

D.P. Matthey, C.T. Pillinger and M.A. Menzies\*

Department of Earth Sciences, The Open University, Walton Hall, Milton Keynes MK7 6AA, U.K.; \* Royal Holloway and Bedford New College, Egham, Surrey, U.K.

## INTRODUCTION

The stable isotopic compositions of both carbon in  $\text{CO}_2$  ( $\delta^{13}\text{C} = -9$  to  $-15$ ‰ rel. to PDB) and hydrogen in  $\text{H}_2\text{O}$  ( $\delta\text{D} = -32$ ‰ to  $-46$ ‰ rel. to SMOW) in back arc basin basalts are different from normal mid-ocean ridge basalts ( $\delta^{13}\text{C} = -6.5$ ‰ and  $\delta\text{D} = -80$ ‰, respectively) [1,2]. This observation provides important evidence for recycling of volatile components from subducted lithosphere and suggests that light element isotope ratios potentially act as sensitive tracers of recycled crustal components in mantle processes. The ubiquitous presence of fluid inclusions in mantle minerals offers a direct means of studying the relationship between mantle volatiles and the petrology and geochemistry of host nodules and magmas. We have used stepped heating, vacuum crushing and high sensitivity mass spectrometry to measure the abundance and isotopic composition of  $\text{CO}_2$  in diopsides separated from exceptionally well preserved mantle nodules.

## SAMPLE LOCALITIES AND ANALYTICAL TECHNIQUES

Carbon abundances and isotope ratios have been determined on diopsides previously characterised for He, Sr, Nd abundances, and  $^3\text{He}/^4\text{He}$ ,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios. Host magmas include kimberlite, carbonatite and a variety of orogenic and anorogenic basaltic hosts from the following localities: 1. Buffontein, South Africa (micaceous garnet lherzolites in kimberlite host); 2. Bullenmerri Maar, Victoria, Australia (garnet lherzolites in basalt host); 3. Foster Crater, Antarctica (pyroxenites and glimmerites in basanite host); 4. Lashaine, Tanzania (garnet lherzolite, pyroxenite in ankaramite, carbonatite host); 5. Auvergne, France (spinel lherzolite in basanite host); 6. Ichinomegata, Japan (spinel lherzolite in basalt host); 7. Geronimo Volcanic Field, Arizona, USA (spinel lherzolite, pyroxenites in basanite host).

Handpicked diopside grains (5-15 mg) were ultrasonically cleaned in 2M HCl, distilled water and dichloromethane, dried at  $110^\circ\text{C}$ , and then degassed in the vacuum system at  $150^\circ\text{C}$  to  $10^{-6}$  torr. Carbon was released from the sample by stepped heating in 1 atmosphere of pure oxygen in  $100^\circ\text{C}$  steps from  $300^\circ\text{C}$  to  $1300^\circ\text{C}$ . Carbon isotopes were measured on  $\text{CO}_2$  using a triple collector static vacuum mass spectrometer to a precision of better than  $\pm 1$ ‰.

## RESULTS

Stepped heating clearly resolves two isotopically distinct carbon components in all the samples. The first component dominates the release profile and is released by oxidation with a maximum release peak at  $400^\circ\text{C}$ . This component has a uniform isotopic composition ( $-28 \pm 2$ ‰) and is believed to be surficial organic contamination. A second isotopically distinct component is released at higher temperatures, usually above  $800^\circ\text{C}$ . This form of carbon is indigenous and may be derived from a number of possible sites. These include 1)  $\text{CO}_2$  (and possibly CO and  $\text{CH}_4$ ) released by the decrepitation of fluid inclusions; 2) molecular  $\text{CO}_2$  (or other gaseous carbon species) contained within the diopside lattice; 3) decomposition of carbonate species, existing within the lattice, as veins or as daughter crystals in fluid inclusions; 4) oxidation of reduced carbon (eg. graphite).

Combined pyrolysis/combustion heating experiments suggest that elemental carbon or CO are not present in the samples studied and that  $\text{CO}_2$  is the principle species released. The source of this  $\text{CO}_2$  is probably from fluid inclusions, or from the lattice. Vacuum crushing experiments confirm that the contents of the pseudo-secondary and secondary fluid inclusions which characterise some samples are pure  $\text{CO}_2$ . Other samples do not contain visible fluid inclusions, do not produce  $\text{CO}_2$  on vacuum crushing and yet release significant quantities  $\text{CO}_2$  at high temperatures ( $> 1000^\circ\text{C}$ ). This carbon must exist as molecular  $\text{CO}_2$  (or  $\text{CO}_3$ ) within the diopside lattice. In general, the origin of  $\text{CO}_2$  released at high temperatures is most likely to be lattice  $\text{CO}_2$ , with a variable contribution from fluid inclusions, according to their abundance, size, and dimensions of their host mineral grain.  $\text{CO}_2$  from fluid inclusions appears to be released over a wide temperature range, and can partially be masked by the low temperature contamination release ( $200^\circ\text{C}$  to  $600^\circ\text{C}$ ). However, carbon released at high temperatures by stepped heating is wholly indigenous, dominantly released from the diopside lattice, and could be closely associated with the crystallisation environment of the diopside.

Carbon abundances, measured by stepped heating or by vacuum crushing can be subject to large errors because of uncertainties as to the efficiency of the extraction technique. Nevertheless, carbon abundances reveal surprisingly good correlations with He and rare earth element (REE) abundances.

Figure 1 is a plot of C versus He for Bullenmerri samples and shows that amphibole bearing xenoliths with elevated  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.7040-0.7065) have high C/He ratios; diopsides from anhydrous lherzolites and pyroxenites with lower, uniform  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.7037-0.7040) have low C/He ratios. Whereas  $^3\text{He}/^4\text{He}$  ratios in diopsides from Bullenmerri are relatively uniform ( $R/R_A = 6 - 10$ ) and are completely decoupled from  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios [3], the C/He and carbon isotope ratios indicate that fluids from different sources are associated with hydrous and anhydrous mantle facies.

Carbon versus Nd for all samples is plotted in Figure 2 (note log-log scale) and shows a broad positive correlation. Diopsides hosted by kimberlite from Bulfontein (South Africa) are amongst the most carbon rich (10 ppm to 425 ppm) and have high C/Nd ratios. Diopsides from Bullenmerri (Australia), Auvergne (France), Foster Crater (Antarctica) and Geronimo (Arizona) generally contain less C (1 ppm to 62 ppm) with a range of lower C/Nd ratios. Light REE enriched diopsides (with Sm/Nd ratios < 0.33) are generally carbon rich and light REE depleted diopsides contain less than 3 ppm C which suggests that under certain circumstances  $\text{CO}_2$  and the light rare earth elements may be coupled.

### C-Nd isotopes in diopsides

Carbon isotopes measured in this study vary from -3‰ to -32‰, but with most data typically falling within the range -8‰ to -12‰.  $\delta^{13}\text{C}$  values appear to vary systematically with REE abundances,  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  particularly in diopsides from Bulfontein and Bullenmerri. Figure 3 shows a plot of  $\delta^{13}\text{C}$  versus  $^{143}\text{Nd}/^{144}\text{Nd}$ . Carbon in diopsides from Bulfontein varies from -8.5‰ to -13‰ and shows a positive correlation with  $^{143}\text{Nd}/^{144}\text{Nd}$ . Similar trends are apparent for diopsides from hydrous and anhydrous lherzolites from Bullenmerri, implying that the trace element enrichment events thus preserved are associated with isotopically light carbon.

### DISCUSSION

Isotopically variable  $\text{CO}_2$  ( $\delta^{13}\text{C}$  ranging from -31‰ to -3‰) occurs in mantle environments closely related to active or recent subduction (eg. back arc basins [1], Ichinomegata and Geronimo (Figure 3)) which strongly implicate a sedimentary carbon component derived from the subducted slab. This isotopic variation (approximately 30 ‰) approaches the range in limiting compositions of carbon in pelagic sediments (ie. organic carbon to marine carbonate). Although diamonds display a similar range in carbon isotopes the variation so far observed in diopsides representing subcontinental lithosphere is more restricted (-8‰ to -15‰) and slightly lower than typical MORB  $\delta^{13}\text{C}$  values. Fluid compositional heterogeneity found within nodule suites and even within single grains, and decoupling of  $^3\text{He}/^4\text{He}$  from solid chemistry and other fluids requires several sources, with at least one source having close affinities with MORB.

A possible interpretation of the C-He-Nd data is that subcontinental lithosphere preserves relict carbon isotope heterogeneity, possibly primordial, but more probably related to ancient subduction events, which has either overwritten, or has been overwritten by, other fluids with MORB-source characteristics.

### References:

1. Mathey D.P., Carr R.H., Wright I.P and Pillinger C.T., 1984. Carbon isotopes in submarine basalts. Earth and Planetary Science Letters, 70, 196-206.
2. Poreda, R., 1985. Helium-3 and deuterium in back-arc basalts: Lau Basin and the Mariana Trough. Earth and Planet. Sci. Letts., 73, 244-254.
3. Porcelli, D.R., O'Nions, R.K. and O'Reilly, S.Y., 1986. Helium and strontium isotopes in ultramafic xenoliths. Chem. Geol., in press.

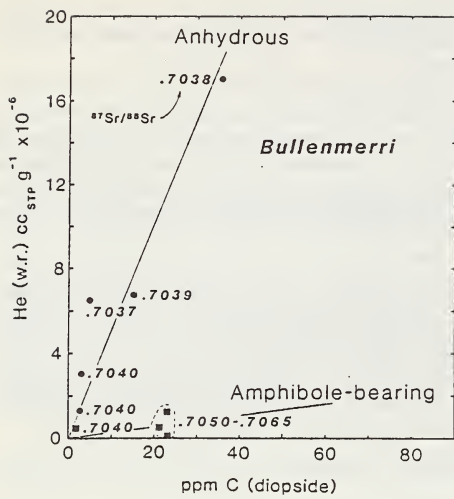


Figure 1

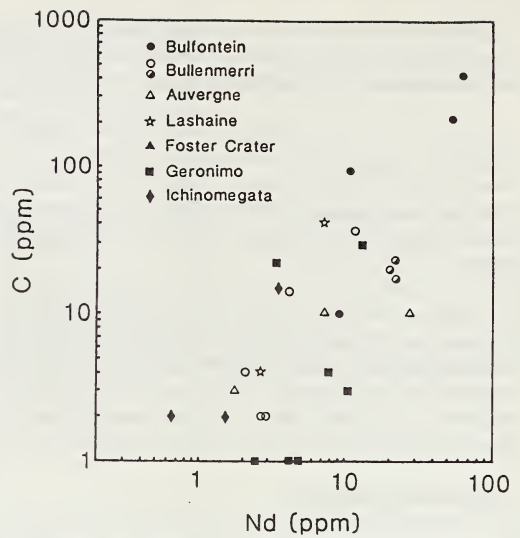


Figure 2

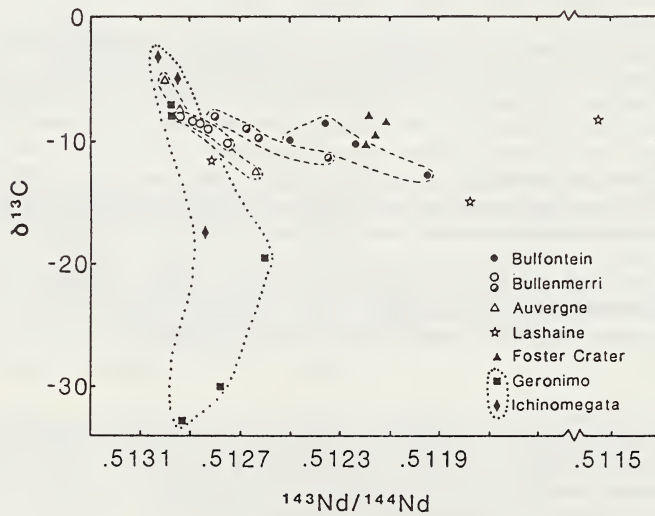


Figure 3