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ISOTOPIC COMPOSITION OF STRONTIUM IN FOUR CARBONATE VEIN-DIKES[1]

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ABSTRACT

The Sr^{87}/Sr^{86} ratios of 8 specimens from the carbonate veins or vein-dikes at Ravalli Co., Montana; the Rocky Boy Stock, Montana; Lemhi Co., Idaho; and Cardiff Uranium Mines, Haliburton Co., Ontario vary from about 0.704 to 0.706 and average 0.7051. Their Sr^{87}/Sr^{86} ratios are in general significantly higher than those of accepted carbonatites, lower than those of most limestones, and similar to those of mafic igneous rocks. Neither isotopic fractionation nor contamination of carbonatitic fluids or magmas with crustal radiogenic strontium appears to be an adequate general explanation for the higher Sr^{87}/Sr^{86} ratios of the four vein-dikes. This may indicate that the vein-dikes studied are not genetically related to massive carbonatite.

INTRODUCTION

Previous work (Powell *et al.*, 1962, 1965) has shown that the Sr^{87}/Sr^{86} ratios of accepted carbonatites vary from about 0.702 to 0.705 and average about 0.7035. (The Sr^{87}/Sr^{86} ratios reported by Powell *et al.* (1962) must be corrected by -0.0030 to account for a consistent error in their analytical procedure.) On the other hand sedimentary and metamorphic carbonate rocks, with the exception of the very old Bulawayan limestone, have Sr^{87}/Sr^{86} ratios which range from about 0.706 or 0.707 upward (Gast, 1960; Hamilton and Deans, 1963; Herzog *et al.*, 1958; Pinson *et al.*, 1958; Powell *et al.*, 1965). The Sr^{87}/Sr^{86} ratios for limestones reported by Hedge and Walthall (1963) appear slightly lower than those reported by other investigators. Hamilton and Deans (1963) have also shown that the Sr^{87}/Sr^{86} ratios of accepted carbonatites are lower than those of most limestones, although their data cannot be compared directly with those of Powell *et al.* (1965) due to interlaboratory discrepancies. Powell *et al.* (1965) suggest that since the Sr^{87}/Sr^{86} ratios of all the accepted carbonatites which have been analyzed are distinctly lower than those of most limestones, this isotopic ratio may serve as an empirical criterion for determining whether carbonate rocks of uncertain classification are carbonatites.

Bailey (1964) and Deans (1964) have called attention to the need for analyses of the Sr^{87}/Sr^{86} ratios of carbonate veins and vein-dikes in order to provide a broader basis for use of the Sr^{87}/Sr^{86} ratio as a criterion for recognition of carbonatite. Accordingly, samples from the carbonate vein-dike occurrences at Ravalli Co., Montana; the Rocky Boy Stock, Montana; Lemhi Co., Idaho; and Cardiff Uranium Mines, Haliburton

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[1] M. I. T. Age Studies No. 59.

Co., Ontario have been obtained and their strontium isotopic compositions determined.

The carbonate rocks at Ravalli Co., Montana have been described by Heinrich and Levinson (1961, p. 1424) as " . . . tabular deposits . . . an inch to 10 feet thick, as much as 450 feet long, and crosscutting as well as conformable." They are not associated with alkalic igneous rocks, and are believed by Heinrich and Levinson to be the result of reaction of hydrothermal solutions of alkalic derivation with dolomitic marble. The carbonate veins in the Rocky Boy Stock, Bearpaw Mountains, Montana are regarded by Pecora (1962) as carbonatites, and in contrast to the other three vein-dike deposits studied, are associated with alkalic igneous rocks. Anderson (1960, p. 1179) characterizes the vein-dike deposits at Lemhi Co., Idaho as " . . . small and tabular . . . " and points to their apparent lack of association with alkalic igneous rocks. Satterly (1957, p. 46) describes the carbonate rocks at the Cardiff Uranium Mines, Ltd., Cardiff Township, Haliburton Co., Ontario as calcite-fluorite-apatite veins with uraninite. They are associated with syenite gneiss but not with alkalic igneous rocks of the type usually associated with carbonatite.

EXPERIMENTAL METHOD

Whole-rock samples were ground in a pre-contaminated steel percussion mortar and approximately one gram was taken for analysis. The samples were dissolved with 2.5N vycor-distilled hydrochloric acid in polypropylene beakers. Strontium was separated from the other elements on a 2×30 cm chromatographic column with Dowex 50W-X8 cation exchange resin and 2.5N vycor-distilled hydrochloric acid as the eluant. The progress of strontium on the column was monitored by the radioactivity of a small amount of Sr^{89} tracer which had been added to the solution. Samples were passed through the ion exchange column twice to insure adequate separation of strontium from calcium. A single analysis indicated the laboratory strontium blank to be on the order of a fraction of a microgram, an insignificant amount compared to that present in the samples.

Mass spectrometric analysis of the samples followed the techniques described by Powell *et al.* (1965). All Sr^{87}/Sr^{86} ratios have been normalized to $Sr^{86}/Sr^{88}=0.1194$. Three different mass spectrometers were used in this study, but 14 of the 18 analyses reported were made on one instrument (denoted I). Several analyses of the interlaboratory strontium isotopic standard (Eimer and Amend $SrCO_3$, lot 492327) have been performed on each of the three instruments. An average value of $Sr^{87}/Sr^{86} = 0.7081$ was obtained from 4 analyses of the standard on instrument I. Sr^{87}/Sr^{86} ratios measured on the other two instruments have been adjusted so that all analyses are expressed relative to a value of $Sr^{87}/Sr^{86} = 0.7081$ for the strontium isotopic standard.

The precision of the analytical technique has been calculated from the duplicate and triplicate analyses listed in Table 1 and from those reported by Powell (1965a). Sr^{87}/Sr^{86} ratios measured on all three of the instruments used were included in this calculation. Following the method for calculation of precision from a series of duplicate analyses given by Youden (1951), the standard deviation of a single analysis of the Sr^{87}/Sr^{86} ratio in this work is ±0.0004, or about 0.06 per cent.

RESULTS

The data obtained for samples from the four carbonate vein or vein-dike deposits are given in Table 1. The mean Sr^{87}/Sr^{86} ratio of the 8 samples listed (R21 is not a vein-dike and is excluded) is 0.7051, relative to a value of 0.7081 for the Sr^{87}/Sr^{86} ratio of the Eimer and Amend interlaboratory strontium isotopic standard. Powell *et al.* (1965) report that the mean Sr^{87}/Sr^{86} ratio of 21 carbonatites, relative to a value of 0.7085 for the standard, is 0.7035. It should be noted that earlier analyses of specimen C4314, from the Rocky Boy Stock, were included in the work of Powell *et al.* (1965). Exclusion of this sample from their data does not significantly change the mean Sr^{87}/Sr^{86} ratio which they obtain for carbonatites. The difference between these two means, making no correction for the slightly different results obtained on the strontium isotopic standard during the two studies, is 0.0016. If such a correction were made the difference would be increased. A standard t test can be applied to determine the significance of the difference between the two means (see Youden, 1951, p. 24). Calculation of t involves the estimated standard deviation of the individual measurements. The weighted average of the standard deviation reported by Powell *et al.* (1965) for 21 samples, ±0.002, and that obtained in this study of 8 vein-dike samples, ±0.0004, is about ±0.0015. The value of t calculated using $\sigma = \pm 0.0015$ is 2.57, which indicates that the difference between the two means is significant at confidence limits greater than 95 per cent (Youden, 1951, p. 119, Table 1, degrees of freedom = 27). The conclusion that the four carbonate vein-dikes have higher Sr^{87}/Sr^{86} ratios than massive carbonatite is strengthened by the results of Powell (1965b) in which 10 massive carbonatites from Ontario were found to have a mean Sr^{87}/Sr^{86} ratio of 0.7028 ± 0.0006 (σ). It should be pointed out, however, that the Sr^{87}/Sr^{86} ratio of vein-dike specimen R55 is identical to those of typical carbonatites.

Although the Sr^{87}/Sr^{86} ratios of the carbonate vein-dikes are generally higher than those of the typical carbonatites, they are distinctly lower than those of most limestones which have been analyzed. In fact the

TABLE I. ISOTOPIC COMPOSITION OF STRONTIUM IN FOUR CARBONATE VEIN-DIKES

Sample Number	Description and Locality	(Sr^{87}/Sr^{86})[1]	Sr^{86}/Sr^{88}
	Ravalli Co., Montana		
R23	Barite-bearing carbonate, Rocky Point #5 deposit, Wood Creek	0.7056	0.1199
		0.7046[2]	0.1184
		0.7051	
R56	Monazite- and ancylite-bearing carbonate; from biotite deposit	0.7060	0.1190
		0.7059	0.1191
		0.7059_5	
R57	Coarse calcite from dike margin, Sheep Creek	0.7048	0.1194
		0.7049	0.1189
		0.7048_5	
	Rocky Boy Stock, Montana		
C4314	Calcite carbonatite, #2 vein	0.7057	0.1195
		0.7061	0.1202
		0.7062	0.1196
		0.7060	
	Lemhi Co., Idaho		
R26	Coarse calcite assoc. with monazite and rutile	0.7050[2]	0.1188
	Cardiff Uranium Mines, Cardiff Twp., Ontario		
R20	Calcite-apatite-fluorite vein	0.7046[2]	0.1196
		0.7048[2]	0.1194
		0.7053	0.1189
		0.7049	
R54	Calcite-apatite-fluorite vein	0.7049	0.1184
		0.7046	0.1193
		0.7047_5	
R55	Pink calcite-apatite-fluorite vein	0.7040	0.1189
		0.7037	0.1186
		0.7038_5	
R21	"Wall-rock marble," recrystallized Grenville?	0.7048	0.1192

[1] All Sr^{87}/Sr^{86} ratios normalized to $Sr^{86}/Sr^{88}=0.1194$.

[2] Analyzed on a second instrument and corrected by -0.0008.

figure of 0.7051 obtained as the mean Sr^{87}/Sr^{86} ratio of the vein-dikes is identical within the analytical precision to the value reported by Faure and Hurley (1963) for the mean Sr^{87}/Sr^{86} ratio of young continental basalts. (The Sr^{87}/Sr^{86} ratios reported by Faure and Hurley must be corrected by -0.0030.)

The differences between the Sr^{87}/Sr^{86} ratios of different specimens from one locality, as for example R56 and R57 from Ravalli County, Montana, are not significant at the 95 per cent confidence level required. The difference between the mean Sr^{87}/Sr^{86} ratio of the specimens from the Cardiff Uranium Mines, Ontario (excluding R21), 0.7046, and that of the specimen from the Rocky Boy Stock, 0.7060, is significant at confidence limits greater than 99 per cent.

Specimen R21 is from the so-called wall-rock marble at the Cardiff Uranium Mines. This marble has been regarded as recrystallized Grenville marble (E. Wm. Heinrich, pers. comm., 1963). The Sr^{87}/Sr^{86} ratio of this sample, 0.7048, is lower than those reported for Grenville marble by Gast (1960), Pinson *et al.* (1958), and Powell *et al.* (1965), but it is identical to the value reported by Krogh (1964). Not only R21, but vein-dike specimens R20 and R54, both from the Cardiff deposits, have Sr^{87}/Sr^{86} ratios identical to those of some specimens of Grenville marble.

DISCUSSION OF RESULTS

The difference between the mean Sr^{87}/Sr^{86} ratio of these four carbonate vein-dikes and those of the accepted carbonatites is not the result of natural fractionation of the strontium isotopes. Although differences between the physical and chemical histories of massive carbonatite and carbonate vein-dikes might have caused their parent materials to fractionate the strontium isotopes to differing extents, the effects of natural and experimental fractionation have been removed by normalizing the observed values of Sr^{87}/Sr^{86} to a constant value of Sr^{86}/Sr^{88}. The difference between the Sr^{87}/Sr^{86} ratios of the typical carbonatites and those of the carbonate vein-dikes must therefore indicate that the two have not been derived from identical source materials.

Since the Sr^{87}/Sr^{86} ratios of near-surface crustal rocks are on the average distinctly higher than those of carbonatites and mafic silicate rocks, it is possible that the higher Sr^{87}/Sr^{86} ratios of the vein-dikes reflect the fact that their source magmas or fluids, although initially the same as those which give rise to massive carbonatite, were contaminated with Sr^{87} from the surrounding wall-rock or country rock. It is reasonable to expect that material deposited in tabular veins or dikes would be more subject to such contamination than rocks formed by crystallization from larger bodies of magma. It should be kept in mind, however, that some of these vein-dikes contain exceptionally large amounts of strontium, making it less likely that contamination could significantly affect their Sr^{87}/Sr^{86} ratios. Heinrich and Levinson (1961, Table 5) list strontium concentrations varying from 2,400 to 17,000 ppm for the deposits at Ravalli County. Pecora (1962) reports that strontium in 12 calcite specimens from the Rocky Boy Stock varies from 18,000 to 40,000 ppm.

A simple calculation can be made to give some idea of the effect of assimilation of crustal rocks on the Sr^{87}/Sr^{86} ratio of carbonatite magma. Gold (1963) reports that average carbonatite contains 0.40 weight per cent strontium oxide, equivalent to about 3500 ppm strontium. Faure and Hurley (1963) estimate that the continental crust contains an average of about 440 ppm strontium with $Sr^{87}/Sr^{86}=0.722$. In the following equation, x and y are the percentages of strontium from average carbonatite and average continental crustal rocks, respectively, that must be mixed to produce a rock with $Sr^{87}/Sr^{86}=0.7051$, the average value found in the vein-dikes.

$$0.7035x + 0.722y = 0.7051$$

Since $x+y=1$, $x=91$ per cent, $y=9$ per cent, and $x/y=10$. In other words, 10 parts of strontium from average carbonatite magma are required for each part of strontium from average continental crustal rocks. The ratio of the concentration of strontium in average carbonatite to that in average continental crustal rocks is about $3500/440=8$. The solution to the equation above shows that in order to produce a rock with $Sr^{87}/Sr^{86}=0.7051$ from the two materials, this ratio must be increased by a factor of $10/8=1.25$. That is, average carbonatite and average continental crustal rocks must be mixed in the proportions $1.25/2.25\times100=55$ per cent, and $1.00/2.25\times100=45$ per cent, respectively. Strontium 87 abundance varies directly with Rb/Sr ratio and is thus inversely proportional to strontium concentration. Repeating this calculation using crustal rocks with larger abundances of Sr^{87} would not greatly change the resulting percentages, since the effect of the higher Sr^{87} abundances of these rocks would be offset by their lower strontium concentrations. In addition, as pointed out above, many carbonate vein-dikes contain considerably larger concentrations of strontium than even the massive carbonatites.

This calculation, although very approximate, shows that typical carbonatite magmas would have to assimilate easily detectable amounts of average continental crustal rocks in order to raise their Sr^{87}/Sr^{86} ratios by even very small amounts. There appears to be no independent evidence to suggest that the carbonatic fluids from which the vein-dikes were deposited have assimilated such relatively large amounts of crustal rocks. Recent experimental work by Deuser and Herzog (1963) and McNutt (1964) suggests that radiogenic Sr^{87} may be less mobile than common strontium, making it appear unlikely that radiogenic Sr^{87} could be preferentially extracted from crustal rocks by carbonatic fluids.

It therefore appears that the higher Sr^{87}/Sr^{86} ratios of the vein-dikes compared with those of massive carbonatite cannot be explained by isotopic fractionation or by contamination involving carbonatite magma as the parent material. It seems probable that the higher Sr^{87}/Sr^{86} ratios of the vein-dikes reflect the fact that their parent material differs fundamentally from that which gives rise to typical carbonatite. It is important to note that the Sr^{87}/Sr^{86} ratios of the vein-dikes, although higher than those of carbonatites, are identical within analytical precision to those of many continental mafic rocks. As a tentative explanation it is suggested that: (1) The typical massive core-type carbonatites are derived from magmas with the over-all composition of carbonatite which have low Sr^{87}/Sr^{86} ratios as a result of their ultimate derivation from great depth where the Rb/Sr ratio is low; (2) The four carbonate veins or vein-dikes studied, three of which are associated neither with alkalic igneous rocks nor massive carbonatite, may be more analogous to pegmatites or hydrothermal veins and have been deposited from fluids or hydrothermal solutions which themselves were derived from mafic and/or alkalic magmas and not from true carbonatite magmas. The parent silicate magmas from which the vein-dikes are believed to have been derived may have been contaminated with crustal rocks, but this is not necessary in order to account for their higher Sr^{87}/Sr^{86} ratios. Contamination of the parent silicate magma is particularly likely, however, in the Rocky Boy Stock where the carbonate veins are associated with potassium-rich alkalic rocks. In the case of the Ravalli County deposits, these carbonatic fluids may well have replaced pre-existing marbles.

More analyses of other carbonate vein-dikes are needed to test this tentative hypothesis. A detailed study of carbonate vein-dikes associated with massive carbonatite, as for example at the complex at Iron Hill, Colorado, would be of particular interest.

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