

D/H, $^{13}\text{C}/^{12}\text{C}$ AND $^{18}\text{O}/^{16}\text{O}$ ISOTOPE STUDIES OF MEGACRYST AND MATRIX MINERALS FROM LESOTHA AND SOUTH AFRICAN KIMBERLITES

S.M.F. SHEPPARD* AND J.B. DAWSON**

*Scottish Universities Research and Reactor Centre, East Kilbride, Glasgow, Scotland.

**Dept. of Geology, The University, St. Andrews, Fife, Scotland.

Hydrogen, carbon and oxygen isotope ratios were determined on phlogopite and serpentine megacrysts, unweathered matrix minerals and yellow altered kimberlite from diatremes in Lesotho (Kao, Matsoku) and South Africa (Monastery, New Elands, Wesselton) and dykes and a sill in Lesotho (Kaunyane) and South Africa (Benfontein, Du Plessis, Premier, Wesselton). In this study we try to (1) set limits on the variability of the D/H and C-13/C-12 ratios of deep-seated hydrogen and carbon, and (2) determine the extent and temperature of any isotopic exchange among the minerals of kimberlite and the country rocks and their associated formation waters.

Isotopic Analyses and Results

Well established analytical methods were used to extract hydrogen, carbon and oxygen quantitatively from minerals after removal of all absorbed or interlayer water at temperatures up to 200°C. Our overall analytical precision is better than ± 0.2 per mil for O-18/O-16 and C-13/C-12, and $\pm 2-3$ per mil for D/H. The majority of our results are presented in Figs. 1 and 2.

Discussion

The hydrogen and oxygen isotope data for the hydrous minerals can be divided into three distinct groups (Fig. 1). Except for the yellow kimberlite from the altered margin of the Benfontein sill (S 437) which plots close to the kaolinite line, none of our Group A and B samples have undergone hydrogen and oxygen isotopic exchange in a low temperature ($<50^\circ\text{C}$) surface or near-surface environment. Similarly all the carbonate data of Fig. 2 support this conclusion except, notably, S437.

All phlogopite megacrysts plot within the Group A field. These are 20 per mil or more enriched in D relative to the Group B serpentine megacrysts and the serpentine - mica matrix including samples from the same hand specimen (Monastery, Wesselton). Glimmerite samples plot within the Group A field. With no evidence to the contrary, Group A data support the proposal that isotopically deep-seated hydrogen is probably in the range - 40 to - 70 per mil and variable from one locality to another (Sheppard and Epstein, 1970)

Most Group B samples coexist with carbonates. These carbonates are enriched, in general, in O-18 relative to the primary igneous carbonatite field (Fig.2). Group B matrix and serpentine minerals are depleted in O-18 relative to "normal" ultramafic rocks (5.4 to 6.6‰, Taylor, 1968) even when corrected for their O-18 rich carbonate content ($<12\%$ by weight). If we assume that O-18 values were originally "normal"

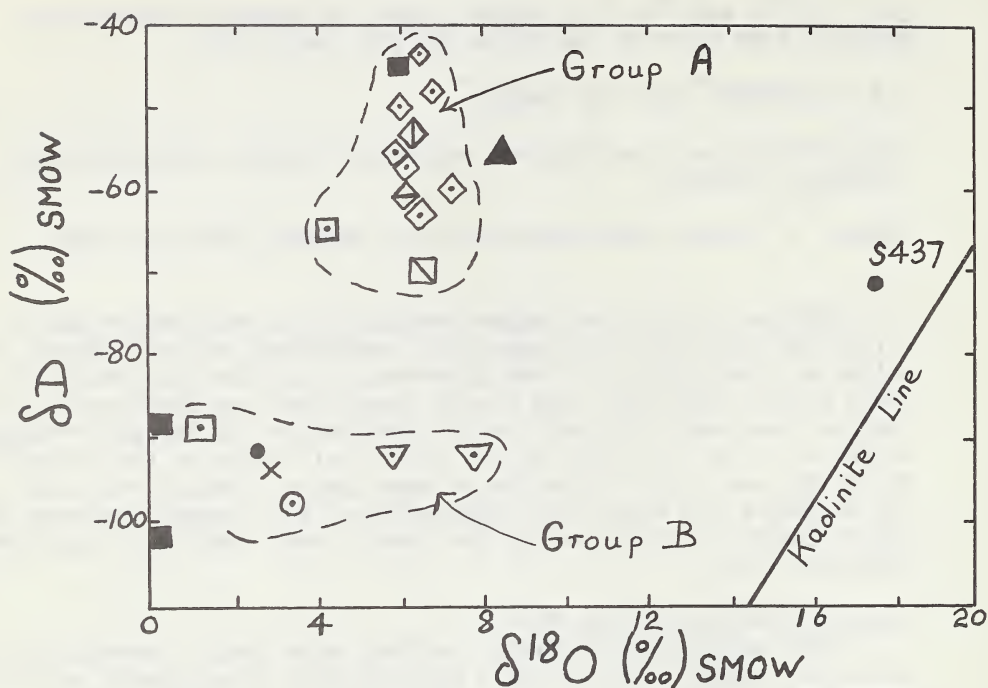


Fig. 1. The $\delta^{18}\text{O}$ vs δD diagram for hydrous minerals from kimberlites from the present study and Sheppard and Epstein (1970). Also plotted is the average δD value for uncontaminated volcanic gases (as water) from Surtsey, Iceland of Arnason and Sigurgeirsson (1968) combined with an assumed $\delta^{18}\text{O}$ value for magmatic water. The kaolinite line of Savin and Epstein (1970), representing the isotopic variation shown by kaolinites from surface weathering environments, is given for reference. Locality symbols are: ∇ Bachelor Lake, \bullet Benfontein, \odot Du Plessis, \diamond Dutoitspan, \square Panna, \diamond Phoenix, \diamond Central and Eastern United States, \blacksquare Wesselton, \blacktriangle Surtsey. * All Group A minerals are biotite-phlogopite megacrysts including glimmerites (Dutoitspan, Wesselton) from diatremes. Group B minerals include serpentine megacrysts (Monastery) and serpentine and/or mica from the kimberlite matrix of a sill, dykes and fragmental kimberlite. Group B $\delta^{18}\text{O}$ are carbonate free "whole rock" values. Group B Wesselton samples are δD values only. Benfontein S437 is yellow altered kimberlite.

* \times Kaunyane, \square Monastery.

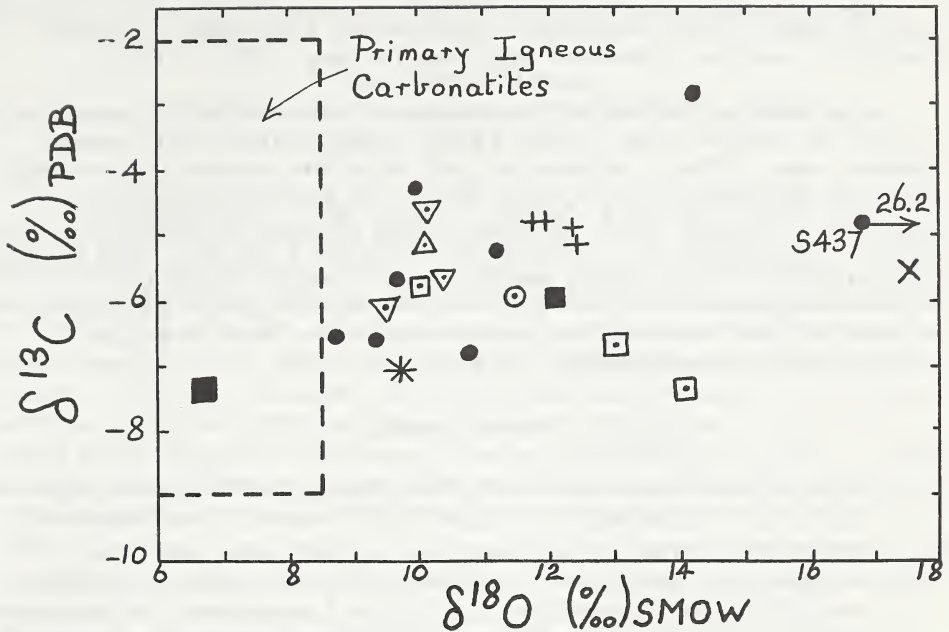


Fig 2. Plot of $\delta^{18}\text{O}$ vs $\delta^{13}\text{C}$ for calcites and dolomites from kimberlites from the present study and Dawson and Hawthorne (1973) compared with the probable field for primary igneous carbonatites (Sheppard and Dawson, 1973). Locality symbols are the same as Fig. 1 except Δ Matsoku, $*$ New Elands, $+$ Premier. The carbonates come from (1) the matrix of a massive black dyke (Wesselton), fragmental kimberlite, a sill and dykes, (2) carbonatite dyke in kimberlite (Premier), (3) carbonated granulite xenoliths (Monastery), and (4) yellow altered kimberlite (S 437).

then low temperature exchange between carbonate and serpentine-mica matrix is a necessary, but, in general, insufficient process to account for these data. Either loss of O-18 rich material, such as a CO_2 rich fluid, or exchange with a low O-18 reservoir, such as meteoric water, is required.

Assuming that the carbonate - serpentine-mica matrix minerals are approximately in equilibrium, then the observed 8 to 14 ‰ fractionations imply temperatures on the order of 150° to 75°C (Wenner and Taylor, 1973; O'Neil et al, 1969). At these temperatures, water in equilibrium with Group B assemblages are isotopically similar to meteoric waters with δD on the order of -40‰ and the O-isotope composition of the matrix is essentially controlled by the ground water reservoir.

A specific and more detailed interpretation of Group B samples and their O-18 data must await more refined studies because of the complexity of the mineralogy and observation of magmatic sedimentation

and flowage differentiation phenomena for some of these specific samples (Dawson and Hawthorne, 1970, 1973).

C-isotope ratios of carbonates are variable both within a single kimberlite (e.g. Benfontein) and among themselves. Their values are within the range for primary igneous carbonatites. This range is similar to that observed for diamonds (Craig, 1953; Vinogradov et al., 1965). Although the carbon isotope data do not conflict with a genetic relation among these carbon sources, a direct comparison may not be valid since the O-isotope ratios of the carbonates appear to have been modified during the post-magmatic processes.

Conclusions

1. The D/H ratios of phlogopite megacrysts (Group A) from 10 different kimberlites are from -40 to -70 per mil.
2. The D/H ratios of serpentine megacrysts and the serpentine-mica matrix (Group B) are 20‰ or more depleted in D relative to Group A, and may be depleted in O-18 by up to 4-5‰ relative to "normal" ultramafic values. Coexisting carbonates tend to be O-18 rich relative to primary igneous values.
3. Calcite-serpentine "isotopic temperatures" for Group B are 75° - 150°C.
4. Group B minerals including carbonates have been isotopically modified assuming "normal" initial O-18/O-16 ratios by either the loss of O-18 rich material (e.g. CO₂) or exchange with low O-18 meteoric waters at T > 75°C.

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