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REVIEWS

The carbon isotope geochemistry of mantle xenoliths

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Abstract

Carbon occurs in mantle samples in several chemical, mineralogical and morphological forms. It has been observed as CO_2, CH_4 and CO in fluid inclusions, as carbonate, graphite, diamond, moissanite, solid solution in silicates, and organic compounds. The total carbon concentration reported for mantle xenoliths varies by four orders of magnitude from below 1 ppm to close to 10 000 ppm. About 40% of these samples contain less than 50 ppm, 70% less than 100 ppm and 95% less than 500 ppm C. Carbon with $\delta^{13}C$ of about $-5‰$ has been identified as a major isotopic composition signature for the mantle (carbonatite and kimberlite carbonates, diamonds and volcanic CO_2 exhalations); it is also observed in mantle xenoliths. However, there may also be a minor signature of C depleted in ^{13}C ($\delta^{13}C = -22‰$ to $-26‰$). Such light carbon has been observed in the dissolution residue of mantle minerals (olivine, pyroxene) and rocks, C fractions that have been interpreted as C dissolved in silicates, in diamonds, graphite, carbide, and hydrocarbons which are thought to be indigenous to the mantle. The data on xenoliths from basalts indicate that their $\delta^{13}C$ distribution is essentially bimodal with peaks at $-5‰$ and $-25‰$ although the geologic occurrence of this light carbon has not yet been clearly delineated. Xenoliths from both hotspot and non-hotspot volcanoes cover the whole C isotopic composition range observed in mantle xenoliths; however, on average, xenoliths from non-hotspot volcanoes contain isotopically lighter carbon. Xenoliths from kimberlites cover the whole isotopic composition range as well, but, on average, probably show the lowest degree of ^{13}C depletion. In addition, the second, low $\delta^{13}C$, mode may occur just above $-20‰$, coincident with the low ^{13}C mode of southern African diamonds. Differences in the C concentration and isotopic composition have been observed between mantle minerals. The data are too few, however, to support firm conclusions on their size, or on how systematic these differences might be. Chemically more fractionated xenoliths tend to have higher $\delta^{13}C$ values than less chemically fractionated ones. Processes that have been considered to be responsible for the considerable $\delta^{13}C$ range in mantle C include the subduction of organic material and degassing. The observations on mantle xenoliths do not provide support for either, but indicate that as yet unexplored thermodynamic isotope effects, probably involving dissolved C in minerals and Si–C bonds, may be responsible for the observed mantle carbon isotope distribution. The occurrence of such isotope effects would help to understand a number of observations on the carbon isotope geochemistry of diamonds. In so far as mantle-degassing models have been based, in part, on the carbon isotopic composition and $C/^3He$ ratios, an understanding of the mantle carbon isotope geochemistry is essential to support or refute their validity. The xenolith data do not support degassing models based on the assumption of limited indigenous carbon isotope variability within the mantle, nor the supposition that all ^{13}C depleted carbon is of surface origin. The relative proportions of mantle C's of differing isotope signature are not known; they will have to be established for well-founded C cycle models to be developed. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Rates of carbon degassing for the Earth have been deduced from the carbon isotope record of volcanic gases, mainly CO_2, in conjunction with He isotopic composition measurements, the determination of their $C/^3He$ ratio and He degassing rates. The gas compositions have been interpreted (e.g. Sano et al., 1997) to be the result of mixing of three components: sedimentary carbonate — organic carbon — mantle carbon. A compilation of volcanic gas data is shown in Fig. 1 along with the expected mixing relationships of these three components. The relative proportions of the three end members are shown in Fig. 2. The collective data appear to indicate a very low contribution of mantle C to volcanic CO_2. One can expect that the relative size of the three components should vary with tectonic setting. A statistical analysis of the ava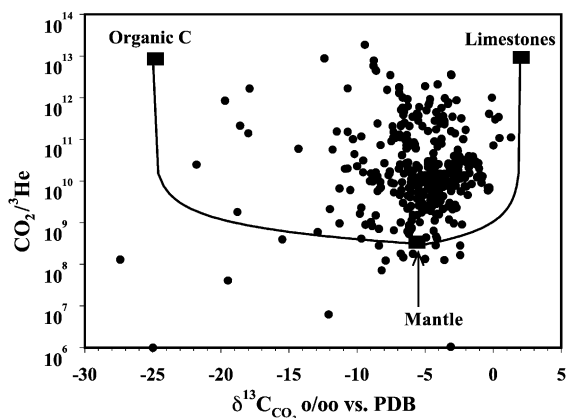ilable data (Table 1) shows, however, that this is not the case. These very surprising results lead one to question the assumptions underlying model computations which include the supposition that the only source of ^{13}C-depleted C in the mantle is organic material, produced by biologic process at the Earth's surface, and subducted into the mantle. It is the aim of this paper to examine this particular assumption.

2. The chemical forms and concentrations of carbon in mantle xenoliths

2.1. Chemical forms

Carbon from mantle samples has been recognized to be present in several oxidation states and chemical and mineralogical forms. These include:

Oxidized C species:	CO_2: in fluid inclusions;
	Carbonates: within fluid inclusions and interstitially;
Neutral C species:	Graphite: in thin films on mineral surfaces, and in cracks as grains; Diamond; Solid solution C: in the crystal lattice of silicates;
Reduced C species:	Organic compounds: on cracks and mineral surfaces and in inclusions; Gaseous Species (CH_4, CO): in inclusions; Moissanite (SiC): in kimberlite matrix and inclusion in diamond.

2.1.1. Oxidized forms of C

2.1.1.1. CO_2. Primary CO_2-rich inclusions in mantle minerals were first recognized by Roedder (1965) and their contents have been typically interpreted as representing mantle fluids trapped during the formation of the minerals. Alternatively, Green and Radcliffe (1975) proposed that the presently observed inclusions were formed secondarily by exsolution and trapping of volatiles originally dissolved in the min-

Fig. 1. Three component mixing model (limestone–sedimentary organic C–mantle C) for volcanic gases based on $CO_2/^3He$ ratio and carbon isotopic composition. The solid line represents binary mixing between mantle and limestone and organic carbon, respectively. Analyses between the binary mixing lines require mixing of three components. The data are from: Allard et al. (1997), Chivas et al. (1987), Fischer et al. (1998), Goff and Janik (1993), Hammouya et al. (1997), Hilton et al. (1998a,b), Ishibashi et al. (1994), Marty and Giggenbach (1990), Marty et al. (1989, 1991), Merlivat et al. (1987), Minissale et al. (1997), Ono et al. (1993), Pedroni et al. (1999), Sano and Marty (1995), Sano and Williams (1996), Sano et al. (1985, 1994, 1995, 1998), Sorey et al. (1998), Sturchio et al. (1993), Taran et al. (1992), Tedesco (1996a,b), Tedesco and Scarsi (1999), Tsunogai et al. (1994), Varekamp et al. (1992), Weinlich et al. (1999), Welhan et al. (1988), Yokoyama et al. (1999).
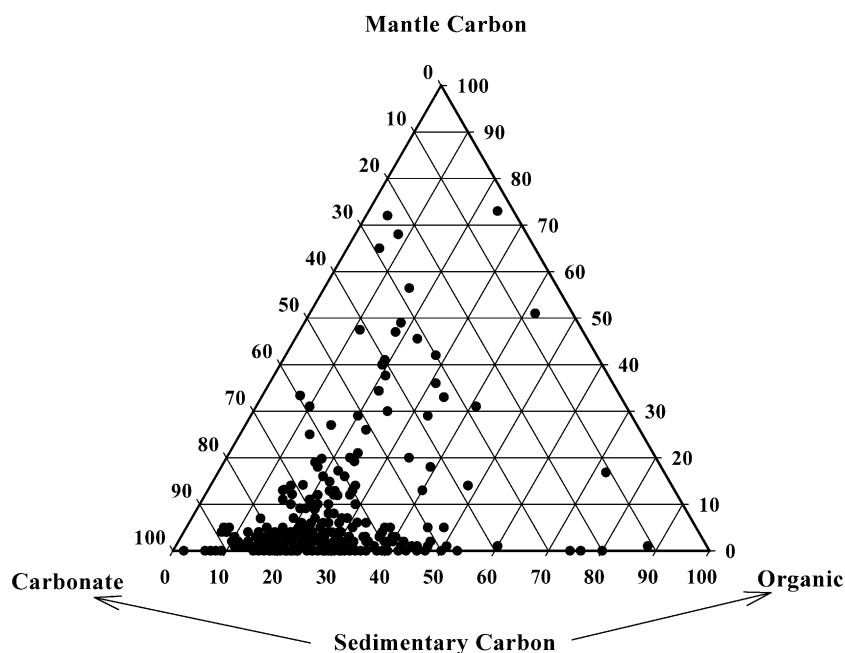
Mantle Carbon

Fig. 2. Relative contributions of sedimentary and mantle carbon components in volcanic gases based on a three component mixing model. The assumed end member compositions (δ^{13}C, $CO_2/^3$He) and sources of data are those of Fig. 1.

erals. The fact that CO_2 is a major constituent of inclusions has been confirmed by a number of authors since then (e.g., Bilal and Touret, 1976; Murck et al., 1978; Touret and Bilal, 1978; Bergman 1981, 1982; Andersen et al., 1984, 1987; Bergman and Dubessy, 1984; Roedder, 1984). In addition, Schrauder and Navon (1993) discovered solid CO_2 in a diamond at

a pressure of 5 GPa, indicating a trapping depth of 220 to 270 km.

2.1.1.2. Carbonates. While carbonates are stable under mantle conditions (Wyllie, 1978; Olafsson and Eggler, 1983), they are rarely encountered in mantle xenoliths. However, carbonates have been observed in

Table 1
Results of model computations for carbon sources in volcanic gases

Setting	Statistic	% Organic	% Carbonate	% Mantle	Carb./Org.
Hotspots, $n = 24$	Mean	21	65	13	3.0
	std	8	17	17	
Divergent margin, $n = 12$	Mean	18	56	26	3.1
	std	6	20	23	
Continental extension, $n = 88$	Mean	25	69	6	2.8
	std	9	14	12	
Convergent margin, $n = 88$	Mean	26	70	4	2.7
	std	13	16	10	

The chosen model parameters ($\delta^{13}C_{mantle} = -5\text{‰}$, $CO_2/^3He_{mantle} = 3 \times 10^8$, $\delta^{13}C_{carbonate} = 2\text{‰}$, $CO_2/^3He_{carbonate} = 1 \times 10^{13}$, $\delta^{13}C_{organic} = -25\text{‰}$, $CO_2/^3He_{organic} = 1 \times 10^{13}$) maximize the mantle contribution for the hotspot samples while fitting all but one sample to the three component model. $n = $ is the number of samples, std = one standard deviation.

mantle-derived garnets, phlogopites, chrome-diopsides and in fluid inclusions in olivine and diamond (McGetchin and Besançon, 1975; Pineau and Javoy, 1975; Rovetta and Mathez, 1982; Andersen et al., 1984; Hervig and Smith, 1981; Smith, 1987; Ionov et al., 1993; Navon et al., 1988). Although carbonate derived from carbonate-rich surface waters may occur in mantle xenoliths, there is no doubt that some carbonates observed in high temperature peridotites are of mantle origin. The composition of the carbonate inclusions is quite variable; while some are Mg- and Fe-rich, others are pure $CaCO_3$ (e.g., McGetchin and Besançon, 1975). Although carbonates are stable under mantle conditions, they do not necessarily remain stable during transport from the mantle to the surface. Berg (1986a,b) has interpreted the brucite/calcite intergrowths in peridotite nodules to represent dolomite from the mantle, metamorphosed by decompression. The reaction may be simplified as:

$$CaMg(CO_3)_2 = CaCO_3 + MgO + CO_2.$$

Gurney (1989) suggested that such a decarbonation reaction could lead to the destruction of carbonate-bearing diamond harzburgites during kimberlite eruption. A different view has been offered by Schulze (1995). The dissociation of carbonates during their removal from the mantle is indicated by the experimental data of Wyllie et al. (1983) (for a review, see Wyllie, 1995).

2.1.2. Neutral C

2.1.2.1. Graphite and diamond.
Carbon in the neutral oxidation state is observed in mantle xenoliths as graphite and diamond and it has been proposed to occur dissolved in minerals (Freund et al., 1980). While eclogites containing diamonds are recovered from kimberlites reasonably frequently, there are only few examples of diamondiferous peridotites. This is surprising, since diamond harzburgites should be the most common diamond host rock in the mantle, judging by the inclusion parageneses most often observed in diamonds, which is peridotitic. Part of the answer to this paradox may lie in the disaggregation of diamondiferous peridotites upon transport to the surface. However, detailed comparisons of xenolith and diamond inclusion chemistry have shown that dia-

monds occurring free in a kimberlite may not necessarily be related directly to diamonds, occurring in mantle xenoliths in the same pipe (Viljoen et al., 1992; Deines et al., 1993).

2.1.2.2. C dissolved in minerals.
The question whether C can be dissolved in upper mantle minerals in the neutral form continues to be debated. Following the observation of submicroscopic inclusions in olivine, this possibility was raised (Green, 1972, 1985; Green and Guegen, 1983). Among the forms in which C occurs in mantle minerals, dissolved carbon is the most difficult to characterize, because it may be present uncharged in interstitial solid solution and would be difficult to detect by spectroscopic or nuclear magnetic resonance methods. Freund et al. (1980) and Freund (1986a,b and references cited there) have suggested that C occurs interstitially or in cation vacancies in mineral lattices. They also proposed that this form of C has relatively high concentrations, has a high mobility in the lattice, and has a tendency to segregate toward crystal surfaces. During the release of this C from the mineral, as a result of decreased solubility due to changes in pressure and temperature, the atomic C would be oxidized by oxygen produced through the decay of OH^- ($2OH^- \Rightarrow O^{2-} + H_2$), also contained in the mineral. While Freund et al. made their original observations on MgO, CaO and SrO, subsequently they extended their work to include olivine for which similar, high C solubility and mobility were proposed. Mathez et al. (1984a), Tsong et al. (1985), and Tsong and Knipping (1986) could not duplicate the earlier results of Freund et al. for olivine. Mathez et al. (1984b) also suggested that the high concentration of C (425 ppm), detected by them in one of the olivine crystals they studied, was due to the presence of submicroscopic inclusions of C on microcracks, rather than C dissolved in the olivine. Additional data on carbon solubility in olivine were published by Tingle and Green (1987) and Tingle et al. (1989) who found that at 1 GPa and 1200 °C, C solubility is below 30 ppm but that C dissolves in excess of 100 ppm at 3 GPa at 1180 to 1530 °C. The authors also observed that while at ambient conditions the diffusivity of C is very low, diffusion at elevated temperatures and pressures is sufficiently high, that depressurization of olivine would cause exsolution of carbon from the mineral. The results obtained by these

authors indicate that mantle minerals, which are nominally volatile free, may constitute a significant C reservoir in the mantle. Hence, while uncertainty exists about the degree to which neutral C can enter olivine, there is experimental evidence that this form of carbon can occur in olivine in excess of 100 ppm at mantle pressures and temperatures. (As part of the review E.A. Mathez has pointed out that he, in cooperation with T.N. Tingle, had made a start at confirming these measurements, which they were unable to do. The results may hence be more uncertain than is apparent from the published literature). For other important mantle minerals such as garnet and pyroxene, the C solubility has not been investigated.

2.1.3. Reduced C

2.1.3.1. CH_4 and CO. While CO_2 is a major constituent of many of the fluid inclusions in mantle minerals, carbon in a reduced state has also been observed; such forms include CH_4 (Melton et al., 1972; Melton and Giardini, 1974), COS (Murck et al., 1978), CO (Bergman and Dubessy, 1984) and hydrocarbons (Tomilenko et al., 1995).

2.1.3.2. Organic compounds. Tomilenko et al. (1995) studied fluid inclusions in diamonds from placers in northeastern Siberia, pyropes from websterite xenoliths from the Mir pipe (Yakutia), and garnet in eclogites from Udachnaya and Obazhenaya (Yakutia). They found that the inclusions in diamonds are located on annealed cracks that do not extend to the surface of the mineral. Along the cracks, graphite occurs. Based on IR spectra and inclusion homogenization temperatures, the authors claimed to have identified *n*-alkanes (C_5 to C_{11}) in some of the inclusions.

The presence of organic compounds on the surfaces of mantle minerals was suggested by Mathez et al. (1984b). While most of the C exists as inclusions of CO_2-rich vapor, it also occurs in all xenoliths (basalt or kimberlite host) as grains and films of carbonaceous matter. Xenoliths from kimberlites (peridotites as well as eclogites) are found to be C-rich compared to those from basalts. The C occurs in xenoliths from kimberlites as calcite or carbonaceous matter associated with serpentine veins and is thought to have been contributed by the kimberlite host. This mantle xenolith C was further characterized by Mathez (1987)

who observed that the films consist of a complex mixture of organic and possibly graphitic compounds and may include alcohols, organic acids or other compounds that are unstable at high temperatures. The cracks were formed during cooling, and the newly formed active surfaces may have facilitated the abiotic formation of the carbonaceous films and carbon compounds from hot volcanic gases. The low temperature compounds are thought to have formed from the high temperature carbon precipitates during cooling. The carbon in cracks observed in the xenoliths is hence considered to be a contaminant from the hosting basaltic or kimberlitic lava and not indigenous to the xenoliths. Similar observations were made by Tingle et al. (1990, 1991) for single crystals of olivine from San Carlos, Arizona, and the Hualalai Volcano, Hawaii, and on peridotite xenoliths and basalts from the Hualalai Volcano, diopside magacrysts from the Jagersfontein kimberlite, and gabbros from the Stillwater and Bushveld intrusions. Carbon compounds on mineral surfaces were characterized by Mathez and Mogk (1998) using time of flight secondary ion mass spectrometry. The pyroxenes from gabbro xenoliths (Haulalai, Hawaii) are covered with indigenous hydrocarbon-rich surface layers in which light C_xH_y fragments as well as molecules of several hundred atomic mass units were detected. In addition to the elements H and C, the major elements (Si, Al, Fe, Mg and Ca) as well as minor and trace elements (B, Li, Na, Ti, Mn, Co, Ni, and Cu) were observed in the layers. The high concentrations of Ni and Cu associated with C suggested to the authors the presence of organometallic compounds; C–N fragments were detected as well.

While most of the cracks in mantle xenoliths on which the carbon films exist appear to have formed during the cooling of their host magma, Pineau and Mathez (1990) described cracks in minerals in websterites that appear to have been partially annealed before the xenoliths were incorporated into the transporting magma. It would follow then that C which occurs in these megascopic inclusion zones would have been introduced into the xenoliths in the mantle and would hence provide more direct information about mantle carbon.

From the perspective developed in theses papers, the interpretation of the $\delta^{13}C$ of C on cracks in mantle xenoliths would need to consider the $\delta^{13}C$ of the host

lava, the isotope fractionation during the precipitation of C from the vapor phase of the basaltic, or kimberlitic melt, as well as the subsequent modification of the isotope composition in the formation of carbon compounds at low temperatures. A comprehensive analysis considering these multiple causes of carbon isotope variability has not been published. The precipitation of the C on the surfaces would also have implications for the local redox conditions, because these must be reducing enough to make the observed carbon compounds stable. The mechanism of C reduction and the attendant isotope effects remain to be investigated.

In contrast to the low temperature origin of hydrocarbons suggested by earlier investigators, Sugisaki and Mimura (1994) proposed that the higher hydrocarbons observed by them in mantle samples are indigenous to the mantle. These authors suggested that the stability of higher hydrocarbons increases with pressure and that they decompose to CH_4 at the lower pressures prevailing when magmas intrude into the crust. The proposed change in the stability of the hydrocarbon compounds with P and T thus would thus resemble that of the carbonates discussed above.

The effect of pressure on chemical equilibria is related to the volume change in a reaction:

$$\left(\frac{\delta\ln K}{\delta P}\right)_T = -\frac{\Delta V}{R \times T}$$

where K is the equilibrium constant, P is pressure, ΔV is the volume change in the reaction, R is the gas constant and T is the temperature in K. Because hydrocarbon generation from elemental carbon can have negative volume changes, their stability would be enhanced through an increase in pressure. This effect has been exploited, e.g., in the synthesis of organic compounds (see, e.g., Klärner et al., 1996). Thermodynamic modeling of the stability of compounds in the system C−H−N−S−O by Zubkov et al. (2000) indicates that heavy hydrocarbons are stable in the upper mantle and that they will decompose under the formation of CH_4 upon decompression. Tomilenko et al. (1998) observed methane and other higher-molecular hydrocarbons in inclusions in diamonds synthesized in the diamond stability field, demonstrating the stability of hydrocarbons under mantle pressure and temperature conditions. There is hence observational and theoretical as well as experimental evidence sug-

gesting that there may be more "organic geochemistry" taking place in the mantle than has been generally assumed.

2.1.3.3. Moissanite. Reduced C occurs in the mantle also in moissanite (SiC). The mineral has been identified from a wide range of mantle conditions and has been separated from mineral concentrates of kimberlites and lamproites (e.g., Jaques et al., 1989; Mathez et al., 1995). In diamonds, moissanite has been found to coexist with peridotitic pyroxenes, (Jaques et al., 1989; Mathez et al., 1995) with eclogitic garnets, clinopyroxenes, and rutile (Jaques et al., 1989), as well as with garnets with exsolved pyroxenes, indicative of an unusually high pressure origin (Moore et al., 1986).

2.2. Concentration of carbon

The total carbon concentration reported for mantle xenoliths varies by four orders of magnitude from below 1 ppm to close to 10 000 ppm (Fig. 3). While about 40% of the samples contain less than 50 ppm, 70% contain less than 100 ppm, 90% less than 300 ppm, and 95% less than 500 ppm C. An extrapolation of these concentrations to the whole mantle has to consider that only a small portion of the mantle is sampled by alkali basalts and kimberlites, the fact that some of the xenoliths are residual and may represent part of the mantle from which carbon has been removed, and that the C content of xenoliths may be altered during their transport from the mantle to the surface. Model-based carbon concentration estimates range from a few hundred to 10 000 ppm (e.g. Javoy et al., 1982; Des Marais, 1985; Marty and Jambon, 1987). Trull et al. (1993) have estimated the C content of the mantle as a whole to be less than 500 ppm.

2.3. Summary

A variety of chemical, mineralogical and morphological forms of C have been recognized in mantle minerals and rocks and several of them can occur together within a given specimen. It has also become clear that the distribution of C, established under mantle conditions, could be altered during transport of xenoliths from the mantle to the surface, and that not necessarily all of the C associated with mantle
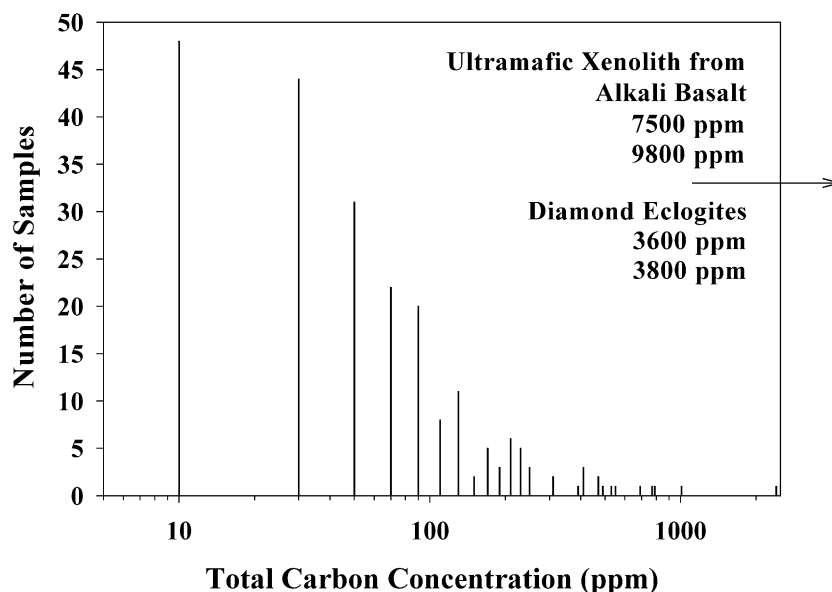
Fig. 3. Total carbon concentration of mantle xenoliths. Frequencies are plotted at mid points of class intervals (0 to 20, 20 to 40 ppm...). Four samples with extreme C contents are not shown as part of the frequency distribution but are indicated in the diagram. Data from: Jaques et al. (1990), Mathez et al. (1984b), Mattey et al. (1989a), Nadeau et al. (1990, 1993), Pineau and Mathez (1990), Pineau et al. (1987), Porcelli et al. (1992), Robinson (1979), Shee et al. (1982), Trull et al. (1993).

minerals is directly derived from the mantle. Introduction of C from the xenolith's host has been considered, however, since the C of the host magma is ultimately also mantle-related, the geochemistry of both C types must be linked. The nature of this linkage remains to be established. In order to understand the carbon isotope geochemistry of the mantle, the isotopic composition, and abundance of the various chemical C forms in mantle xenoliths, as well as the isotopic fractionation among them need to be well characterized. This remains to be accomplished.

3. Carbon isotope measurements

The techniques of measuring the carbon isotopic composition and the interpretation of the results are intimately intertwined. Carbon was extracted from mantle xenoliths by stepwise heating under O_2 (Des Marais and Moore, 1984) or a low temperature combustion step was followed by heating in vacuum without the presence of O_2 (Mattey et al., 1984). Fig. 4A provides an overview of *all* isotopic composition mea-

surements on mantle xenoliths, and includes results for *all* individual heating steps for samples subjected to stepwise heating.

The stepwise combustion procedures have shown that the CO_2 formed below 600 °C is generally depleted in ^{13}C compared to CO_2 formed above 600 °C (e.g. Pineau et al., 1976; Des Marais and Moore, 1984; Mattey et al., 1984). This has led some authors to suggest (e.g., Mattey et al., 1984) that the low temperature CO_2 results from surficial organic contamination, and that C contamination prior to and during the analysis is an important factor. However, when the low temperature combustion results of the analytical data are set aside, significant differences in the interpretation result. In view of the controversial nature of the "correct" interpretation of the analytical data, all results were combined in Fig. 4A. It would be fair to say that in the analyses of mantle materials, fractions of low and high $\delta^{13}C$ are encountered with about equal frequency.

The bimodality of the distribution is remarkably well defined, sharp peaks occur at −5‰ and at −25‰. The peak at −5‰ has been referred to, at
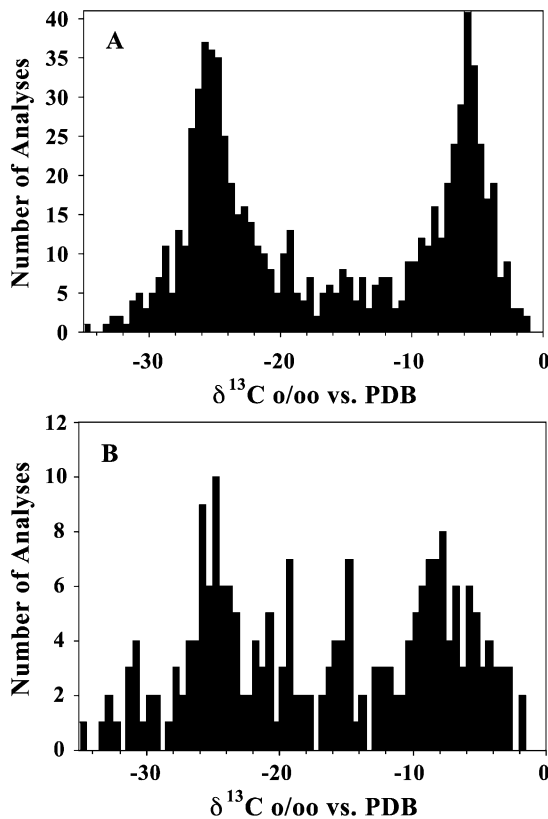
Fig. 4. Summary of $\delta^{13}C$ of whole rock mantle xenoliths and separated minerals, and the relationship of carbon isotopic composition to the extraction temperature. (A) All temperature fractions. (B) Fraction liberated above 1000 °C only. Data from Watanabe et al. (1983), Deines et al. (1984, 1991), Pineau et al. (1987), Wagner et al. (1988), Mattey et al. (1989a), Galimov et al. (1989), Jaques et al. (1990), Leung and Friedman (1990), Nadeau et al. (1990, 1993), Pineau and Mathez (1990), Porcelli et al. (1992), Viljoen et al. (1992, 1994), Trull et al. (1993), Pearson et al. (1994), Sugisaki and Mimura (1994), Mathez et al. (1995), Snyder et al. (1995), Schulze et al. (1997) and Liu et al. (1998).

times, as high-temperature C and the $-25\permil$ as low-temperature C. One school of interpretation has attributed the peak at $-25\permil$ to sample contamination and thus lacking geochemical significance while another suggests that the low $\delta^{13}C$ values are indigenous and carry meaningful information. In order to examine which of these interpretation is appropriate, the $\delta^{13}C$ values for CO_2 formed in stepwise combustion above 1000 °C have been compiled in Fig. 4B. When one considers Fig. 4A and B jointly, the following observations make an attribution of the peak at $-25\permil$ exclusively to secondary organic contamination unlikely:

1. the awareness of researchers of the problem of carbon contamination and the care taken by individual analysts, to minimize it;
2. the high levels of contamination required to produce some of the observed analytical results;
3. the fact that low $\delta^{13}C$ carbon is detected with very different analytical techniques and frequently in the high-temperature combustion fraction (see Fig. 4B);
4. the sharpness of the peak at $-25\permil$ in Fig. 4A, considering the $\delta^{13}C$ range of possible contaminants;
5. the lack of a clear relationship between $\delta^{13}C$ and carbon concentration (see Fig. 12A below, in which two mixing hyperbolae for organic carbon contamination have been shown).

One must conclude that mantle xenoliths contain indigenous ^{13}C-depleted C which needs to be considered as an integral part of the mantle carbon isotope geochemistry.

Fig. 5 summarizes the $\delta^{13}C$ values of the whole-rock xenoliths and that of separated minerals that the reporting authors think best reflect the isotopic composition of the mantle samples. Since some authors consider all of the carbon liberated during the combustion as characteristic for the sample while others report only those fractions (high temperature) that they believe represent "uncontaminated" carbon, the data are not always strictly comparable. However, the major peaks at $-25\permil$ and $-5\permil$ as well as the lack of intermediate $\delta^{13}C$ data remain evident. Naturally any reported $CO_2/^3He$ ratios depend on what fraction of the carbon is interpreted as indigenous to the sample, with attendant consequences for the conclusions. The bimodal nature of the $\delta^{13}C$ distribution is noteworthy and we will investigate, using the available data, whether there are geologic, petrologic or mineralogic variables with which it might be correlated. Because it is conceivable that different parts of the mantle are characterized by different carbon isotopic compositions and that xenoliths-carrying magmas, depending on their tectonic setting and magma source(s), have the potential to sample different parts of the mantle, the avail-
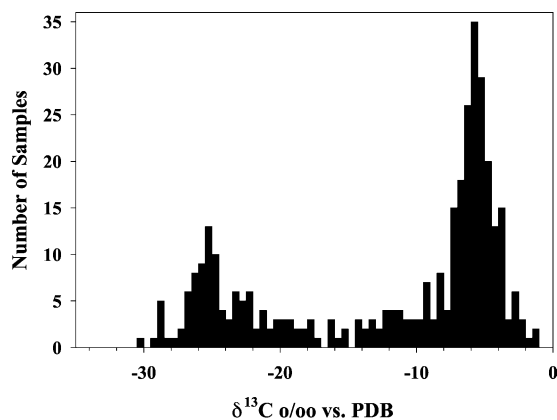
Fig. 5. Summary of $\delta^{13}C$ of whole rock mantle xenoliths and separated minerals as reported by: Watanabe et al. (1983), Deines et al. (1984, 1991), Pineau et al. (1987), Wagner et al. (1988), Mattey et al. (1989a), Galimov et al. (1989), Jaques et al. (1990), Leung and Friedman (1990), Nadeau et al. (1990, 1993), Pineau and Mathez (1990), Porcelli et al. (1992), Viljoen et al. (1992, 1994), Trull et al. (1993), Pearson et al. (1994), Sugisaki and Mimura (1994), Mathez et al. (1995), Snyder et al. (1995), Schulze et al. (1997) and Liu et al. (1998). The figure differs from Fig. 4A in that combustion fractions which were considered by authors to result from "contamination" were not included.

able data were classified into several categories: xenoliths from hotspot basalts, xenoliths from non-hotspot basalts, and kimberlites. The suite of xenoliths from alkali basalts and kimberlites were subdivided according to their petrology.

3.1. Xenoliths from hotspots

The fact that mantle samples can contain C of a wide range in isotopic composition was first shown by Watanabe et al. (1983) for olivine crystals from the Hualalai volcano, Hawaii. The carbon was extracted by three different methods: (1) pyrolysis in the presence of oxygen, (2) dissolution with HCl, and (3) ball milling. The concentration of C, determined by oxidative pyrolysis was about 10 ppm and its $\delta^{13}C = -3.2‰$. The "graphitic" C of the HCl dissolution residue represented a concentration of about 6 ppm of $\delta^{13}C = -26.9‰$. CH_4 was not detected in the samples. Assuming that originally all of the C was present in fluid inclusions as CO and CO_2 and that the disproportionation reaction, $2CO \Rightarrow CO_2 + C$, occurred, an initial CO/CO_2 ratio of about 3 can be determined.

The authors suggested that is consistent with thermodynamic computations at 1200 °C ($CO/CO_2 = 3.12$) using the measured oxygen fugacities of 10^{-12} for Hawaiian olivines (Sato, 1978). At the pyrolysis temperature used (850 °C) oxygen diffusion into the olivine is so slow that the "graphitic" carbon within the olivine is not oxidized. The total isotopic composition of the samples (CO_2, liberated in the pyrolysis plus "graphitic" C, of the dissolution residue) is estimated to be $-12‰$, and thought to represent the isotopic composition of C in the mantle beneath Hawaii. Two olivines from Japanese volcanoes yielded $\delta^{13}C$ values of $-29.4‰$ and $-26.1‰$ using the dissolution method ("graphitic" C). From one of the samples, CO_2 of $-14.3‰$ was liberated by the pyrolysis method; for the second sample, no CO_2 could be detected after oxidizing pyrolysis. The results indicate that within individual xenoliths large differences in $\delta^{13}C$ occur and that the highly ^{13}C-depleted C may reside within minerals.

Subsequent work has indicated that the occurrence of ^{13}C-depleted C may be related to the petrology and mineralogy of the xenoliths. Pineau and Mathez (1990) examined the carbon isotopic composition of mantle xenoliths from the Huakakai Volcano, Hawaii, including websterite, dunite, wherlite, pyroxenite and gabbro, as well as two xenoliths in which two lithologies contact one another. Most of the xenoliths represent deformed cumulates which formed in the same source region, at a depth of about 20 km. Step heating was used to liberate the carbon. Below 900 °C, C is characterized by $\delta^{13}C = -25‰$. The authors suggested that this C is predominantly graphitic and organic material which is present in cracks. They observed that there may be differences in $\delta^{13}C$ among the samples that are related to lithology; i.e., the carbon extracted from wherlites and dunites is more ^{13}C enriched than C extracted from websterites. In the former, C exists mainly in the form of CO_2-rich inclusions in arrays which were interpreted to represent partially annealed microcracks. The websterites have zones of large irregular-shaped inclusions, occupying zones that traverse an entire thin section. These inclusion zones were thought to represent fractures that were annealed at depth. Most of the carbon in the websterites is concentrated in these zones and represents carbonaceous material precipitated from a mantle fluid. The $\delta^{13}C$ record of this material thus indicates

the presence of ^{13}C-depleted C ($-24.8‰$) in the mantle. The observed isotopic composition variability can be explained by multistage isotope fractionation processes involving CO_2 and graphitic carbon, including degassing of a magma and graphite precipitation from CO_2. The $\delta^{13}C$ of the total C in the xenoliths varies from $-7.1‰$ to $-25.7‰$.

In three of the xenoliths, cpx and olivine were separately analyzed. In all cases, the cpx contained more C (C_{cpx}/C_{ol} ratios are 3.6, 5.3, 1.2); also, for every pair cpx is enriched in ^{13}C compared to the olivine ($\Delta13C_{cpx-ol}$ differences are 16‰, 4.7‰, 8.3‰). It is worthy of note that when the total C concentrations of the whole rocks are compared, dunites have on average the lowest C content, and that in the composite wherlite/gabbro there is a significant difference in $\delta^{13}C$ and carbon concentration between the two lithologies. These observations suggest that the mineralogy may exert an influence on both the C concentration as well as the carbon isotopic composition of mantle rocks (Table 2).

Although the joint study of C and He isotopic compositions and concentrations of mantle xenoliths holds promise for the elucidation of the mantle carbon isotope geochemistry and the understanding of the Earth's degassing history, very few data are available. The C and He abundance and isotopic composition of xenoliths from hotspot volcanoes (Hawaii, Réunion and Kerguelen) were measured by Trull et al. (1993). C was extracted from the samples in three to six steps between 200 and 1550 °C in the presence of O_2. Fluid inclusions decrepitate above 900 °C. Isotopically light carbon (to $-29‰$) was observed in several of the samples even in the very high temperature fraction and could represent a mix of volcanic C and biogenic

C from post-eruptive contamination. The authors considered only CO_2 contained in high pressure fluid inclusions whose $\delta^{13}C$ varies between $-1.6‰$ and $-10.8‰$ to be geochemically meaningful; the low $\delta^{13}C$ values were set aside. No evidence for a difference in $\delta^{13}C$ between hotspot xenoliths and MORBs can be detected. The observed range of isotopic compositions can be explained by physicochemical processes of the volcanic system. The CO_2 abundance varies from 1 to 260 ppm and He abundances between 10^{-9} and 10^{-6} cm^3 STP/g; CO_2 and He abundances are correlated. The observed correlation can be interpreted to demonstrate that the two elements are not readily separated during fluid transport in the mantle and therefore would support the use of the CO_2/He ratio to determine global C fluxes. However, this inference can be argued, because a correlation can be maintained while a fractionation of the two elements occurs. The C/[3]He ratio of the xenoliths varies between 2 and 20×10^9 and overlaps that of MORB (1 to 7×10^9). The small range of this ratio in the xenoliths could be an indication that there was not a residual C phase during melting and that no large-scale diffusive transport in the mantle occurred, which would separate the two gases (at magmatic temperatures $D_C < 10^{-12}$ cm^2/s, Tingle et al., 1988 and $D_{He} > 10^{-9}$ cm^2/s, Trull and Kurz, 1993). The similarity of hotspot and ridge C/[3]He ratios is inconsistent with significant recycling of carbon to the upper mantle. Based on the measured C/[4]He ratios, the authors suggested that the C content of the upper mantle is less than 500 ppm (probably in the range 50–250 ppm). While recycling of C to the upper mantle was ruled out, based on the similarity in the C/[3]He ratio of the xenoliths and MORBs, the carbon and helium concentration and isotopic composition systematics permit recycling to the lower mantle; however, direct chemical evidence for deep-mantle C cycling was not presented in the paper.

The multifaceted nature of the relationship, between C geochemistry and He isotopic composition in mantle xenoliths, is also apparent in harzburgites from the Samoan hotspot (Farley, 1995). These xenoliths are characterized by extraordinarily enriched Sr–Nd–Pb isotopic ratios which were attributed to metasomatism by a carbonatitic fluid derived from recycled sediments. However, Meen et al. (1989) presented experimental evidence that CO_2-rich fluids dissolve only

Table 2
Summary of data from Pineau and Mathez (1990)

Rock type		Mean $\delta^{13}C$ (‰)	Std	Mean C (ppm)	Std
Wherlite		−9.2	3.1	182	72
Olivine pyroxenite		−16.0	0.3	103	5
Dunite		−12.9	2.3	72	11
Websterite		−24.8	0.8	154	42
Composite	wherlite	−11.6		182	
	gabbro	−22.2		126	
Composite	websterite	−21.5		54	
	dunite	−20.9		75	

minor amounts of REE and thus cannot have been responsible for the selective enrichment of REE. The inclusions in the xenoliths are dominantly pure CO_2 and have high $^3He/^4He$ ratios (12 times the atmospheric ratio), which is inconsistent with the radiogenic values expected for recycled sediments. In addition, the $C/^3He$ ratio of the inclusion gas is approximately 3×10^9, indistinguishable from typical mantle values, and very much lower than those in sediments ($>10^{11}$). These observations indicate that little of the helium and carbon in the metasomatic fluid could have been derived from the recycled source implied by the Sr–Nd–Pb isotope data. The metasomatic fluid could be a product of mixing of a volatile-rich high $^3He/^4He$ plume melt and recycled sediments within the Samoan hotspot. In order to retain the high $^3He/^4He$ ratios in the mixture, rapid recycling is necessary. The location of the hotspot at the northern end of the Tonga Trench subduction zone could serve as an explanation for the availability of rapidly recycled sediments to mix with the hotspot material. If there is indeed a decoupling of sediment recycling and the $^3He/^4He$ signature, then degassing models based on the $C/^3He$ ratio and $\delta^{13}C$ measurements will become suspect.

A summary of the C isotope record of xenoliths from hotspot volcanoes is shown in Fig. 6A, which indicates a broad range of $\delta^{13}C$ without a pronounced mode.

3.2. Xenoliths from non-hotspot alkali basalts

Ultramafic xenoliths (harzburgite, olivine–orthopyroxinite, orthopyroxenite, websterite and clinopyroxenite) from a Plio-Quaternary Strombolian cone, of alkali basalts (Tissemt, Eggéré, Algerian Sahara) were analyzed by Pineau et al. (1987). The xenoliths contain large (up to 1 mm) graphite flakes. Petrologic, mineralogic and geochemical data suggest that the rocks were derived from a deep crustal intrusive of Precambrian age, and, based on the texture, graphite is thought to form early. After the cumulus crystallization of olivine and orthopyroxene, the graphite co-crystallized with olivine, orthopyroxene and spinel in the inter-cumulus assemblage. $\delta^{13}C$ of the graphites varies from -24.6‰ to -14.4‰. The highest ^{13}C enriched samples are websterites, i.e., the most differentiated xenoliths, which contrasts with the ^{13}C depletion observed in websterites from hotspot basalts.
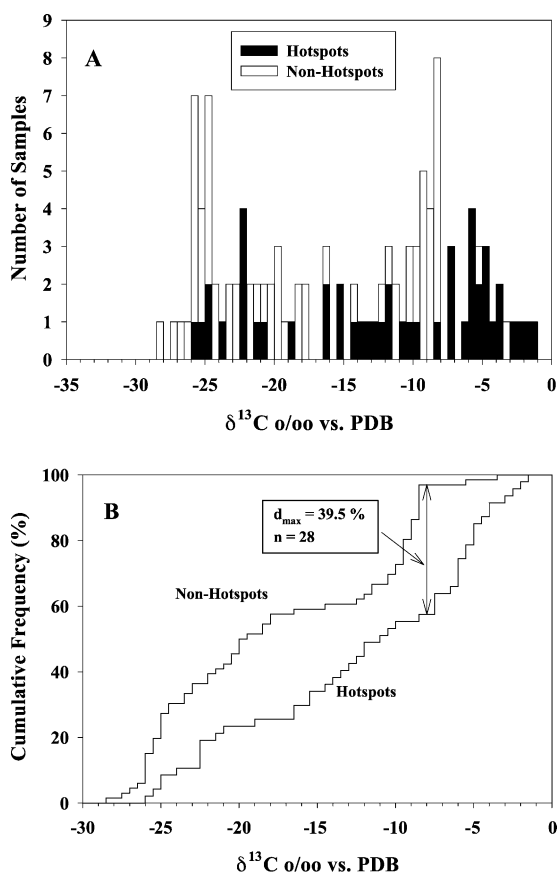

Fig. 6. Comparison of carbon isotopic composition of non-hotspot and hotspot xenoliths. Source of data, see text. (A) Sampling frequency distribution. (B) Cumulative frequency distribution and basis of the non-parametric Kologorov Smirnov test (Miller and Kahn, 1962).

Orthopyroxenites on the other hand contain graphite of $\delta^{13}C$ between -20.2‰ and -24.6‰. Xenoliths, which, based on the geochemical data, may belong to a separate magmatic series have $\delta^{13}C$ values between -20.3‰ and -20.5‰. The carbon concentration of the xenoliths varies widely (383 to 7500 ppm) but the carbon isotopic composition is unrelated to this concentration variation. Acid treatment of the xenoliths liberated CO_2 (42 to 1060 ppm) with $\delta^{13}C$ of -0.8‰ to $+3.5$‰.

The low $\delta^{13}C$ values could be the result of degassing and isotope fractionation in the magmatic crystallization process. It is interesting to note that: (1) while in excess of 70% of the C would have to be

lost in order explain the low $\delta^{13}C$ values of the graphite, still enough C must remain available to supersaturate the magma with respect to C; (2) no relationship between carbon isotopic composition and carbon content of the xenoliths is observed; and (3) the more differentiated xenoliths (websterites) contain isotopically less-fractionated C (if one assumes that the unfractionated C has an isotopic composition of $\delta^{13}C = -5\%$). These features are not in accord with expectations that one would have if degassing is evoked to explain low $\delta^{13}C$ values.

The total isotopic composition of the basaltic host is -4.2% and its carbon concentration 696 ppm. The $\delta^{13}C$ of the basalt was determined by stepwise combustion and large variations with combustion temperatures are noted. For the low temperature fraction, $\delta^{13}C$ values vary from -27.1% to -16.5%, for the 670 to 985 °C fraction from $+1.4\%$ to $+7.3\%$, and for the fraction above 1000 °C from -15.5% to -25.8%. About 200 ppm of the total C of the basalt (about 30%) is characterized by ^{13}C depletion. The C concentration of the host basalt (696 ppm) is much higher than expected for a sub-areal lava (the authors estimated 50 ppm), and was proposed to represent re-mobilized C from disaggregated xenoliths. The isotopic record is suggested to be determined by degassing and oxidation reactions involving CO_2 and CH_4 during the cooling of the magma.

Further studies on peridotitic xenoliths, predominantly spinel lherzolites, from recent to late Tertiary alkali basalts along the northwestern margin of North America were completed by Nadeau et al. (1990). The authors used step heating to extract the carbon and suggested that at least three, but perhaps four, C components may be identified.

(1) Carbon released between 200 and 600 °C represents between 30% and 90% of the total C extracted, has $\delta^{13}C$ between -28% and -23% and could exemplify complex carbon compounds condensed on surfaces of minerals and cracks, similar to the material described by Mathez (1987).

(2) CO_2 released between 600 and 800 °C could be derived from interstitial carbonates. It has variable $\delta^{13}C$ (-9.5% to -31.5%) and concentrations that generally do not exceed 24 ppm.

(3) Carbon extracted from 1000 to 1450 °C could be a mixture of CO_2 from fluid inclusions and the "low-

temperature" fraction C ($\delta^{13}C = -4\%$ to -32.7%). The portion of "low-temperature C" extracted at this temperature is small and does not exceed 10 ppm. Because the light "low-temperature" C could be introduced from the host, it would represent only in part of the C originally present in the xenoliths. Why this "low-temperature" C should be released only above 1000 °C remains unclear. It is likely that this C fraction is actually part of the fourth component mentioned below. Xenoliths that are fluid-inclusion rich release C ($\delta^{13}C$ between -4% and -10%) at the highest combustion temperatures. The concentration of the C released varies between 0.1 and 66 ppm.

(4) A fourth component may represent C dissolved in minerals and has an isotopic signature indistinguishable from that of the "low temperature" C (-23% to -28%).

Porcelli et al. (1992) examined the C/He ratio as well as the isotopic composition of C, He, Nd, Sr and Pb in continental ultramafic xenoliths. The He isotopic composition is within the range of MORB and shows no correlation with the concentration of the trace elements, or their isotopic composition. $\delta^{13}C$ for the xenoliths varies between -3.2% and -17.5%. A correlation between Nd isotopic composition and $\delta^{13}C$ was noted. The C/^{3}He ratios range from 1.3 to 2×10^9 and do not correlate with the He abundance; they are also similar to the ratios observed in MORBs. The correlation between carbon and neodymium isotopic composition may be explainable in terms of a two component mixing model requiring that the LREE-enriched component is coupled with isotopically light C. Mattey et al. (1985) also had noted that light C might be associated with LREE enrichment in xenoliths from Geronimo; however, subsequent work did not confirm this observation (see below). Porcelli et al. (1992) believed that the lighter C isotopic compositions are compatible with contributions from subducted C. The details of how this geochemical association comes about, remain unclear. In addition, Mathez et al. (1984b), who studied the geochemistry of carbon in mantle peridotites, found no clear relationship between abundance of C and the incompatible trace elements. Why the carbon isotopic composition–Nd relationship observed by Porcelli et al. (1992) should record a sedimentary component and the C/^{3}He should not, and why the helium isotopic composition should not be affected by the size of

the sedimentary component remain to be established.

The relationship between C, He, Sr and Nd isotopes in mantle diopsides was examined by Mattey et al. (1989a); step heating was used. The low-temperature component has a $\delta^{13}C$ of $-28‰$ and is attributed to organic contamination. However, the analytical data show that at temperatures as high as 1000 °C significant amounts of light carbon are liberated. Even the highest temperature fraction shows $\delta^{13}C$ values as low as $-11.4‰$. The decreased ^{13}C content in the high-temperature fraction is attributed by the authors to the presence of organic matter introduced into the mantle by subduction, corroborating evidence is not presented. The concentrations of C and Nd are positively correlated in clinopyroxenes. However, when $\delta^{13}C$ and Nd concentrations are considered jointly, one finds that while some of the lower $\delta^{13}C$ values are measured for diopsides of higher Nd concentration, there is no statistically significant correlation. The weighted mean $\delta^{13}C$ for C liberated above 700 °C varies from $-9.5‰$ to $-21.4‰$ and averages $-13.1‰$, another indication of the presence of highly ^{13}C depleted C in mantle samples that cannot readily be explained by contamination.

Liu et al. (1998) liberated CO_2, CO and CH_4 from spinel lherzolites and pyroxenite xenolith from alkali basalts from Damaping, China. The gases were released by pyrolysis at temperatures from 400 to 1400 °C, and measured by GC-MS. The carbon isotopic composition of CO_2 and CO range from $-22‰$ to $-27‰$ and that of the CH_4 from $-30‰$ to $-50‰$.

3.3. Comparison of carbon isotope geochemistry of hotspot and non-hotspot xenoliths

A summary of the $\delta^{13}C$ data for non-hotspot xenoliths is included in Fig. 6A. Carbon from both hotspot and non-hotspot xenoliths shows approximately the same range of $\delta^{13}C$ ($-1‰$ to $-28‰$). While the xenoliths from hotspot volcanoes have a more or less even distribution of samples across this isotopic composition range (note the steady rise of the cumulative $\delta^{13}C$ frequency distribution in Fig. 6B), non-hotspot volcanoes appear to transport to the surface, on average, more xenoliths of low $\delta^{13}C$ than hotspot volcanoes. A non-parametric test (Kolmogorov–Smirnov

test, Miller and Kahn, 1962), indicates that the sampling distributions of hotspot and non-hotspot xenoliths differ significantly (see Fig. 6B).

Xenoliths from basalts were classified by their lithology and their tectonic setting (Fig. 7). The sampling so far is too limited to establish whether there are significant differences in $\delta^{13}C$ among the various rock types. One can note, however, that pyroxenites (Fig. 7D) have no examples of $\delta^{13}C$ values heavier than $-8‰$ and tend to be, as a group, lower in ^{13}C; with this exception, all rock types show examples for low as well as high $\delta^{13}C$ values. Within a particular rock type, however, differences between hotspot and non-hotspot xenoliths may be present. While the few harzburgites and lherzolites from hotspots studied all have $\delta^{13}C$ values above $-6‰$, those from non-hotspots appear to be more ^{13}C depleted (Fig. 7B and C). Hotspot dunites and wherlites (Fig. 7E and G) on the other hand cover a wide range of $\delta^{13}C$. The few analyses available for hotspot websterites (Fig. 7F) suggest that they are characterized by $\delta^{13}C$ of about $-25‰$, while non-hotspot wherlites have higher ^{13}C contents. The available data thus may indicate some regularities in the ^{13}C distribution; however, a clear distinction of greater ^{13}C or lesser ^{13}C enrichment in hotspot compared to non-hotspot xenoliths of a particular lithology cannot be made.

3.4. Xenoliths from kimberlites

Diamond and graphite eclogite xenoliths are more frequently observed in kimberlites than diamond or graphite peridotites. Eclogite xenoliths from the Orapa, Botswana, kimberlite (Deines et al., 1991) contain graphite whose $\delta^{13}C$ range ($\delta^{13}C = -4.6‰$ to $-7.8‰$, 28 samples) is significantly smaller than that of diamond ($-4‰$ to $-22.3‰$, 46 samples). No clear relationship between the $\delta^{13}C$ (graphite or diamond) of the xenolith and eclogite chemistry, which could be interpreted to be subduction related, was found. Only a fraction of the diamonds occurring as individual crystals in the kimberlite host can represent minerals liberated in the breakup of diamondiferous eclogite xenoliths. This conclusion was based on a comparison of the carbon isotope record of Orapa diamond eclogites and the composition of their garnets and pyroxenes with the $\delta^{13}C$ of E-type diamonds, that occur free in the kimberlite, and the
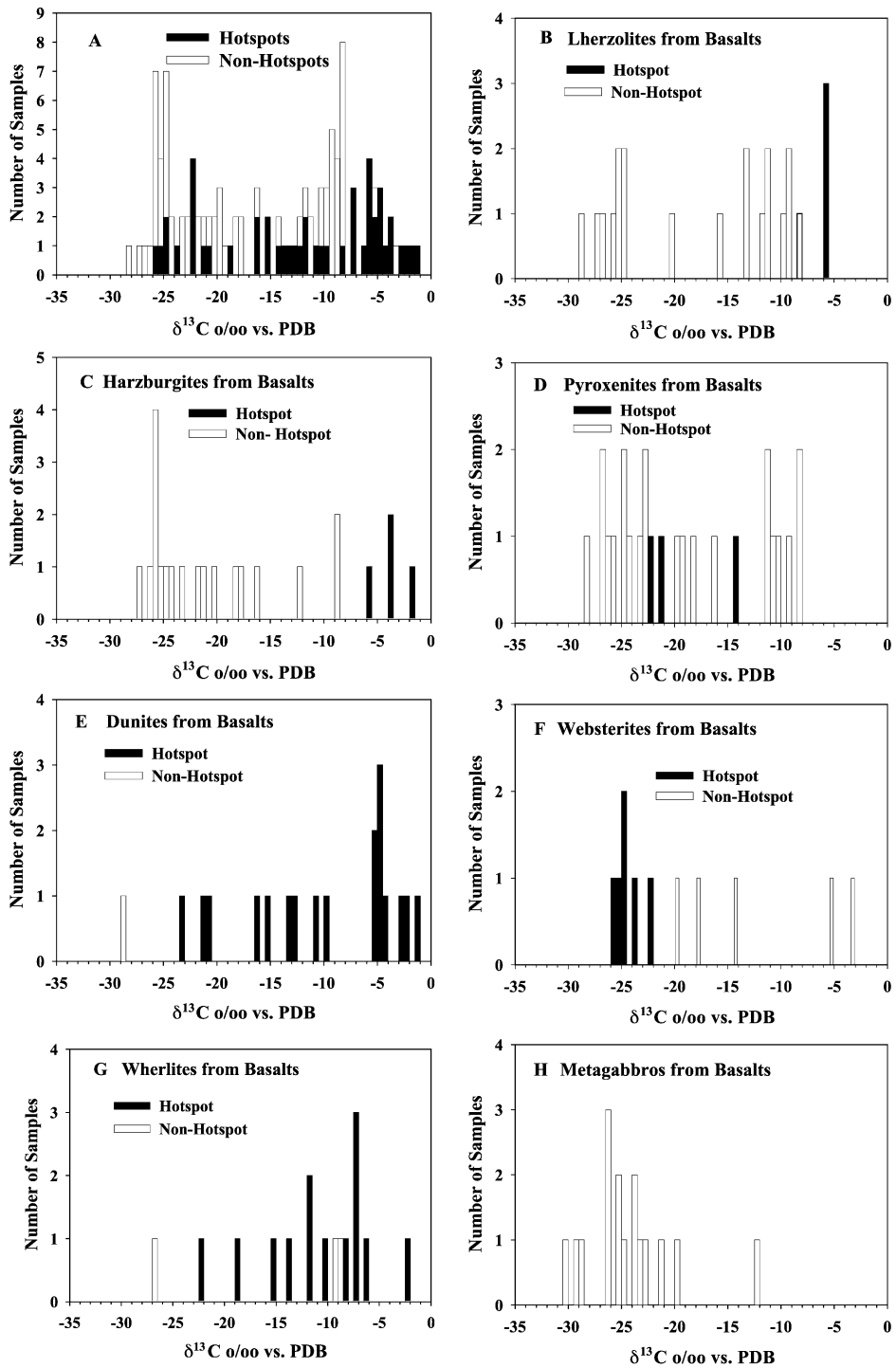
Fig. 7. Carbon isotope composition of xenoliths from alkali basalts distinguished by rock type and tectonic setting.

composition of their silicate inclusions (Deines et al., 1993). Snyder et al. (1995) measured the $\delta^{13}C$ of diamondiferous eclogites from the Udachnaya kimberlite, Siberia, whose $\delta^{13}C$ varies between $-1‰$ and $-7‰$ and Viljoen (1995) reported on one diamond-bearing and eight graphite bearing-eclogite xenoliths from the Bellsbank kimberlites, Cape Province, South Africa. The graphite occurs in discrete prismatic grains and its isotopic composition ranges from $-2.84‰$ to $-7.04‰$ (Schulze et al., 1991). The diamond has an isotopic composition of $-5.39‰$, falling within the range ($-1.7‰$ to $-5.6‰$) reported by Deines (1980) for diamonds occurring free in the Dan Carl Mine kimberlite, thus permitting a common source of the carbon of graphite and diamond. Schulze et al. (1997) reported on the $\delta^{13}C$ of primary graphite from 28 mantle-derived xenoliths from kimberlites in southern Africa and the USA. The suite of samples consisted of 22 eclogites, one wherlite, one lherzolite and three harzurgites. The $\delta^{13}C$ range ($-2.84‰$ to $-14.4‰$) is attributed to the subduction of organic C into the mantle. No evidence for this proposal, other than the $\delta^{13}C$ record, is advanced by the authors. Pearson et al. (1994) characterized graphite in cratonic, lithospheric mantle. Graphite bearing peridotites, clinopyroxenites and eclogite xenoliths from the Kaapvaal craton of southern Africa and the Siberian craton, Russia were examined. The $P-T$ estimates based on silicate equilibria are lower than those of diamondiferous mantle xenoliths and fall almost exclusively within the experimentally determined graphite stability field. $\delta^{13}C$ values fall between $-5.9‰$ and $-19.4‰$ for pyroxene megacrysts.

The total $\delta^{13}C$ range of graphite in eclogites ($-2.8‰$ to $-19.4‰$) reported to date appears to be approximately equal to that of diamond in eclogite xenoliths ($-1‰$ to $-22.3‰$). To determine whether there are significant differences in $\delta^{13}C$ among the xenoliths recovered from different pipes, as they have been reported for diamonds occurring free in the kimberlite (Deines et al., 2001), requires a larger and more systematic data set.

Because mantle peridotites can be expected to be the major host rock of diamonds, their carbon isotope record is of special interest. Carbon isotope measurements on diamondiferous peridotite were first discussed by Jaques et al. (1990) who report $\delta^{13}C = -3.7‰$ and $-5.6‰$ for diamonds from a perido-

tite nodule, from the lamproite at Argyle, Australia. In addition to the eclogitic xenoliths discussed above, Pearson et al. (1994) also carried out measurements on graphite bearing peridotites whose $\delta^{13}C$ values vary between $-3.8‰$ and $-12.3‰$. Schulze et al. (1997) reported the $\delta^{13}C$ of primary graphite from dunite to be $\delta^{13}C = -9.39$ and that of harzburgites $\delta^{13}C$ to vary between $-6.64‰$ and $-10.4‰$.

Comparison of the $\delta^{13}C$ and chemistry of periotite xenoliths with the $\delta^{13}C$ of diamonds and the composition of the peridotitic inclusions from the same kimberlite is particularly instructive. Viljoen et al. (1992) examined diamondiferous harzburgites from the kimberlite at Finsch, South Africa. The mineral chemistry of the peridotites is distinct from that of the P-type mineral inclusions observed in Finsch diamonds occurring free in the kimberlite. The $\delta^{13}C$ of diamonds from harzburgites ($-3.8‰$, $-3.7‰$ and $-3.9‰$), fall in the $\delta^{13}C$ range of diamonds from Finsch lherzolite xenoliths ($-2.76‰$ to $-4.58‰$) reported earlier (Deines et al., 1984). The mean isotopic composition of P-type diamonds occurring free in this kimberlite is $-6.03 \pm 0.97 (1\sigma)‰$ (Deines et al., 1984). The difference in chemistry between P-type diamond inclusions and xenoliths, in conjunction with the difference in $\delta^{13}C$ between diamonds from the xenoliths and P-type diamonds occurring free in the Finsch kimberlite, indicates that the two varieties of diamonds had different C sources and origins. Hence, the P-type diamonds occurring free in the kimberlite cannot have resulted from the breakup of peridotitic xenoliths. A similar conclusion was reached for elcogitic diamonds and diamond eclogites from the Orapa, Botswana kimberlite (see above).

The relationship between the graphite and diamond isotope chemistry in mantle peridotites is of interest as well. A suite of lherzolites and low Ca harburgites from the Roberts Victor kimberlite was investigated by Viljoen et al. (1994). The xenoliths contain graphite and/or diamond. The $\delta^{13}C$ of graphite varies between $-4.2‰$ and $-6.5‰$, while that of diamond has a slightly larger range from $-3.5‰$ to $-7.0‰$. In one of the samples, diamond ($-4.8‰$) and graphite ($-6.5‰$) coexist. The fractionation of $1.7‰$ between the two C polymorphs is in the correct direction (^{13}C enrichment in diamond compared to graphite) but significantly larger than expected ($0.4‰$ at 1000 °C) on the basis of the computations of Bottinga (1969)

(see Fig. 15). More recently, Polyakov and Kharlashina (1994) have argued that the computations of Bottinga did not take into account the effect of pressure, and that graphite and not diamond should be enriched in ^{13}C, the enrichment amounting to about 0.5‰. The observation of Viljoen et al. (1994) hence does not necessarily support the more recent computations. However, isotopic equilibrium between the graphite and diamond grains in a particular xenolith may not be present because there is evidence that chemical and carbon isotope disequilibrium on small spatial scales can occur even within individual diamonds (for a recent summary, see Deines et al., 2001).

The few $\delta^{13}C$ analyses available suggest that carbon isotopic composition range encountered in diamondiferous peridotites (-3.6‰ to -6.5‰) is smaller than that of graphitic peridotites (-3.5‰ to -10.4‰) which extends to lower $\delta^{13}C$ values; the limited data, however, do not support a firm conclusion.

Galimov et al. (1989) examined garnet and spinel websterites from the Udachnaya and Obnazhennaya kimberlite pipes. Estimates for the pressure/temperature of equilibration for the xenoliths are between 27 and 30 kbar, and 880 °C, to 1090 °C. The graphite present forms intergrowths with phlogopite and both minerals are thought to be related to a K- and P-bearing metasomatizing fluid. C was isolated from the rock in three different ways. Graphite was hand picked, CO_2 was liberated by reaction with phosphoric acid, and dispersed carbon was isolated by fusion and dissolution of the silicates, leaving a residue containing carbon (see Table 3). The authors considered that isotopically light C of the graphite may be produced as a result of Rayleigh fractionation, or equilibration with CO_2. Alternatively, the ^{13}C depletion may be a characteristic of the metasomatizing fluid. The light $\delta^{13}C$ of the dispersed C is thought to be produced by a thermodynamic isotope effect between CO_2 and unbonded carbon atoms. Such a fractionation would be characterized by the reduced partition function of CO_2. The reduced partition function of CO_2 in the temperature range 850–1050 °C falls between 1.023 and 1.017 (see below), which would lead to an approximately 20‰ depletion in atomic C with respect to CO_2.

Fig. 8A shows $\delta^{13}C$ determined for xenoliths from kimberlites and includes data for graphite as well as diamond-bearing specimens. The distribution is distinct from that for xenoliths from alkali basalts (Fig.

Table 3
Summary of data from Galimov et al. (1989)

Sample	C form	$\delta^{13}C$
3/85 Udachnaya– Vostochnaya pipe Coarse-grained garnet websterite	graphite	−7.83
	graphite from concentrate	−7.35
	amorphous C from dissolution of cpx grains. 0.09 wt.%	−23.94
	carbonate (0.53 wt.%)	−3.36
4/83 Udachnaya– Vostochnaya pipe coarse-grained garnet websterite	graphite	−10.82
	dissolution residue 0.14 wt.%	−26.46, −26.35
	carbonate 0.08 wt.%	−4.56
74-1002 Obnazhennaya pipe fine-grained spinel websterite	graphite	−22.72
	amorphous carbon concentrate 0.006 wt.%	−21.96
	carbonate 0.005 wt.%	−3.58
	carbonate serpentinized rim	+1.8

7A) but resembles that of diamonds (Fig. 8B). It is interesting to note that while the xenoliths from basalts have a distinct mode at about −25‰, this not the case for either the kimberlite xenoliths, or diamonds from southern Africa. For diamonds, $\delta^{13}C$ values below −25‰ are relatively rare and a mode just above −20‰ is indicated. The difference between the distributions for kimberlite and non-kimberlite xenoliths may reflect in part the different chemical forms of C investigated. While many carbon analyses represented in Fig. 7 are for inclusion CO_2 and finely dispersed carbon, those of Fig. 8 are mainly for graphite grains and diamond. It will require more intensive studies to establish whether there is indeed a significant difference in the $\delta^{13}C$ distribution of the two groups of xenoliths. If a significant isotopic composition difference between the non-hotspot and kimberlite xenoliths could be established, differences in $\delta^{13}C$ with mantle depth would be indicated.

In Fig. 8C–H, kimberlite xenoliths have been classified by their petrography. Diamond and graphite eclogites (Fig. 8C) show a significantly wider $\delta^{13}C$ range than the peridotites (Fig. 8D); however, samples of low ^{13}C content are rare and none with $\delta^{13}C$ values as light as −25‰ have been reported. In eclogites, the range of graphite isotopic compositions is slightly less than that of diamonds. Lherzolite and harzburgite xenoliths from kimberlites (Fig. 8E and F) cover a much more restricted $\delta^{13}C$ range than xenoliths of
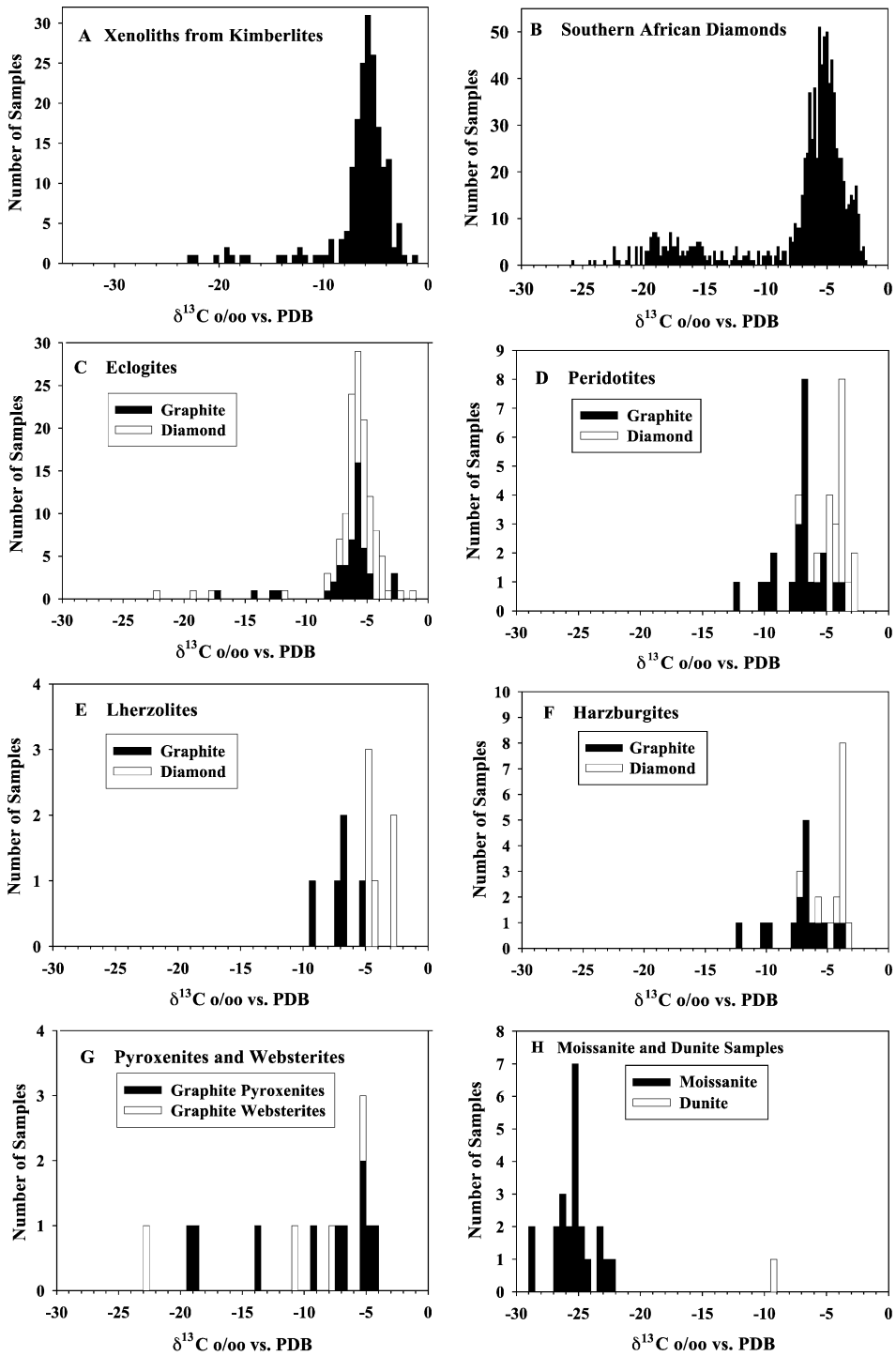
Fig. 8. Carbon isotopic composition of graphitic and diamondiferous xenoliths from kimberlites.

similar petrography from alkali basalts (Fig. 7B and C). One might propose a similarity in $\delta^{13}C$ between diamondiferous lherzolites (Fig. 8E) and harzburgites (Fig. 8F) and hotspot lherzolites (Fig. 7B) and harzburgites (Fig. 7C); however, the data are rather sparse. Graphite appears on average to have slightly lower ^{13}C concentrations than the diamonds from the same lithology, consistent with the computations of Bottinga (1969). Although the data are very limited, the graphite pyroxenites and websterites (Fig. 8G) show $\delta^{13}C$ distributions that are similar to those of pyroxenites (Fig. 7D) and websterites (Fig. 7F) from alkali basalts. While no diamondiferous websterites have been investigated to date, it is interesting to note that diamonds with websteritic inclusions from the Orapa kimberlite, have, with one exception ($-6.9‰$), $\delta^{13}C$ values between $-15.2‰$ and $-22.4‰$ (Deines et al., 1993), and thus resemble in their $\delta^{13}C$ hotspot websterites (see Fig. 7F). Hence, while harzburgites and lherzolites might indicate a relationship between hotspot and kimberlitic xenoliths at one end of the mantle $\delta^{13}C$ spectrum ($-5‰$), websterites might do so at the other ($-20‰$ to $-25‰$).

The presence of moissantite (SiC) has been recognized in mantle related rocks and in P-type as well as E-type diamonds (see above). It was also observed in a graphite lense in the Brighurt gabbro, northern Delaware, by Wagner et al. (1988), who reported the carbon isotopic composition to be $-24.2‰$, while that of the associated graphite is $-22.4‰$. Leung and Friedman (1990) have reported $\delta^{13}C$ of $-24‰$ for silicon carbide from a diatreme near Fuxian in the Liaoning Province of China. Diamonds from the kimberlite have an isotopic composition between $-2.8‰$ and $-4.8‰$ (average $-4.1‰$). Mathez et al. (1995) determined the carbon isotopic composition of SiC from kimberlites of Yakutia, Russia. Nine SiC samples from Aikhal and 14 from Mir fall in the range $-22‰$ to $-29‰$ most of the samples concentrate in the range of $-24‰$ to $-27‰$. The Mir samples have, on average, a lower ^{13}C content ($\delta^{13}C = -25.6‰$) than the samples from Aikhal ($\delta^{13}C = -24.5‰$). Thermodynamic computations by the authors show that in order for moissanite to be stable, the fO_2 under upper mantle P, T conditions would have to be five to six orders of magnitude below that of the Fe–FeO buffer. Causes considered for the occurrence of moissanite include: (1) the

presence of relics of a reduced primordial Earth; (2) the presence of regions in the mantle that are highly reduced and low in ^{13}C; (3) the extension of moissanite stability to higher fO_2 ranges at pressures of the lower mantle, or metastable SiC formation; and (4) the formation of moissanite by metamorphism of reduced, carbonaceous sediment during subduction. The authors believed that the last mechanism is most consistent with their observations.

The similarity in $\delta^{13}C$ moissanite from different kimberlites is noteworthy. It leads to the question whether the observed carbon isotopic compositions are related to a thermodynamic isotope effect and suggests that a comparison be made of $\delta^{13}C$ of diamond and moissanite collected from the same kimberlite. Diamonds from the Aikhal pipe range in $\delta^{13}C$ from $-2‰$ to $-17‰$ with a strong peak at about $-4.5‰$ while Mir diamonds have $\delta^{13}C$ values between $-1‰$ and about $-35‰$. Most samples, however, have $\delta^{13}C$ values between $-4‰$ and $-8‰$ with a pronounced peak at $-6‰$; the very light isotopic composition, particularly around -25 are rare (Galimov, 1991). We find that for the diatreme near Fuxian in the Liaoning Province of China: $\delta^{13}C_{diamond} - \delta^{13}C_{moissanite} = 19.9‰$, for Aikhal: $\delta^{13}C_{diamond} - \delta^{13}C_{moissanite} = 20‰$ and Mir: $\delta^{13}C_{diamond} - \delta^{13}C_{moissanite} = 19.6‰$. For these three kimberlites, there is a consistent difference in $\delta^{13}C$ between average diamond and moissanite carbon isotopic composition close to 20‰. While the limitations of such a comparison are obvious, the result is nevertheless interestingly consistent. The moissanite carbon isotopic composition distribution (Fig. 8H) is distinct form that of all kimberlite xenoliths and the limited available data suggest a correlation between the $\delta^{13}C$ of the mineral and the average diamond from the same kimberlite. In view of these observations, it would be very interesting to measure $\delta^{13}C$ of moissanite inclusions and their P- and E-type diamond hosts.

3.5. Ophiolites and other mantle-related rocks

In the Beni Bousera peridotite massif, Morocco elemental C occurs in octahedral and other cubic symmetry in graphite garnet pyroxenites (Davies et al., 1988). This observation has been interpreted as showing that the carbon represents graphitized diamond and that these rocks resided at some time in the

stability field of diamond. Graphite has $\delta^{13}C$ values between $-19\‰$ and $-20\‰$ which suggested to the authors that this carbon represents a biogenic source. The rocks were interpreted to be recycled oceanic crust which included a significant amount of a sedimentary component. No corroborating evidence was presented to support the hypotheses that the ^{13}C depletion can only be a result of biogenic processes.

Fluid inclusion and mineral isotopic compositions in eclogite facies, metagabbros from the Monviso ophiolite complex (Italian Western Alps) were examined by Nadeau et al. (1993). Whole rocks were studied and the C present in them was interpreted to represent the residual phase of volatile loss (90%) occurring during subduction. The remaining fluid was trapped in omphacite megacrysts that developed at the expense of precursor magmatic pyroxene. The scale of isotopic equilibration observed is small (cm), which led the authors to conclude that the fluids were locally derived, ruling out large-scale mass flushing of isotopically homogeneous fluids during subduction zone metamorphism. The carbon present is thought to be inherited from the metamorphic transformation of the original carbon present in the oceanic crust. Two carbonaceous components can be recognized, condensed carbon which represents the major carbon species and carbonate daughter crystals present in fluid inclusions. The authors used stepped heating in the presence of O_2 to liberate C from the samples and observed that between 18 and 346 ppm of CO_2 was released between 200 and 600 °C. In view of the high concentration, contamination by adsorption was ruled out and the liberated C considered to be condensed carbon indigenous to the sample. The mean value of this C is $-24.6\‰$. The constancy of the isotopic composition during subsequent heating steps indicates that the condensed form of C is the most abundant carbon species. The authors believed to have detected C from carbonates in the 600 to 800 °C fraction; however, the isotopic composition of this carbonate could not be identified. At very high temperature (1200 °C), little CO_2 was liberated. In five samples, the isotopic composition of the highest T fraction (8 to 13.5 ppm CO_2) varied between $-3.4\‰$ and $-7.6\‰$, and was thought to best represent the $\delta^{13}C$ of the daughter carbonate in fluid inclusions. For another eight samples (3 to 35 ppm C), CO_2 had $\delta^{13}C$ values from $-20\‰$ to $-35\‰$ in the highest

temperature fraction, which are indistinguishable from the $\delta^{13}C$ values of the low temperature fraction. The authors did not discuss the origin of the ^{13}C depletion in these meta gabbros. However, the absence of a correlation between $\delta^{13}C$ and the total C concentration, as well as the observation of joint low $\delta^{13}C$ and high C content of the undeformed meta gabbro, rule out ^{13}C depletion as the result of CO_2 loss.

Sugisaki and Mimura (1994) examined a wide range of rock types and demonstrated that mantle derived rocks such as tectonized peridotites in ophiolite sequences and peridotites from alkali basalts contained heavier hydrocarbons (*n*-alkanes), whereas gabbros and granites lacked them. Similarly, cumulate peridotites that were produced by magmatic differentiation (e.g., Stillwater) were found not to contain higher hydrocarbons. Laboratory or geologic contamination, accounting for the presence of the hydrocarbons, was ruled out by the authors and the higher hydrocarbons observed in the xenoliths were thought to be indigenous to the mantle. The authors suggested that the stability of higher hydrocarbons increases with pressure and hence their presence within the mantle is possible. The following sources for higher hydrocarbon compounds were considered. (1) Fischer Tropsch synthesis in the mantle; (2) remnants from meteorites accreting to form the Earth; (3) recycling during subduction. While higher hydrocarbons may survive high *P* and *T* in the mantle, they are thought to decompose to CH_4 at the lower pressures prevailing when magmas intrude into the crust. As a result, peridotite cumulates do not contain higher hydrocarbons than C_4H_{10}. The $\delta^{13}C$ of the mantle hydrocarbons, determined after combustion of material extracted from the rocks, was rather uniform around $-27\‰$. Considering the significant range of $\delta^{13}C$ of organic carbon, the constancy of this isotopic composition is not readily reconcilable with a subduction origin of these organic compounds. In addition, in view of the decreasing stability of hydrocarbons with increasing *P* and *T* (until mantle conditions are reached), one would expect a destruction of the higher hydrocarbons during the subduction process.

4. Discussion

Carbon with $\delta^{13}C$ of about $-5\‰$ has been identified as a major isotopic composition signature for the

mantle (carbonatite and kimberlite carbonates, diamonds and volcanic CO_2 exhalations); this signature is also carried by mantle xenoliths. However, C depleted in ^{13}C ($\delta^{13}C = -22‰$ to $-26‰$) has been observed by several investigators in the dissolution residue of mantle minerals (olivine, pyroxene) and rocks, and in C fractions that have been interpreted as C dissolved in silicates. Xenoliths from hotspot and non-hotspot volcanoes cover the whole C isotopic composition range observed in mantle xenoliths, although on average xenoliths from non-hotspot volcanoes contain isotopically lighter carbon. Differences in the C concentration and isotopic composition have been observed between minerals; the data are too few, however, to support firm conclusions on their size or how systematic these differences might be. Differences in $\delta^{13}C$ between more (higher ^{13}C content) and less fractionated (lower ^{13}C content) mantle xenoliths have been observed as well. Recently, *n*-alkanes, have been extracted from mantle xenoliths and proposed to be indigenous to the mantle. These hydrocarbons have a rather uniform $\delta^{13}C$ values of about $-27‰$, within the carbon isotopic composition range of moissanite recovered from kimberlite.

For some of the xenoliths, helium as well as carbon concentration and isotopic composition have been measured. For volcanic gases, one has used $\delta^{13}C$ together with the $CO_2/^{3}He$ ratio in models to estimate the relative contributions of mantle carbon and sedimentary carbon (carbonate carbon plus organic carbon) (e.g., Sano et al., 1997). Fig. 9 demonstrates that most of the xenoliths data are explainable by such a three-component mixing model. The solid curves in this figure describe the end member mixing (two components) of mantle C with sedimentary carbonate or organic matter. Samples which require three-component mixing plot between the two curves. Significantly different conclusions are reached, however, depending on whether the "low temperature" fraction is or is not included in the computation of the $C/^{3}He$ ratio and the $\delta^{13}C$ of the total C of a sample.

Fig. 10 displays the relative proportions of the three components necessary to obtain the observed carbon isotopic composition and $C/^{3}He$ ratios. The relative size of the end member contributions were evaluated based on the end member characteristics shown in Fig. 9. According to the model computation most ($61\% \pm 20$, std.) of the carbon would have to
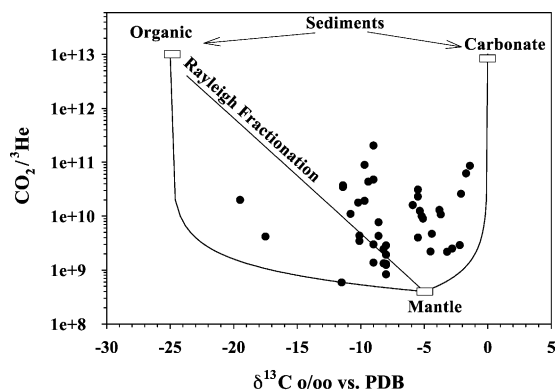

Fig. 9. Three component mixing model for mantle xenoliths based on $CO_2/^{3}He$ ratio and carbon isotopic composition. The solid line represents binary mixing between mantle and limestone and organic carbon respectively. Analyses between the binary mixing lines require mixing of three components. The model parameters are those of Fig. 1. Data from Mattey et al. (1989a), Porcelli et al. (1992), and Trull et al. (1993).

come from sedimentary carbonates and $28\% \pm 15$ std. from organic sediments. It is apparent that, on the basis of the model, one could conclude that only a small fraction of the carbon in the xenoliths would be derived from the mantle ($11\% \pm 14\%$ std.). This conclusion would change significantly, however, if all carbon now observed in the xenoliths would be considered, and a light mantle carbon source would be allowed for. In the studies reporting on the carbon isotope geochemistry of the xenoliths plotted in Figs. 9 and 10, no mention was made that the chemistry of the xenoliths examined, indicated a high sedimentary contribution or was unusual in any way. The possible decoupling of the He isotopic composition from sediment recycling, discussed above, as well as the large isotope variations suggested to have been produced in mantle degassing, put into question the basic assumptions of the model computation, namely that the three end members can be characterized by specific, immutable C and He isotopic compositions as well as constant elemental ratios. Hence, although the He and C concentrations and isotopic compositions may be fitted to a three component mixing model, the appropriateness of the model can be questioned.

The causes of the ^{13}C depletion in mantle C have been debated. Principal mechanisms considered include single or multiple step fractionation involving
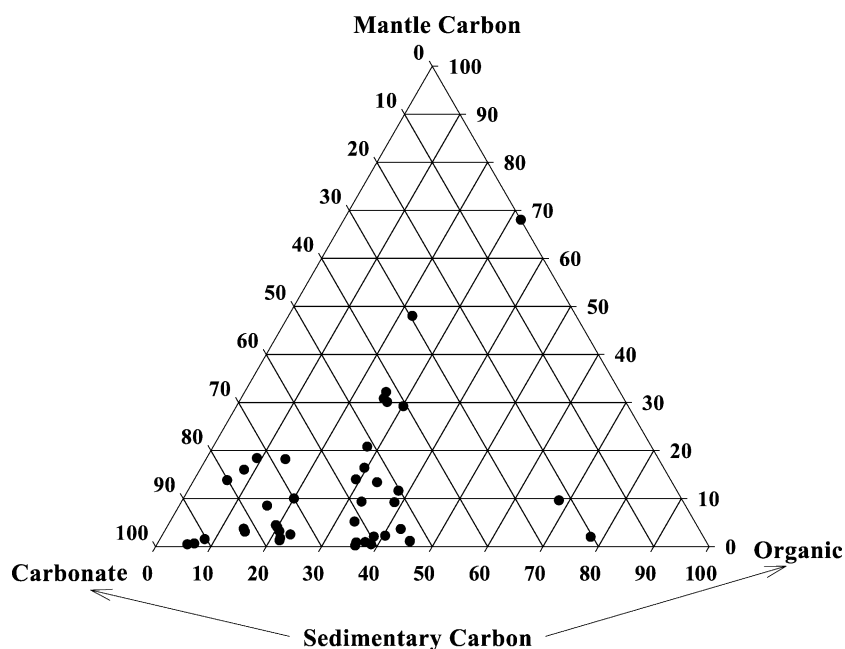
Fig. 10. Relative contributions of sedimentary and mantle carbon components in mantle xenoliths based on a three component mixing model. The assumed end member compositions ($\delta^{13}C$, $CO_2/^3He$) are those of Fig. 1.

carbon phases of differing oxidation states (e.g., CO_2 and reduced carbon, or carbon dissolved in silicate melts, CO, CH_4), magma degassing (loss of CO_2), introduction of biogenic carbon into the mantle, remnant carbon isotope heterogeneity from accretion, and as yet unknown high-temperature fractionation processes characterized by large fractionations. The observed $\delta^{13}C$ distribution places limits on what processes can be rationalized.

As a possible explanation for the wide range in mantle carbon isotopic composition, Javoy (1991) has suggested CO_2 loss from a mantle carbonate phase. Experimental work (e.g., Javoy et al., 1978; Mattey et al., 1990; Mattey, 1991) and observations on natural systems (e.g., Des Marais and Moore, 1984; Javoy and Pineau, 1986; Mattey et al., 1989b) have indicated a several per mil enrichment of ^{13}C in CO_2 compared to C in a melt phase. Degassing of CO_2 would thus result in a significant ^{13}C depletion in the residual carbon in a melt. Depending on the degree of CO_2 loss, the $\delta^{13}C$ values in the residuum could readily be as low as $-20‰$ or more; the ^{13}C depletion has been characterized by a Rayleigh fractionation (RF) proc-

ess. The $\delta^{13}C$ sampling frequency distribution of the residual carbon produced in this way would be a continuous smoothly declining spectrum of carbon isotopic compositions with a high degree of skewness toward low $\delta^{13}C$ values. While both the $\delta^{13}C$ distribution of diamonds (Fig. 8B) and the $\delta^{13}C$ distribution of mantle xenoliths (Fig. 5) have negative skewness, they do not have the form expected for a RF process. This becomes apparent in Fig. 11 where the observed diamond $\delta^{13}C$ distribution is compared with the distribution expected on the basis of Rayleigh fractionation. A reservoir isotopic composition of $-5‰$ with an internal variability of $1‰$ (1σ) and a $2‰$ ($4‰$) fractionation were assumed for the model computations. The diamond $\delta^{13}C$ distributions is distinctly bimodal, showing, compared to the Rayleigh fractionation model, a significant under-representation of $\delta^{13}C$ values between the two modes ($-5‰$ and $-20‰$ to $-25‰$).

If degassing was responsible for the observed large $\delta^{13}C$ range, one also would expect a correlation between $\delta^{13}C$ and the CO_2/He ratio as well as $\delta^{13}C$ and the C concentration. An example of the type of
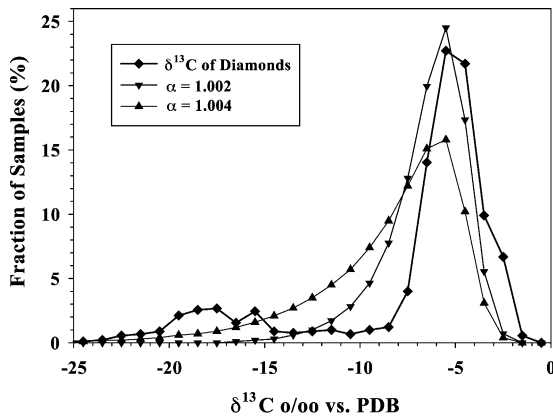
Fig. 11. Comparison of the diamond sampling frequency distribution (solid diamonds), with sampling frequency distributions generated using a Rayleigh fractionation model (solid triangles). Distributions for two different fractionation factors are shown.

relationship expected for a RF process is displayed in Fig. 9. The particular model computations shown are based on the assumption that the reservoir contains initially 1000 ppm C ($\delta^{13}C = -5\%o$), He of a $^3He/^4He$ ratio of 17 times the atmospheric ratio and a $C/^3He$ ratio of 4×10^8. The fractionation process is characterized by a 2‰ fractionation for C isotopes and K_D values of 2 and 3 for the extraction of C and He, respectively. The relationship shown is very insensitive to He isotope fractionation. The respective K_D values were chosen (see also the discussion below) so that the model computations produced $C/^3He-\delta^{13}C$ combinations that fell into the range of observed analytical data. The linear nature of the relationship does not depend, within the observed data range, on the size of the values assumed for the distribution coefficients. Fig. 9 demonstrates that there is no correlation between $\delta^{13}C$ and the $CO_2/^3He$ ratio and that few of the observations would fit a Rayleigh fractionation model, no matter what specific model assumptions would be adopted.

Fig. 12A and B demonstrates that $\delta^{13}C$ is also not related to the carbon concentration of the xenolith or their $CO_2/^4He$ ratio. Fig. 12A shows the expected RF relationships between carbon isotopic composition and concentration for different initial carbon concentrations (C_o) and vapor/melt distribution coefficients (K_D). Based on the experimental work cited above, a ^{13}C

fractionation of 2‰ between vapor and melt is assumed. The C distribution coefficient for the vapor melt separation will be larger than one, however, actual values are not known. Therefore, the results of computations using several, significantly different K_D values have been shown. With increasing K_D values, the
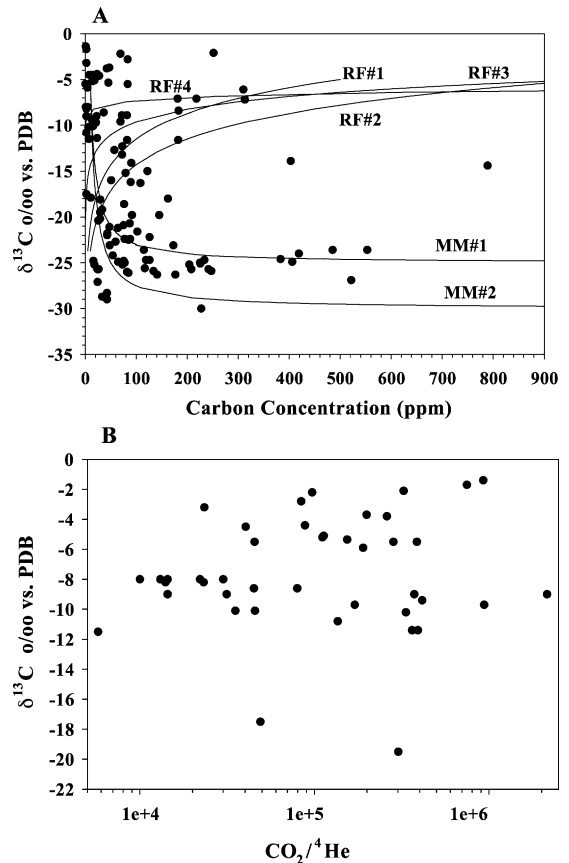

Fig. 12. Relationships between $\delta^{13}C$, C concentration and $CO_2/^4He$ ratio in mantle xenoliths. (A) Comparison of carbon isotopic composition and concentration in mantle xenoliths with Rayleigh Fractionation (RF) and Mixing (MM) Models. For the RF models, the fractionation 1000 $\ln\alpha_{CO_2}-C$ was assumed to be 2‰ and the initial $\delta^{13}C = -5\%o$. The initial C concentration (C_o) and the assumed distribution coefficient for C between the removed and residual phase (K_D) were varied. RF#1 $C_o = 500$ ppm, $K_D = 1.5$, RF#2 $C_o = 1000$ ppm, $K_D = 1.5$, RF#3 $C_o = 1000$ ppm, $K_D = 2$, RF#4 $C_o = 10\,000$, $K_D = 5$. The effect of mixing mantle C ($\delta^{13}C = -5\%o$) with organic C is shown for two different organic C isotopic compositors, MM#1, $\delta^{13}C = -25\%o$, MM#2, $\delta^{13}C = -30\%o$. (B) $\delta^{13}C$ and $CO_2/^4He$ ratio of mantle xenoliths.

model curves become more linear through much of the concentration range and large changes in $\delta^{13}C$ occur only at very low concentrations (e.g., for model RF#4 $\delta^{13}C$ values of $-10‰$ are reached only when the carbon concentration is below 0.5 ppm and values below $-20‰$ when the C concentration falls below 10^{-9} ppm). Most of the measurements are not explainable by a RF model for a range of possible model assumptions. The data thus provide no ready link between degassing and the large $\delta^{13}C$ range in mantle xenoliths.

Subduction has been appealed to frequently in order to explain low $\delta^{13}C$ values observed in mantle materials. The $\delta^{13}C$ distribution for the mantle xenoliths (Fig. 8A) provides some insight for the validity of this proposal as well. The lack of intermediate $\delta^{13}C$ values and, above all, the sharp drop of $\delta^{13}C$ values toward $0‰$ (the average of marine limestones) is not in accord with expectation for the carbon isotope record, if subduction of sediments were to be responsible for the observed $\delta^{13}C$ range in mantle xenoliths. It is interesting to note that this same question arises in the interpretation of the diamond carbon isotope record (Fig. 8B). In the context of a discussion on diamond formation, Galimov (1991) has pointed out that the wide range of $\delta^{13}C$ observed in surficial carbon could be expected to be homogenized during subduction and metamorphism.

Deines (1992) suggested that the probability of retaining carbon with an organic C or limestone C signature during a homogenization process, such as subduction, could be evaluated with the aid of a random mixing model. In such a model, it is assumed that in the subduction of sedimentary carbon, isotope exchange between organic ($-25‰$) and carbonate carbon ($0‰$) may occur to varying degrees (the degree of exchange can be controlled through input variables). One can consider cases of: (1) no mixing, or exchange, (2) the production of a continuous spectrum of isotopic compositions between the end members, or (3) the creation of specific intermediate isotopic compositions. The random sampling of this isotopic composition range is subject to the constraint that the weighted mean isotopic composition of the samples drawn equals $-7‰$ (the weighted mean $\delta^{13}C$ of diamonds). Complete homogenization would lead to one (the weighted mean) isotopic composition ($-7‰$), no

homogenization would lead to two peaks, one at $-25‰$ and one at $0‰$. The structure of the model is outlined in Table 4.

Examples of model computations showing varying degrees of isotopic homogenization are shown in Fig. 13. Fig. 13A–D represents frequency distributions generated when only two reservoir isotopic compositions ($-5‰$ and $-25‰$) are allowed. From Fig. 13A–D, the degree of mixing increases from none (the isotopic compositions of the reservoirs are preserved) to a high degree of mixing, where samples reflecting the pure $-25‰$ reservoir occur with very low frequency. If the number of samples, within a sample were to be increased further, eventually only samples of one isotopic composition would be observed (i.e., the mean isotopic composition of $-7‰$). In Fig. 13E–H, isotopic compositions from $0‰$ to $-25‰$ are allowed to occur, subject to the constraint that their weighted mean be $-7‰$. Again, the degree of homogenization increases from E through G. Fig. 13H represents a special case, in which the model was forced to produce a peak at a specified $\delta^{13}C$ value ($-20‰$). Exploring a large range of scales of homogenization of organic and carbonate carbon isotopic compositions, one finds that there is no way in which the light $\delta^{13}C$ values could be retained ($-25‰$), while producing the major mode of $\delta^{13}C$ values at $-5.5‰$. More importantly, all models which yield a significant fraction of low $\delta^{13}C$ values also produce a high frequency of $\delta^{13}C$ values around $0‰$.

The diamond $\delta^{13}C$ frequency distribution is compared in Fig. 14 with the expected $\delta^{13}C$ distributions, if during subduction organic C ($-25‰$) and limestone C ($0‰$) are mixed and permitted to exchange isotopes. Examples of a lower (Model 1) and higher (Model 2) degree of homogenization are shown, and the mismatch between model and observed distribution is apparent. The model computations demonstrate that the relatively high abundance of low $\delta^{13}C$ values in the diamond sampling frequency distribution is not balanced by a ^{13}C-enriched mantle reservoir as would be expected, if both organic and carbonate sedimentary carbon are subducted in the proportions in which they are present at the Earth's surface. The mismatch is a reflection of a fundamental mass balance problem which is inherent in the chosen boundary conditions

Table 4
Subduction/mixing model

Assumptions	(1) Sedimentary carbon reservoirs are:
	    (a) Carbonates: $\delta^{13}C_c$=(a variable input parameter)
	    (b) Organic Matter: $\delta^{13}C_o$=(a variable input parameter).
	(2) The subducted crustal carbon is a mix of organic and carbonate C with an average
	    $\delta^{13}C_s$=(a variable input parameter).
	(3) During subduction the two C reservoirs may mix or exchange isotopes, and a range in isotopic compositions
	    between the original carbonate and organic C is produced (variable input parameters). If carbonate of a specific
	    isotopic composition is created, there must be a complementary organic C isotopic composition such that
	    their weighted mean equals $\delta^{13}C_s$.
	(4) A specific isotopic composition may be preferentially retained, or formed, to produce an additional mode in the
	    distribution, $\delta^{13}C_m$=(a variable input parameter).

Model computations	(1) Create a 1000-cell table for each possible combination of $\delta^{13}C$ values of carbonate and organic C considered
	    (assumption #3) and fill cells randomly with $\delta^{13}C_{carbonate}$, and $\delta^{13}C_{organic}$ such that mean $\delta^{13}C$ value of the
	    table equals the mean $\delta^{13}C$ value of subducted crustal carbon (assumption #2).
	(2) Draw random samples (number of samples=a variable-input parameter) from each table, compute the mean
	    $\delta^{13}C$ and record the result. The mean $\delta^{13}C$ constitutes a sample. The samples drawn to compute the mean
	    have been termed samples within a sample.
	(3) Repeat step #2 many times (number of repetitions, or samples=a variable-input parameter).
	(4) Construct a sampling frequency distribution from the recorded mean isotopic compositions.

(Table 3). Hence, if one attributes the low $\delta^{13}C$ to the subduction of sedimentary organic carbon, this mass balance problem can be resolved only if one postulates a preferential subduction of ^{13}C depleted C into the mantle. However, no evidence for the preferential subduction of organic C has been presented to date. If it were to be proposed, a rather significant rethinking of the geochemical cycle of C and O would have to be undertaken.

Careful examination of the relationship between the ^{13}C depletion in diamonds and the chemical composition of their silicate and oxide inclusions for well more than 1000 specimens from 10 southern African kimberlites has yielded no support for a subduction origin of light mantle carbon (Deines et al., 2001). Because of the high contributions of limestone to the mantle carbon pool suggested by the model computations shown in Fig. 14, one would expect also a reflection in the chemistry and isotope record ($\delta^{13}C$ values close

to 0‰) of mantle xenoliths, yet none have been reported for the xenoliths reviewed here. Hence, chemical as well as carbon isotope data do not lend support to the subduction hypothesis for the origin of low ^{13}C C in the mantle.

The possibility producing isotopically light carbon in the mantle through large thermodynamic or kinetic isotope effects (e.g., Galimov et al., 1973, 1989) has not been explored in detail. There are several lines of evidence suggesting that thermodynamic isotope effects are a viable mechanism; among them are the following.

(a) The large systematic isotopic composition difference between graphite and the amorphous C obtained from the dissolution of pyroxene grains (see Table 3).

(b) The observations of Sugisaki and Mimura (1994) of highly ^{13}C depleted hydrocarbons in mantle xenoliths.

Fig. 13. Typical $\delta^{13}C$ sampling frequency distributions generated by the random sampling model. Each distribution represents 1000 samples whose mean weighted isotopic composition is $-7‰$. Sedimentary carbonate is assumed to have an isotopic composition of 0‰, and sedimentary organic of $-25‰$. For distributions (A) through (D), it is assumed that only isotopic compositions of 0‰ and $-25‰$ may be mixed, for distributions (E) through (G), the indicated intermediate isotopic compositions can mix, for distribution (H), it was assumed that an isotopic composition of $-20‰$ was preferentially retained.
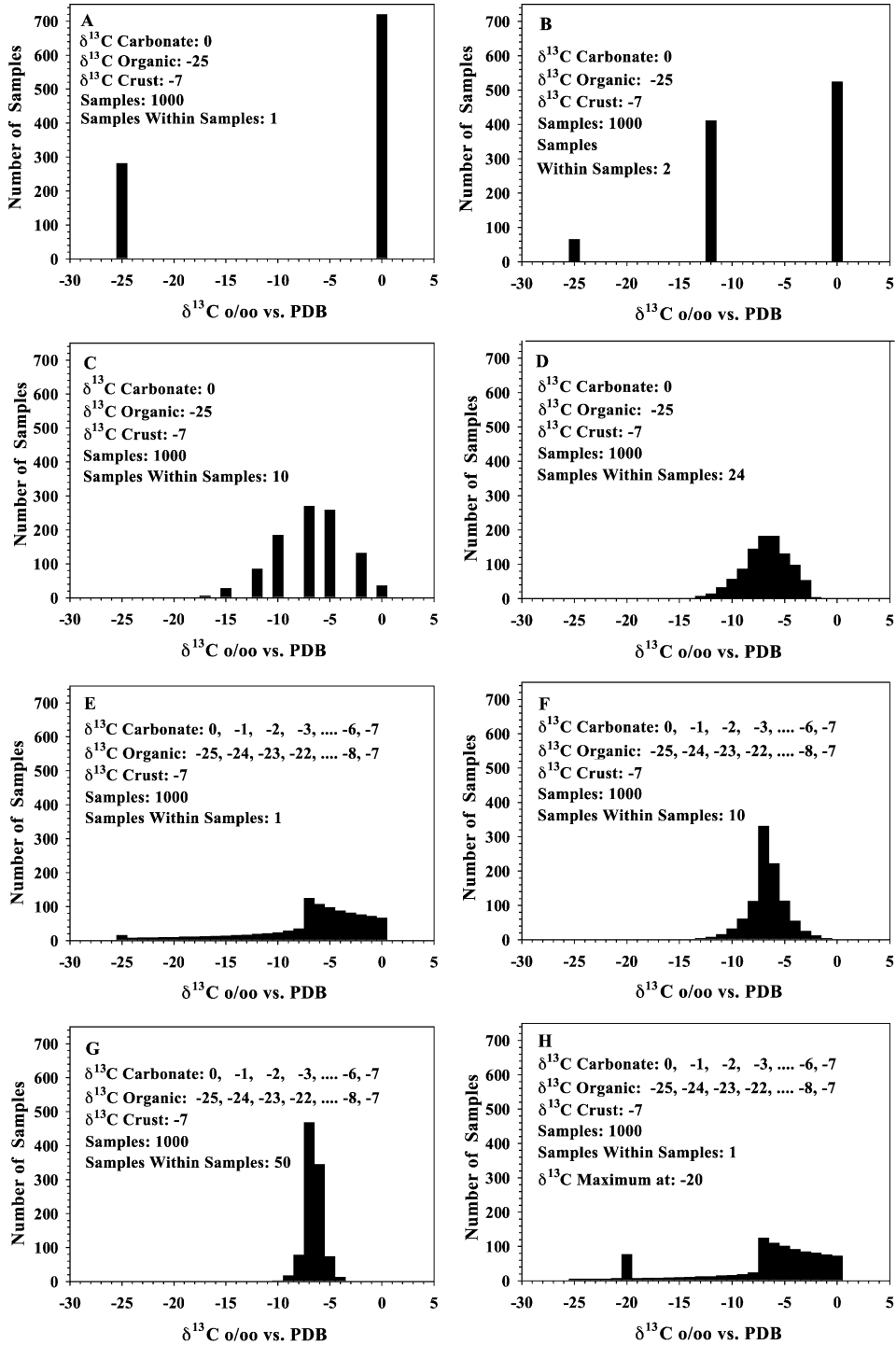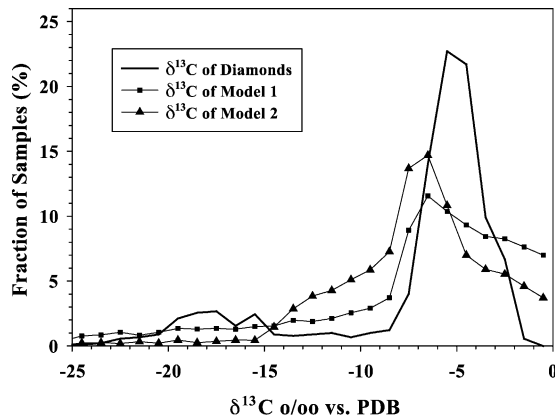
Fig. 14. Comparison of $\delta^{13}C$ sampling frequency distributions generated by random mixing model with the sampling frequency distribution of southern African diamonds. Model 1 and Model 2 represent an example of low and high degrees of homogenization, respectively, see text.

(c) The presence of large systematic isotopic composition differences between diamond and moissanite from the same kimberlite (see above). On average, a depletion of approximately 20‰ in the moissanite compared to diamond is indicated.

(d) The observation of large systematic isotopic composition differences in iron meteorites between graphite on the one hand and cohenite and C dissolved in Ni/Fe (taenite) on the other. The few data reported by Deines and Wickman (1975) suggest an average 13‰ depletion of the iron carbide with respect to graphite and a depletion of 14‰ of the carbon in solid solution in taenite compared to graphite. These data point to a significant isotopic composition difference between graphite and C in solid solution and suggest a large ^{13}C depletion of carbides with respect to graphite as well. These observations are similar to those made on mantle xenoliths (see a and c above).

(e) The results of theoretical computations. The first-principle computations (Fig. 15) demonstrate that in the temperature range 1000 and 1200 °C fractionations between CO_2 and unbonded carbon atoms between 18‰ and 13.5‰ can be expected. The fractionations between carbonate and atomic C (15.5‰ at 1000 °C and 11.5‰ at 1200 °C) and methane and atomic C (12‰ at 1000 °C and 9‰ at 1200 °C) are somewhat smaller; however, they are still

quite large. In all cases, the atomic carbon is depleted in ^{13}C compared to the other chemical species.

A major fraction of the Earth's deep carbon reservoir has $\delta^{13}C$ values around $-5‰$, as manifested by volcanic CO_2, exhalations, gas trapped in volcanic glasses, carbonates in kimberlites and carbonatites, as well as diamonds (Deines, 1992). If, for argument's sake, one would suggest that carbon of this isotopic signature occurred in the mantle as carbonate, carbon dioxide or methane, then the atomic carbon, e.g., C dissolved interstitially in mantle silicates (Tingle et al., 1989), could readily have an isotopic composition between $-25‰$ and $-15‰$, depending on temperature and the chemical form of the carbon with which it is in equilibrium. This is consistent with the data of, e.g., Watanabe et al. (1983), Galimov et al. (1989) and Nadeau et al. (1990). If, upon changes in P and T, the carbon solubility in minerals decreases (Tingle and Green, 1987; Tingle et al., 1988, 1989), carbon of this light isotopic composition would exsolve. The graphite grains in garnets, showing exsolution of pyroxene as a result of pressure reduction (Doukhan et al., 1994), might be an example. If such C would participate in the formation of diamonds, a number of features in their $\delta^{13}C$ distribution could be understood including the difference in the carbon isotope distribution between eclogitic and peridotic diamonds, the independence of the inclusion chemistry and diamond
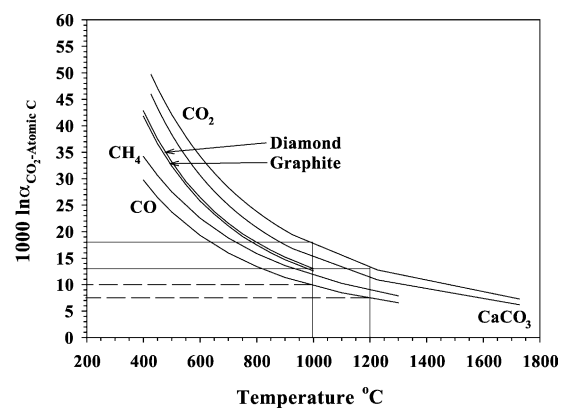

Fig. 15. Computed carbon isotope fractionation between CO_2 (Richet et al., 1977; Chacko et al., 1991), $CaCO_3$ (Chacko et al., 1991), Diamond, Graphite (Bottinga, 1969), CH_4, CO (Richet et al., 1977) and atomic C. The size of the fractionation at 1000 and 1200 °C is indicated for CO_2 and CO.

host $\delta^{13}C$ as well as the very abrupt large changes in $\delta^{13}C$ in some diamonds (for a summary, see Deines et al., 2001).

Detailed studies of diamonds have demonstrated that they have a complex history and there is ample evidence that their growth (C deposition) does not necessarily occur under equilibrium conditions. This raises the possibility that kinetic isotope effects could also contribute to the mantle $\delta^{13}C$ variability. Although to date, little attention has been given to the importance of kinetic isotope effects in mantle carbon geochemistry, their potential significance should not be overlooked. Galimov et al. (1973) measured a fractionation of 25‰ between diamond and the methane from which it precipitated (^{13}C enrichment in the diamond) and a 20‰ fractionation between methane and graphite which was precipitated from it (the graphite being depleted in ^{13}C). In both cases, C precipitation occurred clearly out of isotopic equilibrium.

Theoretical approximations (e.g., Van Hook, 1970) suggest that kinetic isotope effects may be large for C molecules at mantle temperatures. In a diatomic approximation (e.g. CO), one finds for the Harmonic Rate Ratio (HRR) at high temperatures:

$$\ln(\text{HRR}) = \left(\frac{h}{k \times T}\right)^2 \times \frac{1}{24}$$

$$\times \left[(\omega \times c)^2 \times \left[1 - \frac{M_1 \times (M_2 + M)}{M_2 \times (M_1 + M)}\right]\right]$$

$$+ \ln\left[\left[\frac{M_2 \times (M_1 + M)}{M_1 \times (M_2 + M)}\right]^{1/2}\right]$$

where: h = Planck's constant = 6.626×10^{-27} erg s; k = Boltzmann's constant, 1.381×10^{-16} erg/°; T = absolute temperature; ω = wave number for CO = 2170 cm^{-1}; c = velocity of light 2.998×10^{10} cm/s; M_1 = mass of ^{12}C in atomic mass units; M_2 = mass of ^{13}C in atomic mass units; M = mass of ^{16}O in atomic mass units.

In Fig. 16, the kinetic isotope effect for the CO molecules (1000 ln(HRR)) has been shown as a function of temperature, indicating that significant kinetic isotope effects could occur at high temperatures in
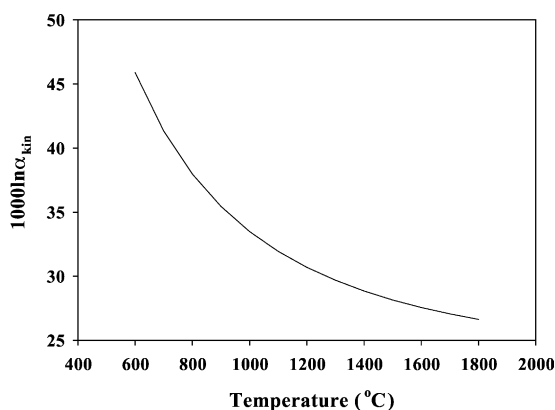

Fig. 16. High temperature approximation of the kinetic isotope effect for the $^{12}C^{16}O/^{13}C^{16}O$ fractionation, see text.

reactions involving CO. Similar size effects are obtained if other C species are considered.

5. Conclusions

The mantle carbon isotope geochemistry less well understood than one might have anticipated and a number of areas for future research can be identified. While C of about -5‰ was recognized early as a major mantle isotopic composition signature, the presence of mantle C depleted in ^{13}C ($\delta^{13}C$ on average = -25‰) must now be considered as a mantle C signature as well. Such light carbon has been observed in diamonds, graphite, carbide, and identified with lesser certainty as hydrocarbons, and C dissolved in mantle minerals. The data on xenoliths from basalts indicate that their $\delta^{13}C$ distribution is essentially bimodal with peaks at -5‰ and -25‰, however, the geologic occurrence of this light carbon has not yet been clearly delineated.

While, on average, xenoliths from non-hotspot volcanoes contain isotopically lighter carbon than xenoliths form hotspots, both xenolith types cover the whole isotopic composition range. Xenoliths from kimberlites cover the whole isotopic composition range as well, but, on average, probably show the lowest degree of ^{13}C depletion. In addition, the second, low $\delta^{13}C$, mode may occur just above -20‰, i.e. where the low ^{13}C mode of southern African diamonds

is located. Further studies will have to confirm this observation. The xenolith data also point to the presence of differences in the C concentration and isotopic composition between mantle minerals. The size of these differences, or how systematic they might be, remains to be determined. Differences in $\delta^{13}C$ between more (higher ^{13}C content) and less fractionated (lower ^{13}C content) mantle xenoliths have been observed as well.

Processes that have been considered to be responsible for the considerable $\delta^{13}C$ range include the subduction of organic material and degassing. The observations on mantle xenoliths do not support either, but provide evidence that as yet unexplored thermodynamic or kinetic isotope effects may occur. The former involve probably dissolved C in minerals, and Si−C bonds, and, because of their magnitude, may be responsible for the observed mantle carbon isotope distribution. The occurrence of such isotope effects would help to understand a number of observations on geochemistry of diamonds. The potential that large kinetic isotope effects contribute to the mantle carbon isotope heterogeneity exists as well. Further research will have to establish their importance.

In so far as mantle degassing models have been based, in part, on carbon isotopic compositions and C/^{3}He ratios, an understanding the mantle carbon isotope geochemistry is essential to support or refute their validity. The xenolith data do not support degassing models based on the assumption of limited carbon isotope variability of C indigenous to the mantle, or the supposition that all ^{13}C depleted carbon is of surface origin. The relative proportions of the mantle C's of differing isotope signatures are not known, however, and will have to be quantified so that well founded C cycle models can be formulated.

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