

Calcio-carbonatite melts and metasomatism in the mantle beneath Mt. Vulture (Southern Italy)

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Abstract

At Mt. Vulture volcano (Basilicata, Italy) calcite globules (5–150 μm) are hosted by silicate glass pools or veins cross-cutting amphibole-bearing, or more common spinel-bearing mantle xenoliths and xenocrysts. The carbonate globules are rounded or elongated and are composed of a mosaic of 2–20 μm crystals, with varying optical orientation. These features are consistent with formation from a quenched calciocarbonatite melt. Where in contact with carbonate amphibole has reacted to form fassaitic pyroxene. Some of these globules contain liquid/gaseous CO_2 bubbles and sulphide inclusions, and are pierced by quench microphenocrysts of silicate phases. The carbonate composition varies from calcite to Mg-calcite (3.8–5.0 wt.% MgO) both within the carbonate globules and from globule to globule. Trace element contents of the carbonate, determined by LAICPMS, are similar to those of carbonatites worldwide including ΣREE up to 123 ppm. The Sr–Nd isotope ratios of the xenolith carbonate are similar to the extrusive carbonatite and silicate rocks of Mt. Vulture testifying to derivation from the same mantle source. Formation of immiscible silicate–carbonatite liquids within mantle xenoliths occurred via disequilibrium immiscibility during their exhumation. © 2007 Published by Elsevier B.V.

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1. Introduction

Carbonate in mantle xenoliths can yield important information about carbonatitic mantle metasomatism and carbonatite magmatogenesis (e.g. Green and Wallace, 1988; Lee and Wyllie, 1998). It is part of the poorly known deep Earth carbon cycle. Unfortunately, such

carbonate is rare because it is usually consumed by decarbonation reaction with mantle peridotite minerals (Green and Wallace, 1988; Dalton and Wood, 1993) or explosively decomposed to CaO and CO_2 during xenolith exhumation (Canil, 1991).

The carbonate described thus far in ultramafic mantle nodules occurs mainly as globular inclusions with micro-mosaic textures in glass veins (Kogarko et al., 1995; Pyle and Haggerty, 1994; Amundsen, 1987; Ionov et al., 1996; Norman, 1998; Ionov (1998), Frezzotti et al., 1994; Laurora et al., 2001, Kogarko, 2003; Moine et al., 2004), and less frequently as interstitial laths in veins with silicate mineral inclusions (Ionov, 1998; Chalot-Prat and Arnold, 1999; Lee et al., 2000; Moine et al., 2004) or as

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composite inclusions (Schiano et al., 1994; Lee et al., 2000; Solovova et al., 2005; Frezzotti et al., 2002).

Twenty percent of the samples in the Mt. Vulture xenoliths–xenocrysts suite contain carbonate inclusions, generally set in silicate glass veins which also contain olivine, clinopyroxene, and often spinel microphenocrysts. There are published accounts of mantle xenoliths from Mt. Vulture volcano by Stoppa and Principe (1998), Jones et al. (2000) and Downes et al. (2002) but this is the first detailed study of carbonate and associate textural features and reactions in the mantle nodules. Three mantle xenoliths and two mantle xenocrysts have been studied in order to establish the nature of the carbonate inclusions and their relationships with the host glass and other minerals in the xenoliths.

2. Geological and petrological notes

Mt. Vulture is located in the Basilicata region, Southern Italy [N40.935 lat; E15.622 long] at the outer edge of the Italian Apennine belt (Lavecchia and Stoppa, 1996; Lavecchia and Boncio, 2000). It is a relatively small alkaline stratovolcano composed mainly of pyroclastic deposits and lava flows of tephritic phonolite, phonofoidite, foidite, melilitite and carbonatite (Stoppa et al., 1999; Beccaluva et al., 2002). Volcanic activity started in the mid-Pleistocene with the emplacement of a phonolitic ignimbritic plateau and ended with the formation of several melilitite–carbonatite diatremes (Giannandrea et al., 2004).

Ultramafic xenoliths and xenocrysts occur in two units at Mt. Vulture: the pyroclastic unit belonging to

the sub-syntheme (Salvador, 1987) of Rionero dated at 612–655 ka (Giannandrea et al., 2004) and the uppermost pyroclastic unit called the Monticchio Lakes Syntheme (acr. MLS previously the Monticchio Lakes Formation), dated at 132 ka (Stoppa and Principe, 1998; Rosatelli et al., 2000, Rosatelli, 2001). The Rionero sub-syntheme (RS) is a succession of foidite to phono-foidite pyroclastic deposits, containing also amphibole xenocrysts, ‘sövite’, uncompahgrite and alkali pyroxenite xenoliths (Rosatelli et al., 2000, Stoppa et al., 2005). The MLS is composed of melilitite–carbonatite lapilli tuff and ash tuff, which contain abundant upper mantle peridotitic xenoliths and their debris (Stoppa and Principe, 1998; Jones et al., 2000), often mantled by melilitite lava and/or carbonatite.

Mt. Vulture mantle nodules are generally anhydrous and mainly spinel-bearing dunites, lherzolites, wehr-lites, and rare harzburgites with porphyroclastic or porphyroclastic–mosaic textures (Stoppa and Principe, 1998; Jones et al., 2000, Rosatelli, 2001; Downes et al., 2002). In a few cases they contain phlogopite. Phlogopite clinopyroxenites and amphibole–peridotite nodules have been found rarely in the MLS but mantle debris from disaggregated nodules are abundant and consist of discrete xenocrysts of Cr-diopside, olivine, pargasitic amphibole and phlogopite. Pyrope garnet has been found in spinel–lherzolite xenoliths (Stoppa and Principe, 1998; Jones et al., 2000) and as an inclusion in olivine xenocrysts in a foiditic bomb from the MLS (Solovova et al., 2005). Veins or interconnected pools of glass are frequent in the xenoliths (Jones et al., 2000, Downes et al., 2002). Carbonate has previously been

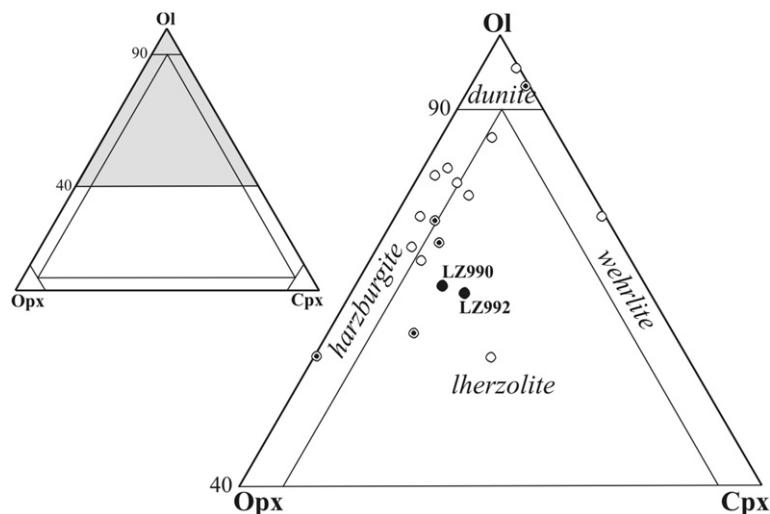


Fig. 1. Classification diagram (Le Maitre, 1989) of Mt. Vulture mantle xenoliths. White circles are mantle xenoliths from Jones et al. (2000) and Downes et al. (2002); those with the black spots contain carbonate.

noted in harzburgites, dunites and lherzolites by Jones et al. (2000) and Downes et al. (2002) in about 25% of Mt. Vulture xenoliths (Fig. 1).

3. Analytical methods

Polished thin sections were prepared using oil as the lubricant in order to avoid any alteration of soluble carbonate. Electron microprobe analyses (EMPA) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LAICPMS) analyses were made at the Natural History Museum London. Wavelength-dispersive (WDS) analyses were performed using a Cameca SX50 electron microprobe. Elements were standardised on a range of natural minerals. Operating conditions were selected according to the material analysed: 15 kV, ~20 nA and 2–15 μm beam diameter to analyse crystalline silicate materials; 15 kV, 10–15 μm spot (where possible) and a lower current of 10 nA to analyse glasses and carbonate. Detection limits were estimated for oxides as three times the standard deviation of the background count, and averaged 0.04 wt.%.

LAICPMS analyses were performed using a Thermo Elemental PlasmaQuad 3 ICP-MS coupled to a frequency quintupled Nd:YAG laser system operating at 213 nm (New Wave Research). The laser had a beam diameter of 15 μm , and was fired at a repetition rate of 10 Hz with a pulse energy of 0.05 mJ per pulse. A 10 ms dwell time was set for each mass with the exception of the HREE (Sm and heavier) for which a 30 ms dwell time was used. Data were collected over a period of 90 s and recorded as a function of time (time resolved analysis). Other details of data processing are reported in Stoppa et al. (2005) and Jeffries (2001). The concentration of Ca determined by EMPA was used as the internal standard for the data processing.

The $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{144}\text{Nd}/^{143}\text{Nd}$ isotopic ratios of carbonate in sample LZ992 were obtained after thoroughly removing the melilitite coating. To leach the carbonate fraction, powdered sample was treated with ultrapure HCl (2.0 mol%) for a short time until bubbling ceased (method in Castorina et al., 2000; data courtesy of Prof. Castorina, Università la Sapienza — Rome).

4. Petrography of the Mt. Vulture xenoliths and xenocrysts

The assemblages of the three xenoliths and two xenocrysts described in detail here are given in Table 1. In these samples carbonate forms rounded to patchy interstitial inclusions in glass veins or pools within the xenoliths/xenocrysts. The glass also contains quench

Table 1
Assemblages in Vulture carbonate-bearing ultramafic xenoliths and xenocrysts

Sample	Rock type	Location	Primary assemblage	Secondary assemblage
AP991	Amphibole peridotite	MLS	ol ₅₇ +amph ₂₆ +cpx ₇ +phl ₅	gl+cc+ol+cpx+sp
AX993	Amphibole xenocryst	RS	Amph ₉₆ +ap ₁	gl+cc+cpx
DX994	Diopside xenocryst	MLS	cpx ₉₈ +phl ₁ +sp _{0.2}	cc+gl
LZ990	sp-lherzolite	MLS	ol ₆₄ +opx ₂₁ +cpx ₁₃ +sp _{0.5}	gl+cc+ol+cpx+sp+ap
LZ992	sp-lherzolite	MLS	ol ₆₅ +opx ₂₃ +cpx ₁₀ +sp _{0.6}	gl+cc+ol+cpx

In the *primary* and *secondary assemblage* columns the phase sequence is in order of abundance and the numbers refer to their modal %. Estimate of modal composition of primary assemblage was made with image analysis technique (Tarquini and Armienti, 2003). Uncertainty on modal composition of about $\pm 3\%$ for each primary phase, but spinel; amph=amphibole; ol=olivine, cpx=clinopyroxene; opx=orthopyroxene; sp=spinel; phl=phlogopite; gl=glass; cc=carbonate; ap=apatite. MLS — Monticchio Lakes Synthème, RS=Rionero sub-synthème.

microphenocrysts of olivine, clinopyroxene, spinel and rare apatite together with rare rounded sulphide inclusions. Liquid and gaseous CO₂ inclusions have also been observed (Kogarko personal communication).

4.1. Sample AP991

Sample AP991 (~8 cm in diameter) from MLS is a porphyroclastic phlogopite-bearing amphibole peridotite with a primary assemblage of coarse-grained olivine and amphibole surrounded by fine-grained neoblastic clinopyroxene, phlogopite, and olivine (Table 1). Amphibole, coarse olivine and phlogopite show mosaic extinction and kink bands. Intergranular glass pools, glass inclusions in the grains and silicate glass veins containing carbonate inclusions occur throughout the sample. Sets of fractures in the coarse-grained primary olivine are decorated by thin silicate glass films that sometimes rim pools of carbonate. Sometimes the carbonate contains rounded voids (Fig. 2c) that probably contained a volatile phase that escaped during the thin section preparation. Amphibole and phlogopite show embayed or ragged margins where they contact with glass. Larger pools of reddish-brown glass with carbonate globules and rounded bleb-like voids are frequent inside the amphibole and are often interconnected (Fig. 2b). They also contain carbonate, secondary microphenocrysts of skeletal olivine, euhedral clinopyroxene and deep green, euhedral spinel (Fig. 2a).

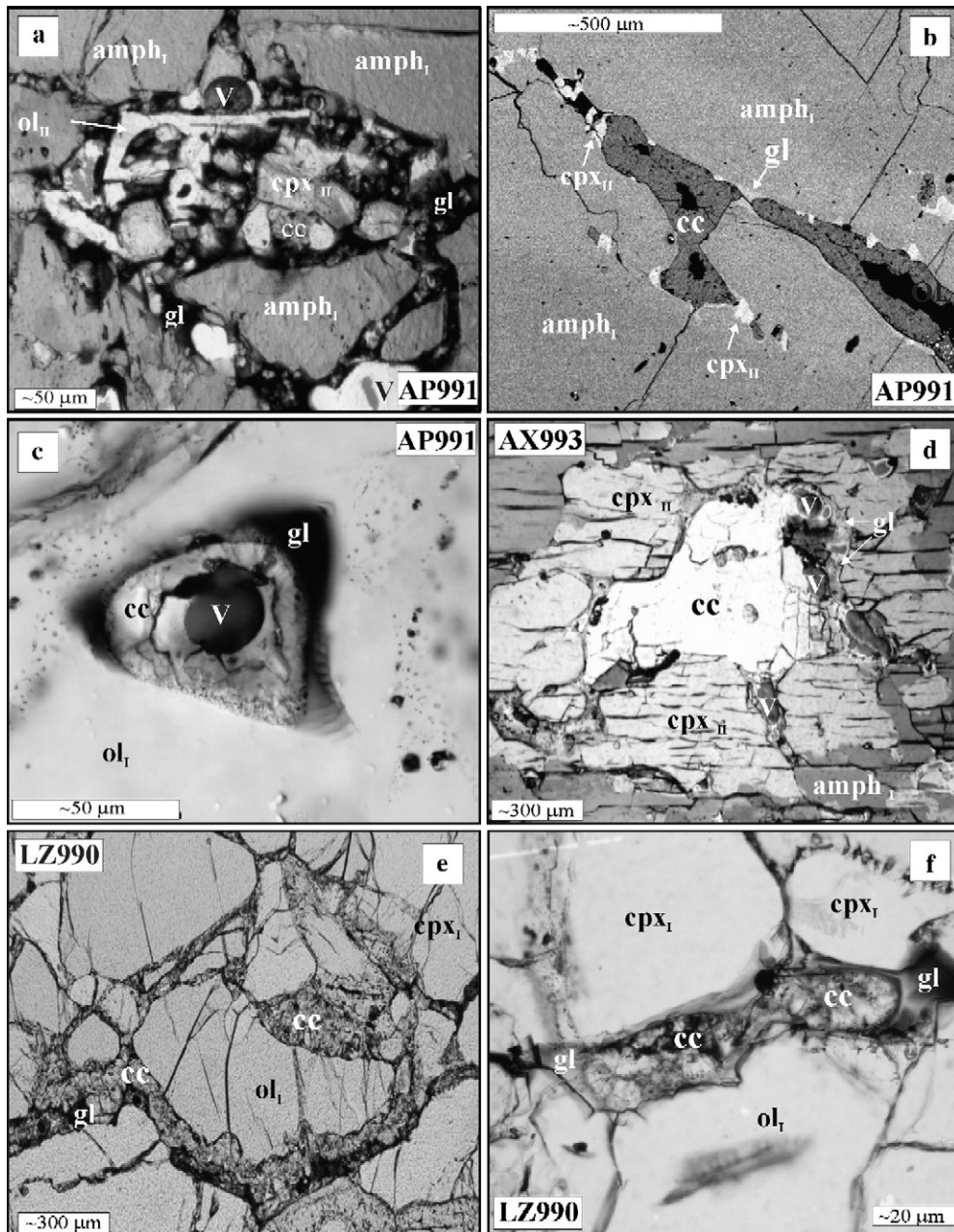


Fig. 2. a) Sample AP991, glass (gl) pool within a primary amphibole (amph₁) crystal. The dark-brown silicate glass pool contains quench (second generation) skeletal olivine (ol₁₁), clinopyroxene (cpx₁₁) crystals, carbonate globules (cc) and empty rounded vugs (V). b) Sample AP991, carbonate vein in primary amphibole. Small fassaite clinopyroxene crystallised at the carbonate–amphibole contact. c) Sample AP991, composite inclusion in primary olivine composed of glass and carbonate, the latter contains a rounded empty vug in the centre. d) Sample AX993, epitaxial clinopyroxene growing on amphibole, note the consistent cleavage on both minerals. In the centre there is mosaic calcite surrounded by glass containing rounded vugs. e) Sample LZ990, glass–carbonate vein surrounding a resorbed primary olivine crystal. f) Sample LZ990, detail of an intergranular glass–carbonate inclusion and carbonate with a pinch-off structure.

4.2. Amphibole xenocryst AX993

Amphibole xenocryst AX993 (~6 cm in diameter) from RS is a shiny black, dense fragment of pargasite

amphibole with good cleavage and inclusions of mm-long whitish/colourless apatite needles. Amphibole portions are in optical continuity but some areas within the amphibole are replaced by clinopyroxene. The main

cleavage system of clinopyroxene and amphibole is concordant, and the contact between the two minerals is lobate and indistinct (Fig. 2d). At the centre of these areas there are structures formed by a patch of mosaic calcite in the centre, partially surrounded by reddish

glass with small carbonate inclusions and rounded voids (Table 1, Fig. 2d).

AP991 and AX993 do not contain Cr-spinel and their modal composition is unusual for normal peridotite mantle. However they can be considered representative

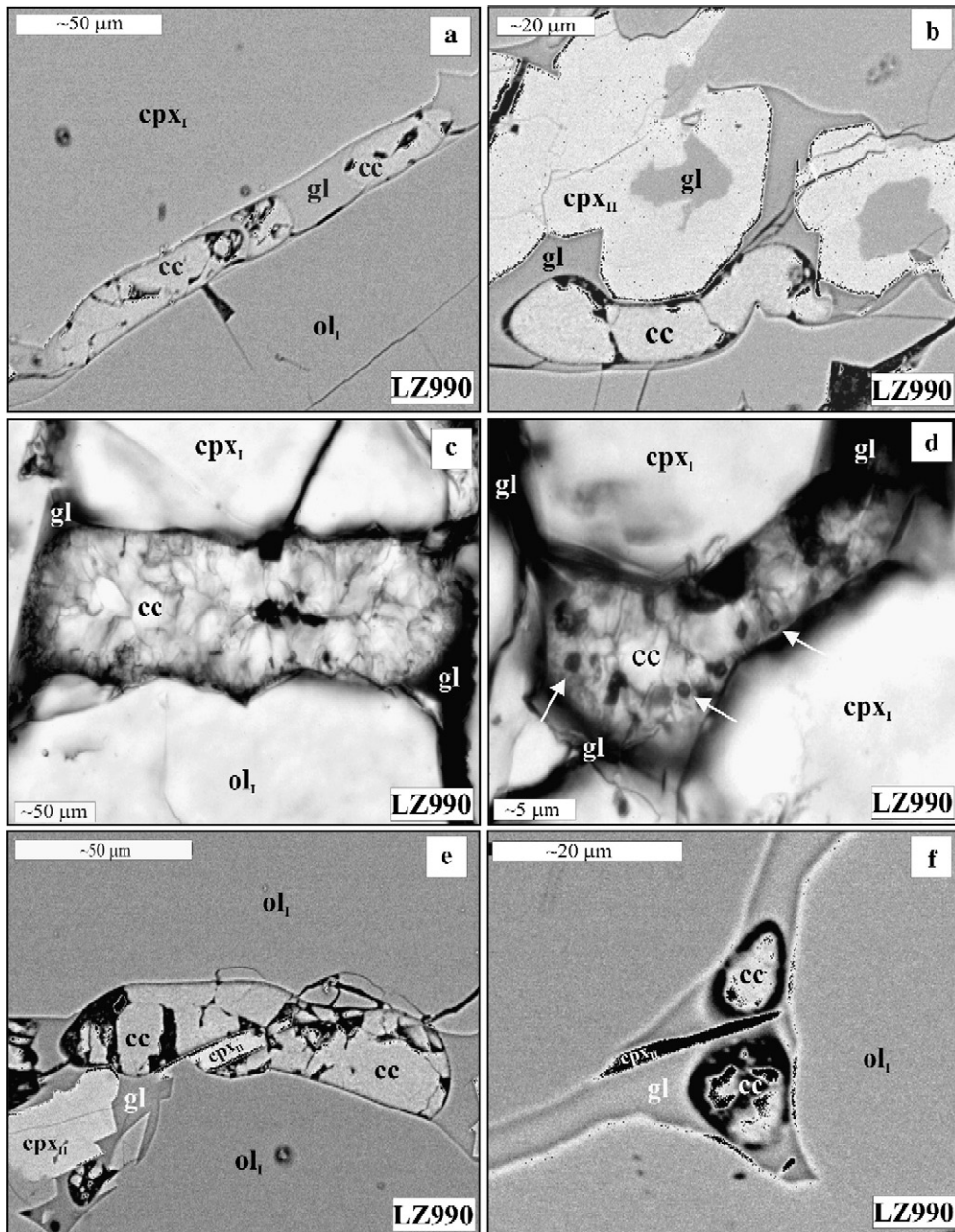


Fig. 3. Sample LZ990: a) BSE image of interstitial glass (gl) vein containing elongated carbonate (cc) inclusions, their morphology suggests a pinch-out structure; b) kidney-shaped carbonate inclusion in a glass pool containing quench clinopyroxenes (cpx_{II}) with glass inclusions; c) detail of a carbonate globule (cc) surrounded by dark glass (gl) the carbonate globule is composed of an interlocking aggregate of fine-grained calcite; d) carbonate globule containing small, black rounded CO₂ inclusion (white arrows); e) carbonate globule pierced by a quench clinopyroxene microphenocryst (cpx_{II}); f) small (quench) clinopyroxenes (cpx) dividing a carbonate globule set in a silicate glass.

of pegmatoid amphibole–phlogopite-bearing peridotite veins in the Mt. Vulture lithosphere (Rosatelli, 2001).

4.3. Sample DX994

Sample DX994 (~2 cm in diameter) from MLS consists of several fragments of a fractured green Cr-diopside xenocryst that have undulose extinction and contain small phlogopite laths and euhedral apatite scattered throughout. Trains of tubicules and sieve-textured glassy inclusions are widespread. The xenocrysts contain several small (<100 μm) rounded carbonate inclusions rimmed with a silicate glass film (Table 1), similar to carbonate inclusions described in lherzolitic diopside macrocrysts from Lac de Gras kimberlite (Van Achteberg et al., 2002).

4.4. Sample LZ990

Sample LZ990 (~5 cm in diameter) from MLS is a porphyroclastic spinel lherzolite cross-cut by two carbonate-bearing glass veins of ~1 mm diameter (Fig. 2e). Along the veins, primary olivine and clinopyroxene show resorption morphologies (Fig. 2e), while orthopyroxene grains have scalloped or ragged

contacts. The Cr-spinel grains have a sieve texture made of fine-grained spinel set in a darker glassy matrix. Locally, larger glassy pools within the veins contain relicts of primary diopside poikilitically enclosing olivine. Thinner veinlets spread from the main veins to form a pervasive network in the central portion of the xenolith. Glass veins locally widen to form pools, suggesting migration and local accumulation of the liquid throughout the xenolith (Fig. 2f). The brownish glass contains abundant euhedral microphenocrysts of clinopyroxene, olivine, rare Cr-spinel, and rounded or elongated carbonate inclusions, along with apatite needles, sulphide blebs, CO₂ inclusions and circular voids (Fig. 3a to f). Away from the veins, the primary mineral assemblage is characterised by granoblastic triple junctions and does not show any pyrometamorphic textures. EMPA analyses of primary minerals in contact have been used to calculate temperature and pressure equilibration values for this xenolith using the pyroxene–spinel and enstatite–spinel geothermobarometers of Mercier (1980), for direct comparison with the results of Jones et al. (2000). The calculated temperature varies from 1082 °C to 1125 °C and the pressure varies from 1.7 to 2.2 GPa. This is within the range of Mt. Vulture mantle xenoliths, previously given as 1050–1150 °C and 1.4 and 2.2 GPa (Jones et al., 2000).

Table 2
Representative EMPA analyses of olivine

Sample	LZ990				AP991				
	ol _I	ol _I	ol _{II}	ol _{II}	ol _I	ol _I	ol _I	ol _{II}	ol _{II}
	#31	#32	#59	#77	#61	#64	#2	#71	#79
SiO ₂	40.77	41.08	40.90	41.72	41.19	41.34	41.15	41.26	41.26
FeO*	9.87	10.34	10.86	9.94	12.34	10.64	11.76	12.27	12.25
MgO	48.78	48.97	48.32	49.08	45.70	46.75	46.96	46.02	45.87
MnO	0.19	0.19	0.18	0.21	0.24	0.22	0.21	0.16	0.21
CaO	0.15	0.13	0.16	0.16	0.28	0.60	0.50	0.33	0.38
Cr ₂ O ₃	bdl	bdl	0.13	0.09	bdl	bdl	0.06	bdl	bdl
NiO	0.31	0.25	0.20	0.13	0.12	0.15	0.13	0.14	0.07
Total	100.12	100.96	100.74	101.33	99.95	99.82	100.81	100.46	100.10
<i>Cation calculation on the basis of 4 oxygens</i>									
Si	0.999	1.000	1.000	1.008	1.020	1.018	1.009	1.016	1.019
Fe	0.202	0.211	0.222	0.201	0.255	0.219	0.241	0.253	0.253
Mg	1.783	1.777	1.762	1.769	1.687	1.716	1.717	1.689	1.690
Mn	0.004	0.004	0.004	0.004	0.005	0.005	0.004	0.003	0.004
Ca	0.004	0.003	0.004	0.004	0.007	0.016	0.013	0.009	0.010
Cr			0.006	0.004			0.003	0.002	
Ni	0.006	0.005	0.004	0.003	0.002	0.003	0.003	0.003	0.001
Sum	2.998	3.000	3.002	2.993	2.977	2.977	2.990	2.974	2.978
Mg#	0.90	0.89	0.89	0.90	0.87	0.89	0.88	0.87	0.87
Ca#	0.21	0.19	0.23	0.23	0.43	0.91	0.76	0.51	0.59

FeO* = total iron; bdl = below detection limits (<0.04 wt.%) Mg# = Mg/(Mg + Fe), Ca# = 100 (Ca/Ca + Mg). ol_I = olivine porphyroblasts; ol_{II} = olivine microphenocrysts in the glass.

4.5. Sample LZ992

Sample LZ992 (8 cm diameter) from MLS is a porphyroclastic spinel lherzolite with carbonate-bearing glass veins similar to LZ990. This sample was selected for measurement of Sr–Nd isotopic ratios in the carbonate inclusions because it was very similar to LZ990 and contained ca. 1% modal carbonate.

5. Carbonate texture petrography

Carbonate inclusions within the silicate glass are 5–150 μm , with a variety of shapes from rounded to ovoid, budded to elongate or ameboid (Figs. 2 and 3). The glass forms veins that cross-cut the ultramafic xenoliths and xenocrysts. In a few cases a kind of neck-off morphology was observed between two closely spaced carbonate ovoid inclusions in the glass (Fig. 2f). Small carbonate veinlets interconnect with the carbonate inclusions running either within the interstitial glass or through the host-mineral fractures. In some cases carbonate in the veins is more abundant than glass, especially when the glass contains abundant silicate microphenocrysts (Fig. 3b). The carbonate inclusions are composed of an interlocking aggregate of fine-grained calcite crystals (<20 μm ; Fig. 3c) that often have different optical orientations. They are sometimes incomplete with irregular voids resulting from preparation of the thin section (Figs. 2b, 3f). Sometimes, within the carbonate and the glass there are dark, dense rounded inclusions with a bright core interpreted as high pressure liquid-gaseous CO_2 inclusions (Lia Kogarko personal communication; Fig. 3d; Andersen and Neumann, 2001). Carbonate is rarely in direct contact with the host xenolith primary minerals or quenched microphenocrysts in the glass. A film of silicate glass is always interposed and the carbonate–glass contact is always sharp. However, in sample AP991 small clinopyroxene crystal overgrowths were observed on amphibole where the carbonate is directly in contact with the host primary amphibole (Fig. 2b). In LZ990 carbonate globules are sometimes pierced (Fig. 3e) or divided (Fig. 3f) by quenched clinopyroxene needles nucleated on the surface of the primary xenolith minerals and growing toward the centre of the glass vein.

6. Mineral chemistry of the veins and comparison with porphyroclasts olivine

Olivine compositions in glass and porphyroclasts are consistent between and within the samples (Table 2). The NiO content, $\text{Ca\#} [=100(\text{Ca}/\text{Ca} + \text{Mg})]$

and $\text{Mg\#} [= (\text{Mg}/\text{Mg} + \text{Fe}^*)]$ of olivine microphenocrysts in the glass (ol_{II}) generally fall within the field of the primary olivine (ol_{I} , Fig. 4) for each sample. However olivine in AP991 has lower Mg and Ni and higher Ca than LZ990 which falls in the field of olivine in lherzolites and wehrlites from Mt. Vulture (Rosatelli, 2001).

7. Clinopyroxene

Primary porphyroclastic clinopyroxene (cpx_{I}) and microphenocrysts (cpx_{II}) in the glass of LZ990 and DX994 are aluminian chromian-diopside or -augite (sec. Morimoto, 1988) (Table 3, Fig. 5a). In LZ990 primary porphyroblastic clinopyroxene and secondary microphenocrysts differ only in having slightly higher FeO^* (total iron) and Al_2O_3 in the microphenocrysts. In samples AP991 and AX993 the micro clinopyroxenes (cpx_{II}) are Ca-rich and plot above Wo_{50} , reaching Wo_{55} (Table 3, Fig. 5a). These clinopyroxenes are also richer in Al_2O_3

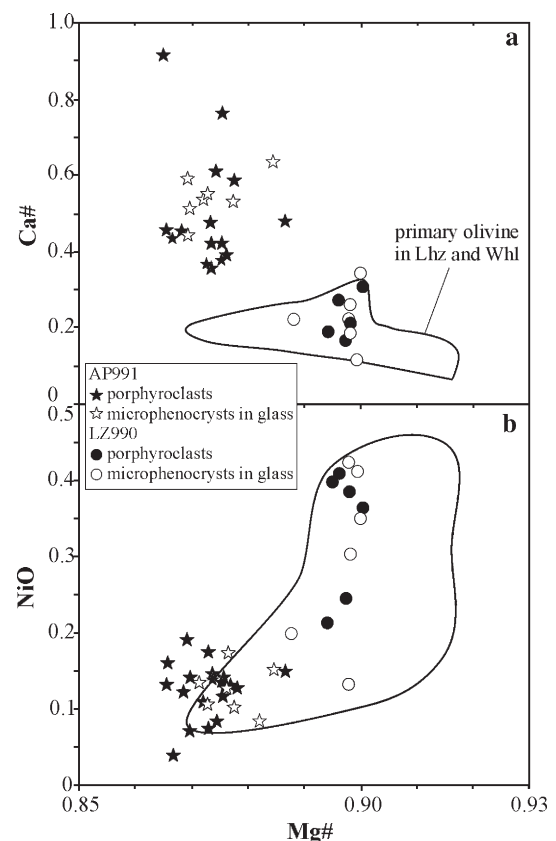


Fig. 4. Olivine microphenocrysts (ol_{II}) compared with host xenolith porphyroblast olivine (ol_{I}). a) $\text{Mg\#}$ vs $100 \times \text{Ca\#}$; b) $\text{Mg\#}$ vs NiO . Fields of data of primary porphyroblast olivine in lherzolite and wehrlites from Mt. Vulture are from Jones et al. (2000); Rosatelli (2001).

Table 3

Representative EMPA analyses of clinopyroxene

Sample	AX993	AX993	AP991	AP991	AP991	AP991	DX994	DX994	LZ990	LZ990	LZ990	LZ990	LZ990
	cpx _{III}	cpx _{III}	cpx _{II}	cpx _{III}	cpx _{III}	cpx _{III}	cpx _I	cpx _I	cpx _I	cpx _I	cpx _{II}	cpx _{II}	cpx _{II}
	1	2	3	4	5	6	7	8	9	10	11	12	13
SiO ₂	45.92	43.09	46.10	38.08	43.98	42.69	51.87	50.95	51.73	52.16	51.59	52.56	53.49
TiO ₂	1.75	1.97	1.80	4.37	2.67	2.29	0.33	0.50	0.43	0.31	0.42	0.39	0.34
Al ₂ O ₃	7.99	10.20	10.61	15.59	11.45	13.20	3.57	3.56	5.44	5.58	5.01	3.92	3.83
FeO*	7.39	9.95	4.64	8.14	6.59	7.12	3.09	3.14	3.28	3.62	4.36	4.11	3.67
Cr ₂ O ₃	bdl	bdl	bdl	bdl	bdl	bdl	0.64	0.45	1.03	0.95	1.83	1.18	1.57
MnO	0.15	0.18	0.08	0.08	0.06	0.05	0.08	0.10	0.16	0.06	0.14	0.13	0.19
MgO	11.55	10.07	12.97	9.14	11.64	10.56	16.90	16.32	16.25	16.54	17.71	17.69	17.70
CaO	24.47	23.57	23.94	24.04	24.40	24.49	22.22	24.32	20.40	19.45	17.59	18.72	19.12
Na ₂ O	0.44	0.44	0.39	0.27	0.27	0.31	0.52	0.23	0.86	1.07	0.82	0.78	0.81
Total	99.66	99.47	100.53	99.71	101.06	100.71	99.24	99.58	99.59	99.74	99.48	99.49	100.71

Cation calculation based on 6 oxygens

Si ⁴⁺	1.713	1.623	1.682	1.430	1.613	1.573	1.895	1.863	1.883	1.891	1.879	1.913	1.922
Al ^{IV}	0.287	0.377	0.318	0.570	0.387	0.427	0.105	0.138	0.117	0.109	0.122	0.087	0.078
ΣT site	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Al ^{VI}	0.064	0.076	0.138	0.120	0.108	0.147	0.049	0.016	0.116	0.129	0.094	0.081	0.084
Fe ³⁺	0.156	0.220	0.108	0.222	0.150	0.174	0.056	0.096	0.007	0.010	0.009	0.005	
Ti ⁴⁺	0.049	0.056	0.049	0.123	0.074	0.064	0.009	0.014	0.012	0.009	0.012	0.011	0.009
Mg ²⁺	0.642	0.565	0.705	0.512	0.636	0.580	0.868	0.861	0.835	0.825	0.834	0.870	0.863
Fe ²⁺	0.074	0.083		0.023	0.032	0.036		0.001					
Mn ²⁺	0.005												
Cr ³⁺							0.019	0.013	0.030	0.027	0.053	0.034	0.044
ΣM1 site	0.990	1.000	1.000	1.000	1.000	1.000	1.000	1.001	1.000	1.000	1.000	1.000	1.000
Mg ²⁺			0.001				0.052	0.028	0.046	0.068	0.128	0.090	0.086
Fe ²⁺		0.011	0.034	0.011	0.020	0.009	0.039		0.093	0.100	0.124	0.121	0.110
Mn ²⁺		0.006	0.002	0.003	0.002	0.002	0.003	0.003	0.005	0.002	0.004	0.004	0.006
Ca ²⁺	0.978	0.951	0.936	0.967	0.959	0.967	0.870	0.953	0.795	0.755	0.686	0.730	0.736
Na ⁺	0.032	0.032	0.028	0.020	0.019	0.022	0.037	0.016	0.061	0.075	0.058	0.055	0.056
ΣM2 site	1.010	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	0.993
ΣCat.s	4.053	4.075	4.036	4.075	4.051	4.059	4.019	4.032	4.002	4.003	4.003	4.002	3.993
Mg#	0.90	0.86	0.95	0.94	0.92	0.93	0.96	1.00	0.90	0.90	0.89	0.89	0.90

End members

En	34.61	30.80	39.51	29.45	35.37	32.81	48.77	45.81	49.48	50.76	53.86	52.75	52.68
Wo	52.71	51.82	52.43	55.69	53.30	54.70	46.10	49.08	44.65	42.90	38.45	40.14	40.88
Fs	12.67	17.39	8.06	14.86	11.33	12.49	5.13	5.11	5.88	6.35	7.68	7.11	6.44
Ae	3.21	3.21	2.75	1.96	1.92	2.21	3.70	1.64	0.72	0.99	0.87	0.45	—
Jd	—	—	—	—	—	—	—	—	5.35	6.49	4.95	5.07	5.64
Ka	—	0.57	0.24	0.25	0.18	0.15	0.25	0.32	0.49	0.19	0.44	0.41	0.56
CaTi	9.92	11.16	9.88	24.68	14.72	12.70	1.84	2.76	2.36	1.70	2.30	2.14	1.83
CaCr	—	—	—	—	—	—	1.85	1.30	2.97	2.72	5.27	3.40	4.47
CaTs	6.46	7.62	13.81	12.01	10.81	14.66	4.87	1.59	6.28	6.42	4.41	3.04	2.81
CaFe	12.57	18.79	8.04	20.21	13.04	15.23	1.88	7.96					
ΣCaTsk	28.95	37.57	31.73	56.90	38.57	42.59	8.59	12.31	8.64	8.12	6.71	5.18	4.64
Jo	0.47	—	—	—	—	—	—	—	—	—	—	—	—
Di	59.88	50.39	61.85	38.57	56.10	51.51	76.54	81.64	67.93	64.68	56.62	64.43	64.97
Hd	7.48	7.17	—	1.26	1.22	2.60	—	—	—	—	—	—	—
En	—	—	0.07	—	—	—	5.22	2.79	4.64	6.82	12.75	8.99	8.61
Fs	—	1.09	—	1.06	2.01	0.94	—	—	—	—	—	—	—
Fs–En	—	—	3.36	—	—	—	3.85	—	9.26	9.99	12.39	12.07	11.11

IMA names: 1–3 aluminian subsilicic ferroan diopside; 4 aluminian titanian subsilicic ferroan diopside; 5 titanian subsilicic ferroan diopside; 6 aluminian subsilicic ferroan diopside; 7 aluminian chromian diopside; 8 aluminian chromian ferroan diopside; 9–11 aluminian chromian [Magnesium-rich] augite; 12–13 chromian [Magnesium-rich] augite. FeO*=total iron; bdl=below detection limits (<0.04 wt.%). Mg#=Mg/(Mg+Fe). cpx_I=clinopyroxene porphyroclasts; cpx_{II}=clinopyroxene microphenocrysts in the glass, cpx_{III} from reaction carbonate–amphibole.

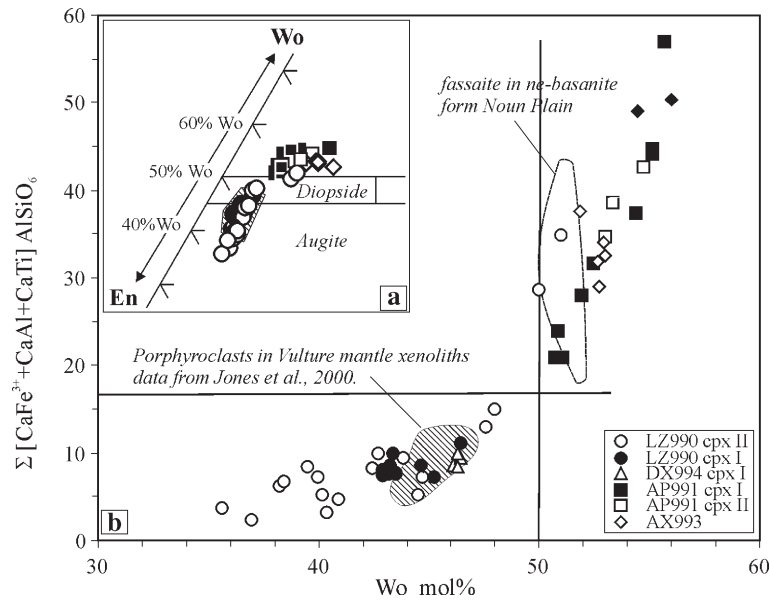


Fig. 5. a) En–Wo–Fs classification diagram for clinopyroxenes in the sample studied and compared with primary peridotitic clinopyroxene compositional field (data from Jones et al., 2000). Clinopyroxene compositional diagram. b) Wo mol% versus the sum of CaAlSiAlO_6 (CaAl mol%) + CaTiAlSiAlO_6 (CaTi mol%) + $\text{CaFe}^{3+}\text{AlSiAlO}_6$ (CaFe³⁺ mol%) of the clinopyroxenes in mantle xenoliths (Wo mol% < 50; $[\text{CaFe}^{3+} + \text{CaAl} + \text{CaTi}]$ mol% < 17) and from the reaction amphibole–carbonate along with fassaite compositions from Noun Plain (Cameroon, Wandji et al., 2000) (Wo mol% > 50; $[\text{CaFe}^{3+} + \text{CaAl} + \text{CaTi}]$ mol% > 17).

(8–14 wt.% vs 4–10 wt.%), and Fe^{3+} ($\text{Fe}^{3+}/\text{Fe}^{2+} > 1.5$) than diopside–augite, while TiO_2 is within the diopside compositional range of 0.3–3.4 wt.% (Wandji et al., 2000). Adopting the IMA classification (Morimoto, 1988), the AP991 and AX993 clinopyroxenes are aluminian and/or titanian-subsilicic-ferroan-diopside (Table 3). Alternatively, these clinopyroxenes can be classified as fassaite because, although the diopside end-member is dominant (51–65%, Table 3 analysis 1–6), the fassaite components are important CaAlSiAlO_6 (CaTs = 6.5–16.6%), $\text{CaFe}^{3+}\text{AlSiAlO}_6$ (CaFe³⁺ = 7.6–17%) and CaTiAlSiAlO_6 (CaTi = 7.6–17.4%) and together contribute more than 17% of the end-member composition (Fig. 5b). Although fassaite is considered an obsolete term (Morimoto, 1988), in this case it is preferred in order to distinguish the pyroxene compositions (Huckenholz, 1973; Deer et al., 1997; Wandji et al., 2000). The Ti-content of this fassaite is lower than that reported from extrusive rocks. This unusual clinopyroxene composition for a mantle peridotite rock, suggests that it is a product of amphibole–Ca-carbonatite melt reaction at high pressure.

8. Apatite

Apatite in the glass and amphibole has a fairly constant composition (Table 4). Secondary apatite needles near the carbonate blebs in sample LZ990 differ

from the larger primary apatite inclusions in amphibole xenocryst AX993 in having up to 1.55 wt.% SrO (Table 4).

9. Glass

The silicate glasses in the xenoliths and xenocrysts cover a broad compositional range from foidite to dacite and trachyte in the TAS diagram (Le Bas et al., 1986) (Table 5, Fig. 6). In spite of the chemical variability between different glassy pools X-ray mapping by EPMA confirmed that individual pools are homogeneous. All the glasses contain appreciable amounts of P, S and Ba, along with detectable F and sometimes Cl. Water and CO_2 (volatile) contents are probably low because analysis totals are close to 100 wt.%. The glasses in the MLS xenoliths have higher Al_2O_3 and alkalis and lower MgO than the host melilitite (Stoppa and Principe, 1998). In general, glass composition varies in relation to the primary mineral assemblage of the xenolith, and this suggests that these glasses have undergone negligible contamination from the host magma.

Glasses associated with amphibole (AP991 and AX993) tend to cluster in the foidite field and differ from the other glasses in having a silica-undersaturated composition and metaluminous character [$\text{A}/\text{CNK} < 1$ and $\text{NK}/\text{A} = \text{apaitic index (AI)} < 1$; $\text{A} = \text{Al}_2\text{O}_3$, $\text{C} = \text{CaO}$,

Table 4
Selected EMPA analyses of apatite

Sample	LZ990	AX993	AX993	AX993
Analysis	#1	#12	#13	#4
SiO ₂	1.90	1.21	1.00	1.22
FeO*	0.34	0.09	0.08	0.14
MnO	–	0.07	–	0.05
MgO	0.22	0.08	0.11	0.13
SrO	1.05	0.50	0.51	0.51
CaO	53.50	55.10	55.20	55.34
Na ₂ O	0.22	0.16	0.20	0.21
P ₂ O ₅	39.85	39.44	39.73	38.77
SO ₃	1.78	1.38	1.11	1.40
F	–	2.96	2.72	3.13
Cl	0.50	0.20	0.26	0.21
Sum	99.36	101.21	100.93	101.13
O=F+Cl	0.11	1.29	1.2	1.37
Total	99.25	99.92	99.73	99.76
Fe ²⁺	0.048	0.013	0.011	0.019
Mn	–	0.010	–	0.007
Mg	0.056	0.020	0.027	0.032
Sr	0.103	0.048	0.049	0.049
Ca	9.721	9.854	9.849	9.820
Na	0.072	0.052	0.065	0.067
Si	0.322	0.202	0.167	0.202
P	5.722	5.574	5.601	5.436
S	0.226	0.173	0.139	0.174
Cations	16.270	15.950	15.910	15.810
CF	–	1.562	1.432	1.639
CCl	0.144	0.057	0.073	0.059

FeO*=total iron; –=below detection limit (<0.05 wt.%).

Cation calculation based on Fe²⁺+Mn+Mg+Sr+Ca+Na=10.

N=Na₂O, K=K₂O], i.e. high alkalis, CaO and Al₂O₃, with low MgO and FeO* (=total iron). The glasses associated with amphibole in AP991 have K₂O/Na₂O ratios ≤ 0.5 , whereas in the same peridotite sample, glass associated with, or containing phlogopite relicts, has K₂O/Na₂O ratios of 1–1.5 (Fig. 7). Their compositions are consistent with a partial melting contribution of the hydrous phase in the primary mantle assemblage (Gorring and Kay, 2000). However, glass in AX993 differs again in having high K₂O that produces high K₂O/Na₂O ratios that are not consistent with these observations. The difference may be accounted for by considering that the reaction products include clinopyroxene as well as glass and its crystallisation may have taken up Na in preference to K.

Glass in sample LZ990 and in previously reported anhydrous xenoliths (Jones et al., 2000) is different from glass associated with the hydrous minerals. It has peraluminous, intermediate composition, alkaline to subalkaline character, and has variable alkali ratios but most analyses average around 1.

10. Carbonate

The carbonate is calcite, with MgO ≤ 1.8 wt.%, or Mg-calcite with MgO contents between 2.5 and 6.4 wt.% (Table 6, Fig. 8), similar to calcite compositions in Mt. Vulture carbonatites (Stoppa and Principe, 1998; Rosatelli et al., 2000). FeO* is always low, generally <0.5 wt.%. The Mg# (=Mg/Mg+Fe*) of the carbonate is generally >0.7 but in AP991 ranges from 0.78 to 0.20. SrO is on average 0.35 wt.% but reaches 0.9 wt.% in the microcrystalline carbonate globules in the glass associated with fassaitic clinopyroxene produced by reaction of carbonate with amphibole (Table 6, #10) and up to 0.75 wt.% in glasses in the veined lherzolite LZ990 (e.g. Table 6, #15) where apatite needles are also present. Carbonate within a single or in closely spaced globules may be variable in composition, particularly in MgO and SrO (Fig. 8). SiO₂ is generally low or absent but in analysis # 15 reaches 1 wt.%. Alkalies and Al are absent. Traces of P and S may be present but both F and Cl are always below detection limits. The presence of P in some analyses may imply the presence of sub-micron apatite within the carbonate globules, although it is common to find minor quantities of P in carbonates in mantle xenoliths (Kogarko et al., 1995; Moine et al., 2004) or in rapidly quenched calcite in extrusive carbonatites (Stoppa et al., 2005).

11. Carbonate and glass trace element and Sr–Nd isotope geochemistry

Trace element, including rare earth element (REE) determinations of carbonate and glass in LZ990 are reported in Table 7. The carbonate has a constant trace element composition despite variation in major element chemistry (Fig. 9 and Table 6). Trace element patterns normalised to primitive mantle are characterised by negative anomalies for some HFSE (Ta, Zr, Hf, Ti), but not Nb (except for analysis #6), and positive anomalies for LILE such as Sr. Two analyses (#2 and #6) also have negative Th anomalies. The incompatible element content of the carbonate is substantially lower than ‘average intrusive calciocarbonatite’ (Woolley and Kempe, 1989, Fig. 9) but the shape and relative depletions are mostly similar. The difference between ‘average calciocarbonatite’ and the carbonates in LZ990 may be related to the more primitive nature of the latter. The ‘average Ca-carbonatite’ is calculated from intrusive rocks that have undergone differentiation that could have resulted in increased concentrations of trace elements (Woolley and Kempe, 1989; Ionov and Harmer, 2002).

Table 5
Representative EMPA analyses of glass and CIPW norm recalculations

Sample	AP991				AX993				LZ990			
	#43	#44	#55	#5	#7	#9	#10	#11	#4	#7	#22	#35
SiO ₂	37.64	41.37	40.29	44.61	45.79	46.46	37.81	42.71	55.81	54.98	58.53	62.42
Al ₂ O ₃	18.53	20.93	16.22	22.01	21.39	22.03	17.48	26.63	19.06	18.58	19.47	19.38
TiO ₂	0.97	0.86	1.21	1.18	0.61	0.65	0.62	0.57	1.56	1.56	1.35	1.20
Cr ₂ O ₃	nd	nd	nd	nd	nd	nd	Nd	nd	bdl	0.05	0.04	0.11
FeO*	7.67	7.75	10.06	6.95	3.45	3.01	6.21	5.42	4.94	5.14	3.63	2.86
MgO	2.14	4.26	7.86	2.20	0.75	0.75	0.71	0.42	2.21	2.33	1.95	1.55
MnO	0.18	0.21	0.16	0.14	0.23	0.29	0.21	0.15	0.10	0.09	0.11	bdl
CaO	11.32	8.69	13.78	8.09	7.31	7.68	13.67	4.22	6.47	6.81	5.49	3.59
Na ₂ O	5.01	10.18	4.67	6.32	7.48	6.53	4.41	5.71	2.69	2.72	2.33	1.84
K ₂ O	5.72	4.62	3.35	6.38	8.67	7.97	6.08	7.18	2.65	2.39	2.59	2.71
BaO	0.28	0.22	0.27	0.29	0.45	0.47	0.49	0.42	0.39	0.31	0.21	0.14
SO ₃	0.35	0.27	0.36	0.29	0.43	0.32	0.32	3.39	0.12	0.46	0.04	0.08
P ₂ O ₅	0.92	0.73	1.13	0.64	0.60	0.51	0.31	0.55	1.26	1.13	1.11	1.00
F	0.16	0.23	0.34	0.17	0.43	0.48	0.33	0.27	nd	nd	nd	nd
Cl	0.42	0.37	0.36	0.27	0.68	0.71	0.56	0.88	0.47	0.38	0.39	0.21
Total	91.38	100.07	100.06	99.10	98.28	97.85	89.21	98.50	97.75	96.93	97.26	97.12
K/Na	1.14	0.45	0.72	1.05	1.16	1.22	1.38	1.26	0.99	0.88	1.11	1.48
TA	10.73	14.80	8.02	12.70	16.15	14.50	10.49	12.88	5.34	5.11	4.92	4.55
AI	0.58	0.71	0.49	0.56	0.75	0.66	0.60	0.48	0.28	0.28	0.25	0.23
A/CNK	0.84	0.89	0.74	1.02	0.91	0.99	0.72	1.56	1.61	1.56	1.87	2.38
MgO#	0.22	0.35	0.44	0.27	0.18	0.20	0.10	0.07	0.31	0.31	0.35	0.35
<i>CIPW norm composition</i>												
Quartz									15.1	13.8	23.1	34.6
Corundum								3.3	3.1	1.9	5.7	9.6
Orthoclase						0.4		19.6	16.2	14.7	15.8	16.6
Albite									23.5	24.0	20.4	16.1
Anorthite	12.4		13.5	13.0		7.5	11.3	18.5	24.7	27.6	20.7	11.7
Nepheline	25.4	44.5	21.6	29.4	34.7	31.2	23.1	27.9				
Leucite	60.8	54.8	41.9	31.3	53.9	38.8	77.6	20.1				
Acmite		3.7			1.4							
Diopside	36.4	31.8	39.1	19.6	28.5	24.2	55.2					
hypersthene								9.8	10.5	7.7	5.7	
Olivine		4.1	9.4	2.6				6.4				
Magnetite	2.3	0.2	2.8	2.0	0.3	1.0	1.9	1.6	1.6	1.7	1.2	1.0
Hematite												
Ilmenite	2.0	1.6	2.3	2.3	1.2	1.3	1.3	1.2	3.1	3.1	2.7	2.4
Apatite	2.2	1.6	2.5	1.4	1.4	1.2	0.8	1.3	2.8	2.6	2.5	2.3

nd=not determined. bdl — below detection limit (<0.04 wt.%). FeO*=total iron; TA (Total Alkalies)=Na₂O+K₂O; AI (Agpaitic Index)=TA/Al₂O₃; A/CNK=Al₂O₃/CaO+Na₂O+K₂O; MgO#=MgO/(MgO+FeO*) (from wt.% values normalised to 100).

The Mt. Vulture mantle carbonate has very similar trace element patterns to carbonate in mantle xenoliths from Kerguelen and Patagonia (Fig. 9). The main differences are the negative Nb anomaly and overall higher REE contents in the Kerguelen carbonates as well as the U peak in the Patagonian sample. Kerguelen also shows a very strong Ti-trough. Compared with Mongolian carbonate globules (sample BY42 of Ionov and Harmer, 2002), the Mt. Vulture mantle carbonate has an overall lower trace element content but similar pattern with the exception of Th (Fig. 9). In contrast, Spitsbergen carbonate (Ionov et al., 1993) is strongly depleted in in-

compatible elements, up to 1 or 2 orders of magnitude lower than the Mt. Vulture mantle carbonate.

There is considerable variation in the REE contents of carbonate in mantle xenoliths although all patterns are at least slightly light REE-enriched (Fig. 10a and b). The Σ REE in the Mt. Vulture mantle carbonate (all from LZ990) varies from 66 to 123 ppm and La/Yb ratios are 46 to 90 (average ~62), similar to Kerguelen mantle carbonate (La/Yb ratio ~60). The Mt. Vulture mantle carbonate is relatively rich in REE and partially overlaps with Kerguelen mantle carbonates which have the highest REE (Moine et al., 2004). It is also 2–9 times

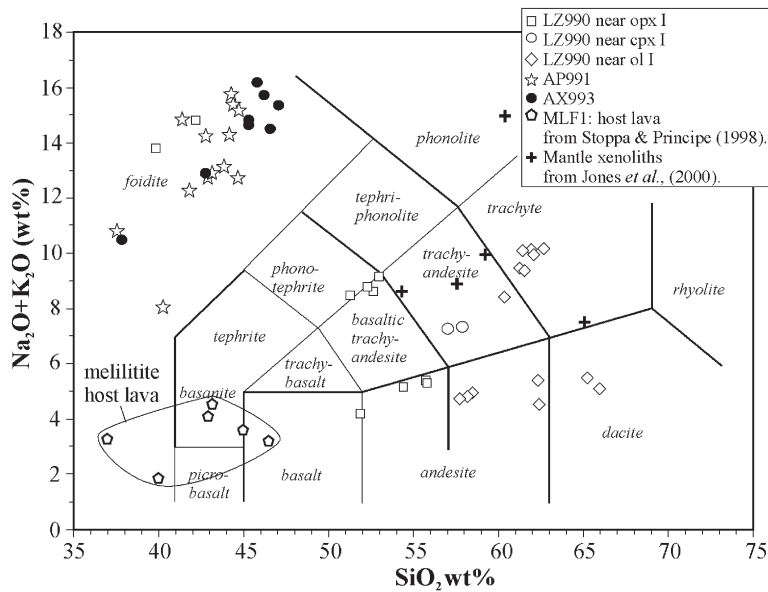


Fig. 6. TAS diagram (Le Bas et al., 1986) for intra-xenolith glasses containing carbonate inclusions compared with the host melilitite glass and other intra-xenolith glasses from Jones et al. (2000).

higher than mantle carbonates from Tanzania, Patagonia and Hungary (Lee et al., 2000; Laurora et al., 2001; Demény et al., 2004) and two orders of magnitude higher than Spitsbergen mantle carbonate (Ionov et al., 1993).

Carbonates in a Mongolian mantle xenolith (BY-42 of Ionov and Harmer, 2002) have very variable REE concentrations both lower and higher than those of Mt. Vulture xenolith carbonates (Fig. 9a). In particular the composition of the fine-grained aggregate of Mg-calcite, dolomite, amphibole, oxides, olivine and clinopyroxene found in the Mongolian xenolith is richer in REE, especially in MREE and HREE than carbonate globules in Mt. Vulture xenoliths. This is reflected in a La/Yb ratio ≈ 16 (Yb concentration inferred from the linear variation of the HREE), much lower than Mt. Vulture and Kerguelen mantle carbonates. The Mongolian carbonates have been interpreted as a mantle crystal cumulate and it was inferred that all carbonates in mantle xenoliths worldwide are crystal cumulates rather than trapped carbonatite liquids. In contrast, carbonatite melt inclusions in xenoliths from Hungary have lower REE contents even than the limestone from which they possibly originated (Demény et al., 2004). Thus variations in REE content of mantle carbonate globular inclusions clearly reflect different carbonate melt sources or trace element enrichment processes (i.e. degree of partial melting). Therefore we suggest that carbonate geochemistry alone is not conclusive for the discrimination of solidus or liquidus nature of carbonate trapped in mantle xenoliths.

The silicate glass in Mt. Vulture xenolith LZ990 is richer in trace elements, including REE but not Sr and Nb, than the carbonate globule it contains (Fig. 9). However the overall pattern is parallel to that of the

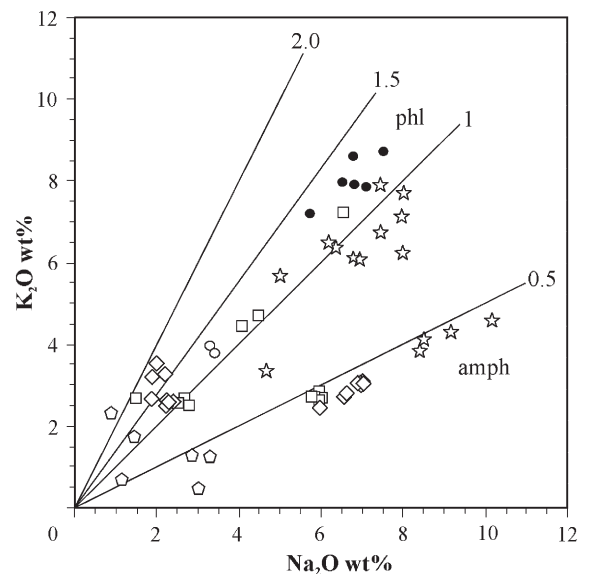


Fig. 7. Na_2O vs K_2O for Mt. Vulture intra-xenolith glasses and host melilitite glass. Glasses associated with, or containing, phlogopite relicts have $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios between 1 and 1.5, while glasses associated with amphibole have $\text{K}_2\text{O}/\text{Na}_2\text{O}$ ratios ≤ 0.5 . In sample AP991, glass occurring in the fine-grained matrix where phlogopite is abundant shows an alkali ratio around 1. The glass in LZ990 has a variable alkali ratio. Legend as Fig. 5.

Table 6

Representative EMPA analyses of carbonate in the globules

	AP991	AP991	AP991	AP991	AP991	AP991	AP991	AX993	AX993	AX993	DX994	LZ990	LZ990	LZ990	LZ990
	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14	#15
SiO ₂	bdl	bdl	0.06	0.06	0.10	0.31	0.12	bdl	bdl	0.05	0.06	bdl	0.07	0.93	1.01
FeO*	0.29	0.30	0.23	0.31	0.26	0.19	0.44	0.11	bdl	bdl	bdl	0.25	0.13	0.39	0.33
MgO	0.47	4.97	0.24	4.47	0.04	2.47	4.49	bdl	bdl	bdl	1.35	1.60	0.98	1.26	6.44
MnO	bdl	bdl	bdl	0.04	bdl	bdl	bdl	0.08	0.07	0.07	0.05	bdl	bdl	bdl	bdl
CaO	55.04	50.97	54.50	50.65	55.16	52.58	51.84	55.51	55.69	56.33	53.26	51.42	51.68	52.11	48.52
SrO	0.28	0.46	0.17	0.39	0.13	0.30	0.41	0.41	0.38	0.89	0.63	0.37	0.33	0.23	0.75
BaO	0.09	0.06	bdl	bdl	0.08	bdl	bdl	bdl	0.08	bdl	bdl	bdl	bdl	bdl	bdl
P ₂ O ₅	0.13	bdl	0.12	0.12	0.30	0.06	0.06	bdl	bdl	bdl	0.37	0.20	0.32	0.06	bdl
Total	56.17	56.76	55.20	55.91	55.76	55.86	57.30	56.11	56.20	57.33	55.35	53.64	53.19	54.92	57.05
Mg#	0.74	0.97	0.65	0.96	0.20	0.96	0.95	—	—	—	—	0.92	0.93	0.85	0.97
Ca#	0.98	0.88	0.99	0.89	1.00	0.94	0.89	1.00	1.00	1.00	0.97	0.96	0.97	0.96	0.83

FeO* = total iron; bdl = below detection limits (<0.04 wt.%). Mg# = Mg/(Mg + Fe²⁺). Ca# = (Ca/Ca + Mg).

carbonate. Ionov (1998) found a similar pattern, with higher trace elements in glass, in Spitsbergen and Mongolian peridotite xenoliths.

The ⁸⁷Sr/⁸⁶Sr (0.705816 ± 4) and ¹⁴⁴Nd/¹⁴³Nd (0.512641 ± 3) ratios of the carbonate globules in LZ992 are plotted on Fig. 11, together with unpublished whole rock data (courtesy of Keith Bell and Francesca Castorina) from the Mt. Vulture lavas and pyroclastic rocks. Data for clinopyroxene separates from Mt. Vulture mantle xenoliths are from Downes et al. (2002). Sr–Nd isotopic compositions of two carbonatite coatings of cored MLS lapilli and two ‘sövite’ xenoliths from the RS (Rosatelli et al., 2000) are also plotted. The

clinopyroxene data trends from the depleted quadrant towards the enriched quadrant. This trend has been interpreted as the result of ancient mantle depletion via basaltic magma extraction and subsequent refertilisation (Downes et al., 2002). The Mt. Vulture xenolith carbonate, lapilli carbonatite tuffs and ‘sövite’ plot close together and within the field of Mt. Vulture lavas within the enriched quadrants (Fig. 11b) and appear to be in isotopic equilibrium.

12. Discussion

Several different models have been proposed to explain the presence of carbonate inclusions in mantle xenoliths.

1. Ionov (1998), Lee et al. (2000), and Ionov and Harmer (2002) suggested on the basis of texture, major and trace element compositions, that carbonate in peridotite xenoliths from Spitsbergen, Mongolia, Tanzania and generally worldwide, is cumulate, having crystallised from a transient carbonatitic melt.
2. Moine et al. (2004) interpreted carbonate inclusions in amphibole–clinopyroxene–spinel dunite mantle xenoliths from Kerguelen as quenched, evolved carbonatite melts.
3. Carbonate inclusions Canary Islands, Fernando de Naronha Island (Brazil) and from East Antarctica have been interpreted as trapped Ca-carbonatite melt formed through mantle carbonatization and wehrlitization caused by Na-dolomitic melts followed by partial melting of this metasomatic assemblage (Kogarko, 2003).
4. Laurora et al. (2001) concluded that carbonate globules in mantle xenoliths from Southern Patagonia are quenched carbonate melt produced via

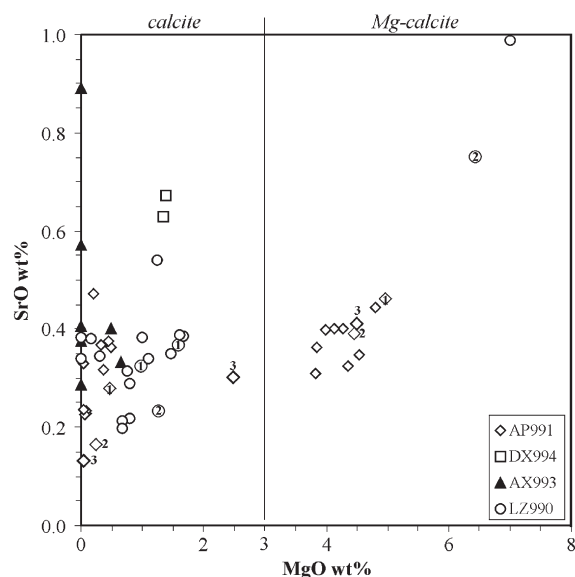


Fig. 8. MgO vs SrO of the carbonate inclusions in intra-xenolith glass. Corresponding numbers label different compositions determined within a single carbonate globule or closely spaced globules.

Table 7
LAICPMS of carbonate inclusions and glass

LZ990	Carbonate #2	Carbonate #4	Carbonate #5	Carbonate #6	Glass #7
Ti	176	232	1763	511	12509
V	3.9	4.5	46.2	41.3	490.8
Mn	37.7	36.2	173.5	141.2	656.7
Co	1.0	1.9	3.7	7.3	9.0
Zn	53.4	79.7	109.3	24.3	44.4
Rb	1.0	1.3	6.7	0.4	133.3
Sr	3916	4587	5219	3144	1699
Y	8.3	10.5	10.4	10.7	40.7
Zr	5.4	10.8	48.2	8.9	332.6
Nb	127.3	161.1	211.0	3.9	105.5
Cs	0.1	0.1	0.2	<0.1	7.4
Ba	141	175	387	212	4426
La	20.1	26.5	39.3	28.7	158.4
Ce	28.9	15.9	42.2	16.4	234.7
Pr	3.3	4.9	6.1	4.8	26.4
Nd	9.8	12.5	24.2	20.2	99.7
Sm	1.5	1.9	3.9	4.1	18.9
Eu	0.4	0.4	0.9	1.1	4.3
Gd	1.2	1.5	2.8	2.9	9.4
Tb	0.2	0.2	0.3	0.3	1.1
Dy	0.9	1.4	1.7	1.8	7.5
Ho	0.2	0.3	0.3	0.3	1.1
Er	0.4	0.4	0.7	0.7	4.1
Tm	0.1	0.1	0.1	0.1	<0.3
Yb	0.4	0.6	0.4	<0.4	4.1
Lu	0.1	0.1	0.1	<0.07	0.4
Hf	0.4	<0.2	0.7	<0.4	5.8
Ta	0.5	0.4	1.0	<0.14	4.1
Pb	5.0	6.7	10.8	8.2	32.0
Th	2.1	1.8	5.6	0.3	36.8
U	1.0	2.0	1.7	2.0	5.4
ΣREE	67.5	66.5	122.9	81.5	570.2
La/Yb	48.2	46.9	90.5	<62.1	38.7

< detection limits (3σ).

immiscibility from a carbonated silicate melt that originated by partial melting of mantle amphibole and addition of CO₂.

5. Van Achterbergh et al. (2004) suggested that silicate–carbonate globules in a garnet lherzolite xenolith from a Canadian kimberlite are products of unmixing in response to a sudden change in pressure and/or temperature related to kimberlite emplacement.

12.1. The nature of the carbonate inclusions

The precipitation of calcite from surficial waters percolating through the tuffs is ruled out. *In situ* dissolution and/or re-crystallisation of carbonate would not have preserved the fluid inclusions. Both alkali silicate glass and magmatic carbonates are easily altered in the presence of a CO₂-rich percolating pore water (Maccodanald et al., 1993) but the Mt. Vulture material is fresh,

and in addition there are no hydrothermal minerals (such as zeolites) associated with the carbonate.

The microstructures and features of these xenoliths lead us to conclude that the calcite and silicate glass formed from two immiscible liquids. Firstly, the morphology of the carbonate globules and their geometrical relationships with the host silicate glass are similar to those observed in other xenoliths where immiscibility has been proposed (e.g. Kogarko et al., 1995) and in experiments with separation of immiscible silicate and carbonate liquids (e.g. Minarik, 1998). In experimental charges rounded to elliptical carbonate occurs as a solid phase in equilibrium with silicate glass but it is formed as a “single crystal or a mosaic of crystals each with optical continuity and sets of parallel cleavage” (Brooker and Hamilton, 1990; Lee et al., 1994). Uniform extinction is also observed in carbonate in some mantle xenoliths (e.g. Lee et al., 2000). In the Mt. Vulture xenoliths the globules are filled with a mosaic of carbonate crystals, generally with different optical orientations. This has been suggested to be a dendritic texture (Lee et al., 2000) and although it differs from the experimental observations, it is similar to the immiscible carbonate observed with silicate glass in extrusive carbonatites (Bailey et al., 2005b; Bailey et al., 2005a).

The Mt. Vulture carbonate globules are rounded or elongated similar to those in Hungarian mantle xenoliths, suggesting that the carbonate contained in the globules and the host glass behaved plastically (Demény et al., 2004). They are also similar to the globular, amoeboid or dumbbell-shaped carbonates observed in extrusive carbonatites (e.g. Bailey et al., 2005a, 2005b).

The contact between carbonate blebs and glass in Mt. Vulture xenoliths is always smooth, curved and sharp, indicating a complete physical separation as in immiscible silicate–carbonate liquid pairs from experimental studies (e.g. Freestone and Hamilton, 1980) and natural occurrences such as at Oldoinyo Lengai (Dawson, 1989; Church and Jones, 1995). This implies that both the carbonate and the glass were liquid and in physical equilibrium when quenching occurred.

The liquid nature of the carbonate is also strongly supported by the fact that carbonate globules may be pierced or divided by quenched clinopyroxene microphenocrysts (Fig. 3e and f). The most reasonable interpretation of this texture is that the crystals grew rapidly in conditions of undercooling (quenching) and pierced the carbonate globules when they were still liquid. Additionally, the carbonate globules are rarely in direct contact with the silicate minerals, but are separated from them by a film of silicate glass. This is consistent with the different melt–solid interfacial energy between

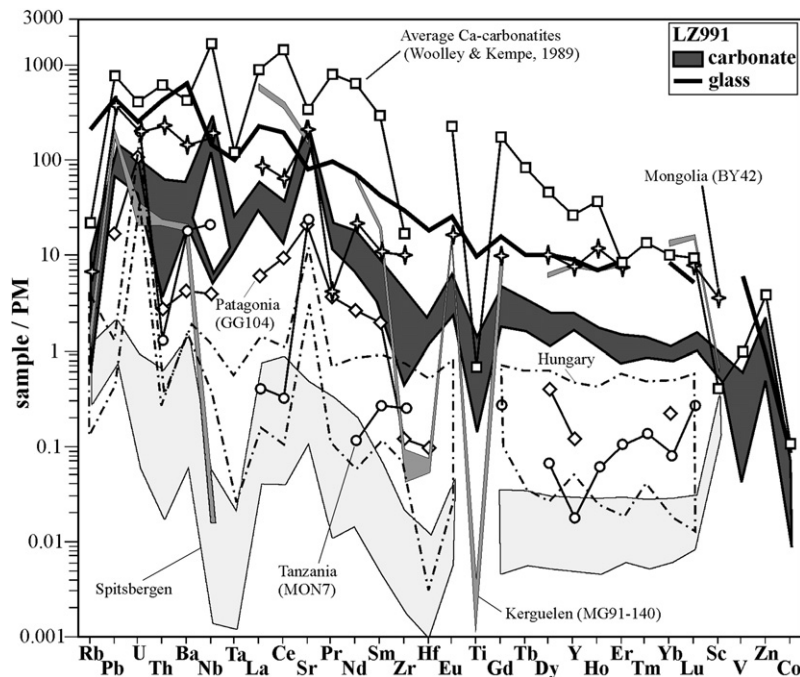


Fig. 9. Primitive mantle (Sun and McDonough, 1989) normalized trace elements variation in the carbonate and glass in the Mt. Vulture xenolith LZ990 compared with average Ca-carbonatites of Woolley and Kempe (1989) and carbonate in mantle xenoliths from Tanzania (Lee et al., 2000) Patagonia (Laurora et al., 2001), Kerguelen Island (Moine et al., 2004), Hungary (Demény et al., 2004), Spitsbergen (Ionov et al., 1993) and Mongolia (Ionov and Harmer, 2002).

silicate and carbonate liquids. In fact, the higher wetting capacity of the silicate melt prevents the carbonate melt from contacting the silicate mineral phases (Minarik, 1998) as noted in other carbonate–silicate occurrences in mantle xenoliths (e.g. Kogarko et al., 1995; Ionov et al., 1996; Pyle and Haggerty, 1994).

The lack of zoning in the silicate glass pools containing carbonate inclusions also supports complete chemical separation. Variations in calcite composition within and between the globules (Figs. 8 and 10) suggest disequilibrium (Ionov, 1998) and are consistent with variable MgO contents in extrusive carbonatites (Bailey et al., 2005b). These compositional variations may be the result of rapid quenching of the segregated carbonatite liquid. Quenching is also testified by the glass trapped in clinopyroxene microphenocrysts in the glass veinlets.

The reaction relationship between amphibole and carbonate (Fig. 2b), forming small clinopyroxene crystals along the amphibole–carbonate globule contact, suggests a high temperature environment and, again, the liquid nature of the carbonate. This kind of reaction has been also postulated by Laurora et al. (2001) and Moine et al. (2004).

The presence of similar dense CO₂ and sulphide inclusions in both the silicate glass and the carbonate

globules (Fig. 3b) suggests that carbonate and glass are fresh and genetically related (Moine et al., 2004).

12.2. The origin of carbonate inclusions

We have interpreted the calcite/Mg-calcite globules and associated silicate glass in Mt. Vulture xenoliths as genetically related, immiscibly separated quenched liquids. However, the experimentally constrained equilibrium liquid immiscibility fields at mantle conditions (Lee and Wyllie, 1998) indicate that alkali-poor carbonatites *cannot* be formed from a parental carbonated silicate melt. Thus the Mt. Vulture xenolith/xenocryst carbonate globules hosted in silicate minerals and glass veins have compositions within the experimentally constrained “forbidden” volume for high pressure, equilibrium carbonate liquids (Lee and Wyllie, 1998). Despite this apparent contradiction, we point to a number of observations now in which calcite carbonatite appears to be immiscible with silicate at mantle conditions. We think it is likely that the carbonate globules in the silicate glass veins were not formed via equilibrium immiscible separation but via a disequilibrium process, such as suggested previously by Van Achterbergh et al. (2004). A possible sequence of events is given below.

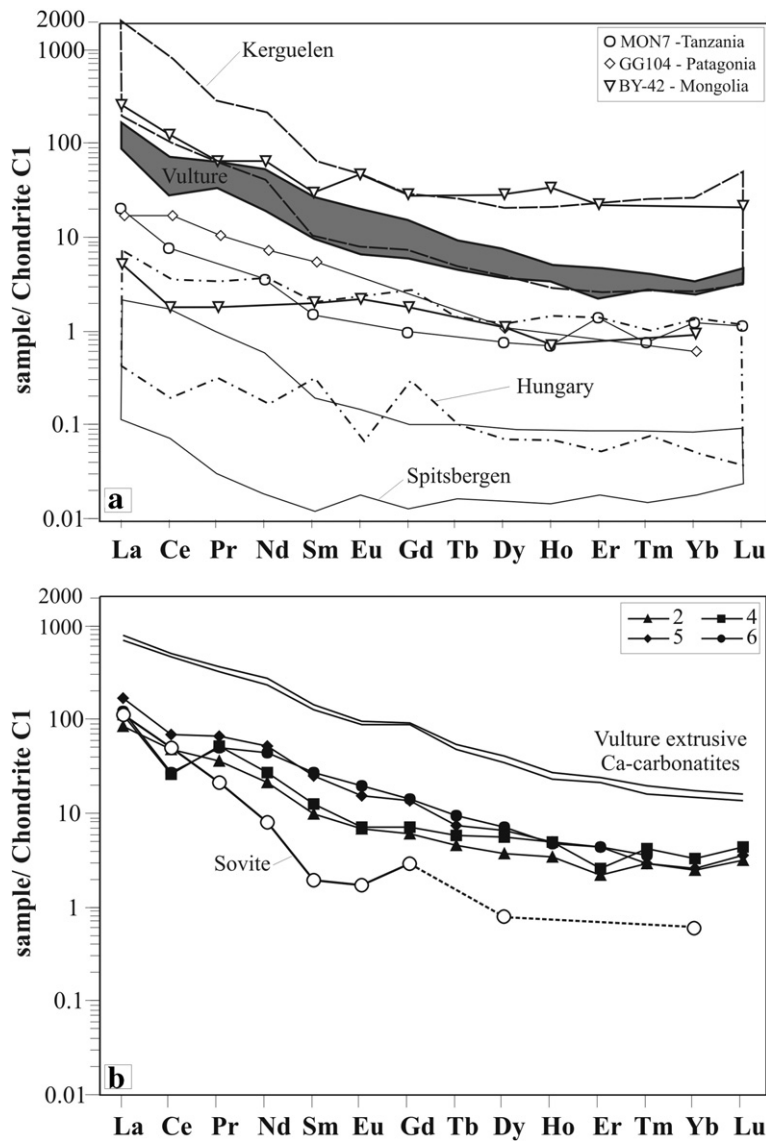


Fig. 10. a) REE variation in the LZ990 xenolith carbonate inclusions compared with similar occurrences in Kerguelen, Spitsbergen, Patagonia and Tanzania mantle xenoliths. b) REE of the xenolith carbonate inclusions compared with extrusive and intrusive (sövite) Ca-carbonatite rocks at Mt. Vulture (Stoppa and Woolley, 1997; Stoppa and Principe, 1998).

According to the evidence recorded in the xenoliths, we suggest that the lithospheric mantle beneath Mt. Vulture experienced multiple infiltration of small batch, carbonated silicate melts. A viable mechanism of melt infiltration and spreading would be via crack propagation and/or thermal fracturing (Frezzotti et al., 2002).

At least one such melt was trapped as inclusions in olivine (Fig. 2c), followed by a weak deformation event as recorded in the same olivine grain.

Subsequently a new carbonated silicate melt batch intruded the mantle forming the vein network in samples

LZ990 and AP991, just prior to the MLS eruption that exhumed the mantle xenoliths.

The presence of carbonate and carbonate–silicate glass inclusions in Mt. Vulture amphibole peridotite xenoliths and diopside xenocrysts that show deformation textures implies that they were trapped before the last mantle deformation event. Furthermore the carbonate-bearing amphibole xenocryst from the (older) RS pyroclastics suggests that carbonatite liquids were present in the mantle beneath Mt. Vulture before the main melilitite–carbonatite eruptions of MLS.

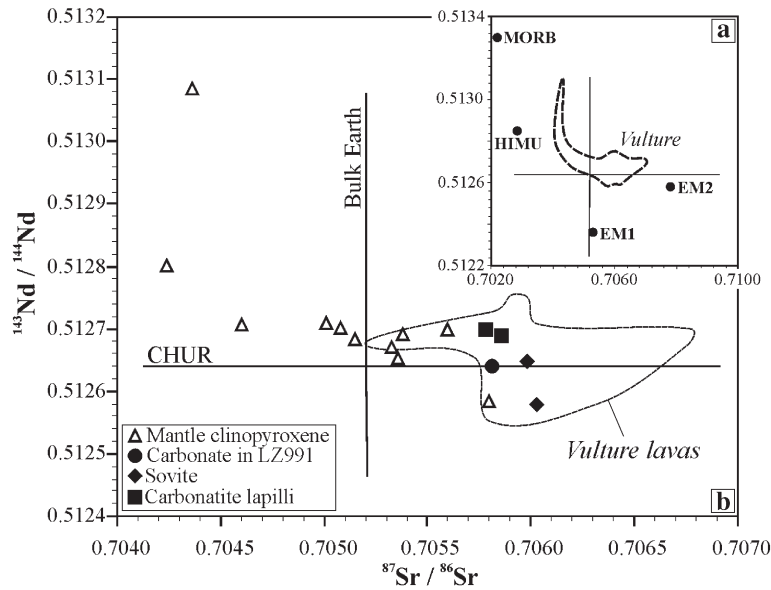


Fig. 11. Inset a): Field of Mt. Vulture data with respect to the common OIB end members (Hofmann, 1997); b) detail of A. The mantle clinopyroxenes define a trend from the depleted quadrant to the enriched quadrant ending in correspondence with the carbonate in mantle xenolith LZ991 and the other carbonatite occurrences at Mt. Vulture. The field of the Mt. Vulture alkaline lavas overlaps the carbonatite data.

The formation of immiscible silicate–carbonatite liquids occurred during the decompression on the way to the surface (Van Achterbergh et al., 2004) in both the veins and mineral inclusions. Rapid exhumation of the xenoliths and subsequent quenching prevented chemical equilibration of the two immiscible liquids and probably favoured wall rock partial melting as observed in primary peridotite phases (as in LZ990 and AP991) that were already in near solidus conditions as recorded in the xenoliths (Jones et al., 2000). This modified the composition of the silicate liquid but almost completely prevented the carbonate liquid from reacting with the host peridotite minerals. In fact the absence of reaction between carbonate and host xenolith minerals when there is glass interposed suggests that formation of silicate glass pockets and films along grain boundaries should have the same effect as wehrlitization of the mantle wall-rocks for the preservation of Ca-carbonatite melts (Green and Wallace, 1988).

The relatively low content of trace elements in the carbonate globules may reflect the short time between the separation of immiscible melts and quenching which prevented chemical equilibration with the glass, and evolution of carbonatite melt through crystal fractionation. The short time gap between partial melting and quenching is also testified by the heterogeneity of the glasses within single xenoliths, indicating there was insufficient time to reach chemical equilibrium via diffusive homogenization. Furthermore the carbonatite

melt formed did not have time to react extensively with amphibole (see AX993 and AP991), but produced only small overgrowths of fassaitic clinopyroxene in sample AP991 (Fig. 2b).

12.3. Relationship between mantle calcite globules and extrusive carbonatite at Mt. Vulture

At Mt. Vulture there are fine-grained extrusive carbonatitic tuffs in the MLS (Stoppa and Principe, 1998) and rare coarse-grained ‘sövite’ xenoliths in the RS (Rosatelli, 2000), giving a rare opportunity to compare mantle carbonate with local carbonatite *s.s.* While there is a substantial isotopic equilibrium between the carbonate globules in the xenoliths, the extrusive carbonatite and the ‘sövite’ xenolith, there is a wide variation in REE contents (Fig. 10b). The carbonatite tuffs are one order of magnitude richer in REE than the mantle carbonate globules (Fig. 10b). However the overall patterns are parallel and similar in LREE–HREE fractionation, with La/Yb ratios averaging ~ 62 for the carbonate globules and ~ 64 for the carbonatite tuffs. These geochemical features and the Sr–Nd isotopic equilibrium suggest that mantle carbonate and extrusive carbonate are closely related, and likely to be from the same mantle source.

The difference in absolute REE abundances is difficult to explain given the high velocity of the eruption of extrusive carbonatite, which would have given very

little time for any melt fractionation. One possibility is that fractionational crystallisation of calcite took place in the mantle before eruption (Ionov and Harmer, 2002); another is that the carbonate globules and the extrusive carbonatite were formed from parental melts originating from slightly different enriched mantle domains (Ionov and Harmer, 2002) or by different degrees of partial melting.

12.4. Consideration of lithosphere metasomatism beneath Mt. Vulture

Following the detailed analyses made here, preliminary work on 300 xenoliths from Mt. Vulture has confirmed that 60 contain carbonate. This figure of 20% is consistent with the 4 out of 16 xenoliths studied in Downes et al. (2002) that contain carbonate. The presence of carbonated silicate melts in the mantle beneath Mt. Vulture suggests that the enrichment of the lithospheric mantle in incompatible trace elements and LREE may be caused by infiltration of such melts. Enrichment in incompatible elements, as well as in ^{87}Sr , has been observed previously by Downes et al. (2002) and related to metasomatism beneath Mt. Vulture induced by a subduction-related silicate melt because of the similarity between the compositions of Vulture mantle clinopyroxene and those of other regions of Europe (such as North Hessia xenoliths and Finero massif) that have been interpreted as subduction-related. However, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the carbonate globules is similar to the most enriched mantle clinopyroxene (Fig. 11) and we suggest that carbonated silicate or carbonatite melts rather than a 'subduction-related silicate melt' may have been the agent of this metasomatism.

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