666. *Determination of the Age of Igneous Rocks.*

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In view of the importance of determinations of age in geochemical prospecting for ore deposits, an attempt has been made to determine geological age directly in rock samples. Owing to the extremely small amounts of the relevant elements occurring in rocks, mass-spectrographic analysis of the inactive end-products is not practicable and the determinations of age have been made by two independent methods, *viz.*, the " lead " and the " strontium " method. As spectrographic methods are not sensitive enough for lead, it was determined by a polarographic method. Except for samples of a granite and a granulite from the Carboniferous, the two methods gave fairly concordant results.

In connection with a proposed geochemical method for prospecting for ore deposits (Miholić, *Intern. Geol. Congress, Report of the XVIIIth Session*, Part II, p. 86) the need arises for a simple and direct method for the determination of the geological age of igneous rocks accompanying the metalliferous faults and joints. At present only radioactive methods are available for this purpose, but since igneous rocks contain the relevant elements only in traces, no isotopic analysis of the end-products of the radioactive disintegrations is possible as is the case in determinations of age in minerals. This entails serious sources of error, as the rocks might contain *ab initio* non-radiogenic isotopes of those end-products. Tertiary igneous rocks, for instance, are unusually rich in lead (Holmes, *Proc. Roy. Irish Acad.*, 1936, **46**, *B*, 89), and according to Sahama (*Bull. Geol. Comm. Finlande*, 1945, **135**), younger granites contain up to 0·01% of lead oxide. Strontium also shows a tendency to accumulate in younger rocks, whereas the older rocks seem to be richer in yttrium (Rankama, *ibid.*, 1946, **137**). Another source of error affecting results in the opposite direction has to be sought in the possibility of losses of the relevant elements either through leaching or through the diffusion of a gaseous end-product (helium) or a gaseous link in a a radioactive series. This applies principally to the uranium, and to a lesser degree to the thorium radioactive series. López de Azcona (*Anal. Soc. Fís. Quím.*, 1948, *B*, **5**, 571) has studied in detail this source of error and given a table of corrections to be applied for losses of radon through diffusion.

It is therefore important that the age determination of a rock should be made by several independent methods for comparison. Two such methods are at present available. First, there are the well-known " helium " and " lead " methods, proposed by Strutt (*Proc. Roy. Soc.*, 1908, *A*, **81**, 272) and Boltwood (*Amer. J. Sci.*, 1907, **23**, 77) and based on the radioactive disintegration of uranium and thorium giving helium and lead as inactive end-products, and secondly, there is the new " strontium " method worked out by Hahn and Walling (*Z. anorg. Chem.*, 1938, **236**, 78) and based on the radioactive disintegration of the rubidium isotope ^{87}Rb into the inactive strontium isotope ^{87}Sr.

A third possible method can be devised based upon the disintegration of the radioactive samarium isotope ^{152}Sm, which gives the inactive neodymium isotope ^{148}Nd with emission of an α-particle, as first suggested by Wahl (*Geol. Rundschau*, 1942, **32**, 550). Ordinary samarium contains 26·63% of ^{152}Sm (Inghram, Hess, and Hayden, *Physical Rev.*, 1948, **73**, 180), and as the half-life of ^{152}Sm is $2{\cdot}5 \times 10^{11}$ years, this gives an apparent half-life for ordinary samarium of $9{\cdot}4 \times 10^{11}$ years. Joly (*J.*, 1924, **125**, 905), investigating pleochroic haloes in the micas of Ytterby, found haloes which did not correspond to those of any known radioactive element. One sort, occurring very rarely and called by him hibernium haloes, had a radius of 0·0052 mm., corresponding to a range in air of 1·04 cm., which agrees well with the calculated range of 1·13 cm. for the α-particles of samarium in air (Haenny, Najar, and Gailloud, *Helv. Physica Acta*, 1949, **22**, 611). According to Roentgen-spectrographic determinations by Sahama and Vähätalo (Sahama, *loc. cit.*, p. 39), igneous rocks contain 0·0001—0·0007% of Sm_2O_3 and 0·0005—0·0036% of Nd_2O_3, which indicates a considerable amount of non-radiogenic neodymium in rocks and would necessitate its isotopic analysis. López de Azcona (*Bol. Inst. geol. min. España*, 1941, **55**, 277), working with arc excitation of samples of sulphates diluted with mercuric oxide or with sodium chloride, found for the samarium line 3218·60 A. a sensitivity of 0·005% Sm, and for the neodymium line 4012·25 A. also a sensitivity of 0·005% Nd. With spark excitation and concentrated solutions of the samples, the sensitivity could be increased, but would still be far from satisfactory. For all those reasons the method is as yet unsuitable for determinations of age in rocks; it is however, being tested for such determinations in minerals.

EXPERIMENTAL.

In order to determine the suitability of the different radioactive methods for the purpose in view, samples of igneous rock from different localities and of different age were chosen. It was also endeavoured to choose samples whose geological age was still controversial in order that the present paper might also be a contribution to the knowledge of the stratigraphical position of the investigated rocks.

In view of the increased importance attributed to the trace elements in rocks, the determinations were not confined to elements necessary fo the age determination proper, but a number of other trace elements has also been determined. Complete analyses of the rocks are recorded in Table I.

The elements common in silicates were determined according to Hillebrand (" The Analysis of Silicate and Carbonate Rocks," Washington, 1919).

Uranium was determined radiometrically by a standard emanation method; this did not allow of a greater precision than about ±10%, but as the precision for the other elements relevant for the age determination of rocks by the " lead " method (thorium and lead) was also not high owing to their extremely small amounts, it was not deemed necessary to make the determinations of uranium with any greater precision. The emanation from a solution of a 2-g. sample was allowed to accumulate for one month in a 100-ml. flask; this was then connected with the ionization chamber, and the radon distributed evenly in the whole system by means of an atomizer. In order to minimize back-ground ionization, the measurements were made in a country house outside the town. The radon was allowed to come to equilibrium for 3 hours, and the rate of fall of the charged quartz fibres of a Wulf electrometer was read every ½ hour. From the values obtained the amount of radon in milimicrocuries was calculated by a modified formula (Schmidt, *Physikal. Z.*, 1905, **6**, 561), *viz.*:

$$\mathrm{Rn} = \frac{I_{\mathrm{max.}}C \times 100(l_1 + l_2 + l_3)}{60al_3}\left(1 + \delta_T\frac{l_0}{l_1}\right)\frac{100}{300} \times 0{\cdot}364$$

In this expression, $I_{\mathrm{max.}}$ is the fall of the electric charge on the fibres due to the ionization by radon in volts per minute, C the capacitance of the ionization chamber with the electrometer (3·55 cm.), l_0 the volume of the solution of the sample (50 ml.), l_1 that of the air in the flask (50 ml.), l_2 the volume of air in the connections, etc. (300 ml.), l_3 that of air in the ionization chamber (1000 ml.), δ_T the coefficient of distribution of radon between air and water at the temperature T, and a the amount of sample (2 g.). From these data and the half-life of uranium, $4{\cdot}51 \times 10^9$ years, and of radium, 1590 years, we obtain for the amount of uranium, in p.p.m.: $\mathrm{U} = \mathrm{Rn} \times 29{\cdot}9$.

Zirconia, baryta, and the rare earths (containing thoria) were determined in a 2-g. sample according to Washington (" The Chemical Analysis of Rock," 4th edn., New York, 1930, p. 257). Thorium in the ignited rare earths was separated as the oxynitrate, Th_2O_7,N_2O_5, which was dissolved and reprecipitated and finally ignited to ThO_2, the amount of which was subtracted from the weight of the rare earths.

TABLE I.

A. Gneiss granite, pink, coarse-grained, from Forshem, near Kinnekulle, Sweden.
B. Gneiss granite, pink, fine-grained, from same district.
C. Gneiss granite, grey, fine-grained, from same district.
D. Green schist, fine-grained, from the Western part of Mt. Medvednica, near Zagreb, Croatia.
E. Green schist, fine-grained, from the Eastern part of Mt. Medvednica.
F. Granite, light-grey, fine-grained, from Mt. Bukulja, N.W. Serbia.
G. Granulite, almost white, with long conspicuous crystals of tourmaline, from same mountain.

	A.	B.	C.	D.	E.	F.	G.
SiO_2	74·93	75·03	60·65	48·14	48·63	73·18	75·05
TiO_2	0·23	0·23	0·57	1·11	1·21	0·15	0·07
Al_2O_3	12·15	12·50	18·30	15·47	17·17	15·05	14·53
Fe_2O_3	2·22	1·88	2·41	5·17	6·92	1·36	0·58
FeO	0·11	0·18	2·49	4·32	1·17	0·30	0·20
MnO	0·14	0·28	0·15	0·014	0·024	0·27	0·022
MgO	0·03	0·12	2·28	5·75	6·50	0·05	0·20
CaO	1·08	0·67	4·65	12·47	10·79	1·62	1·09
BaO	0·052	0·025	0·11	0·027	0·0089	0·018	0·011
Na_2O	5·34	5·25	3·36	2·34	2·45	4·79	4·73
K_2O	3·31	3·25	2·64	0·15	0·09	2·17	2·38
P_2O_5	0·029	0·022	0·29	0·21	0·29	0·16	0·087
ZrO_2	0·038	0·14	0·083	0·039	0·022	0·038	0·039
$(Ce,Y)_2O_3$	0·072	0·049	0·056	0·21	0·050	0·027	0·24
FeS_2	0·095	0·047	0·10	0·31	1·32	0·091	0·047
CO_2	—	—	0·049	1·12	—	—	—
$H_2O +$	0·14	0·20	1·82	3·05	3·52	0·59	0·46
$H_2O -$	0·01	0·02	0·03	0·19	0·07	0·08	0·03
	99·98	99·89	100·04	100·09	100·23	99·93	99·77
Trace elements (in p.p.m.) :							
Cu	7·63	3·44	19·86	60·25	59·65	4·92	6·44
Pb	8·93	2·26	1·09	2·24	1·80	2·00	12·1
Cd	0·91	0·06	9·55	2·27	0·23	2·77	1·81
Sn	10	41	28	41	16	69	56
Zn	116	131	187	39·3	28·7	86·0	57·2
U	2·93	4·91	2·47	1·82	2·89	3·11	2·73
Th	125·0	20·6	10·2	57·1	44·0	88·2	132·3
Sr	8·3	6·0	29·0	12·0	14·0	0·85	0·55
Rb	1400	1000	5000	3700	4100	800	520

For the determination of trace metals in rocks the spectrographic method is usually employed. This gives excellent results with the alkali and the alkaline-earth metals, but is less sensitive for heavy metals. Lead, for instance, can be determined spectrographically only in amounts greater than 0·001%, which is considerably higher than the average lead content of the rocks. For this reason the author used a polarographic method that has proved very satisfactory in the determination of traces of heavy metals in mineral waters (Miholić, *Rad. Acad. Sci. Zagreb*, 1945, **278**, 195). A 50-g. sample of the finely ground rock was decomposed with hydrofluoric and nitric acid, the solution evaporated to dryness, and the residue taken up with water and acidified with nitric acid; the heavy metals were precipitated with hydrogen sulphide, and the precipitate, after removal of tin as thiostannate, was dissolved in nitric acid, excess of acid removed by evaporation to dryness, and copper, lead, and cadmium determined polarographically in a 0·3M-solution of sodium potassium tartrate. From the filtrate of the hydrogen sulphide precipitate, iron, aluminium, and titanium were removed by the basic carbonate method, and zinc and manganese deposited by ammonium sulphide. The deposit was dissolved in hydrochloric acid, evaporated to dryness, taken up with 5 ml. of water and 5 ml. of a saturated solution of potassium chloride, and polarographed for zinc and manganese. Details of the polarographic procedure for the determination of trace metals have been published elsewhere (Miholić, *Mikrochem.*, in the press).

The solution containing the thiostannate was acidified with acetic acid and filtered hot through a porcelain filter crucible. The precipitate was dissolved in a 50% solution of potassium hydroxide and oxidized with hydrogen peroxide; nitric acid was added to a slight acid reaction, the solution heated for 3 hours on a water-bath, and the precipitate filtered off, ignited, and weighed as SnO_2.

Rubidium and strontium were determined spectrographically in 2-g. samples of rock which had been decomposed by hydrofluoric and nitric acid. The final volume of the solution was 10 ml. The elements were determined with a Zeiss Universal Quartz Spectrograph using 8000-volt a.c. The distance of the electrodes (high-purity carbon rods 50 mm. long and 3 mm. in diameter) was 3 mm. After a pre-sparking of one minute, the sample (0·3 ml. of the solution) was placed on the lower electrode provided with a bored recess, and then the spark was continued for a further minute during which the exposure was made. The sample was photographed on the same plate with exposures of standards made by 500-, 1000-, and 5000-fold dilution of a standard solution containing 2·823 g. of rubidium chloride and

0·01449 g. of strontium nitrate dissolved in 10 ml. of water. This ratio between rubidium and strontium (1 : 0·003) corresponds to the age of 1000 million years (cf. Ahrens, *Trans. Geol. Soc. S. Africa*, 1947, **50**, 23). The spectra were recorded on Foma Gradual plates which were developed in quinol developer for 4 minutes at 20°. A Zeiss non-recording microphotometer, the full scale deflection of which is 50 cm., was used for the evaluation of line intensities. The slit in the photometer was arranged so that an unexposed part of the photographic plate gave a deflection on the scale of 250 (d_0). The plate was then moved slowly in a horizontal direction and when the spectral line passed the slit the minimum deflection (d) was noted. The difference ($d_0 - d$) was taken as a measure of the blackening of the plate.

For the determination of rubidium the line at 4201·85 A., and for strontium that at 4077·71 A., was used. As both lines are within a cyanogen band, the head of which is at 4216 A., interference from that band was to be expected. Potassium chloride was therefore added to both sample and standards so that the solution contained 1% of KCl. With this the cyanogen emission was effectively quenched and satisfactory measurements could be made even on faint lines.

For every element to be determined the values ($d_0 - d$) were plotted logarithmically as abscissæ on a graph. The ordinates represented the concentrations of the three standard solutions also on a logarithmic scale, and a straight line was obtained on the graph from which the concentration of the unknown was read.

The analytical results are summarized in Table I.

From the data for uranium, thorium, and lead in Table I the relations U/(U + Th) and Pb/(U + Th) were calculated, and from the values obtained the geological age according to the "lead" method was read from Wickman's nomogram (*Sveriges geol. Unders.*, 1944, *C*, **458**). The results are given in Table II, which shows also the ratio Rb/Sr and the geological age according to the "strontium" method calculated from $T = [\ln N_0/(N_0 - 1)]/\lambda$, where N_0 is the amount of rubidium at $T = 0$, and $N_0 - 1$ its amount at the time T, the amount of strontium formed during that time by the radioactive disintegration of rubidium being taken as unity.

TABLE II.

				Geological age (10^6 yrs.) according to :	
	U/(U + Th).	Pb/(U + Th).	Rb/Sr.	"lead" method.	"strontium" method.
A	0·0228	0·694	169	1420	1570
B	0·193	0·0886	168	1325	1570
C	0·195	0·0860	171	1280	1570
D	0·0309	0·0380	310	790	1010
E	0·0616	0·0384	292	750	1010
F	0·0341	0·0219	940	(430)	185
G	0·0202	0·0893	945	(1810)	185

DISCUSSION.

Except for the granite, and particularly for the granulite of Mt. Bukulja, both of which obviously contain non-radiogenic lead, the age determination by the "lead" and by the "strontium" method agree fairly well in view of the sources of error inseparable from this kind of determination. The absolute geological age (in millions of years) can be correlated as follows with the relative age of geological formations: Early Pre-Cambrian 3350—1500, Middle Pre-Cambrian 1500—1000, Late Pre-Cambrian 1000—500, Silurian 500—310, Devonian, 310—280, Carboniferous 280—220, Permian 220—190, Triassic 190—150, Jurassic 150—110, Cretaceous 110—70, Tertiary 70—1, Quaternary 1—0.

The relative age of the Swedish gneiss granites has been estimated very differently by various geologists. Some (Törnebohm, Sederholm, Eskola) consider them to be older than the Leptite formation or even a remnant of the primary earth's crust; others (Högbom, De Geer, Holmquist) place them in the Middle Pre-Cambrian, or consider them of Late Pre-Cambrian age (Nathorst). The above determinations establish them as belonging to the Middle Pre-Cambrian.

The green schists of Mt. Medvednica occupy a key position in the stratigraphy of N.W. Croatia and have been generally considered (Foetterle, Pilar, Gorjanović) to be of Silurian age. Only Kišpatić believed them to be Late Pre-Cambrian. His opinion has now been confirmed by the determination of their absolute age.

The granite intrusion of Mt. Bukulja in N.W. Serbia has been classified as Cretaceous by Kossmat and as Cretaceous or Older Tertiary by Pilger. Žujović (*Ann. geol. Pénin. balc.*, 1924, **7**, Annexe, p. 9), however, considered it as Carboniferous. The values for the absolute geological age obtained by the "strontium" method are nearer to his estimate than to those of the other geologists.

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