

A STUDY OF THE DISTRIBUTION OF TRACES OF COPPER, LEAD, AND ZINC IN THE MINERALS OF A PRECAMBRIAN GRANITE¹

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ABSTRACT

A specimen of Precambrian granite from the Grenville subprovince of Eastern Ontario, Canada, was found to contain 4.(5) p.p.m. copper, 12 p.p.m. lead, and 29 p.p.m. zinc. The ferromagnesian minerals and magnetite show a higher concentration of copper and zinc than quartz and feldspar. Feldspar, the ferromagnesian minerals, and magnetite show a higher concentration of lead than quartz.

A minor amount of copper and about 40 per cent of the zinc were found in an easily leachable form.

The metals were determined colorimetrically using the mixed-colour dithizone method. Analyses of standard granite G-1, using the same method, resulted in values within the range of published results.

INTRODUCTION

Studies on the nature of the distribution of traces of metals in the minerals of igneous rocks, contribute to a better understanding of the behaviour of these metals during the different geologic processes that result in their mobilization and their possible concentration. The present work is a study of the nature of the distribution of traces of copper, lead, and zinc in the minerals of a granite.

There are two general modes of occurrence of traces of copper, lead, and zinc in igneous rocks. One mode is by being combined in the major minerals of the rock. This combination can take place by atomic substitution or by interstitial solid solution. The other mode is when these elements are present as separate minerals of submicroscopic size, i.e., sulphides, native metals, and oxides.

Goldschmidt (1937) proposed a series of empirical rules as a general guide for the mutual replacement of ions in magmatic minerals. Goldschmidt's rules are based on a consideration of ionic size and charge.

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These rules have been restated by Mason (1958, p. 129) as follows: (1) If two ions have the same radius and the same charge, they will enter a given crystal structure with equal facility. (2) If two ions have different radii and the same charge, the smaller ion will enter a given crystal structure more readily. (3) If two ions have similar radii and different charge, the ion with the higher charge will enter a given crystal structure more readily. These rules have been found not to be universally valid because of the fact that the bonding in most minerals is not exclusively ionic (Shaw, 1953, and Ringwood, 1955).

Several studies have been carried out on the nature of the distribution of traces of these three metals in igneous rocks.

Copper

Newhouse (1936) and Ramdohr (1940) observed that copper occurs, chiefly, as sulphides in igneous rocks. Sandell & Goldich (1943, p. 102) found that the copper in samples from the Greenstone and Kearsage flows, Michigan, is not combined in the silicates but rather is chiefly in the form of sulphides. Wager & Mitchell (1951) have shown that in some of the Skaergaard basic rocks the copper is present in the silicate minerals, and in others it is mainly present as sulphides. Cornwall & Rose (1957) found that disseminated copper sulphides and native copper were common in the Greenstone and other flows, Michigan. Cornwall & Rose also found that copper is most abundant in the minerals that contain ferrous iron.

Lead

Tilton *et al.* (1955) found that 40 per cent of the lead of a pulverized Precambrian granite can be removed by stirring with 6N hydrochloric acid. Tauson & Kravchenko (1956) found that 30–50 per cent of the lead of granites, granodiorites, and tonalites can be removed by leaching in boiling dilute hydrochloric acid. However, Tauson & Kravchenko found that only 12–18 per cent of the lead of K-feldspars, separated from granites, can be removed by this leaching method.

Zinc

Tauson & Kravchenko (1956) found that 67–94 per cent of the zinc of granites and granodiorites can be removed by leaching in boiling dilute hydrochloric acid. They also found that 70–80 per cent of the zinc of biotite samples separated from granites can be removed by the same leaching method.

The general conclusion of the workers cited above regarding the nature of the distribution of traces of copper, lead, and zinc in igneous

rocks and minerals could be summarized as follows: traces of these metals occur in combination in the silicate minerals and as separate minerals, such as sulphides.

In connection with the gross composition of the leaching products, Brown & Silver (1956) reported that pulverized igneous rocks ranging from tonalites to granites and of diverse ages and geographic origins responded rather uniformly to a 50-minute dilute (1N) nitric acid leaching. 0.1–0.6 per cent of the rock by weight was found to be soluble.

The present investigation was undertaken in order to find the concentration of traces of copper, lead, and zinc in the minerals of a specimen of a Precambrian granite, and to study the nature of the combination of these metals in the rock.

The study was carried out on the Deloro granite whose structural geology and petrology were studied in detail by Saha (1957). This investigator concluded that this pluton resulted from the crystallization of a magma. The present study deals with only the major minerals of the Deloro granite. These minerals, which make up 99.5 per cent of the rock, are quartz, feldspar, biotite, chlorite, and magnetite.

The Deloro pluton is one of several granitic bodies of the Precambrian Grenville subprovince of eastern Ontario, Canada. This pluton consists, mainly, of a north striking body of perthite granite with a syenite rim along the western margin and an adjoining smaller body of granophyric granite to the east. It has an area of 20 square miles and is located near the southern border of the Canadian Shield in Marmora and Madoc Townships, Hastings County, Ontario. The 50 lb. specimen that was used for the present study was obtained from a quarry in the middle of the southern part of the perthite granite body along Highway 7.

The perthite granite was described by Saha (1957) as consisting essentially of perthite and quartz together with some albite, an alkali amphibole, biotite, magnetite, and various accessory minerals including calcite, zircon, sphene, and pyrite. The perthite grains, usually subhedral, are coarse intergrowths of microcline and albite in about equal proportions. Amphibole is commonly altered to biotite and chlorite. In the specimen under study the amphibole has been completely altered to biotite and chlorite. Magnetite and sphene are usually associated with the patches of biotite and chlorite. Quartz usually occurs as coarse anhedral grains.

Chemical methods essentially as described by Sandell (1937, and 1950) were used for determining the metals. The samples were completely decomposed in strong acids and the metals were extracted and determined with dithizone using the mixed-colour method.

REAGENTS AND APPARATUS

Laboratory distilled water, carbon tetrachloride, hydrochloric acid, and nitric acid were distilled in an all-glass (Pyrex) still. C.P. sulphuric acid and perchloric acid were used without further purification.

Acetate Buffer. Sodium acetate was mixed with doubly distilled water and the reacting metals were removed by shaking with a dithizone solution.

Ammonia Solution. Ammonia gas was bubbled through doubly distilled water.

Dithizone. Dithizone was purified according to the procedure of Sandell (1950, p. 107). Dithizone solutions were made by dissolving dithizone in distilled carbon tetrachloride.

Hydrofluoric acid. Hydrofluoric acid was purified with strontium chloride according to the procedure of Rosenqvist (1942).

Potassium Cyanide Solution. Potassium cyanide was dissolved in doubly distilled water and the solution was tested with dithizone for freedom from metals.

Potassium Iodide Solution. Potassium iodide was dissolved in doubly distilled water and the solution was shaken with dithizone solution to remove reacting metals.

Sodium Citrate Solution. Sodium citrate was dissolved in doubly distilled water and the solution was shaken with dithizone to remove reacting metals.

Sodium Thiosulphate Solution. Sodium thiosulphate was dissolved in doubly distilled water.

Standard Copper Solutions. Copper solutions were prepared by dissolving Specpure copper in nitric acid.

Standard Lead Solutions. Lead solutions were prepared by dissolving lead nitrate in nitric acid.

Standard Zinc Solutions. Zinc solutions were prepared by dissolving 30 mesh reagent grade zinc in hydrochloric acid.

Sieves. Sieves with stainless steel screens were used.

Glassware. Pyrex glassware was used throughout for handling solutions of rocks and minerals as well as for handling leaching solutions. The glassware was treated after each use with dichromate-sulphuric acid cleaning solution and thoroughly rinsed with tap water. This was followed by rinsings with 1 to 99 nitric acid followed by rinsings with doubly distilled water. Finally the glassware was dried in air. Dithizone extractions were carried out in Squibb type and globe shaped separatory funnels.

Cotton. Cotton was prepared according to the method of Maynes & McBryde (1957).

Colorimeter. A Bausch and Lomb Spectronic 20 colorimeter was used to measure the per cent transmittancy of the dithiozone solutions. The colorimeter cells consisted of specially selected $\frac{1}{2}$ -inch test tubes fitted with ground glass stoppers to minimize evaporation losses of carbon tetrachloride. Measurements were made at wavelengths that are the minimum transmittancies of the dithizonates of copper, lead, and zinc. These wavelengths were checked by means of the diffraction grating monochromator.

EXPERIMENTAL WORK

Sample Preparation

The specimen of Deloro granite was broken by means of a vise to smaller pieces weighing 100–150 grams. The smaller pieces were heated

to 585° C. and quenched in doubly distilled water in order to partially break down the rock into its constituent minerals. The heat-treated samples were next ground in a Coors alumina mortar.

The ground samples were sieved through stainless steel screens into fractions with the same size range. Four mineral-rich concentrates were prepared from these fractions: (1) a quartz-rich, (2) a feldspar-rich, (3) a biotite-chlorite-rich, and (4) a magnetite-rich concentrate. To prepare the quartz-, feldspar-, and biotite-chlorite-rich concentrates, the fractions were first freed from magnetite by means of an Alnico horseshoe magnet and then were concentrated with the different minerals by means of a Frantz isodynamic magnetic separator. The magnetite-rich concentrate was prepared from another fraction by means of the horseshoe magnet. Next each concentrate was freed from the accessory minerals by a heavy liquid separation using tetrabromethane.

The mineral content, expressed in volume per cent, of the different mineral-rich concentrates was determined by counting the number of grains, of the same size range, under the binocular and petrographic microscopes. The mineral content, converted to weight per cent, of these concentrates is shown in Table 1.

Mineral-rich concentrates were used for metal analysis rather than hand-picked "pure" mineral samples in order to: (1) prepare larger more representative samples with minimum time and handling, since minimum handling lowers the chances of contamination, and (2) have the metal content of the samples in a closely related order of magnitude, so that essentially the same procedure could be used for all determinations.

Metal Analysis of Granite and Minerals

Approximately 0.25 gram of rock or mineral concentrate powder was decomposed with perchloric acid, hydrofluoric acid, and sodium carbonate. The resulting solutions were extracted with an 0.01 per cent

TABLE 1. MINERAL CONTENT OF MINERAL-RICH CONCENTRATES

Concentrate	Per cent by weight			
	Quartz	Feldspar	Biotite-Chlorite	Magnetite
Quartz-rich	66.1	33.0	0.9	0.0
Feldspar-rich	19.5	79.8	0.7	0.0
Biotite-Chlorite-rich	15.5	49.0	35.5	0.0
Magnetite-rich	1.1	3.4	2.0	93.5

carbon tetrachloride solution of dithizone in a slightly basic medium in the presence of citrate. Copper, lead, and zinc form dithizonates which are soluble in the carbon tetrachloride while the major constituents of the sample remain in the aqueous phase. The carbon tetrachloride layer was separated and was shaken with 0.02 N hydrochloric acid to transfer lead and zinc to the aqueous phase leaving copper in the carbon tetrachloride.

Known amounts of copper, lead, and zinc were mixed together in a solution and were subsequently determined by using the procedure adopted in the present work for the extraction, separation, and determination of these metals. The results are shown in Table 2.

The carbon tetrachloride containing the copper was next shaken with a potassium iodide solution in 0.01 N hydrochloric acid to remove any bismuth or silver that may have been present with the copper. The carbon

TABLE 2. DETERMINATION OF KNOWN AMOUNTS OF COPPER, LEAD, AND ZINC

Taken (microgram)	Found (microgram)		Error (per cent)
	Found	Corrected for blank	
COPPER			
0.0	0.3		
5.0	4.7	4.4	-12
5.0	6.4	6.1	+22
LEAD			
0.0	0.0		
5.0	4.8	4.8	-4
ZINC			
0.0	0.4		
5.0	6.4	6.0	+20
5.0	4.7	4.3	-14

tetrachloride containing the copper was next evaporated and the residue was heated with a mixture of sulphuric and perchloric acids to destroy the cupric dithizonate and the excess dithizone. The resulting copper was determined in 0.01 sulphuric acid by shaking with 0.001 per cent dithizone in carbon tetrachloride and measuring the per cent transmittancy of the copper dithizonate-dithizone solution at 545 millimicrons. When the copper dithizonate-dithizone solution was not clear, it was filtered through cotton before the transmittancy measurement was made. A blank was run at the same time as the sample in order to correct for the copper contributed by the reagents. The amount of copper present

in the sample was now determined, with reference to a standard curve, and was expressed in parts per million (p.p.m.).

An aliquot of the aqueous phase (0.02 N hydrochloric acid) containing lead and zinc was shaken with 0.001 per cent dithizone, in the presence of citrate and cyanide, for the determination of lead. The pH was 9–10. The cyanide prevents the reaction of interfering metals. The transmittancy of the lead dithizonate-dithizone solution was measured at 525 millimicrons. A blank was run at the same time as the sample in order to apply a correction for the lead contributed by the reagents. The amount of lead was now determined, with reference to a standard curve, and was expressed in parts per million.

Another aliquot of the aqueous phase (0.02 N hydrochloric acid) containing lead and zinc was shaken with 0.001 per cent dithizone, in the presence of thiosulphate, for the determination of zinc. The pH was 4–5.5. The thiosulphate prevents the reaction of interfering metals. The transmittancy of the zinc dithizonate-dithizone solution was measured at 535 millimicrons. A blank was run at the same time as the sample in order to apply a correction for the zinc contributed by the reagents. The amount of zinc was now determined, with reference to a standard curve, and was expressed in parts per million.

The results of the determination of copper, lead, and zinc in the granite specimen are shown in Table 3.

TABLE 3. COPPER, LEAD, AND ZINC CONTENTS OF GRANITE

Metal	p.p.m.			Arithmetic Mean (p.p.m.)
	1	2	3	
Copper	4	5		4. (5)
Lead	15	9		12
Zinc	27	30	29	29

The three metals were also determined in the mineral-rich concentrates. Two determinations were made for each metal in each concentrate and the arithmetic mean of the two determinations was obtained. The per cent deviation of the duplicate analyses ranged from 0 to 29. Using this mean value of the duplicate analyses and the mineral content of the mineral-rich concentrates (Table 1), the metal content of the quartz, feldspar, biotite-chlorite, and magnetite was calculated. The results are shown in Table 4. The weight per cent of the different minerals in the granite, neglecting the accessory minerals, was determined by modal

analysis followed by a specific gravity correction. These results are also shown in Table 4.

TABLE 4. COPPER, LEAD, AND ZINC CONTENTS OF MINERALS OF GRANITE

Mineral	Per cent mineral in granite by weight	Metal content of mineral (p.p.m.)	Amount of metal in mineral in 1 gram of granite (microgram)	Metal content of bulk granite, from Table 3 (p.p.m.)
COPPER				
Quartz	26.4	2	0.5	
Feldspar	67.3	7	4.7	
Biotite-Chlorite	4.2	13	0.5	
Magnetite	2.0	14	0.3	
			6.0	4. (5)
LEAD				
Quartz	26.4	0	0.0	
Feldspar	67.3	18	12.1	
Biotite-Chlorite	4.2	23	1.0	
Magnetite	2.0	27	0.5	
			13.6	12
ZINC				
Quartz	26.4	4	1.1	
Feldspar	67.3	15	10.1	
Biotite-Chlorite	4.2	294	12.3	
Magnetite	2.0	137	2.7	
			26.2	29

Leaching of Ground Granite

The ground Deloro granite was subjected to leaching by a dilute acid as a step in studying the nature of the distribution of the traces of copper, lead, and zinc in the rock. It is known that dilute acids used for leaching ground granites hardly affect the silicate minerals but dissolve minor amounts of alteration minerals, certain accessory minerals, and some submicroscopic material dispersed along fractures and grain boundaries (Brown *et al.* 1953*a* and *b*, and Tauson & Kravchenko, 1956).

After a preliminary test to explore the leachability of the metals, 19 grams of -42 mesh granite, having a grain size distribution as shown in Table 5 were leached with 0.5 N nitric acid at room temperature. Samples of the leaching solution were withdrawn and analysed for their metal content at given times after the beginning of leaching. The first sample was withdrawn 1.3 minutes after the beginning of the leaching

TABLE 5. GRAIN SIZE DISTRIBUTION OF GROUND GRANITE USED IN LEACHING TESTS

Grain size (mesh)	Weight per cent
-42 + 100	59.2
-100 + 150	13.8
-150 + 200	7.5
-200	19.6
	100.1

and the following samples were withdrawn at approximately 13-hour intervals after the withdrawal of the first sample. A correction was applied due to the metals present in a blank. Citrate was added to the leaching solutions and copper, lead, and zinc were determined as in the case of acid solutions resulting from the decomposition of rock samples as is outlined above.

The results are shown in Figs. 1 and 2. The portion of metal leached, shown in these figures and expressed in per cent of total metal leached and in parts per million, is in relation to the arithmetic mean of the total metal content of the rock (Table 3).

In order to obtain a measure of the consistency of the leaching method, the residue that remained after the completion of the leaching experiment was analysed. The results are shown in Table 6. The results for lead are inconclusive as the determination of this metal in the leaching samples was not successful. However, the analysis of the residue showed a loss of about 65 per cent of the lead as a result of the leaching.

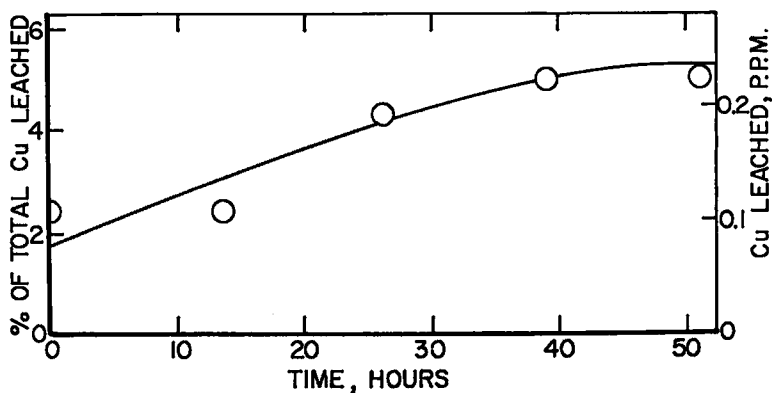


FIG. 1. Leaching of copper from ground granite in 0.5N nitric acid at room temperature.

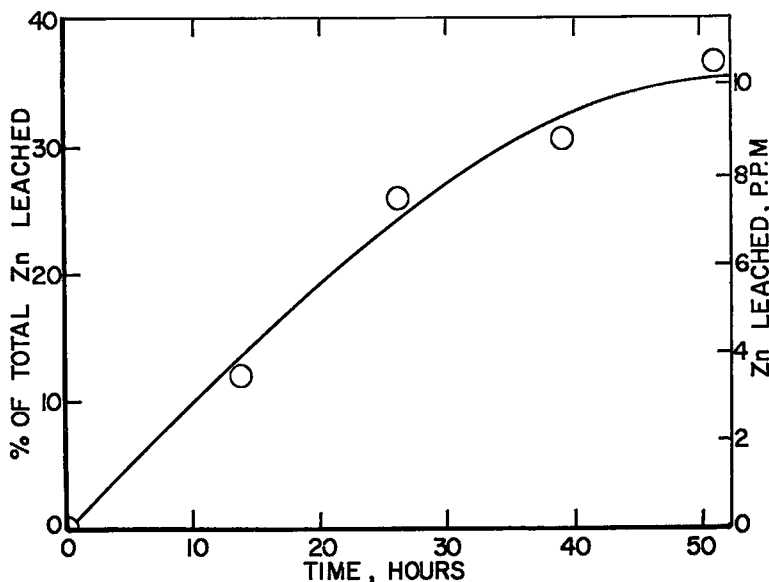


FIG. 2. Leaching of zinc from ground granite in 0.5N nitric acid at room temperature.

TABLE 6. COPPER, LEAD, AND ZINC CONTENTS OF LEACHING RESIDUE

	Copper	Lead	Zinc
(Metal in residue/metal in rock before leaching) $\times 100$	111	36	49
(Metal leached in 51.15 hours/metal in rock before leaching) $\times 100$	5	—	37
Total	116	—	86

Reproducibilities and Analysis of Granite G-1

Besides the duplicate and triplicate analyses carried out in this laboratory for the purpose of obtaining a measure of the reproducibilities of the determinations, a sample analysed chemically in this laboratory was analysed spectrographically in another laboratory. The result of a single analysis of the leaching residue for lead was 4 p.p.m. On the other hand the results of duplicate spectrographic analyses of the same residue obtained in the Department of Mineral Sciences of the Pennsylvania State University were 5.2 and 4.6 p.p.m.

Fairbairn (1951) discussed the use of two rocks as standards for the determination of major and minor constituents of igneous rocks. One of

these two rocks is granite G-1 from Westerly, Rhode Island. A sample of this granite, obtained through the courtesy of the Ontario Department of Mines, was analysed in this laboratory for copper, lead, and zinc in order to compare the results with those of other workers. This granite was analysed by using the same method as that used in analysing the granite and mineral samples of the Deloro specimen. The results are shown and compared with the results of other workers in Table 7.

TABLE 7. COPPER, LEAD, AND ZINC CONTENTS OF GRANITE G-1

	Copper (p.p.m.)	Lead (p.p.m.)	Zinc (p.p.m.)
Range previously reported (Ahrens & Fleischer, 1960; Carmichael & McDonald, 1961; Hamaguchi <i>et al.</i> , 1961)	5-25	14-56	26-55
Recommended value by Ahrens & Fleischer (1960)	13	50	40
This laboratory	13, 10	31, 35	52, 53

DISCUSSION OF RESULTS

In the granite specimen investigated, the copper content, 4.(5) p.p.m., is lower than the average, 16 p.p.m., found by Sandell & Goldich (1943) in silicic rocks. The lead content, 12 p.p.m., is also lower than the average for granites, 20 p.p.m., given by Wedepohl (1956). Finally the zinc content, 29 p.p.m., is also lower than the average, 45 p.p.m., for granites, granodiorites, quartz monzonites, and quartz diorites given by Wedepohl (1953).

The granite specimen contained rounded acid-intermediate volcanic inclusions. One of these inclusions, which measured about 1.5 inches in diameter, was removed from the granite and analysed for copper, lead, and zinc. It was found to contain 9 p.p.m. copper, 4 p.p.m. lead, and 105 p.p.m. zinc. Thus there is a marked difference in the metal content of the inclusion compared to the enclosing granite. This difference is in accordance with the trend in the content of these metals in acidic and basic rocks, i.e., the more basic rocks contain more copper, less lead, and more zinc than the acidic ones (Sandell & Goldich, 1943; Wedepohl, 1953; Wedepohl, 1956).

The copper content of the minerals of the granite (Table 4) shows that this metal is more concentrated in biotite-chlorite and magnetite than in quartz and feldspar. The fact that the concentration of copper (ionic radius = 0.72 Å, Ahrens, 1952) is greater in the minerals that contain

ferrous iron (ionic radius = $0.74 \text{ \AA}$) and magnesium (ionic radius = $0.66 \text{ \AA}$) generally agrees with the empirical rules of Goldschmidt.

The leaching curve of copper (Fig. 1) shows a sharp rise up to 0.02 hours followed by a gentler rise. It also shows that only about 5 per cent of the total copper present in the rock was leached. The shape of the curve seems to indicate that little, if any, more copper would have been extracted if the leaching test had been carried out for a longer period of time than the period of the present investigation. Thus, it is concluded that most of the copper in this granite substitutes in the structure of the major minerals.

The lead content of the minerals of the granite (Table 4) shows that lead is more concentrated in feldspar, biotite-chlorite, and magnetite than in quartz. One possible explanation for the concentration of lead (ionic radius = $1.20 \text{ \AA}$) in feldspar and biotite is its substitution for potassium (ionic radius = $1.33 \text{ \AA}$) according to the rules of Goldschmidt. The high lead concentration in magnetite, however, is possibly due to the presence of lead-rich inclusions. There are no cation positions in magnetite for which lead can substitute according to the rules of Goldschmidt. The ionic sizes of ferrous iron and ferric iron are too small compared to the ionic size of lead.

The leaching results of lead are inconclusive because the determination of lead in the leaching solutions was not successful. The leaching residue, however, showed that about 65 per cent of the lead was extracted by leaching.

The zinc content of the minerals of the granite (Table 4) shows that this metal is more concentrated in biotite-chlorite and magnetite than in quartz and feldspar. Thus it appears that the structural positions of ferrous iron (ionic radius = $0.74 \text{ \AA}$) and magnesium (ionic radius = $0.66 \text{ \AA}$) in biotite and chlorite, and the structural position of ferrous iron in magnetite, influence the concentration of zinc (ionic radius = $0.74 \text{ \AA}$) in these minerals according to the rules of Goldschmidt.

The leaching curve of zinc (Fig. 2) shows a gradual rise from time 0.02 hour until the end of the test. The curve shows that approximately 40 per cent of the total zinc present in the rock was extracted. Also, the shape of the curve indicates that more zinc would have been extracted if the test had been carried out for a longer period of time. Thus it is concluded that at least about 40 per cent of the zinc does not substitute in the structure of the major minerals of the granite, but rather occurs in an easily leachable form.

It can be generalized, for the specific elements and rock specimen investigated, that the factors that influenced the type of combination of the three trace elements included, (a) the similarity of the ionic size

and charge of the trace elements to the host elements in the minerals (Goldschmidt, 1937), and (b) the tendency of these trace elements to form covalent bonds compared to the host elements in the minerals (Ringwood, 1955). The results of this study indicate that traces of copper, lead, and zinc substitute in the structure of the major minerals of the granite but also occur in some easily leachable form. Both factors mentioned above have influenced this combination. Thus the similarity of the ionic sizes and charges of copper, lead, and zinc to the host elements of ferrous iron, magnesium, and potassium in biotite, chlorite, magnetite, and feldspar, influenced the substitution of the trace elements for the host elements. In addition, the Cu-O, Pb-O, Zn-O bonds are more covalent than the Fe-O, K-O, Fe-O bonds respectively (Ringwood, 1955). Therefore copper, lead, and zinc did not enter the structure of the silicate minerals as readily as iron and potassium and thus some accumulated and crystallized in some interstitial and easily leachable minerals.

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