

## Subducted carbonates, metasomatism of mantle wedges, and possible connections to diamond formation: An example from California

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### ABSTRACT

We investigated calcite globules and veins in two spinel-garnet peridotite xenoliths from the sub-Sierra Nevada mantle. The studied xenoliths were entrained in a Miocene (11 Ma) volcanic plug. These carbonates are associated spatially with silicate glass inclusions, suggesting that they are primary inclusions—inclusions that formed at high temperature in the mantle and not at or close to the Earth's surface. The host peridotites represent samples of the lithospheric mantle wedge beneath the Mesozoic California magmatic arc, as indicated by radiogenic isotopic ratios measured on clinopyroxene separates [ $^{87}\text{Sr}/^{86}\text{Sr}(11\text{ Ma}) = 0.7058\text{--}0.7061$ ,  $\epsilon_{\text{Nd}}(11\text{ Ma}) = -1.9$  to  $-0.7$ ]. Mineral chemistry of the peridotite major phases is typical of a mantle section that was depleted of melt. The  $\delta^{18}\text{O}$  values of olivine and orthopyroxene from the two samples are also typical of mantle rocks ( $\delta^{18}\text{O} = 6\text{--}6.5\text{‰}$ ). In contrast, calcite veins have  $\delta^{18}\text{O}$  of  $18\text{--}20\text{‰}$  and  $\delta^{13}\text{C}$  of  $-14\text{‰}$ , arguing for a subducted sedimentary origin for these carbonates. Presumably, the carbonates were expelled from the downgoing slab and fluxed into the overlying mantle wedge as  $\text{CO}_2$ - or  $\text{CO}_2\text{-H}_2\text{O}$ -rich fluids or melts. The trace-element patterns of two analyzed calcite veins are typical of the arc signatures (e.g., depletions in high-field-strength elements) seen in calc-alkaline magmatic rocks worldwide. However, the cores of peridotite clinopyroxenes do not show that pattern, suggesting that the arc-like trace element signature was introduced via the recycled carbonate agent. A connection between mantle wedge carbonation and diamond formation in a subduction environment is proposed based on these observations.

### INTRODUCTION

Mantle metasomatism at subduction zones is thought to be one of the key processes that leads to arc magmatism (Davies and Stevenson 1992). Fluids released by the downgoing slab are thought to flux into the upper plate (the mantle wedge) and depress the peridotite solidus (e.g., Wyllie 1984). Although these fluids are primarily aqueous, carbonic fluids also can play an important role in mantle metasomatism and melting (Wood et al., 1996). In fact,  $\text{CO}_2$  fluxes in arc volcanoes are larger than those at mid-ocean ridges (Sano and Williams 1996; Marty and Tolstikhin 1998), making arc volcanoes the largest deep reservoir releasing  $\text{CO}_2$  into the atmosphere. Carbon-isotopic ratios are used to estimate that about 80% of the  $\text{CO}_2$  inventory in arc volcanoes is derived from recycled sediments, i.e., organic sediment and marine limestones (Marty and Tolstikhin 1998), the remaining being primary mantle carbon. These observations indicate that  $\text{CO}_2$  fluxing in the mantle wedge may be an important ingredient in generating arc magmas. However, available experimental (e.g., Molina and Poli 2000) and thermodynamic (e.g., Kerrick and Connolly 1998, 2001) data indicate that decarbonation takes place at higher temperatures than dehydration in the slab and that carbonate rocks may persist in the slab at depths greater than those sampled by arc volcanoes. Overall, quantifying carbonate recycling at subduction zones is a particularly important challenge, given the need to understand the role of fluids in arc

magmatism as well as the atmospheric carbon cycle over geologic timescales. It is also plausible that much of the recycled  $\text{CO}_2$  in arc volcanoes may be derived from sedimentary sections that were emplaced in the lower crust beneath arcs via shortening and not from the subducted slab; this hypothesis has yet to be tested (Stern 2002). The issue of how much  $\text{CO}_2$  is released from the slab into the upper mantle and ultimately in arc volcanoes is very much unresolved and currently suffers from little direct (observational) evidence.

Rare direct observations on upper-mantle xenoliths from arc environments confirm the presence of carbonic fluids in the mantle. In this study, we present new trace-element and isotopic analyses from carbonated peridotite xenoliths from the central Sierra Nevada, California (Dodge et al. 1988). This is the first report of calcite-bearing peridotites from this locality. Crustal and mantle xenoliths from Miocene pipes in the central Sierra Nevada represent fragments of the Mesozoic-Cenozoic sub-arc lithosphere (Ducea and Saleeby 1998) of this classic Cordilleran subduction zone (Dickinson 1981). We use isotopic tracers to show that the carbonates are recycled via the subducted Farallon slab, and that they imprint an arc-like trace-element signature on peridotite clinopyroxenes, a signature that the pyroxenes did not possess originally. Carbonate fluxing may have also been responsible for generation of sub-arc diamonds in California.

### SAMPLES AND TECHNIQUES

The Sierra Nevada batholith is a typical Mesozoic Cordilleran magmatic arc, composed primarily of tonalitic and granodioritic plutons. Granitoid rocks are

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known from present-day surface exposures to extend to a depth of at least 30 km in the Cretaceous crustal column (Saleeby 1990; Ducea 2001). Samples of more deeply seated rocks representing the lower crust and the upper mantle beneath the arc are entrained as xenoliths in volcanic rocks of Miocene age from the central Sierra Nevada (Dodge et al. 1988; Mukhopadhyay and Manton 1994; Ducea and Saleeby 1998). They include granulite- and eclogite-facies rocks of the arc root, as well as spinel-garnet and garnet-bearing peridotites that represent samples of the mantle wedge beneath the arc (Ducea and Saleeby 1998).

Two large (5–8 cm in diameter) calcite-bearing spinel-garnet peridotites (BC115 and BC125) from the Miocene (11.1 Ma) Big Creek trachyandesitic pipe (Dodge et al. 1988; Mukhopadhyay and Manton 1994; Ducea and Saleeby 1996, 1998; Lee et al. 2000a) in the Huntington Lake area, central Sierra Nevada [37°13' N, 119° 16' W, see also Ducea and Saleeby (1996) for a location map], were selected for analysis. The samples are typical of the central Sierra Nevada peridotite suite and contain spinels that are rimmed by garnets. Calcite veins make up about 3–5% of the analyzed samples. Calcite crystals are found as globules and micro-veins that are up to 0.7 cm in diameter and 0.4 cm in width, respectively (Fig. 1). In a few cases, carbonate veins either following grain boundaries or filling fractures connect patches and globules of carbonates to each other. Secondary, small euhedral olivine and spinel crystals are associated with the carbonates, typically within the carbonate. Carbonate crystals are found in spatial connection with aluminosilicate glass inclusions (Fig. 1). Major-element analyses of these glasses (see below) show that they are basaltic in composition and are distinct from the host lavas.

Electron-microprobe analyses on minerals were carried out at the University of Arizona using the Cameca SX50 microprobe equipped with 5 wavelength-dispersive spectrometers (using LiF, PET, and TAP crystals). Counting times for each element were 30 seconds at an accelerating potential of 15 kV and a beam current of 10 nA. Measurements with oxide totals outside of the range  $100 \pm 1\%$  were discarded from the analyzed silicates.

Trace-element analyses were performed on carbonates mechanically separated from the peridotites, as well as clinopyroxene separates (about 80 mg). The following acid-leaching routine obtained a rim fraction of clinopyroxenes: unbroken clinopyroxene grains were first leached in mild, cold 2.5 M HCl for two hours. This step was performed to eliminate any additional carbonate that may reside at clinopyroxene grain boundaries; then the leachate was discarded and the grains were dried out and inspected optically. The clean grains without any grain boundary staining were used for the next step, a second leaching carried out in a hot (150 °C) mixture of concentrated HF and HNO<sub>3</sub>; after two weeks of dissolution, about 1/3 of the clinopyroxene mass was dissolved—the leachate was used for the clinopyroxene rim fractions. The undissolved clinopyroxene grains were then dried out, weighed, crushed into a powder, and dissolved in the same manner—the dissolved samples were analyzed as the “clinopyroxene core” fractions. About 10% of the dissolved core and rim samples were used for trace-element determinations in an ICP-MS instrument, the remainder being eluted in standard chromatographic columns for thermal ionization mass spectrometry (TIMS) analyses. For both fractions, the elution procedures for radiogenic isotopic analyses are as in Ducea and Saleeby (1998).

Trace-element determinations were performed at Caltech on an Elan Ar-source quadrupole ICP-MS. Well-known USGS standards were used for calibrating the ICP-MS instrument. Strontium and Nd isotopes were measured using the techniques described in Ducea and Saleeby (1998). Isotopic analyses were performed at Caltech on a VG Sector TIMS instrument (Ducea and Saleeby 1998) and replicated at the University of Arizona on a Sector 54 VG instrument (Ducea et al. 2002).

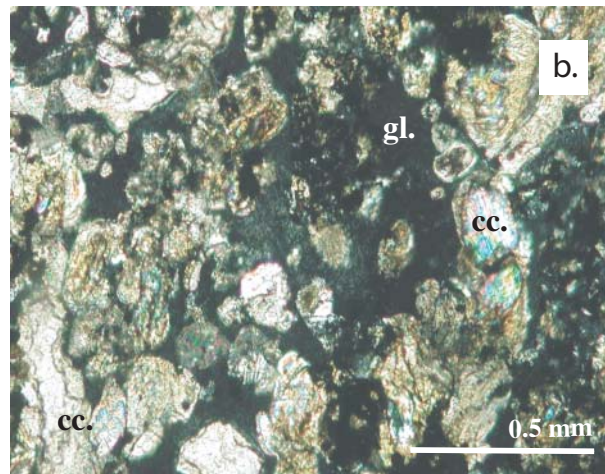
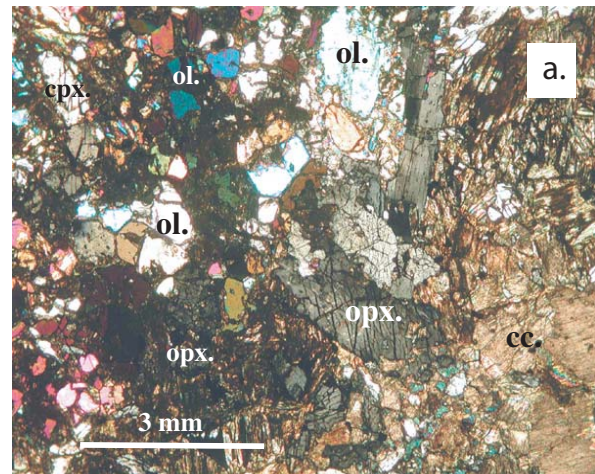
Olivine mineral separates (1–2 mg) were analyzed for O-isotopic ratios at Caltech, following the techniques of Holt and Taylor (1998). The O was extracted using a laser fluorination line, followed by analysis of isotopic ratios of major minerals, expressed as  $\delta^{18}\text{O}$  in per mil relative to SMOW. The extracted O was converted to CO<sub>2</sub> using a heated carbon rod. This CO<sub>2</sub> was analyzed with a Finnigan MAT252 mass spectrometer. Precision is better than 0.2‰ (1 $\sigma$ ) for the olivine separates analyzed in this study. Carbon- and O-isotopic measurements on calcite mechanically separated from the xenoliths were performed at University of Southern California using the techniques outlined in Woods et al. (1999).

## RESULTS

### Peridotites

The two analyzed peridotites have mineral chemistries typical of the sub-Sierra Nevada mantle, as known from previously reported data (Mukhopadhyay 1989; Ducea and Saleeby 1996, 1998). Olivines are Fo<sub>91</sub> in BC115 and Fo<sub>92</sub> in BC125 (Table 1),

which is close to the average of peridotites in the central Sierra Nevada Miocene suites. These rocks are thought to be melt-depleted, possibly via several episodes of melting, but certainly during the formation of the overlying Sierra Nevada magmatic arc (Lee et al. 2000). The samples yielded equilibration temperatures of 950–1000 °C (using Brey and Kohler 1990), which are typical of mantle peridotites from Big Creek (Dodge et al. 1988, Mukhopadhyay and Manton 1994; Ducea and Saleeby 1996). The equilibration pressure determined on BC115 is  $26 \pm 2$  kbar, and was determined using the Al-in-orthopyroxene barometer (Harley 1984). The high pressure measured in BC115 is consistent with the fact that the spinel-garnet transition can be as deep as 100 km beneath active continental margins (O'Neill, 1981; Robinson and Wood 1998). BC125 did not yield a reliable



**FIGURE 1.** Photomicrographs. (a) Cross-polarized view of peridotite BC115 showing calcite vein material in the lower right corner of the section. Note the porphyroclastic texture of the peridotite. (b) Detailed view of a silicate glass pocket from BC125; the glass, which is isotropic, is intermixed with calcite. Abbreviations: ol = olivine, opx = orthopyroxene, cpx = clinopyroxene, cc = calcite, gl = aluminosilicate glass.

pressure, possibly because the garnet, which is rimming spinel, is not in equilibrium with the orthopyroxene; however, the similarity in the overall compositions of BC115 and BC125 makes it likely that BC125 has been sampled from a similar depth. Radiogenic isotopic ratios on separated clinopyroxenes—age corrected to 11 Ma—are  $^{87}\text{Sr}/^{86}\text{Sr} = 0.7058\text{--}0.7061$ , and  $^{143}\text{Nd}/^{144}\text{Nd} = 0.51254\text{--}0.51260$  or  $\epsilon_{\text{Nd}} = -1.9$  to  $-0.7$  (Table 2). These numbers are consistent with previously measured ratios on sub-Sierra Nevada peridotites (e.g., Dodge et al. 1988; Mukhopadhyay and Manton 1994; Ducea and Saleeby 1998) and are indicative of a lithospheric mantle origin for the peridotites. The  $\delta^{18}\text{O}$  measured on olivine from the two peridotites (6.4 and 6.5‰) are within the range, although on the high side of O-isotopic ratios measured worldwide, of olivines from the continental mantle (e.g., Rosenbaum et al. 1994, for a review). The oceanic mantle, in contrast, is characterized by a much more limited range of  $\delta^{18}\text{O}$ , all measured olivines being close to a value of  $5.2 \pm 0.2\text{‰}$ . Trace element patterns (Table 3) measured on clinopyroxene cores are similar to other measurements on peridotite clinopyroxenes from the Sierra Nevada (Domenick et al. 1983; Ducea 1998), and are slightly enriched in incompatible elements (Fig. 2) on a chondrite-normalized diagram. Clinopyroxene rims have significantly higher (up to 5 $\times$ ) concentrations of incompatible trace elements relative to their cores (Fig. 2), and display negative anomalies of the high-field-strength elements (Nb, Ta, Zr, and Ti). The rims of the clinopyroxenes have been chemically modified by metasomatism.

### Carbonates

The analyzed carbonate vein material in both samples is calcite containing only a small amount of MgO (<0.7 wt%). The almost pure  $\text{CaCO}_3$  composition of these carbonates is indicative of the fact that these globules cannot represent frozen carbonatite melts, because carbonate melts could not have had more than 80%  $\text{CaCO}_3$  (e.g., Lee and Wyllie 1996; Wyllie and Lee 1998). The Mg. no. of the calcite is ~90, which suggests that the carbonate veins have equilibrated—in this respect—with the olivine-rich, peridotite matrix. Age-corrected Sr- and Nd-isotopic ratios ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.7081\text{--}0.7083$ , and  $^{143}\text{Nd}/^{144}\text{Nd} = 0.51221\text{--}0.51223$  or  $\epsilon_{\text{Nd}} = -8.3$  to  $-8.0$ ) are distinct from the values measured on clinopyroxene separates and are within the range of Cenozoic Pacific waters (Faure 1986). The  $\delta^{18}\text{O}$  values are very high (18.6–20.5‰), and clearly indicate a sedimentary origin for the precursor of the carbonate. Moreover, the negative values of  $\delta^{13}\text{C}$  (–14.1 and –14.3‰) suggest that at least a component of the  $\text{CO}_2$  present in these carbonates may have formed originally in an organic environment. A recent study by Deines (2002) has pointed out that, alternatively, low-C isotopic ratios in mantle rocks may be produced via fractionation due to “unexplored thermodynamic effects” in Si-C bonds within the mantle, but the combination of O- and C-isotopic ratios on these carbonates gives us confidence that their precursor  $\text{CO}_2$  formed at or near the surface of the Earth.

Chondrite-normalized trace-element patterns of carbonate veins (Figs. 2 and 3) show negative anomalies of the high-field-strength elements such as Nb, Ta, Zr, and Ti. The overall concentrations of trace elements in the analyzed calcite vein materials are typical of trace-element concentrations in sedimentary

carbonates and muds (Sammartano et al. 2002). In contrast, those of mantle-derived, primitive carbonatites tend to be significantly (an order of magnitude) more enriched in incompatible elements (e.g., Bell 1989).

### Silicate glass

Major-element compositions of glass inclusions found in BC115 and BC125 (as well as the host trachyandesite from

**TABLE 1.** Olivine major-element compositions in carbonated peridotites BC115 and BC125

	BC115 olivine core	BC115 olivine rim	BC125 olivine core	BC125 olivine rim
<b>Oxide wt%</b>				
MgO	50.46	51.45	50.80	50.96
SiO <sub>2</sub>	40.35	40.32	40.52	40.64
CaO	0.01	0.03	0.02	0.01
MnO	0.11	0.16	0.11	0.11
FeO	9.37	7.35	8.79	8.88
Total	100.31	99.49	100.25	100.26
<b>Atomic proportions (based on 4 O atoms)</b>				
Mg	1.836	1.874	1.844	1.844
Si	0.985	0.981	0.987	0.986
Ca	0.00017	0.0083	0.0005	0.00017
Mn	0.00217	0.0033	0.0022	0.0023
Fe	0.191	0.150	0.179	0.180
Mg. No.	0.91	0.93	0.91	0.91

Notes: Analytical techniques and errors are described in text.

**TABLE 2.** Isotopic compositions

Sample	$^{87}\text{Sr}/^{86}\text{Sr}_{11}$ *	$^{143}\text{Nd}/^{144}\text{Nd}_{11}$ *	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$
<b>BC115</b>				
Olivine				6.4
Clinopyroxene	0.705821	0.512601		
Calcite vein	0.708112	0.512231	–14.3	18.6
<b>BC125</b>				
Olivine				6.5
Clinopyroxene	0.706105	0.512538		
Calcite vein	0.708323	0.512212	–14.1	20.5

\*Strontium and Neodymium isotopic data are age corrected to 11 Ma, the age of the eruption of the host lava. The Sr isotopic ratios of standards and samples were normalized to  $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ , whereas the Nd isotopic ratios were normalized to  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ . Sr and Nd standards are identical to values previously measured on the same batches of standards. The estimated analytical  $\pm 2\sigma$  uncertainties for samples analyzed in this study are  $^{87}\text{Sr}/^{86}\text{Sr} = 0.002\%$  and  $^{143}\text{Nd}/^{144}\text{Nd} = 0.002\text{--}0.003\%$ .

**TABLE 3.** Trace-element concentrations of clinopyroxene cores, rims, and calcite veins (ppm)

Element	BC115			BC125		
	Cpx core	Cpx rim	Calcite	Cpx core	Cpx rim	Calcite
Ba	37.11	43.77	139.30	90.03	151.55	179.85
Rb	8.77	11.81	58.25	6.65	6.39	17.39
Th	0.05	0.11	1.14	0.11	0.18	0.95
U	0.09	0.19	1.26	0.15	0.28	1.80
Nb	1.97	0.47	0.13	1.96	0.81	0.36
Ta	0.12	0.02	0.00	0.09	0.04	0.02
La	0.81	1.89	14.13	1.65	9.22	55.28
Ce	1.57	3.00	18.56	1.93	8.14	76.24
Sr	25.77	78.45	308.55	28.70	69.90	377.06
Nd	1.09	1.70	8.70	1.03	3.51	21.34
Sm	0.22	0.35	1.81	0.20	0.58	7.62
Eu	0.08	0.10	0.42	0.08	0.20	1.43
Gd	0.26	0.34	1.38	0.32	0.92	3.23
P	0.11	0.14	0.31	0.11	0.17	0.59
Zr	4.35	3.36	1.51	5.34	3.55	2.92
Hf	0.12	0.11	0.04	0.15	0.12	0.08
Ti	0.03	0.03	0.02	0.05	0.04	0.03
Yb	0.16	0.17	0.47	0.24	0.23	1.22

Note: See text for analytical details and uncertainties.

Ducea 1998) are reported in Table 4. The compositions are alkali-basaltic, and suggest that these glasses are partial melts of the upper mantle, most likely a metasomatized section (e.g., phlogopite or amphibole present). Although the spatial association of carbonate with silicate glass is obvious, textural evidence is ambiguous as to whether these carbonates were immiscible melts or co-existing CO<sub>2</sub>-rich fluids. Experimental petrologic data (e.g., Wyllie and Lee 1998) suggest it is highly unlikely that immiscible carbonatite melts would form from silicate glasses with the compositions measured here. Instead, they are most likely the product of partial melting of the host peridotite after it was fluxed with CO<sub>2</sub>-rich fluids.

## INTERPRETATIONS

### Primary origin of carbonates

The low  $\delta^{13}\text{C}$  and high  $\delta^{18}\text{O}$  of the analyzed carbonate material may be suspected to be surficial in origin, i.e., that the veins formed after the xenoliths were brought up to the surface or during volcanic entrainment and ascent. There are two significant observations that argue for a mantle origin of the calcite vein material: (1) spatially, the calcite crystals are associated with silicate glass inclusions having the composition of partial

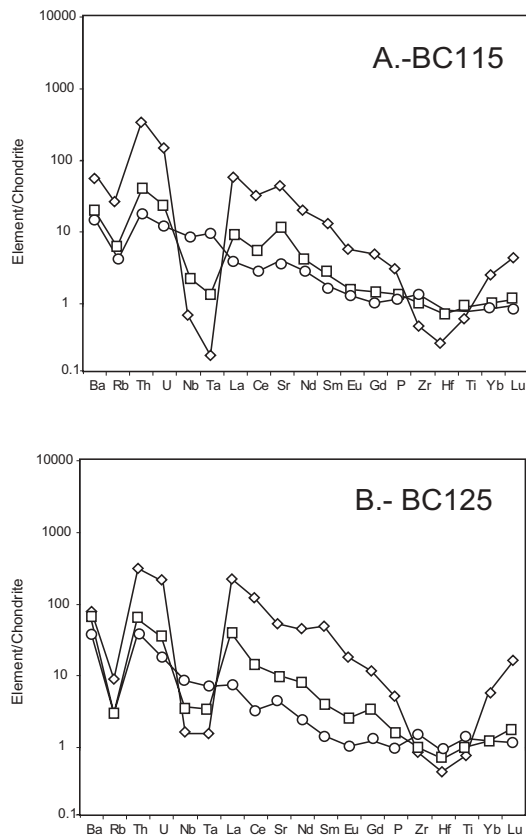
melts—silicate glass is only found in close proximity (mm) to the carbonates; and (2) the calcite veins are restricted to the xenoliths and do not cut into the host trachyandesite; moreover, we did not observe calcite crystals in the host trachyandesite. The silicate glasses measured in samples BC115 and BC125 are former melts percolating through the upper mantle; they are significantly different in major-element compositions from the host trachyandesite (Table 4). While available experimental petrology data (e.g., Wyllie and Lee 1998) show that calcites with the composition reported here are unlikely to have formed as immiscible melts from silicate liquids, the carbonates had to have formed at high temperature in the presence of silicate melt, most likely as a separate CO<sub>2</sub> or CO<sub>2</sub>-H<sub>2</sub>O rich phase. We therefore interpret the calcite globules and veins to have formed while their host peridotites resided in the upper mantle.

### Timing of carbonate metasomatism

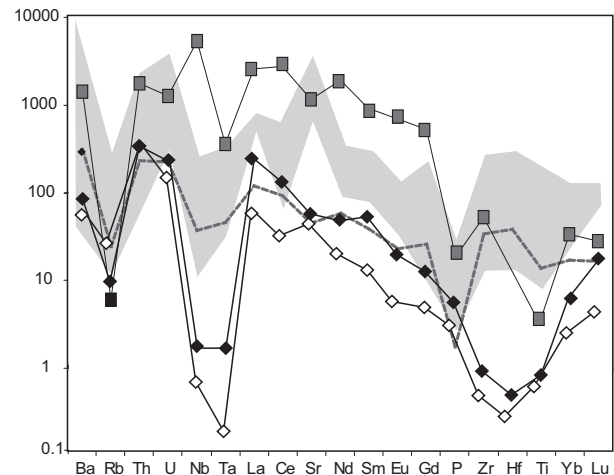
High-temperature, O-isotopic equilibrium between calcite and olivine requires a  $\Delta < 3\text{‰}$  at 1000–1200 °C (Clayton et al. 1989), which was not achieved in our samples. The lack of stable-isotopic equilibrium between the calcite and peridotites indicate that fluxing of peridotites with the carbonate fluid took place shortly ( $< 10^6$  yr) before the eruption of the host volcanic plug at 11.1 Ma (Dodge et al. 1988). A similar disequilibrium was used to argue for Cenozoic metasomatism of the Slave province mantle lithosphere with carbonatite melts (van Acherbergh et al. 2002).

### Sedimentary origin of the carbonate precursors

The stable-isotopic ratios of the measured calcite unambiguously demonstrate a sedimentary origin for the carbonates. The low  $\delta^{13}\text{C}$  is typical of organic sediments. A low  $\delta^{13}\text{C}$  carbon has been found in many mantle xenoliths [see Deines (2002) for a review], although none of the determinations were made on



**FIGURE 2.** Trace-element concentrations normalized to chondritic values: calcite veins (diamond symbols), clinopyroxene rims (square symbols), and clinopyroxene cores (circles) from peridotites: (A) BC115, and (B) BC125. Chondrite normalization values are from McDonough (1995).



**FIGURE 3.** Trace-element concentrations normalized to chondritic values (McDonough 1995)—calcite veins in Sierran peridotites (BC115 = open diamonds, BC125 = filled diamonds) are compared to the host Big Creek trachyandesite (dashed line, Ducea, unpublished), average carbonatites [filled squares, after Woolley and Kempe (1989)], and an average of deep sea carbonates [shaded field, after www.earthref.org; Plank and Langmuir (1998); Sammartano et al. (2001)].

**TABLE 4.** Major-element compositions of glass inclusions from xenoliths and of host trachyandesite

Element	BC115*	BC125*	BC150†
SiO <sub>2</sub>	48.18	49.88	57.70
TiO <sub>2</sub>	1.82	1.35	0.66
Al <sub>2</sub> O <sub>3</sub>	14.48	13.50	13.01
FeO‡	8.32	8.65	5.60
MgO	9.11	9.88	8.50
CaO	9.66	8.25	5.10
Na <sub>2</sub> O	4.54	2.23	3.2
K <sub>2</sub> O	1.99	3.89	2.41
P <sub>2</sub> O <sub>5</sub>	0.77	0.55	0.35
Total	98.87	98.18	96.57

\* Average of 5 microprobe analyses.

† From Ducea (1998), XF analysis.

‡ FeO as total iron.

carbonates—instead, data were obtained on graphite, diamond, CO<sub>2</sub>-rich inclusions, or silicate mantle minerals. We interpret the stable-isotopic signatures on carbonate veins to indicate that the source of the C and O was a surficial, organic component that was recycled into the mantle via subduction and then released into the mantle wedge.

The Nd-isotopic ratios measured on the two carbonates are consistent with a Pacific ocean origin and a Cenozoic age of the sediment (Shaw and Wasserburg 1985). Moreover, the Sr-isotopic ratios, if in equilibrium with Pacific water and not modified during metamorphism, subduction, and decarbonation, would indicate a 30–35 Ma age for the sediment, using the curve for oceanic Sr-isotopic composition from Faure (1986); this predates the age of the xenolith entrainment by ~20–25 My.

### Comparison to typical carbonatites

The concentrations of incompatible trace elements measured on the calcites in BC115 and BC125 are significantly lower than typical mantle-derived carbonatites (Bell 1989) or cumulates from carbonatite melts (Lee et al. 2000b). Additionally, the anomalous negative spikes of the high-field-strength elements is not consistent with trace-element patterns in carbonatites worldwide. Based on these observations, one may argue that these carbonate vein materials were not melts percolating through the upper mantle, but CO<sub>2</sub>-rich fluids. However, the presence of accompanying silicate glass pockets (Fig. 1) in BC115 suggests that a melt phase was in fact present. A water-rich fluid could also be the carrier of dissolved carbonate. Distinguishing upper mantle carbonate “melt” from CO<sub>2</sub>-rich or H<sub>2</sub>O- and CO<sub>2</sub>-rich “fluid” based on textural and chemical criteria may be impossible; the important observation is that these calcite veins are different in trace-element concentration and C and O isotopes from most carbonatites worldwide (Woolley and Kempe 1989; Woolley et al. 2001).

## DISCUSSION

### Release of subducted CO<sub>2</sub> in the mantle wedge

Release of volatiles from the subducted slab into the mantle wedge (Tatsumi and Eggins 1995; Schmidt and Poli 1998) is a critical process in triggering arc melting (Davies and Stevenson 1992). Water is clearly the most important volatile and its release by dehydration metamorphic reactions has been studied extensively [see Stern (2002) for a review]. The release of CO<sub>2</sub> is not

well understood, despite many observations suggesting that CO<sub>2</sub> fluxes in arc volcanoes are significant (Sano and Williams 1996; Marty and Tolstikhin 1998). Some carbonate phases previously observed in peridotite xenoliths, e.g., from beneath the Slave craton (van Acherbergh et al. 2002) and the Alpine peridotite of Finero (Zanetti et al. 1999) potentially could have formed by slab decarbonation reactions at some point in the geologic past, but a direct link could not be established due to the antiquity of the postulated subduction events. To our knowledge, the only other direct observation of carbonated peridotites from beneath a modern subduction zone is from the Tabar-Lihir-Tanga-Feni arc (Papua New Guinea), first described by McInnes and Cameron (1994). The petrology and origin of these xenoliths was described further in Gregoire et al. (2001) and McInnes et al. (2001). In detail, there are differences between the carbonates reported here and the carbonate- and sulfate-bearing aluminosilicate melts reported by McInnes and Cameron: (1) their liquids have a sulfate component that we did not observe; (2) the aluminosilicate glasses are phonolitic, whereas ours are basaltic; and (3) there is an overall higher diversity of metasomatic minerals in their xenoliths (including apatite, phlogopite, amphibole, magnesio-chromite, etc.).

Calcite veins described in this paper can be linked directly to the subduction of the Farallon plate beneath western North America and provide some direct qualitative evidence that subducted sedimentary carbonates can be released in the mantle wedge. The Sierra Nevada was the main magmatic arc at this latitude for much of the Mesozoic, but it became the forearc as magmatism migrated inland during the Laramide orogeny (Saleeby 2003). Subsequently, arc magmatism swept back toward the location of the Sierra Nevada as a result of slab roll back (Dickinson 1981), although a new magmatic arc never fully redeveloped at the latitude of central California. Subduction was in its waning stages beneath central California at the latitude of Big Creek and at the time of the eruption of the pipe, according to the most recent plate kinematic reconstructions (Atwater and Stock 1998). In the Miocene, central California was in the process of developing a slab window while the plate margin ultimately became a major transform boundary between the Pacific and North American plates (the San Andreas fault). Therefore, these carbonates were released from the downgoing slab into the wedge of this subduction zone during the final few Ma of subduction beneath central California.

### Subducted carbonates and arc signatures

The analyzed calcite veins have typically higher concentrations of incompatible elements than the peridotite clinopyroxenes as measured in their core fractions. The clinopyroxene rims have interacted with the metasomatizing carbonate veins, resulting in trace-element concentrations intermediate between the calcite and clinopyroxene cores. One of the most interesting chemical characteristics of the analyzed carbonate veins is that they carry trace-element signatures typical of arc volcanoes (Pearce and Peate 1995) and arc magmas in general. As a metasomatic agent, the carbonate fluid has apparently interacted with the matrix peridotite and imprinted the “arc” chemical signature onto the clinopyroxene rims. Because the studied peridotites represent fragments of the mantle wedge of a long-lived subduction zone,

we speculate that carbonates recycled via subduction may contribute to generating negative HFSE anomalies in mantle wedge regions of subduction zones

### A connection to sub-arc diamonds?

Several major rivers from the Sierra Nevada contain diamondiferous sediments of Paleocene to Miocene ages (Kopf et al. 1990; Heylman 1999) that are thought to have a proximal, i.e., Sierran, origin based on their crystal size and habit. Recently, diamonds have been identified in the trachyandesitic Miocene pipe of Leek Springs from the northern Sierra Nevada (<http://www.diademresources.com>), north of, but compositionally almost identical to the pipe of Big Creek. Recently published experimental data show that percolation of carbonate through a mantle column can lead to diamond formation (Arima et al. 2002). The anomalously low thermal budget of any subduction zone increases the stability field of diamond relative to graphite to shallower depths than in cratonic areas, potentially as shallow as 90–100 km. Big Creek peridotite xenoliths may or may not be too shallow to preserve diamonds; however, future investigations of the C-bearing phases and reactions in Miocene central Sierra Nevada peridotites could provide further insights into the possible link between carbonate metasomatism and diamond formation in a mantle wedge environment.

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