

# Evidence for stable isotope and chemical disequilibrium associated with diamond formation in the mantle

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## Introduction

Syngenetic inclusions in diamond have remained isolated from diffusive exchange since encapsulation and therefore record mantle conditions during diamond growth. These inclusions are too small for  $\delta^{18}\text{O}$  analysis using conventional fluorination techniques. Recent advances in laser ablation techniques for the microanalysis of oxygen isotopes in silicates has made possible the analysis of very small samples, either *in situ* or as single grains (see Matthey & Macpherson, 1993 and references cited therein). The technique developed by Matthey & Macpherson (1993) has been extended to include analysis of single grain diamond inclusions weighing between 40 $\mu\text{g}$  and 350 $\mu\text{g}$ . The  $\delta^{18}\text{O}$  data, when combined with microprobe and *REE* data for the same inclusions and  $\delta^{13}\text{C}$  data for the host diamond, act as very important tools in the understanding of chemical and isotopic processes which are operative during diamond formation.

## Methods

84 diamonds from Finsch Mine, RSA, were cracked open to release the inclusions. All inclusions weighing >40 $\mu\text{g}$  (below which the precision is unacceptable) were analysed for  $\delta^{18}\text{O}$  by laser fluorination (LF). Over the weight range of the inclusions the 'house' GP 143 garnet standard gives a mean  $\delta^{18}\text{O}$  of  $7.20 \pm 0.64\%$  (2sd,  $n=110$ ) compared to  $7.21 \pm 0.19\%$  (2sd,  $n=30$ ) for samples weighing >1mg. Smaller inclusions were grouped together for LF analysis based on the  $\delta^{13}\text{C}$  of the host diamonds being within 0.5‰ of each other. In this way it was possible to analyse 24 individual inclusions and 7 groups of inclusions from a total of 39 diamonds. Microprobe analyses were performed on the remaining small inclusions. A small fragment was saved for microprobe analysis if the larger inclusions fractured during release from the diamond. Fluoride residues were extracted after

the laser fluorination of 11 of the largest garnet inclusions and their *REE* concentrations analysed by isotope dilution (Thirlwall, 1982).

## Isotope results

$\delta^{13}\text{C}$  for the host diamonds fall in the range  $-8.4\%$  to  $-2.7\%$  for both peridotitic and eclogitic affinities, but the oxygen isotopes show significant variations between the two groups. The  $\delta^{18}\text{O}$  for peridotitic garnet and olivine inclusions fall in the range 4.6‰ to 5.6‰, with means of 5.00‰ and 5.25‰, respectively. The eclogitic garnets have higher and more variable values ranging from 5.7‰ to 8.0‰. Five additional peridotitic and eclogitic garnet inclusions from Kimberley, RSA, and Udachnaya, Siberia, also conform to the Finsch ranges.

## Comparison of laser fluorination (LF) nodule and inclusion data

High precision LF oxygen isotope data has been obtained for over 160 mantle nodules (see Matthey *et al.*, this volume). These data show that significant isotopic disequilibrium is rare (Matthey *et al.*, submitted), the notable exception, discussed here, is between olivine and garnet in rare diamondiferous peridotites and as inclusions in diamond. The peridotitic minerals, especially olivine, are essentially uniform in terms of  $\delta^{18}\text{O}$  values and inter-mineral fractionations. Garnet  $\delta^{18}\text{O}$  values in non-diamondiferous peridotites average  $5.43 \pm 0.05\%$  (2se,  $n=31$ ), but in diamondiferous peridotites this is  $5.21 \pm 0.12\%$  (2se,  $n=13$ ). The peridotitic garnet inclusions average  $5.00 \pm 0.21\%$  (2se,  $n=13$ ). For both diamondiferous peridotites and inclusions there is a group of values around 5.4‰, but the remainder have values <5.1‰. Many garnet inclusions are therefore more depleted in  $^{18}\text{O}$  than co-existing olivines (averaging 5.2‰ for both inclusions and nodules), which indicates that subtle disequilibrium effects

	(early forming?)				(late forming?)
	Garnet	Clinopyroxene	Garnet	Clinopyroxene	clinopyroxene
$\delta^{13}\text{C}$	-8.4‰	-8‰	-6‰	-6‰	-3‰
$\delta^{18}\text{O}$	+8.0‰		6-7‰	+5.9‰	+4.7‰
FeO (wt.%)	23	8.5	17-20	6.5	4.5
MnO (wt.%)	> 1.0	> 0.3	0.4-0.5	0.2	0.2
CaO (wt.%)	< 6	< 11	7-10	15	17.5
Jadeite component		> 40	30	15	

may be associated with the presence of diamond.

Eclogite nodules possess a range of LF  $\delta^{18}\text{O}$  values from 2.4‰ to 7.5‰.  $\delta^{18}\text{O}_{\text{gt-cpx}}$  values average 0.31‰. Non-diamondiferous eclogites have values covering the full range and a mean  $\delta^{18}\text{O}_{\text{gt-cpx}}$  of  $0.35 \pm 0.05\%$  (2se,  $n=31$ ). Most samples yield isotopic temperatures of 1000–1200°C. Diamondiferous eclogites are restricted to values  $> 4.7\%$  and have a mean  $\delta^{18}\text{O}_{\text{gt-cpx}}$  of  $0.25 \pm 0.05\%$  (2se,  $n=24$ ). Most yield unrealistically high isotopic temperatures because of the small fractionations and may represent disequilibrium assemblages. All the eclogitic garnet inclusions have  $\delta^{18}\text{O}$  values which are heavier than the LF values for garnets in peridotitic mantle.

### Discussion

The disequilibrium effect whereby the oxygen isotopic composition of garnets in diamondiferous peridotites and diamonds changes from equilibrium values of 5.4–5.6‰ to lower values is related to both *LREE* enrichment and changing Ca content. Using a simple Rayleigh fractionation model for formation of the Finsch peridotitic diamonds from a single  $\text{CO}_2$ - or carbonate-bearing fluid indicates that the diamonds with the heaviest  $\delta^{13}\text{C}$  values ( $\approx -3\%$ ) were the last to form. This enrichment in  $^{13}\text{C}$  corresponds with an enrichment in Ca and depletion in  $^{18}\text{O}$  in the garnet inclusions. The end result of these chemical changes are the presence of rare diopside inclusions only in the heaviest diamonds (noted also at Premier and Koffiefontein by Deines *et al.*, 1984, 1991). A diopside inclusion from Finsch also has the lightest  $\delta^{18}\text{O}$  value of 4.1‰. In addition the Fe content of olivines increases with changing  $\delta^{13}\text{C}$  from  $\text{Fo}_{94}$  for -6‰ diamonds to  $\text{Fo}_{91}$  for a -3‰ diamond.

The eclogitic diamonds and inclusions from Finsch show many similar chemical changes to the peridotitic inclusions. Eclogitic garnet inclusions with heavy  $\delta^{18}\text{O}$  values (7.5–8.0‰) and inclusions in diamonds with  $\delta^{13}\text{C}$  lighter than -6.5‰ have extreme chemistry (see table) which is not matched by the chemistry of any nodules from the literature or this study. The chemistry of these garnets and clinopyroxenes is matched only by inclusions in the group of  $^{13}\text{C}$ -depleted diamonds from Roberts Victor (Deines *et al.*, 1987). Increasing  $^{13}\text{C}$ -

enrichment in the diamonds and decreasing inclusion  $\delta^{18}\text{O}$  are associated with Ca enrichment and Fe and Mn depletion in the inclusions. This culminates with eclogitic diamonds containing clinopyroxene of close to diopside composition (only 15% jadeite component, see above).

These chemical changes again suggest the interaction of the eclogite with a  $\text{CO}_2$ - or carbonate-bearing fluid during diamond growth. The *REE* profiles of the eclogitic garnet inclusions are flat to slightly *LREE* depleted, similar to MORB profiles. The high  $\delta^{18}\text{O}$  values for these inclusions also have affinities with upper layers of oceanic crust. The  $\delta^{13}\text{C}$  values provide no indication of a source and all Finsch diamonds could have formed from a mantle-derived fluid.

### Conclusions

Isotopic and chemical disequilibrium characteristics are retained in some (early formed) peridotitic and eclogitic inclusions in Finsch diamonds. This disequilibrium may have resulted from the initial interaction of the host lithologies with the infiltrating diamond-forming fluid. With time the fluid and host would move toward equilibrium, the trapped inclusions representing snapshots of this process. These continuing changes in the host rock could account for many of the anomalies in chemistry between the inclusions and diamondiferous nodules, such as Ca content in peridotitic garnets. It is also possible that much of the observed disequilibrium in diamondiferous peridotite nodules results from a later fluid interaction, perhaps associated with movement and accumulation of proto-kimberlite melts. Detailed oxygen isotope and chemical profiles across zoned sub-calcic garnets are required to strengthen the inclusion-nodule disequilibrium relationships and further develop the model. The overall tendencies during the period of diamond growth are toward  $^{18}\text{O}$ -depletion,  $^{13}\text{C}$ -enrichment and Ca-enrichment in garnet and pyroxene inclusions of both peridotitic and eclogitic affinity at Finsch. This suggests that a common process, possibly involving exchange reactions between host rock and a carbonate-rich fluid, was involved during the major period of diamond growth.