

Chemical Geology 233 (2006) 346–357



www.elsevier.com/locate/chemgeo

Short communication

# Magmatic origin of low-Ca olivine in subduction-related magmas: Co-existence of contrasting magmas

Vadim S. Kamenetsky <sup>a,b,\*</sup>, Marlina Elburg <sup>b,c</sup>, Richard Arculus <sup>d</sup>, Rainer Thomas <sup>e</sup>

<sup>a</sup> ARC Centre of Excellence in Ore Deposits and School of Earth Sciences, University of Tasmania, Hobart, Tasmania 7001, Australia b Max Planck Institute for Chemistry, Geochemistry Division, Mainz, Germany <sup>c</sup> Departmen

<sup>d</sup> Department of Earth and Marine Sciences, Australian National University, Canberra, ACT 0200, Australia Corpor GeoForschungsZentrum Potsdam, Telegrafenberg B 120, Potsdam, D-14473, Germany

Received 17 October 2005; received in revised form 15 March 2006; accepted 16 March 2006

## Abstract

Unravelling the origin of different components contributing to subduction-related magmas is a prerequisite to understanding the sources and processes involved in their origins. Mafic, high-Ca subduction-related magmas from geographically-diverse areas (Indonesia, Solomon Islands, Kamchatka, Valu Fa Ridge) contain two populations of olivine crystals, of which only the high-Ca population (CaO =  $0.3-0.5$  wt.%) crystallized from the melt that dominantly contributed to the whole rock composition. Forsteriterich (Fo<sub>90–94</sub>), low-Ca (CaO<0.15 wt.%), high-Ni (NiO>0.3 wt.%) olivine crystals, which constitute 16–37 vol.% of total olivine population, are generally interpreted as mantle or lithospheric xenocrysts. However, in these samples, the olivine shape and chemical zoning, the composition of included minerals (orthopyroxene, clinoenstatite and Cr-spinel) and presence of melt inclusions, are indications that these crystals are phenocrysts from a mafic magma with high silica and low calcium contents. The coexistence of contrasting magmas (mafic high-Ca silica-poor versus low-Ca silica-rich) within a number of arc systems and their mixing may not be a rare event, and should be taken into account when developing models of arc petrogenesis. © 2006 Elsevier B.V. All rights reserved.

Keywords: Island-arc magmas; Picrites; Olivine; Clinoenstatite; Magmatic inclusions; Xenocrysts; Mantle

## 1. Introduction

It is now widely accepted that any volcanic rock represents a mixture of different batches of silicate melts and one or more generations of crystals. The melt batches contributing to the bulk composition of a vol-

(V.S. Kamenetsky).

canic rock can ultimately originate from different mantle and crustal sources (i.e., primary melts), but in most cases the mixing melts are already affected by the processes in the magmatic plumbing conduit, such as mixing, crystallization, assimilation, degassing etc. Magma generating processes and chemical diversity of magmatic sources in subduction-related environments (island arcs, back arc basins) are more complex than in other tectonic settings. Moreover, insights into subduction-related primary magmas and their sources are generally hampered by the scarcity of primitive olivine-bearing rocks.

<sup>⁎</sup> Corresponding author. ARC Centre of Excellence in Ore Deposits and School of Earth Sciences, University of Tasmania, Hobart, Tasmania 7001, Australia. Tel.: +61 3 62267649; fax: +61 362232547.

E-mail address: [Dima.Kamenetsky@utas.edu.au](mailto:Dima.Kamenetsky@utas.edu.au)

<sup>0009-2541/\$ -</sup> see front matter © 2006 Elsevier B.V. All rights reserved. doi[:10.1016/j.chemgeo.2006.03.010](http://dx.doi.org/10.1016/j.chemgeo.2006.03.010)

<span id="page-1-0"></span>Table 1 Whole rock compositions of picritic samples from south Sulawesi, eastern Kamchatka, Solomon Islands and Valu Fa Ridge

	Location S. Sulawesi	Ε. Kamchatka		Solomon Isl. Valu Fa Ridge 22.3°S, 176.5°W SO67-240	
	5.3°S, 119.7°E	55°N, 159.5°E	8.2°S, 157.5°E		
Sample	Tnv96-1	<b>KB10</b>	R44692		
wt.%					
SiO <sub>2</sub>	46.70	41.61	45.70	50.52	
TiO <sub>2</sub>	0.53	0.34	0.35	0.42	
Al2O <sub>3</sub>	9.12	4.80	7.20	9.95	
$Fe2O3*$	10.04	9.99	10.21	9.73	
MnO	0.16	0.17	0.18	0.15	
MgO	20.23	30.05	25.20	17.31	
CaO	10.64	6.00	8.00	11.46	
Na <sub>2</sub> O	1.47	0.29	1.32	0.87	
$K_2O$	1.68	2.38	0.83	0.31	
$P_2O_5$	0.29	0.22	0.18	0.10	
LOI	1.71	5.01	0.58	0.66	
Total	102.57	100.86	99.75	101.48	
CaO/	1.17	1.25	1.11	1.15	
$Al_2O_3$					
ppm					
Cr	1308	1980	1744	n.a.	
Ni	644	1170	860	423	
Ba	497	455	111	46	
Nb	3.3	1.1	1	1.8	
Ce	27.9	12.6	12.1	12.4	
Sr	750	220	614	285	
Zr	57	24	28	18	

Analysis of R44692 from [Ramsay et al. \(1984\);](#page-11-0) this composition is similar to the sample we studied (M262) on the basis of modal mineral abundances. The extreme MgO, Ni and Cr contents indicate that the compositions are influenced by accumulation of olivine and Cr-spinel. n.a. — not analysed;  $Fe<sub>2</sub>O<sub>3</sub><sup>*</sup>$  — total Fe.

Existing data show that high-magnesian olivine crystals in primitive arc volcanic rocks can belong to more than one population ([Danyushevsky et al., 1995;](#page-10-0) [Kamenetsky et al., 1995b, 1997; Reubi et al., 2002](#page-10-0)). Different populations of primitive olivine point towards the co-existence of compositionally diverse magmas, and, by inference, the involvement of different protoliths or melting processes. These minerals can therefore act as probes of normally inaccessible, protolith areas, such as the upper mantle. In our studies of magmas from geographically-dispersed but representative samples of subduction-related environments (Indonesia, Solomon Islands, Kamchatka, Valu Fa Ridge) we have found several instances of forsterite-rich low-Ca olivine crystals, coexisting with phenocrystic olivine with higher-Ca contents at similar forsterite contents. We suggest these occurrences may not be rare. Since the study by [Simkin](#page-11-0) [and Smith \(1970\)](#page-11-0) most workers have interpreted high-

forsterite, low-Ca, high-Ni olivine crystals as mantle xenocrysts ([Ramsay et al., 1984; Cameron, 1985;](#page-11-0) [Boudier, 1991; Hirano et al., 2004; Schuth et al., 2004;](#page-11-0) [Rohrbach et al., 2005](#page-11-0)), that is, crystals which did not grow from magmatic liquids, but which were picked up accidentally from the mantle through which the magma ascended. The extent of Ca substitution in olivine is a function of pressure, host magma chemical composition (especially Ca, Si and alkalies), and forsterite content of olivine ([Simkin and Smith, 1970; Stormer, 1973;](#page-11-0) [Watson, 1979; Jurewicz and Watson, 1988; Libourel,](#page-11-0) [1999\)](#page-11-0); if it is assumed that most parental basaltic arc magmas have similar Ca contents, then low-Ca olivine is most likely to be derived from relatively low-temperature peridotitic wall-rock captured during magma ascent. In this situation, low-Ca olivine crystals would not convey any information about magmatic processes or sources. In this contribution we will present evidence for the magmatic origin of these low-Ca olivines, and formulate criteria by which phenocrystic low-Ca olivine can be distinguished from xenocrystic olivine.

## 2. Sample location and whole rock compositions

The four studied picritic samples (Table 1) from the New Georgia Group of the Solomon Islands ([Ramsay et](#page-11-0) [al., 1984; Schuth et al., 2004; Rohrbach et al., 2005](#page-11-0)), eastern Kamchatka, Far East Russia ([Kamenetsky et al.,](#page-11-0) [1995b](#page-11-0)), southern Sulawesi, Indonesia ([Elburg and](#page-10-0) [Foden, 1999](#page-10-0)) and the Valu Fa Ridge, Lau Basin [\(Kamenetsky et al., 1997\)](#page-11-0), although different in detail, come from broadly subduction-related environments. These olivine  $\pm$  clinopyroxene phyric rocks (up to 40 vol.  $%$  of olivine, [Fig. 1\)](#page-2-0) have relatively high contents of K, Ba, and Sr, and low values for Nb, Zr, and Ti, and thus are rare examples of primitive arc magmas. All samples have Ca-rich whole rock compositions (CaO/Al<sub>2</sub>O<sub>3</sub>>1), and studies of olivine-hosted melt inclusions confirm that highly calcic melts contributed to the whole rock/ groundmass compositions [\(Kamenetsky et al., 1995b,](#page-11-0) [1997; Elburg et al., 2004](#page-11-0)).

#### 3. Mineral relationships and compositions

The majority of olivine phenocrysts have CaO contents  $(0.25-0.4 \text{ wt.})\%$  and up to 0.5 wt. $\%$  CaO in the Sulawesi samples) that are higher than those of typical subduction-related magmas (0.15–0.25 wt.%, [Sigurds](#page-11-0)[son et al., 1993; Smith and Leeman, 2005](#page-11-0)), as would be expected from olivine that crystallized from high-calcium liquids [\(Beattie, 1993](#page-10-0)), and was in equilibrium with clinopyroxene at high temperatures and shallow depths

<span id="page-2-0"></span>

Fig. 1. Photographs of polished sections (∼0.1 mm thick) of olivine-phyric and olivine clinopyroxene-phyric picrites from eastern Kamchatka (A) and Solomon Islands (B), respectively, demonstrating the abundance and morphology of olivine crystals. Scale bars are 1 cm.



Fig. 2. CaO (wt.%) versus forsterite contents of olivine cores from the four samples studied. The symbols are larger than the analytical errors. Simplified evolution of olivine compositions in primitive volcanic suites is represented by the trend lines  $(I - low$ -Ca boninites;  $II - high$ -Ca boninites; III — island arc tholeiites, IV — basalts in mid-ocean rifts and oceanic islands). The variability of CaO content for a given Fo is within 20 rel.% along the trends shown. A field of mantle olivine compositions is also shown. Data for fractionation ( $Ol \pm Cpx \pm Pl$ ) trend lines from [Sigurdsson et al. \(1993\),](#page-11-0) [Kamenetsky and Crawford \(1998\)](#page-11-0), [Kamenetsky et al. \(1998\)](#page-11-0), and Kamenetsky (unpublished).

[\(Köhler and Brey, 1990](#page-11-0)). However, a large proportion of olivine cores in the grains studied (from 16% in the Solomon Islands to 37% in the Valu Fa Ridge, [Fig. 2\)](#page-2-0) have low-CaO (0.02–0.15 wt.%) and high-NiO (up to 0.5 wt.%) compositions. The boundary of 0.15 wt.% CaO between "low-Ca" and "high-Ca" olivine groups is tentative (i.e., for the purpose of this presentation only). In reality, a continuum of compositions exists in every sample ([Fig. 2](#page-2-0)). The olivine crystals show considerable variation of CaO at a given Fo across the entire Fo range, and such variability is at odds with compositional trends observed for primitive olivine in common rocks

from intra-oceanic island arcs, mid-oceanic rifts and ocean islands ([Fig. 2\)](#page-2-0). The low-Ca olivine tends to be more Fo-rich (90–94) than associated high-Ca olivine (Fo 85–91; [Fig. 2](#page-2-0)). The exception is the Valu Fa Ridge sample which has rare low-Ca olivine grains with Fo as low as 85 [\(Fig. 2\)](#page-2-0).

No difference in shape or size is observed between high- and low-Ca olivine; both varieties are usually present as euhedral 0.3–10 mm crystals [\(Fig. 1\)](#page-2-0). Backscattered electron and X-ray imaging show that a single crystal can be strongly zoned with gradual compositional variations up to 10 mol% Fo, and up to 0.2 wt.% CaO and NiO ([Fig. 3\)](#page-5-0). The high-Fo and low-Ca compositions are typical of olivine cores, and never occur at the olivine rims. Some low-Ca cores have identifiable crystal faces, giving them a euhedral–subhedral appearance [\(Fig. 3](#page-5-0)), and some are rounded or ovoid, but still aligned with the whole crystal outlines ([Fig. 3C](#page-5-0),D). In some cases, a low-Ca core  $(0.08 \text{ wt.})$  is mantled by olivine with even lower CaO (0.05 wt.%), with CaO contents then smoothly increasing from the core to 0.15 to 0.2 wt.% in the outer rim ([Fig. 3](#page-5-0)A), giving the profile an inverse saddleshape. NiO and Fo contents are correlated negatively with CaO and also yield saddle-shaped profiles. In the case of two or several attached crystals with low Ca cores, the size (volume) of olivine with similarly low CaO is proportional to the volume of entire crystals [\(Fig. 3](#page-5-0)B,D). In the olivine grains with normal zoning, CaO compositional profiles show smaller core plateaus than those of Fo and NiO [\(Fig. 3C](#page-5-0)), or even lack a core plateau [\(Fig. 3D](#page-5-0)).

The high-Ca olivine contains inclusions of melt, Crspinel, high-Ca pyroxene and occasionally orthopyroxene. The low-Ca olivine contains inclusions of melt, fluid, and orthopyroxene ([Fig. 4](#page-5-0)) and rarely euhedral Crspinel; inclusions of high-Ca pyroxene have not been found. Inclusions of melt in low-Ca olivine are very abundant, but because of their dominantly small size  $(< 5 \mu m)$  heating stage experiments and quantitative analysis were unsuccessful. Clinoenstatite is found in

both low- and high-Ca olivine from Solomon Islands and Kamchatka ([Kamenetsky et al., 1995b\)](#page-11-0). It is recognised by typical polysynthetic twinning ([Fig. 4](#page-5-0)G, H) and a characteristic Raman spectrum [\(Fig. 5](#page-7-0)), which is identical to that of clinoenstatite from low-Ca boninites in New Caledonia [\(Sameshima et al., 1983](#page-11-0)). Orthopyroxene and clinoenstatite (low-Ca pyroxene) are always euhedral in shape and only found as olivinehosted inclusions (up to 100 μm in size), often in clusters of several grains, and never as a phenocryst phase. The low-Ca pyroxene inclusions are always rimmed by silicic glass ([Fig. 4C](#page-5-0)–G), and are typically contained within clear olivine, whereas the host olivine away from the pyroxene inclusions is clouded with micro-inclusions  $(0.5 \mu m)$  of glass, vapour bubbles and Cr-spinel crystal [\(Fig. 3](#page-5-0)A,B). Melt and vapour inclusions are also often present within orthopyroxene inclusions [\(Fig. 4D](#page-5-0)–F).

Low-Ca pyroxene inclusions and their host olivine from all studied samples are well equilibrated in terms of Fe–Mg, as demonstrated by their correlated Mg#  $(100 * Mg/(Mg + Fe))$  and Fo [\(Fig. 6](#page-7-0), [Table 2](#page-8-0)). A fair positive correlation between CaO contents of coexisting low-Ca pyroxene and olivine exists overall, but it is not as good for individual samples ([Fig. 6](#page-7-0), [Table 2](#page-8-0)). A distinctive feature of most analysed inclusions of low-Ca pyroxene is their low  $\text{Al}_2\text{O}_3$  (<1 wt.%) abundances [\(Fig. 7,](#page-9-0) [Table 2](#page-8-0)).

Cr-spinel inclusions in "dusty" areas of low-Ca olivine [\(Figs. 3](#page-5-0) and [4](#page-5-0)A,B) are typically present as very small euhedral plates in association with micro-inclusions of melt and fluid bubbles (see also [Rohrbach et al.,](#page-11-0) [2005\)](#page-11-0), whereas individual larger grains suitable for analysis are very rare. A few grains large enough to be analysed have the characteristics typical of primitive Crspinel in island-arc volcanic rocks, i.e.  $Mg# > 50$ , Cr#  $(100 * Cr/(Cr + Al)) \sim 80$ , TiO<sub>2</sub> 0.15–0.5 wt.%, and  $Fe^{2+}/Fe^{3+} < 2.5$  ([Table 3](#page-9-0)).

# 4. Discussion and conclusions

#### 4.1. Mantle xenocrysts versus magmatic phenocrysts

The common belief that olivine with  $CaO<0.1$  wt.% must have been derived from mantle peridotites is based on the work by [Simkin and Smith \(1970\).](#page-11-0) However, a number of primitive mantle-derived magmas from different tectonic environments are now known to crystallise low-Ca olivine at shallow depths; the most notable examples include carbonatites, kimberlites and low-Ca boninites (e.g., [Crawford, 1980; Walker and Cameron,](#page-10-0) [1983; Skinner, 1989; Fedortchouk and Canil, 2004](#page-10-0)).



<span id="page-5-0"></span>

Fig. 4. Magmatic inclusions in low-Ca olivine from Solomon Islands (A, B, D, E, H), south Sulawesi (C), Valu Fa Ridge (F) and Kamchatka (G). A and B represent boxed areas on Fig. 3A and B, respectively; the 'dusty' appearance of olivine reflects the presence of numerous tiny inclusions of silicate glass, vapour and spinel. Note polysynthetic twinning characteristic of clinoenstatite on G and H (photographed in polarized light), and magmatic glass and vapour inclusions in orthopyroxene inclusions on D–F. opx — orthopyroxene, gl —glass, b — vapour bubble; mi — melt inclusions. Scale bars are 40 μm.

Although many features of the low-Ca olivine crystals in the subduction-related picrites could be interpreted to result from re-equilibration of mantle, lithospheric and crustal xenocrysts with a hot, highCa magma ([Costa and Dungan, 2005; Rohrbach](#page-10-0) [et al., 2005](#page-10-0)), the following observations provide strong evidence that this is not the case for the samples studied:

Fig. 3. Optical images, X-ray maps and electron microprobe profiles (taken along dotted lines indicated on optical images) of olivine crystals from the Solomon Islands picrites. The boxed areas with magmatic inclusions on A and B are shown in Fig. 4A and B, respectively. Orthopyroxene inclusions are circled on C, D.



- <span id="page-7-0"></span>1. Mantle olivine is typically anhedral in shape, since it is essentially a metamorphic, not a magmatic mineral. Therefore, one would expect the low-Ca cores of euhedral crystals to have anhedral outlines if they were mantle xenocrysts. In contrast, the low-Ca cores always show either euhedral to subhedral outlines or ellipsoidal shape, aligned crystallographically ([Fig. 3](#page-5-0)), and completely lack deformation features, such as kink bands, which are common in olivine xenocrysts. Significantly, aggregates of low-Ca olivine grains, common in intraplate alkali basalts and kimberlites, are not present in the subductionrelated picrites.
- 2. Subhedral and ovoid shapes of the low-Ca olivine cores and the features of compositional profiles across them [\(Fig. 3](#page-5-0)) argue against mechanical abrasion and/ or partial resorption of peridotitic olivine xenocrysts in the transporting magma, followed by overgrowth by liquidus high-Ca olivine. Instead we propose that observed euhedral shapes of olivine crystals with low-Ca cores are original shapes of olivine grains that were entirely high-Fo, high-Ni and low-Ca in composition. Smooth, continuously changing composi-tions from cores to rims (Fo, Ni, Ca — [Fig. 3,](#page-5-0) and Cr and Mn, not shown) reflect both diffusive partial reequilibration [\(Costa and Dungan, 2005](#page-10-0)) of earlier phenocrysts with the lower-Mg# and higher-Ca magma that delivered them to the surface and crystallisation growth from the same magma. The latter is evident in those compositional profiles where the concentration gradient of slower diffusing Ca is steeper than gradients of faster diffusing Fe–Mg, Ni and Mn ([Fig. 3](#page-5-0)D). The extent of diffusive re-equilibration and crystallisation overgrowth can be different for individual crystals in the rock, but is roughly similar for two or several adjacent crystals [\(Fig. 3B](#page-5-0),D). In other words, for adjacent crystals of variable size, distances from a point in the core with a given CaO content to the outer rim are similar [\(Fig.](#page-5-0) [3B](#page-5-0),D). This strongly implies that adjacent low-Ca olivine grains were euhedral prior to their reequilibration.
- 3. The presence of a high-Fo, high-Ni and low-Ca mantle on the core with somewhat lower Ca and higher Fo and NiO (inverted saddle-shaped elemental profiles, [Fig. 3A](#page-5-0)) is inconsistent with the origin for low-Ca olivine from disintegrated peridotitic xeno-



Fig. 6. Compositional relationships between low-Ca pyroxene inclusions and their host olivine. Note that orthopyroxene inclusions are slightly more Mg-rich that host olivines (i.e.,  $Kd \ge 1$ ), and this is consistent with the experimental data on Fe–Mg partitioning between olivine and orthopyroxene at magmatic temperatures [\(von Seckendorff](#page-11-0) [and O'Neill, 1993\)](#page-11-0).

liths, since mantle xenocrysts would be expected to have homogeneous compositions, resulting from long equilibration times. This type of zoning is more likely to reflect olivine growth from a magmatic liquid with a fluctuating, but still low-Ca, composition.

4. In every studied picrite the range of Fo in low-Ca olivine is significant [\(Fig. 2,](#page-2-0) up to ∼9 mol% Fo in the Valu Fa sample), and such a large range of Fo contents is uncommon for mantle xenocrysts and would require sampling from vastly different peridotite lithologies. Moreover, the low-Fo end of the array is outside the compositional range of mantle olivine. The range of Fo in olivine from a given rock is commonly attributed to magma fractionation due to crystallisation. The absence of xenoliths and xenocrysts of other

Fig. 5. Comparison of the Raman spectra of the clinoenstatite inclusion from the Solomon Islands picrite M262 ([Table 2,](#page-8-0) n. 5) and a clinoenstatite microphenocryst in a glassy low-Ca boninite lava from New Caledonia (collected by Tony Crawford). The Raman probe (GFZ, Potsdam) consists of a Dilor XY Laser Raman Triple 800 mm spectrometer equipped with an Olympus optical microscope. The Raman spectra are nearly similar to the spectrum of synthetic clinoenstatite [\(Lin, 2004](#page-11-0)). According to [Lin \(2004\)](#page-11-0) the most discernible feature for differentiation of clino- and orthoenstatite are the bands with medium intensity at 344 and 371 cm<sup>-1</sup> for clinoenstatite and the single band at 343 cm<sup>-1</sup> for orthoenstatite.

<span id="page-8-0"></span>peridotitic minerals (orthopyroxene, clinopyroxene, spinel or garnet) in the rocks studied, and their apparent scarcity in other subduction-related volcanic magmas, are noteworthy.

- 5. Low-Ca, high-Mg# pyroxene inclusions in forsteritic olivine are not regularly recorded in magmatic rocks, except boninites, but orthopyroxene and olivine are commonly associated in peridotites. However, low  $Al_2O_3$  contents (<1 wt.%) in most low-Ca pyroxene inclusions are not typical of orthopyroxene in harzburgites from supra-subduction zones [\(Bonatti and Michael, 1989; Niu and](#page-10-0) [Hekinian, 1997; Parkinson and Pearce, 1998;](#page-10-0) [Morishita et al., 2003\)](#page-10-0), and have not been recorded from abyssal peridotites [\(Fig. 7\)](#page-9-0). The idea, advocated above, of partial equilibration of low-Ca olivine with a high-Ca magma, explains the occurrence of low-Ca pyroxene inclusions in relatively high-Ca olivine. Although CaO abundances of coexisting low-Ca pyroxene inclusions and olivine are positively correlated, the correlation is not as good as their Fe–Mg relationships [\(Fig. 6\)](#page-7-0). However, such a retarded re-equilibration of trace elements compared to major elements is to be expected. Melt inclusions in orthopyroxene and glass mantles with shrinkage bubbles around orthopyroxene ([Fig. 4](#page-5-0)) further support magmatic crystallisation.
- 6. Clinoenstatite has never been recorded in mantle xenoliths and abyssal or ophiolite peridotites. The polysynthetic twinning of the clinoenstatite [\(Figs. 4,](#page-5-0) [and 5](#page-5-0)) indicates that it inverted from protoenstatite [\(Iishi and Kitayama, 1995\)](#page-10-0), a mineral whose stability field is limited to relatively low pressure  $(< 1$  GPa) and high temperatures  $(>1000-1250$  °C). On the other hand, clinoenstatite, co-crystallising with low-Ca high-Fo olivine, is typical of low-Ca boninitic magmas in the western Pacific [\(Dallwitz et al., 1966; Crawford,](#page-10-0) [1980; Komatsu, 1980; Shiraki et al., 1980; Sameshima](#page-10-0) [et al., 1983\)](#page-10-0). It has been stated for the low-Ca olivine– clinoenstatite assemblage in the Solomon Island picrites that "olivines with clinoenstatite inclusions should be magmatic in origin and may have been liquidus phases of a low-Ca boninitic melt" [\(Rohrbach](#page-11-0) [et al., 2005\)](#page-11-0). It cannot be excluded that inclusions of orthopyroxene were originally trapped as clinoenstatite. The occurrence of clinoenstatite in relatively calcic olivine (Table 2, n. 5) suggests that the host olivine was once low-Ca in composition.
- 7. Low-Ca olivine is occasionally sprinkled with minute melt, fluid and Cr-spinel inclusions ([Figs. 3A,B](#page-5-0) [and 4A](#page-5-0),B). This provides additional support for the

Table 2

Representative compositions of low-Ca pyroxene inclusions and their host olivine in picrites from south Sulawesi (1, 2), eastern Kamchatka (3, 4), Solomon Islands (5, 6) and Valu Fa Ridge (7)

$\cal N$	$\mathbf{1}$	$\mathfrak{2}$	3	$\overline{4}$	5	6	7
Grain	Tnv96- 1 ol88	Tnv96- 1 ol944	KB9/ $11 -$ Cen	<b>KB74</b> 2/11	M262- Cen	$19-1$ 0 <sup>11</sup>	SO <sub>35</sub> 98
SiO <sub>2</sub>	57.98	57.75	57.45	57.49	56.80	57.30	56.56
TiO <sub>2</sub>	0.09	0.09	0.02	0.01	$\mathbf{0}$	0.03	0.04
$Al_2O_3$	1.46	0.21	0.18	0.26	0.33	0.31	0.29
FeO	5.00	4.76	5.04	3.93	6.88	5.22	5.05
MnO	0.07	0.09	0.13	0.08	0.19	0.12	0.09
MgO	34.18	35.71	35.25	37.02	34.30	35.67	36.09
CaO	1.25	0.71	0.66	0.30	0.59	0.27	0.42
Na <sub>2</sub> O	0.03	0.07	0.05	0.04	$\mathbf{0}$	0.02	0.11
$Cr_2O_3$	n.a.	0.13	0.17	0.02	0.11	0.1	$\overline{0}$
N <sub>i</sub> O	n.a.	0.11	n.a.	0.13	n.a.	0.12	0.19
Total	100.06	99.63	98.95	99.28	99.20	99.16	98.84
$Mg#$ , mol%	92.4	93.1	92.6	94.4	89.9	92.4	92.7
Host olivine							
SiO <sub>2</sub>	40.49	40.16	41.41	41.94	40.49	40.39	40.43
FeO	7.82	7.12	7.42	6.09	11.39	8.54	8.04
MnO	0.11	0.08	0.11	0.10	0.21	0.14	0.13
MgO	51.31	50.93	50.07	52.99	48.42	50.26	50.6
CaO	0.09	0.07	0.15	0.05	0.23	0.05	0.09
NiO	0.38	0.43	0.38	0.44	0.26	0.38	0.41
$Cr_2O_3$	0.06	0.04	0.05	0.07	0.03	n.a.	0.06
Total	100.26	98.83	99.59	101.68	101.04	99.76	99.76
Fo. mol%	92.1	92.7	92.3	93.9	88.3	91.3	91.8

Compositions of clinoenstatite are in columns 3 (see [Fig. 4](#page-5-0)E) and 5 (see [Figs. 4F and 5](#page-5-0)). Analyses were performed on a JEOL 8200 electron microprobe at the Max Planck Institute for Chemistry (Mainz, Germany), using an accelerating voltage of 20 kV and a current of 20 nA. On-peak counting times for Ca in olivine were 60 s, for Ni 120 s. CaO contents of olivine at the 0.1% level have a 2-sigma standard deviation of 12% relative. n.a. — not analysed. Fo and  $Mg# - 100 * Mg/(Mg + Fe).$ 

inferred magmatic origin of the low-Ca olivine. Crspinel inclusions are euhedral, unlike anhedral and vermicular spinel in harzburgites [\(Matsumoto and](#page-11-0) [Arai, 2001\)](#page-11-0), and have higher TiO<sub>2</sub> and lower Fe<sup>2+</sup>/  $Fe<sup>3+</sup>$  than mantle spinel, but well within the field of spinel from volcanic rocks [\(Kamenetsky et al.,](#page-11-0) [2001](#page-11-0)).

# 4.2. Contrasting melt compositions in a single magmatic system

The magmatic origin of the low-Ca olivine that is present in the high-Ca rocks [\(Table 1](#page-1-0)) indicates that at least two types of magma must have passed through the volcanic plumbing system. The dominant component is

<span id="page-9-0"></span>

Fig. 7. Relationships between Al<sub>2</sub>O<sub>3</sub> and Mg# in low-Ca pyroxene inclusions hosted by olivine phenocrysts in the subduction-related picrites. Compositions of orthopyroxene from abyssal peridotites [\(Dick, 1989](#page-10-0)) and from mantle harzburgites in the supra-subduction zone ophiolitic complexes (Horoman, Japan, [Morishita et al., 2003](#page-11-0); Izu–Bonin–Mariana forearc, ODP Leg 125, [Parkinson and Pearce, 1998](#page-11-0); New Caledonia, S. Meffre, unpublished) are shown for comparison.

the high-Ca magma, from which phenocrysts of high-Ca olivine and clinopyroxene and the groundmass crystallised. The low-Ca olivine points to the presence of another magma with a contrasting composition, and the continuum of CaO contents in olivine of a given rock [\(Fig. 2\)](#page-2-0) and often within a single olivine phenocryst [\(Fig.](#page-5-0) [3\)](#page-5-0) suggests mixing of two types of magma and diffusive re-equilibration and overgrowth of earlier formed olivine. The coexistence of magnesian low-Ca olivine with orthopyroxene and/or clinoenstatite indicates that this magma must have been both rich in silica and magnesium; the low CaO content of the olivine is likely to be a direct reflection of the reduced calcium and high silica contents of the melt [\(Libourel, 1999\)](#page-11-0). This agrees with correlated CaO in olivine and  $CaO/Al<sub>2</sub>O<sub>3</sub>$  in melt inclusions from the studied and other magmatic suites [\(Kame](#page-11-0)[netsky et al., 1995a; Kamenetsky and Clocchiatti, 1996;](#page-11-0) [Kamenetsky et al., 1997; Kamenetsky and Crawford,](#page-11-0) [1998\)](#page-11-0).

The low-Ca olivine, which originated from a supposedly low-Ca, high-Si magma, could have become included into the rock-forming high-Ca magmas either from the earlier cumulates or during mixing of two contrasting magmas. The second possibility is preferred given the fact that low-Ca and high-Ca olivine in the studied rocks are linked by the intermediate CaO compositions (i.e., between  $0.15$  and  $0.25$  wt.%), and proportions of such "transitional" olivine are significant in all studied rocks [\(Fig. 2](#page-2-0)). Therefore, the absence of clear relationships between Fo and CaO in the olivine cores [\(Fig. 1](#page-2-0)) suggests that a number of parental melt compositions, resulting from mixing of the tentatively defined "low-Ca" and high-Ca" endmembers, were present in the magmatic system.

Table 3

Compositions of Cr-spinel inclusions and their host low-Ca olivine in picrites from eastern Kamchatka (1, 2) and Solomon Islands (3, 4)

N	1	2	3	4
Grain	KB9 ol2/1	K74/5	M262 gr1	M262 gr41
TiO <sub>2</sub>	0.32	0.45	0.19	0.16
$Al_2O_3$	6.20	10.29	6.10	6.70
$Cr_2O_3$	57.34	47.37	57.51	56.64
Fe <sub>2</sub> O <sub>3</sub>	9.61	13.87	9.00	8.17
FeO	10.88	10.93	16.56	16.65
MnO	0.17	0.16	0.30	0.31
MgO	15.6	14.67	10.78	10.67
Total	100.12	97.74	100.44	99.30
$Mg#$ , mol%	74.3	70.5	53.7	53.3
$Cr#$ , mol%	86.1	75.5	86.4	85.0
$Fe^{2+}/Fe^{3+}$	0.98	0.88	2.04	2.26
Host olivine				
SiO <sub>2</sub>	41.61	41.24	41.21	41.17
FeO	6.32	6.50	6.64	8.77
MnO	0.10	0.14	n.a.	0.16
MgO	52.07	50.4	51.9	49.55
CaO	0.12	0.10	0.08	0.12
N <sub>i</sub> O	0.43	0.42	n.a.	0.38
$Cr_2O_3$	0.08	0.09	n.a.	0.05
Total	100.73	98.89	99.83	100.20
Fo, $mol\%$	93.6	93.3	93.3	91.0

 $Fe<sub>2</sub>O<sub>3</sub>$  is calculated on the basis of stoichiometry. n.a. — not analysed. Fo and Mg#  $- 100$ <sup>\*</sup> Mg/(Mg + Fe); Cr#  $- 100$ <sup>\*</sup> Cr/(Cr + Al).

<span id="page-10-0"></span>The origin of subduction-related magmas, unusually depleted in Ca (e.g., low-Ca boninites) and unusually enriched Ca (e.g., ankaramites), compared to melts derived from common peridotite mantle, is still a matter of considerable debate in the literature (Della-Pasqua and Varne, 1997; Schiano et al., 2000; Kamenetsky et al., 2002; Green et al., 2004; Médard et al., 2004; Schmidt et al., 2004). Low CaO/Al<sub>2</sub>O<sub>3</sub>, silicic high Mg# melt, saturated in forsteritic low-Ca olivine and magnesian orthopyroxene, seems to be common and present in a large proportion relative to the rock-forming melt. What is its origin?

While most workers agree on the importance of the mantle in generating basaltic magmas, alternative views, advocating the role of localised dissolutionreaction-mixing processes in the magmatic plumbing system, have been increasingly gaining support from the studies of intrusive parts of ophiolites (Bédard, 1993; Bédard et al., 2000) and melt inclusions in magmatic phenocrysts (Danyushevsky et al., 2004). Such processes are driven by the chemical interaction of hot mantle-derived magmas with wall rocks in a magmatic conduit, and primarily involve congruent and incongruent dissolution of mineral constituents of crustal rocks, melt mixing and crystallisation. What is most significant in the light of our findings is that a variety of magma types may coexist in the same magmatic system, and thus their origins are probably related. Future research on deciphering this phenomenon should involve detailed mineralogical and magmatic inclusion studies.

## Acknowledgments

This work was funded by an EU Marie Curie Fellowship to MAE, and a Friedrich Wilhelm Bessel Award (A. von Humboldt Foundation, Germany) and an Australian Professorial Fellowship and Discovery Grant to VSK. Al Hofmann and Alex Sobolev are thanked for providing access to instrumentation at the MPI. Discussions with Leonid Danyushevsky help to clarify issues related to modifications of mantlederived magmas in the crust. Discussions with Carsten Münker, Arno Rohrbach and Chris Ballhaus about xenocrystic vs phenocrystic origin of low-Ca olivine are appreciated. Previous versions of this manuscript benefited from reviews by Ian Smith, Jon Davidson, Paul Wallace, Hugh O'Neill and two anonymous reviewers. We are grateful to Fidel Costa and anonymous reviewer for their thoughtful comments that improved this manuscript, and Roberta Rudnick for editorial handling. [RR]

#### References

- Beattie, P., 1993. Olivine-melt and orthopyroxene-melt equilibria. Contrib. Mineral. Petrol. 115, 103–111.
- Bédard, J.H., 1993. Oceanic crust as a reactive filter: synkinematic intrusion, hybridization, and assimilation in an ophiolitic magma chamber, western Newfoundland. Geology 21, 77–80.
- Bédard, J.H., Hébert, R., Berclaz, A., Varfalvy, V., 2000. Syntexis and the genesis of lower oceanic crust. In: Dilek, Y., Moores, E.M., Elthon, D., Nicolas, A. (Eds.), Ophiolites and oceanic crust: new insights from field studies and the ocean drilling program. Geol. Soc. America, Boulder, Colorado, Spec. Pap., vol. 349, pp. 105–119.
- Bonatti, E., Michael, P.J., 1989. Mantle peridotites from continental rifts to ocean basins to subduction zones. Earth Planet. Sci. Lett. 91, 297–311.
- Boudier, F., 1991. Olivine xenocrysts in picritic magmas: an experimental and microstructural study. Contrib. Mineral. Petrol. 109, 114–123.
- Cameron, W.E., 1985. Petrology and origin of primitive lavas from the Troodos ophiolite, Cyprus. Contrib. Mineral. Petrol. 89, 239–255.
- Costa, F., Dungan, M., 2005. Short time scales of magmatic assimilation from diffusion modeling of multiple elements in olivine. Geology 33, 837–840.
- Crawford, A.J., 1980. A clinoenstatite-bearing cumulate olivine pyroxenite from Howqua, Victoria. Contrib. Mineral. Petrol. 75, 353–367.
- Dallwitz, W.B., Green, D.H., Thompson, J.E., 1966. Clinoenstatite in a volcanic rock from the Cape Vogel area, Papua. J. Petrol. 7, 375–403.
- Danyushevsky, L.V., Sobolev, A.V., Falloon, T.J., 1995. North Tongan high-Ca boninite petrogenesis: the role of Samoan plume and subduction zone — transform fault transition. J. Geodyn. 20, 219–241.
- Danyushevsky, L.V., Leslie, R.A.J., Crawford, A.J., Durance, P., 2004. Melt inclusions in primitive olivine phenocrysts: the role of localized reaction processes in the origin of anomalous compositions. J. Petrol. 45, 2531–2553.
- Della-Pasqua, F., Varne, R., 1997. Primitive ankaramitic magmas in volcanic arcs: a melt-inclusion approach. Can. Mineral. 35, 291–312.
- Dick, H.J.B., 1989. Abyssal peridotites, very slow spreading ridges and ocean ridge interaction. In: Saunders, A.D., Norry, M.J. (Eds.), Magmatism in the Ocean Basins. Geol. Soc. Spec. Publ., London, vol. 42, pp. 71–105.
- Elburg, M.A., Foden, J., 1999. Geochemical response to varying tectonic settings: an example from southern Sulawesi (Indonesia). Geochim. Cosmochim. Acta 63, 1155–1172.
- Elburg, M., Kamenetsky, V., Sobolev, A., 2004. Depleted and enriched components in high-K arc magmas: evidence from magmatic inclusions in olivine phenocrysts. In: McPhie, J., McGoldrick, P. (Eds.), Dynamic Earth: Past, Present and Future. Geol. Soc. Australia, Hobart, Abstracts, vol. 73, p. 265.
- Fedortchouk, Y., Canil, D., 2004. Intensive variables in kimberlite magmas, Lac de Gras, Canada and implications for diamond survival. J. Petrol. 45, 1725–1745.
- Green, D.H., Schmidt, M.W., Hibberson, W.O., 2004. Island-arc ankaramites: primitive melts from fluxed refractory lherzolitic mantle. J. Petrol. 45, 391–403.
- Hirano, N., Yamamoto, J., Kagi, H., Ishii, T., 2004. Young, olivine xenocryst-bearing alkali-basalt from the oceanward slope of the Japan Trench. Contrib. Mineral. Petrol. 148, 47–54.
- Iishi, K., Kitayama, K., 1995. Stability of high clinoenstatite. Neues Jahrb. Mineral., Monatsh. 1995 (H.2), 65–74.
- <span id="page-11-0"></span>Jurewicz, A.J.G., Watson, E.B., 1988. Cations in olivine, Part 1: calcium partitioning and calcium–magnesium distribution between olivines and coexisting melts, with petrologic applications. Contrib. Mineral. Petrol. 99, 176–185.
- Kamenetsky, V., Clocchiatti, R., 1996. Primitive magmatism of Mt Etna: insights from mineralogy and melt inclusions. Earth Planet. Sci. Lett. 142, 553–572.
- Kamenetsky, V., Crawford, A.J., 1998. Melt-peridotite reaction recorded in the chemistry of spinel and melt inclusions in basalt from 43°N, Mid-Atlantic Ridge. Earth Planet. Sci. Lett. 164, 345–352.
- Kamenetsky, V.S., Métrich, N., Cioni, R., 1995a. Potassic primary melts of Vulsini (Roman Province): evidence from mineralogy and melt inclusions. Contrib. Mineral. Petrol. 120, 186–196.
- Kamenetsky, V.S., Sobolev, A.V., Joron, J.-L., Semet, M.P., 1995b. Petrology and geochemistry of Cretaceous ultramafic volcanics from eastern Kamchatka. J. Petrol. 36, 637–662.
- Kamenetsky, V.S., Crawford, A.J., Eggins, S.M., Mühe, R., 1997. Phenocryst and melt inclusion chemistry of near-axis seamounts, Valu Fa Ridge, Lau Basin: insight into mantle wedge melting and the addition of subduction components. Earth Planet. Sci. Lett. 151, 205–223.
- Kamenetsky, V.S., Eggins, S.M., Crawford, A.J., Green, D.H., Gasparon, M., Falloon, T.J., 1998. Calcic melt inclusions in primitive olivine at 43°N MAR: evidence for melt-rock reaction/ melting involving clinopyroxene-rich lithologies during MORB generation. Earth Planet. Sci. Lett. 160, 115–132.
- Kamenetsky, V.S., Crawford, A.J., Meffre, S., 2001. Factors controlling chemistry of magmatic spinel: an empirical study of associated olivine, Cr-spinel and melt inclusions from primitive rocks. J. Petrol. 42, 655–671.
- Kamenetsky, V.S., Sobolev, A.V., Eggins, S.M., Crawford, A.J., Arculus, R.J., 2002. Olivine-enriched melt inclusions in chromites from low-Ca boninites, Cape Vogel, Papua New Guinea: evidence for ultramafic magma, refractory mantle source and enriched components. Chem. Geol. 183, 287–303.
- Köhler, T.P., Brey, G.P., 1990. Calcium exchange between olivine and clinopyroxene calibrated as a geothermobarometer for natural peridotites from 2 to 60 kb with applications. Geochim. Cosmochim. Acta 54, 2375–2388.
- Komatsu, M., 1980. Clinoenstatite in volcanic rocks from the Bonin Islands. Contrib. Mineral. Petrol. 74, 329–338.
- Libourel, G., 1999. Systematics of calcium partitioning between olivine and silicate melt: implications for melt structure and calcium content of magmatic olivines. Contrib. Mineral. Petrol. 136, 63–80.
- Lin, C.-C., 2004. Pressure-induced polymorphism in enstatite  $(MgSiO<sub>3</sub>)$  at room temperature: clinoenstatite and orthoenstatite. J. Phys. Chem. Solids 65, 913–921.
- Matsumoto, I., Arai, S., 2001. Morphological and chemical variations of chromian spinel in dunite–harzburgite complexes from the Sangun zone (SW Japan): implications for mantle/melt reaction and chromitite formation processes. Mineral. Petrol. 73, 305–323.
- Médard, E., Schmidt, M.W., Schiano, P., 2004. Liquidus surfaces of ultracalcic primitive melts: formation conditions and sources. Contrib. Mineral. Petrol. 148, 201–215.
- Morishita, T., Arai, S., Green, D.H., 2003. Evolution of low-Al orthopyroxene in the Horoman Peridotite, Japan: an unusual indicator of metasomatizing fluids. J. Petrol. 44, 1237–1246.
- Niu, Y., Hekinian, R., 1997. Spreading-rate dependence of the extent of mantle melting beneath ocean ridges. Nature 385, 326–329.
- Parkinson, I.J., Pearce, J.A., 1998. Peridotites from the Izu–Bonin– Mariana forearc (ODP Leg 125): evidence for mantle melting and melt-mantle interaction from a supra-subduction zone setting. J. Petrol. 39, 1577–1618.
- Ramsay, W.R.H., Crawford, A.J., Foden, J.D., 1984. Field setting, mineralogy, chemistry, and genesis of arc picrites, New Georgia, Solomon Islands. Contrib. Mineral. Petrol. 88, 386–402.
- Reubi, O., Nicholls, I.A., Kamenetsky, V.S., 2002. Early mixing and mingling in the evolution of basaltic magmas: evidence from phenocryst assemblages, Slamet Volcano, Java, Indonesia. J. Volcanol. Geotherm. Res. 119, 255–274.
- Rohrbach, A., Schuth, S., Ballhaus, C., Münker, C., Matveev, S., Qopoto, C., 2005. Petrological constraints on the origin of arc picrites, New Georgia Group, Solomon Islands. Contrib. Mineral. Petrol. 149, 685–698.
- Sameshima, T., Paris, J.-P., Black, P.M., Heming, R.F., 1983. Clinoenstatite-bearing lava from Népoui, New Caledonia. Am. Mineral. 68, 1076–1082.
- Schiano, P., J.M., E., Hutcheon, I.D., Stolper, E.M., 2000. Primitive CaOrich, silica undersaturated melts in island arcs: evidence for the involvement of clinopyroxene-rich lithologies in the petrogenesis of arc magmas. Geochem. Geophys. Geosyst. 1 (1999GC000032).
- Schmidt, M.W., Green, D.H., Hibberson, W.O., 2004. Ultra-calcic magmas generated from Ca-depleted mantle: an experimental study on the origin of ankaramites. J. Petrol. 45, 531–554.
- Schuth, S., Rohrbach, A., Münker, C., Ballhaus, C., Garbe-Schönberg, D., Qopoto, C., 2004. Geochemical constraints on the petrogenesis of arc picrites and basalt, New Georgia Group, Solomon Islands. Contrib. Mineral. Petrol. 148, 288–304.
- Shiraki, K., Kuroda, N., Urano, H., Maruyama, S., 1980. Clinoenstatite in boninites from the Bonin Islands, Japan. Nature 285, 31–32.
- Sigurdsson, I.A., Kamenetsky, V.S., Crawford, A.J., Eggins, S.M., Zlobin, S.K., 1993. Primitive island arc and oceanic lavas from the Hunter ridge-Hunter fracture zone. Evidence from glass, olivine and spinel compositions. Mineral. Petrol. 47, 149–169.
- Simkin, T., Smith, J.V., 1970. Minor-element distribution in olivine. J. Geol. 78, 304–325.
- Skinner, E.M.W., 1989. Contrasting Group I and Group II kimberlite petrology: towards a genetic model for kimberlites. In: Ross, J., et al. (Ed.), Kimberlites and related rocks: their composition, occurrence, origin and emplacement, vol. 1. Blackwell Scientific Publications, Sydney, pp. 528–544.
- Smith, D.R., Leeman, W.P., 2005. Chromian spinel-olivine phase chemistry and the origin of primitive basalts of the southern Washington Cascades. J. Volcanol. Geotherm. Res. 140, 49–66.
- Stormer, J.C., 1973. Calcium zoning in olivine and its relationship to silica activity and pressure. Geochim. Cosmochim. Acta 37, 1815–1821.
- von Seckendorff, V., O'Neill, H.St.C., 1993. An experimental study of Fe–Mg partitioning between olivine and orthopyroxene at 1173, 1273 and 1423 K and 1.6 GPa. Contrib. Mineral. Petrol. 113, 196–207.
- Walker, D.A., Cameron, W.E., 1983. Boninite primary magmas: evidence from Cape Vogel Peninsula, PNG. Contrib. Mineral. Petrol. 83, 150–158.
- Watson, E.B., 1979. Calcium content of forsterite coexisting with silicate liquid in the system  $Na<sub>2</sub>O-CaO-MgO-Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>$ . Am. Mineral. 64, 824–829.