivity due largely to uranium. Larsen gives  $c = 2480$  as an average value for zircon. Even a large error in the assumed Th/U ratio however, results in a relatively small error in the calculated age.

## RECOVERY OF ACCESSORY ZIRCON

One of the major problems of dating rocks from their accessory mineral content is that of recovering a sufficient quantity of material with which to work. The task is laborious because comparatively large rock samples are required. The method outlined below was designed to speed recovery of heavy accessory minerals and differs somewhat from standard procedures.

The samples described were all from the Kenora area of northwestern Ontario (fig. 1). They consisted of granites and granodiorites ranging in size from 20 to 50 lbs. nominal weight.

### Crushing and Grinding

A laboratory jaw crusher was used to reduce the sample to about 1/4 inch maximum diameter. The sample was then passed through a disc-grinder (Braun Pulverizer) set to reduce the material to 100 percent minus 65 mesh. One pass through the disc-grinder was sufficient. Further reduction resulted in too much fine material ie. minus 325 mesh, which was difficult to work with in the final stages of separation.

Generally, material coarser than plus 150 mesh contains little free zircon and grinding would be more effective with a 150 mesh screen in closed circuit with the pulverizer, the coarse material being returned for further grinding.

### Heavy Mineral Concentration

Heavy liquids and to some extent flotation are usually



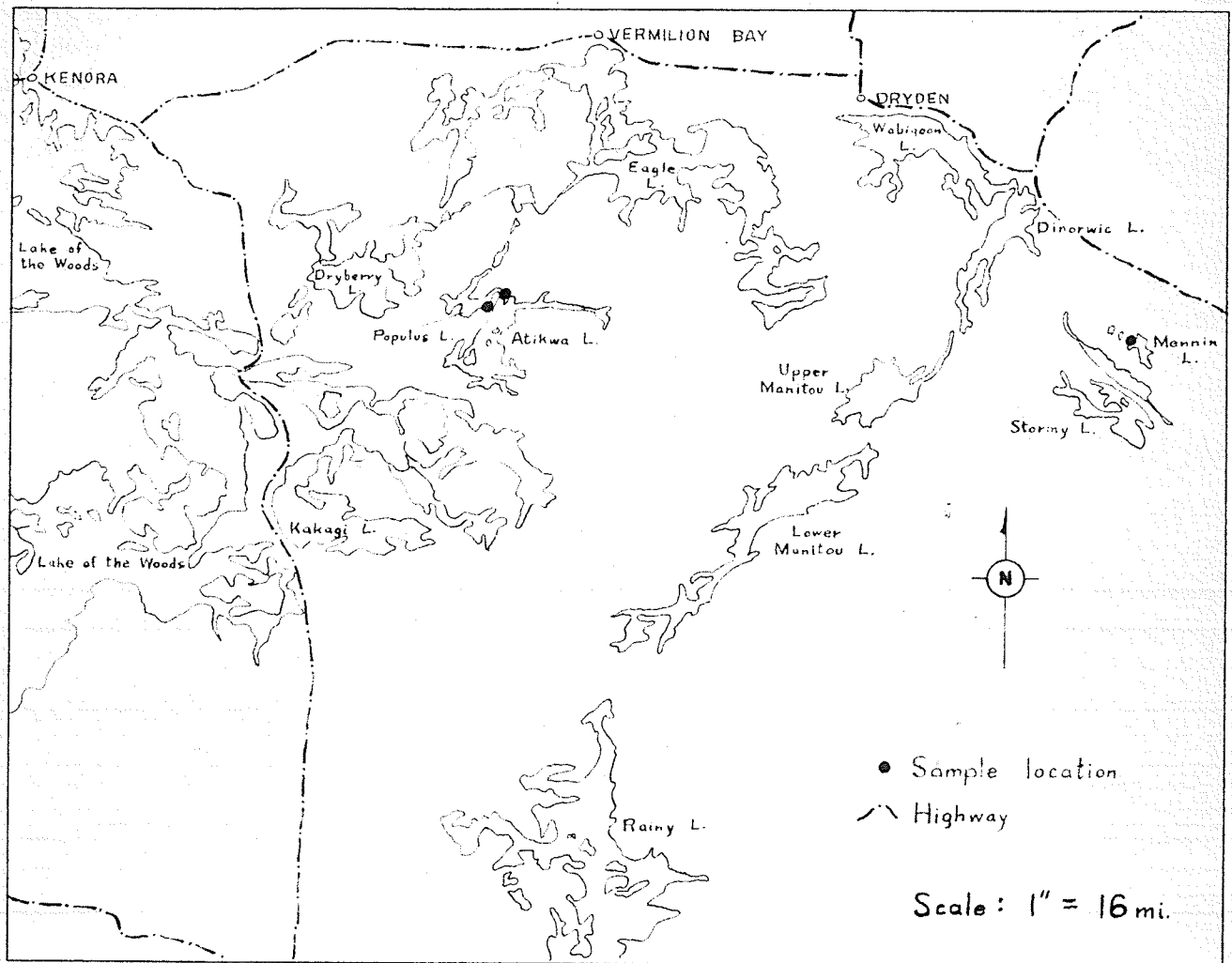


Fig. 1

Map showing sample locations in northwestern Ontario.

used to separate the large bulk of waste material from the relatively minor amount of heavy constituents. However, the use of heavy liquids in quantity is slow, expensive, and not particularly efficient. The method used largely eliminates heavy liquid separations.

The Haultain Superpanner was developed by Prof. H.E.T. Haultain of the University of Toronto for laboratory research on gold ores. This device provides a rapid means of recovering the heavy mineral fraction from large rock samples. With a little practice more than 99 percent of the original sample can be discarded in one operation.

The ground sample was screened through a nest of Tyler standard sieves to obtain +100, +150, +200, and -200 mesh fractions. These screen fractions are kept separate through the entire concentrating procedure. Each screen fraction was panned separately starting with +200 mesh which was found to be the coarsest size that may be expected to contain a significant amount of zircon. If zircon is abundant in this fraction the +150 mesh material is panned next. The coarser the zircons recovered the better, because in the final stages a certain amount of hand picking is usually necessary. If examination of the +200 fraction shows a scarcity of zircon the -200 mesh size must be panned.

It was usually convenient to take two separate fractions from the Superpanner "tip" concentrate: one "high grade"

fraction (No.1 concentrate) at the extreme tip, and a second (No.2 concentrate) immediately behind this. Depending on the heavy mineral constituents of the individual rock, zircon is more abundant in one or other of the concentrates. For example, usually the zircon is abundant in the No.1 concentrate but if the granite is high in sulphides this concentrate will be largely sulphides.

Magnetite was readily removed during the panning operation. A strong permanent magnet covered with a sheet of paper was passed over the tip just before removing the concentrates. If magnetite is not removed here it causes trouble when the concentrates are dried, coating the grains with rusty oxide and sticking them together. Magnetite will also clog the Franz isodynamic separator if it is too abundant.

#### Magnetic Separation

After drying, the concentrates were passed through a Franz separator. With the inclined feed attachment the separator was set with a forward tilt of  $30^{\circ}$ , a side tilt of  $7^{\circ}$ , and a current of 0.2 amps. in the electromagnet. The sample was run through twice at this setting and the procedure repeated, increasing the current in 0.2 amp. increments up to 1.0 amp. A large part of the magnetic minerals including most of the sphene was removed at this point and the current was then raised to 1.8 amps. (full current). Side tilt was reduced to  $5^{\circ}$  and then to  $3^{\circ}$ . All magnetic fractions had to be examined under the microscope. At  $3^{\circ}$  the zircon usually began to appear

in quantity in the magnetic fraction. Zircon apparently becomes more magnetic with increasing uranium content (Webber, Hurley, and Fairairn, 1956).

#### Heavy Liquids

The No.2 concentrates were put through a bromoform separation to eliminate light minerals which usually contaminate this fraction. The "sink" was examined carefully and if zircon was present the fraction was added to the corresponding No.1 concentrate. If the "sink" did not contain zircon it was discarded.

Clerici solution was used for the final separation. The specific gravity of zircon ranges from 3.9 to 5.0, due partly to composition but mainly to the degree of metamictness (Holland and Gottfried, 1955). The sink consisted mainly of zircon and sulphides; apatite floated. The -200 mesh concentrate was screened through a 325 mesh sieve and only the +325 fraction separated with Clerici solution.

The zircon-sulphide concentrates were treated with a hot, strong solution of nitric acid. This dissolved the sulphides. The few impurities left were hand-picked under the microscope. The acid treatment also served to remove surface lead contamination. Pyrite becomes magnetic after heating for a few minutes above 450°C and may be removed with a hand magnet. This method was not used however, because the zircon was to be X-rayed and there was the possibility of thermal annealing

of the zircon structure. It is important that the zircon concentrate be as pure as possible. Larsen notes that pyrite may contain as much as 100 ppm. of lead.

Separation of grains finer than +325 mesh by settling in Clerici solution is not practical. The viscosity of the solution makes the process extremely slow and the resulting separations are poor. Zircon is often abundant in this fine material and would be well worth recovering. Acid treatment appears to be the most feasible method. However, hot, strong acids must be used for considerable periods and the effect on zircon is not known. A sample of Ceylon gem zircon treated with 1:1 aqua regia at 80°C for 1/2 hour showed a negligible change in determined age (Gottfried, Senftle, and Waring, 1956). Probably only badly metamict zircon would be much affected.

#### Zircon Concentrates

Table 1 describes briefly the rocks from which the zircon came and the amount of zircon recovered from each.

The final concentrates were largely whole zircon crystals. It appears that the crystals were small enough so that even the violent grinding action of the pulverizer merely "popped" them free from enclosing mineral grains.

Most zircons collected were brown to reddish brown. Birefringence was considerably lower than normal probably because of their metamict condition which was substantiated by X-ray photographs. Zoning was noted in crystals from each sample

and was not characteristic of any one sample.

Table 1

Sample Description and Amount of Zircon Recovered

<u>Locality and Description</u>	<u>Wt. of Sample</u>	<u>Wt. of Zircon</u>
Mennin Lake, Ont.- medium grained biotite granite. Slightly altered texture.	50 lb.	650 mg.
Tail Bay, Atikwa Lake, Ont. - coarse grained biotite granite. Fresh texture.	48 lb.	trace
Populus Lake, Ont.- coarse grained biotite granite. Fresh texture.	35 lb.	90 mg.
*Dryberry Lake, Ont.(older) - fine to medium grained gneissic biotite granodiorite. Altered texture.	20 lb.	65 mg.
*Dryberry Lake, Ont.(younger) - coarse, pink, pegmatitic granite. Fresh texture.	20 lb.	trace
*Supplied by Mr. S.N. Watowich, Falconbridge Nickel Mines Ltd., Kenora, Ontario.		

The Dryberry Lake granodiorite yielded two distinct varieties of zircon, one brown and cloudy, the other clear and colorless. They were about equally abundant but separation was not attempted due to limited time and the small amount of material available.

Thin sections from several of the rock samples were examined. A single thin section is not a reliable indicator of the amount of zircon occurring in a rock. Brief descriptions of the thin sections are given below.

Mennin Lake, Ont. - Biotite granite

Orthoclase, the predominant feldspar, has strongly sericitized and kaolinized cores with fresher rims. A small amount of plagioclase and fresh-looking microcline are present. Quartz is fractured

and shows wavy extinction. Grain boundaries of feldspars and quartz are not sharp. A few small patches of ragged biotite, muscovite, and finely recrystallized quartz and feldspar occur. Accessory minerals include apatite, epidote, clinozoisite, sphene, and magnetite. Pleochroic haloes are common in biotite and most are caused by sphene. Only one zircon crystal was identified.

Tail Bay, Atikwa Lake, Ont. - Biotite granite

Orthoclase has kaolinized cores with fresh rims. Plagioclase is altered similarly but is less abundant. Microcline is fresh. Quartz is abundant in large clear grains commonly showing wavy extinction. Accessory minerals include biotite, muscovite, epidote, sphene, apatite, magnetite, and hematite. Pleochroic haloes occur in biotite but the mineral causing them was not identified. Zircon was not seen.

Populus Lake, Ont. - Biotite granite

Orthoclase and plagioclase are strongly sericitized and kaolinized. Quartz is abundant, occurring in large grains and granular masses. Accessory minerals include biotite, muscovite, epidote, magnetite, and hematite. Three tiny zircon crystals enclosed by biotite were noted.

## RADIOACTIVITY MEASUREMENTS

The alpha activity of the zircon samples was measured with a scintillation counter. The method was similar to that proposed by Kulp, Holland, and Volchok (1952) for a thin source.

The electronic equipment has been described by Turnock (1956). The method of mounting the sample is shown in fig.2. The sample tray was a sheet of plastic with a circle inscribed on it about one inch larger in diameter than the sensitive face of the photomultiplier tube. The inscribed area was smeared with a very light film of silicone fluid, the sample tray weighed, and the finely ground sample (-325 mesh) spread on with the aid of a camels hair brush. Excess material was shaken off, the little powder which had fallen outside the inscribed circle was trimmed, and the sample plus tray was weighed. Samples ground in preparation for counting were allowed to stand for at least a week before the alpha count was taken to allow the sample to approach equilibrium with respect to radon and thoron.

A remarkably even distribution of grains can be obtained with concentrations as low as  $0.3 \text{ mg./cm}^2$ . The work of Kulp et al (1952) shows that for samples well down in the thin source range ( $<1.0 \text{ mg./cm}^2$ ), the counting rate is proportional to sample thickness ie. essentially all alpha particles are able to escape from within the source.

Ag activated ZnS was used as a scintillator. The face of the photomultiplier tube was smeared with a light film of sil-