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29 January 1971

## **Oxygen Isotope Ratios in Eclogites from Kimberlites**

Abstract. The oxygen isotope compositions ( $\delta^{18}O$ ) of eclogitic xenoliths from the Roberts Victor kimberlite range from 2 to 8 per mil relative to SMOW (standard mean ocean water). This surprising variation appears to be due to fractional crystallization: the eclogites rich in oxygen-18 represent early crystal accumulates; the eclogites poor in oxygen-18 represent residual liquids. Crystalmelt partitioning probably exceeded 3 per mil and is interpreted to be pressuredependent. Anomalous enrichment of oxygen-18 in cumulate eclogites relative to ultramafic xenoliths suggests that crystal-melt partitioning increased after meltformation but prior to crystallization.

Ultramafic xenoliths from kimberlite pipes have  $\delta^{18}$ O values ranging from 5 to 6 per mil relative to SMOW (standard mean ocean water) (Fig. 1). The great majority of ultramafic and mafic igneous rocks from other parts of the world have  $\delta^{18}$ O values between 5 and 7 per mil (1). The upper mantle thus appears to be fairly uniform in isotopic composition. The  $\delta^{18}$ O values less than 5 per mil found in a few igneous rocks have been attributed to isotopic interaction with meteoric waters at igneous temperatures (1, 2). They have not been attributed to fractional crystallization because measured phenocryst-ground-

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C-values

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mass fractionations in lavas are very small (3) and because there is seldom any simple relation between isotopic compositions and the differentiation sequence (1). However, the  $\delta^{18}$ O values of eclogitic xenoliths from the Roberts Victor kimberlite, South Africa, range from 2 to 8 per mil, and the evidence shown in Fig. 1 and described below leaves little doubt that isotopic fractional crystallization has been operative at eclogitic pressures within the mantle.

The Roberts Victor eclogites can be subdivided into three groups on the basis of their textures and chemistries (4): group I, a set of early crystal ac-

cumulates containing clinopyroxene and garnet; group II, a set of subsequent crystal accumulates containing subordinate amounts of kyanite or rutile in addition to clinopyroxene and garnet; and group III, a set of "liquids" which resulted from the progressive removal of the above-mentioned crystals (these "liquids" solidified into assemblages of clinopyroxene and garnet). The probable sequences of differentiation within these groups are shown in Figs 1 and 2. The differences in oxygen isotope compositions between the three groups and the variation within group III can be accounted for by a progressive depletion of <sup>18</sup>O in the melt due to removal of <sup>18</sup>O-enriched crystals (5). Although it is not possible to uniquely associate specific crystal accumulates with specific "liquids," changes in the chemical trends (4) suggest that the transition from group I eclogites to group II eclogites occurred when the liquid had a composition similar to that of samples 26 and 47. The trends in Fig. 1 imply that isotopic partitioning between crystals and melt increased during differentiation and amounted to 3.0 per mil at the time of the transition. We submit that the isotopic partitioning increased in response to an increase in pressure, although we are aware that the influence of pressure on isotopic fractionation is generally assumed to be negligible. An interpretation invoking



eclogites plotted against their C values (C = CaO, see Fig. 2). Samples 4A, 65, and 54 do not conform to the chemical and isotopic patterns determined for the other rocks and may

represent independent magmatic episodes. The histogram shows disO values of ultramafic xenoliths from South African Fig. 2 (right). An ACF diagram showing the projected chemistries of eclogites from the Roberts Victor kimberlites. mine (4). Arrows indicate the directions of differentiation within the three groups. The three off-trend samples are 4A, 65, and 54 (see Fig. 1). In molecular proportions,  $A = Al_2O_3 + Fe_2O_3 - Na_2O - K_2O$ ; C = CaO; and F = MgO + FeO + MnO. 4 JUNE 1971

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<sup>11.</sup> Supported by the National Research Council Canada under grant A3940. I thank C. O.

contamination of the group III "liquids" by <sup>18</sup>O-poor, calcium-rich material is not a plausible alternative because it would require that contamination followed crystallization of the cumulate eclogites and, therefore, could not account for the calcium enrichment of the cumulate eclogites. Furthermore, the existence of an <sup>18</sup>O-poor contaminant in the mantle would be more puzzling than the process of igneous differentiation espoused here.

The <sup>18</sup>O enrichment of the low-calcium cumulate eclogites relative to ultramafic xenoliths is most perplexing. Petrologists and geochemists agree that mafic melts are derived from ultramafic rocks by partial melting, that the melts are initially in equilibrium with their sources, and that the first crystals to form from the melts should also be in equilibrium with the source rocks unless the melts move from their origins and crystallize under different conditions. What set of circumstances would allow a partial melt to precipitate crystals enriched in <sup>18</sup>O relative to ultramafic rocks? Fractional crystallization apparently has the opposite effect. A decrease in pressure and temperature also would have the opposite effect because crystal-melt fractionations have been found to be insignificant under crustal igneous conditions (1, 3), but are here

shown to be significantly positive under the high pressures at which the eclogites crystallized. In the absence of plausible alternatives we suggest that the melt crystallized under higher pressures than those at which it formed. Conceivably, the density of a deepseated partial melt could be greater than that of its source and thereby account for its downward migration (6).

Changes in the content of volatile substances in the melt may have some bearing on the above questions, but the available experimental evidence indicates that isotopic fractionations between CO<sub>2</sub>, H<sub>2</sub>O, and silicates are less than 5 per mil at igneous temperatures (7) and are thus probably too small to be important. In addition, the great majority of unweathered carbonatites have rather ordinary isotopic compositions, ranging from 6 to 9 per mil (8), yet these rocks are thought to be genetically associated with products of extreme differentiation that are rich in volatile substances.

In our discussion we have neglected isotopic partitioning between the solid phases (olivine, pyroxene, and garnet) because the extent of such partitioning at igneous temperatures is small. The average pyroxene-garnet fractionation in eight eclogites from the Roberts Victor mine is 0.2 per mil, and the average

Table 1. Roberts Victor eclogites. In molecular proportions,  $A = Al_2O_3 + Fe_2O_3 - Na_2O - Na_2O_3 + Fe_2O_3 + F$  $K_2O$ ; C = CaO; F = MgO + FeO + MnO.

Sample	Α	С	T	$\delta^{18}$ O (per mil)		
			Г	Garnet	Pyroxene	
		Gr	oup I eclogites	·		
4	11.3	29.7	59.0		6.8	
4A	16.1	25.6	58.3	$8.0 \pm 0.1*$		
7	14.2	24.5	61.3		6.4	
38	8.8	37.2	54.0	6.2		
50	13.7	25.4	60.9		6.1	
63	10.0	31.0	59.0		6.8	
64	14.2	24.3	61.5	6.6	7.2	
71	15.2	24.0	60.8	6.5	7.0	
		Gro	up II eclosites			
13	16.3	29.0	54.7	5.8		
15	17.9	29.2	52.9		6.0	
44	18.6	24.4	57.0		6.4	
53	7.8	47.2	45.0	5.4	011	
65	15.8	27.6	56.6	6.8		
		Grot	up III eclogites			
6	15.5	30.8	53.7	3.8		
8A	12.5	25.6	61.9	5,3	5.3	
22	15.6	31.8	52.6		4.3	
26	16.0	33.1	51.0	3.2	3.2	
30	14.8	28.5	56.7		4.3	
37	15.5	38.1	46.4	3.1		
41	13.3	42.2	44.5	$2.2 \pm 0.1*$		
47	16.2	33.6	50.4	3.3	3.2	
54	14.6	32.3	53.1	$2.6 \pm 0.3^{*}$	$2.5 \pm 0.1*$	
61	15.7	32.7	51.8		3.4	

\* When two analyses were performed, the average deviation from the mean is given.

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Table 2. Ultramafic xenoliths from kimberlites. Abbreviations: R, sample from Roberts Victor mine; BF, sample from Bultfontein mine; U. sample from Kimberly area.

Sample	Composi-	$\delta^{18}$ O (per mil)		
No.	tion	Garnet	Pyroxene	
RVGP	Garnet,			
	lherzolite	5.7		
R77	Garnet,			
	Iherzolite	5.2	5.3	
BF8	Garnet.			
	lherzolite	5.5	5.3	
BF9	Garnet.			
	peridotite	5.6	5.7	
BF10	Peridotite		5.1	
BF5	Garnet.			
	Iherzolite	5.7	5.6	
U5	Peridotite		5.8	

of two pyroxene-olivine fractionations is 0.3 per mil (8). Corrections for these fractionations are included in Fig. 1 (9).

Two grospydite garnets from highly differentiated eclogites occurring in the kimberlites of Yakutia, U.S.S.R., were found to have  $\delta^{18}$ O values of 6.3 per mil (54.3 percent grossularite) and 6.0 per mil (72.1 percent grossularite). These eclogites are similar to the group II eclogites from the Roberts Victor mine, but are more calcic (10).

If the hypothesis is valid that crystalmelt partioning increases with pressure, the mean isotopic composition of the earth need not be that of the upper mantle, and the <sup>18</sup>O/<sup>16</sup>O ratios of basaltic melts can be expected to decrease with increasing depth of origin. This latter prediction will be tested when more analyses of unweathered basalts become available. Our analytical data are presented in Tables 1 and 2.

## G. D. GARLICK

Department of Geology, Humboldt State College, Arcata, California 95521 I. D. MACGREGOR

University of California, Davis 95616

D. E. VOGEL

Rutgers University,

New Brunswick, New Jersey 08903

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- 11 January 1971; revised 11 March 1971

## **Fossil Fuels as a Source of Mercury Pollution**

Abstract. The upper limit of the quantity of mercury released by weathering processes is approximately 230 metric tons per year. The quantity of mercury released by burning of coal is estimated to be of the order of 3000 tons per year, a quantity comparable to that emitted as waste from industrial processes.

Mercury is toxic to humans and animals and is therefore a very dangerous pollutant to our environment. Its presence in the tissues of wildlife has been studied in Sweden and found excessively high. The eggs of many wild birds do not hatch and numerous animals die because of mercury poisoning (1). Especially high mercury concentrations have been found in fish; older fish of larger size have relatively higher concentrations, which indicates that mercury accumulates in tissues (2, 3). This buildup of mercury in the biomass is a recent phenomenon (2).

One suspected source of pollution has been mercury-containing fungicides used in treatment of grain seeds. The treated seeds are highly poisonous to grain-eating birds and are available to them abundantly during the seeding seasons. However, the amounts used are much too small to explain high mercury contents in wildlife except in the graineating birds (2 to 3 mg per hectare of mercury every 4 to 5 years; 0.5 mg per metric ton of topsoil per year (4). A large part of the mercury found in the environment is apparently derived from industrially produced mercury, approximately 10,000 tons per year (5), most of which is eventually discarded in waste streams. However, another possible source of mercury could be fossil fuels and ores (other than mercury ores proper). Although the concentration of mercury in fuels is small (6), fuels are consumed at an enormous rate; consequently, they must be considered as a possibly significant source of mercury release into the environment.

The amount of mercury in coal is not well known. To obtain a preliminary value, 36 American coals were analyzed (Table 1) by means of a mercury vapor detector (7) that had been modified to eliminate organic vapors,

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which interfere in the detection process. In this procedure, the sample is burned in oxygen and the fumes are passed through hot (650° to 700°C) silver wire coils to complete the oxidation, after which a heated (150°C) gold amalgamator traps mercury while most of the other fumes pass through. To remove

Fable	1.	Mercury	content	of	36	American
coals.						

Locality (counties)	$\begin{array}{c} \mathrm{Hg} \\ (\times 10^{-9}\mathrm{g/g}) \end{array}$
Letcher (Ky.)	250
Knox (Ill.)	230
Saline (Ill.)	240
Northumberland (Pa.)	595
Northumberland (Pa.)	245
Northumberland (Pa.)	120
Richland (Mont.)	33,000
Pierce (Wash.)	510
Campbell (Wyo.)	18,600
Washington (Pa.)	240
Franklin (Pa.)	1,200
Franklin (Pa.)	10,500
Franklin (Pa.)	6,400
Franklin (Pa.)	4,900
Somerset (Pa.)	540
Somerset (Pa.)	340
Cambria (Pa.)	1,460
Nicholas (W. Va.)	6,540
Clay (W. Va.)	22,800
Clay (W. Va.)	3,700
Cambria (Pa.)	1,450
Cambria (Pa.)	460
Cambria (Pa.)	90
Cambria (Pa.)	630
Cambria (Pa.)	160
McDowell (W. Va.)	80
McDowell (W. Va.)	70
Jefferson (Ala.)	80
Jefferson (Ala.)	920
Harrison (Tex.)	380
LeFlore (Okla.)	110
Pitkin (Colo.)	220
Parke (Ind.)	310
Moultrie (Ill.)	210
Knox (Ill.)	90
Grundy (Ill.)	190

the remaining organics, mercury is released by heating and is re-amalgamated in a second trap; the mercury is again released by heating and is measured in the mercury vapor detector. Some organic fumes that pass through the first amalgamator are not completely oxidized and could cause some loss of mercury; also some mercury could be lost as oxide. Consequently, the values in Table 1 are biased on the low side.

The analyses were performed on a relatively small number of samples that are not representative; even within one deposit, the mercury distribution is probably not uniform. The mercury content of the Illinois coal samples that were analyzed (average,  $194 \times 10^{-9}$ g/g) is in good agreement with analyses done at the Geological Survey of Illinois (average,  $180 \times 10^{-9}$  g/g) (8). The average of the results (3.3 parts per million) can be hardly applied to the total coal production. If we apply a more conservative estimate of 1 part per million to the yearly world production of coal  $[3 \times 10^9$  tons per year (5)], we may conclude that 3000 tons of mercury per year are released to the environment by the burning of coal.

The mercury content of oils is not known and remains to be evaluated. The mercury content of ores (excluding mercury ores proper) is most likely higher than in coals. The tonnage of ores mined annually is, however, much smaller than that of coal.

The upper limit for the natural release of mercury due to chemical weathering can be estimated by comparison with corresponding figures for sodium. The sodium leached by weathering is almost completely carried to the sea by rivers,  $8 \times 10^7$  tons per year (runoff of rivers,  $3.2 \times 10^{13}$  tons per year; noncyclic sodium in river waters, 2.5 parts per million) (9). In the weathered rock masses, the ratio of mercury to sodium can be assumed to be the same as the ratio of their lithospheric abundances  $(2.8 \times 10^{-6})$  (6, 10), which yields an upper limit of 230 tons per year for leached mercury. The amount of mercury actually released is probably less than this estimate because proportionally more mercury than sodium is absorbed on clays, hydroxides, organics, and so forth.

The release of mercury into the environment during the combustion of coal is much larger than the amount released by weathering. Detailed studies of the distribution of mercury near power plants and other major users of