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Contamination of mafic magma by partial melting of dolomitic xenoliths

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ABSTRACT

Mg-skarns enclosed in dunite cumulates of the Neo-Proterozoic Ioko-Dovyren intrusion (northern Baikal region, Russia) can be traced to silica-poor dolomitic host rock layers. The dominant minerals of the skarns are brucite (pseudomorph after periclase), forsterite and Cr-poor spinel. Rapid heating of quartz-poor dolomitic xenoliths led to the formation of minor olivine, followed by the breakdown of dolomite to calcite and periclase. Xenoliths were partially melted upon further heating resulting in a calcite melt. This low-density melt was quantitatively squeezed out, mixed with the surrounding mafic magma and

left behind periclase and olivine. This caused the crystallization of new olivine with elevated CaO contents in zones above skarn-bearing horizons. Mixing of calcite melt with the surrounding mafic magma also resulted in the crystallization of Ca-rich clinopyroxene instead of plagioclase. The mineralogy of contaminated dunite cumulates is consistent with assimilation of approximately 4wt% CaO by the Ioko-Dovyren mafic magma.

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Introduction

Ascending basaltic melts can experience significant crustal contamination in continental environments. Mineralogical and geochemical indications of basalt contamination by silica-rich crustal material were detected in many zoned plutons and layered intrusions (e.g. Reiners *et al.*, 1996; Tegner *et al.*, 1999). Contamination of mafic magma by carbonate material has been described less frequently (e.g. Tilley, 1952; Joesten, 1977; Baker and Black, 1980; Joesten *et al.*, 1994; Owens, 2000). These studies only describe the interaction of mafic magmas and siliceous limestones along their contacts, and suggest local assimilation of large amounts of calcite (> 13wt%) by the mafic magma. Contamination of the mafic magma resulted in the resorption of igneous minerals (olivine, clinopyroxene), and the crystallization of Ca–Al-rich clinopyroxene, wollastonite and nepheline. To our knowledge, melting of calcite has never been directly inferred.

In this paper, we report the results of petrological investigations on Mg-skarn-bearing dunitic cumulates that are part of the Neo-Proterozoic

Ioko-Dovyren intrusion of the northern Baikal region in Eastern Siberia (Fig. 1). We present a model for the evolution of Mg-rich skarns from silica-poor dolomite based on the extraction of a calcite melt from the xenoliths and mineralogical evidence for mixing of the mafic magma with this calcite melt.

Geological background

The Ioko-Dovyren layered intrusion is located at the south-eastern margin of the East Siberian Platform within the Olokit trough (see, e.g. Konnikov *et al.*, 1994, for details). The intrusion is roughly 26 km long and about 3.5 km thick. The subvertical dip of the magmatic layering is concordant with the enclosing low-grade Neo-Proterozoic sandstones, schists and carbonate host rocks. The tilting is the result of deformation during post-intrusive regional metamorphism at ~ 550 Ma. The intrusion is divided into four major zones based on the dominant cumulate type (Fig. 1). From bottom to top these are (1) the plagiolherzolite zone, (2) the dunite zone, (3) the troctolite zone and (4) the gabbro/gabbro-norite zone (Konnikov *et al.*, 1994).

Xenoliths of Mg-rich skarns range from a few centimetres up to 20 m in size. They occur in the dunite zone and can be traced through the plagiolherzolite zone. Pressure values between 0.5 and 1.5 kbar have been

estimated based on mineral assemblages of skarns (see Kislov, 1998). The present communication is limited to the Mg-skarn-bearing dunite zone.

Results

Mineral composition of the dunitic cumulates

The cumulate rocks of the dunite zone contain spinel and olivine as cumulus minerals, and plagioclase and/or clinopyroxene as intercumulus phases. The intercumulus minerals represent typically less than 15wt%. A crystallization sequence of spinel, followed by olivine, plagioclase and finally clinopyroxene is indicated. A few samples contain Fe–Ni–Cu sulphides. Alteration of the igneous assemblage to chlorite and serpentine is restricted to late brittle faults.

Compositions of minerals are presented in Table 1. Both cumulus and intercumulus minerals are chemically homogeneous. The forsterite content of cumulus olivines varies between 85.7 and 89.5 mol%. Their NiO content rhythmically varies between 0.09 and 0.25wt% as a function of location within the profile (Fig. 2). Samples collected close to the skarns have olivines with high Fo content between 89.5 and 91.2 mol% and low NiO content between 0.03 and 0.11wt%. The weight fraction of CaO of olivine is generally lower than 0.34wt%,

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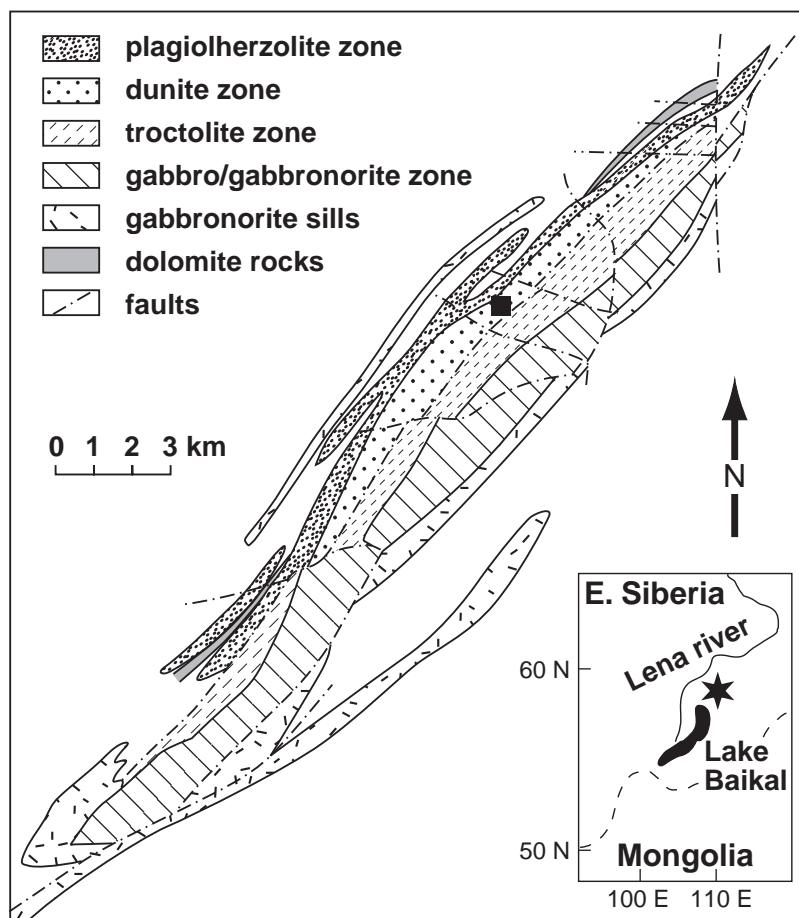


Fig. 1 Schematic geological map of the Ioko-Dovyren intrusion (modified after Konnikov *et al.*, 1994); star – study area; square – location of the cross-section investigated.

but increases in and above the two skarn-bearing horizons to > 0.34wt% (Fig. 2).

Spinel inclusions in cumulus olivine show a large variation of the chromium number [$cr\# = 100 \times Cr/(Cr + Al)$], ranging from 24 to 71. The magnesium number of spinel [$mg\# = 100 \times Mg/(Mg + Fe^{2+})$] is between 33 and 60.

Intercumulus plagioclase (An 42–90) is restricted to samples below and within the first few metres of the lowermost Mg-skarn horizon. Clinopyroxene is the dominating intercumulus mineral. Clinopyroxenes of the first skarn-rich horizon and in the hangingwall of the second skarn-rich horizon are enriched in Ca-Tschermak's component and contain 2–4 mol% of this molecule. This compares to lower contents of

< 2 mol% in uncontaminated samples.

Mineral composition of the Mg-skarns

The Mg-skarns are texturally and mineralogically zoned. The cores of the xenoliths are composed of fine-grained aggregates of brucite replacing coarse (> 3 mm) periclase. The original periclase triple junctions and to a lesser degree the remaining grain boundaries are lined with Fo-rich olivine and Mg-rich, Cr-free spinel (see Fig. 3a and Table 1).

The rims of the skarn bodies are composed of very fine-grained (< 0.2 mm) olivine and spinel (Fig. 3b and Table 1). The olivine composition is similar to those of the skarn core. Spinel is enriched in FeO,

and depleted in MgO and Al₂O₃ at the rim of the skarns. The magnesium number of spinel ranges from 94 to 95.

Discussion

Metamorphic evolution of the xenoliths

The dunite layers containing Mg-skarns can be traced to dolomite host rocks of the contact aureole. Hence these dolomite rocks were the protolith of the Mg-skarn xenoliths. The dolomite host rocks consist of dolomite (more than 87wt%), some calcite (less than 5wt%), and detrital quartz and sheet silicates (Gurulev, 1983).

A $T-X$ (CO₂) diagram was calculated for quartz-poor rocks typical of the host rock dolomites in the system MgO–CaO–SiO₂–H₂O–CO₂ assuming calcite saturation at a pressure of 1 kbar (Fig. 4). Quartz will be consumed resulting in the formation of calcite and tremolite. Tremolite in turn will react with remaining dolomite to forsterite + calcite at a temperature below 570 °C. Hence the assemblage dolomite + calcite + forsterite is present at 600 °C at X (CO₂) values larger than 0.15. Dolomite will decompose completely to calcite and periclase, releasing significant amounts of CO₂ at temperatures between 620 °C and 800 °C. At even higher temperatures, Ca-bearing minerals such as monticellite and merwinite could form from calcite and olivine. The calcite melting curve after Wyllie (1965) was superimposed onto the diagram using Schreinemaker's analysis. The intersection of the calcite melting curve with reaction (3) is uncertain. Since the Mg-skarns are completely free of CaO, all calcium must have been extracted from the original dolomite xenoliths. We suggest partial melting of the dolomite xenoliths and the extraction of the calcite-rich partial melt as a reliable process. Although much CO₂ is produced during dolomite breakdown, the release of H₂O and other volatiles, like sulphur, from the crystallizing mafic magma may flush the xenolith. This would result in a water-rich fluid composition. At 1200 °C, which is the temperature at

Table 1. Composition of minerals (wt%); n.d. –not determined

	Dunite, uncontaminated				Dunite, contaminated			Skarn, core		Skarn, rim	
	Spl	Ol	Cpx	Pl	Spl	Ol	Cpx	Spl	Ol	Spl	Ol
SiO ₂	0.00	40.24	52.04	47.21	0.00	40.06	50.21	0.05	42.44	0.00	41.93
TiO ₂	1.75	n.d.	0.97	n.d.	0.32	n.d.	0.52	0.95	n.d.	2.09	n.d.
Al ₂ O ₃	12.15	0.02	2.50	32.85	36.30	0.02	5.80	57.72	0.03	40.17	0.02
Cr ₂ O ₃	45.26	0.09	0.95	n.d.	23.99	0.08	1.36	0.04	0.02	0.43	0.06
FeO	33.48	12.48	3.62	0.24	25.93	12.57	3.56	13.51	1.29	32.17	1.41
NiO	n.d.	0.24	n.d.	n.d.	n.d.	0.16	n.d.	n.d.	0.01	n.d.	0.03
MnO	0.37	0.20	0.13	n.d.	0.25	0.22	0.04	0.08	0.08	0.17	0.11
MgO	6.80	46.67	17.16	n.d.	13.76	46.22	14.55	26.42	55.37	24.60	55.59
ZnO	0.28	n.d.	n.d.	n.d.	0.17	n.d.	n.d.	0.00	n.d.	0.00	n.d.
CaO	n.d.	0.09	22.10	16.99	n.d.	0.82	23.28	n.d.	1.00	n.d.	0.26
Na ₂ O	n.d.	n.d.	0.48	2.03	n.d.	n.d.	0.62	n.d.	n.d.	n.d.	n.d.
K ₂ O	n.d.	n.d.	0.00	0.12	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.
total	100.10	100.03	99.95	99.43	100.71	100.14	99.95	98.77	100.23	99.63	99.40

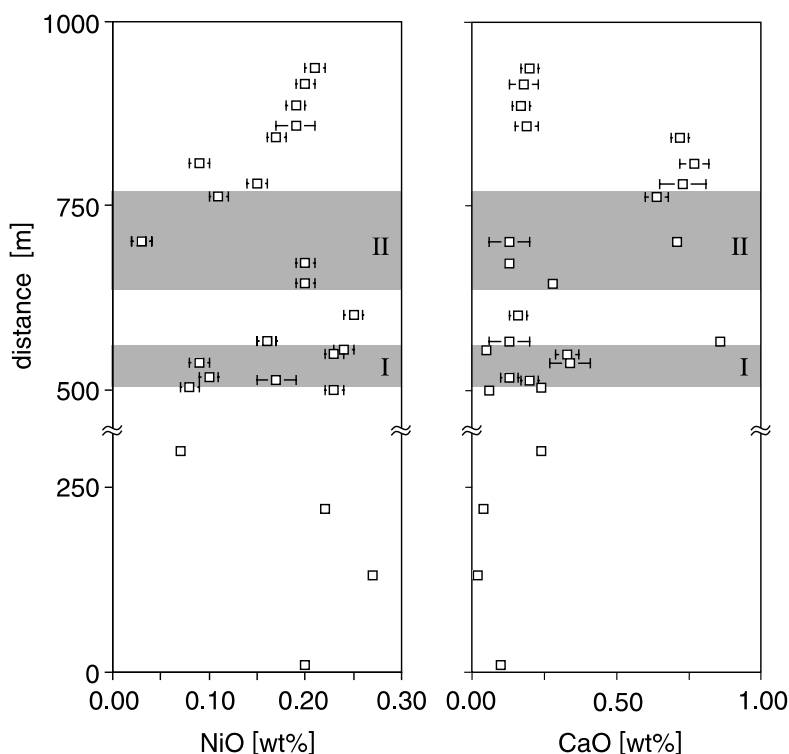


Fig. 2 Average NiO and CaO content of olivine (in wt%) from dunite cumulates is plotted against sample positions along a cross-section through the dunite zone (in metres). Many xenoliths occur in the two grey horizons (labelled I and II). The profile is interrupted between 300 and 500 m. The repeated increase of the NiO content of olivine is characteristic for multiple replenishment of the magma chamber (cf. Irvine, 1980). Low NiO contents indicate crystallization from evolved magma batches. High CaO contents of olivine are typically correlated with low NiO contents.

which intercumulus plagioclase forms in the uncontaminated dunite, calcite will melt even with little or no H₂O present [$X(\text{CO}_2) > 0.6$]. Modelling results indicate a magma temperature

between 1260 and 1180 °C (Wenzel *et al.*, 2001), so it is indeed likely that all calcite in the xenolith melted (Fig. 4). The low-density (about 2000 kg m⁻³) and low-viscosity

(about 10⁻³ Pa.s) calcite melt (Genge *et al.*, 1995) will rapidly be squeezed out of the collapsing xenolith by the surrounding heavy crystal mush. Overall, dolomite breakdown and extraction of calcite melt would result in a volume reduction of about 70vol%.

Olivine and spinel fill the interstices between the brucite pseudomorphs of periclase in the xenoliths. Both minerals did not crystallize from the mafic magma. Olivine is more enriched in MgO and stronger depleted in NiO than any olivine of the dunites (see Table 1). Skarn spinel is almost Cr-free, in contrast to spinel of the dunites which is Cr-rich. Mass balance calculations show that the contents of SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO and MgO of the periclase–forsterite–spinel skarns agree well with the concentration of these oxides obtained by assuming complete loss of calcite and CO₂ from the original silica-poor dolomite (Gurulev, 1983). Olivine and spinel formed most likely during prograde metamorphism of the Si–Al–Fe-bearing dolomite rocks. In contrast, the fine-grained forsterite–spinel skarn rims probably crystallized from the mafic magma at elevated oxygen fugacity equal to the HM buffer (Wenzel *et al.*, unpubl. obs.).

Mineralogical evidence for mixing of mafic magma and calcite melt

The composition of olivine and clinopyroxene of skarn-bearing horizons indeed reflect mixing of calcite melt (extracted from the xenoliths) and

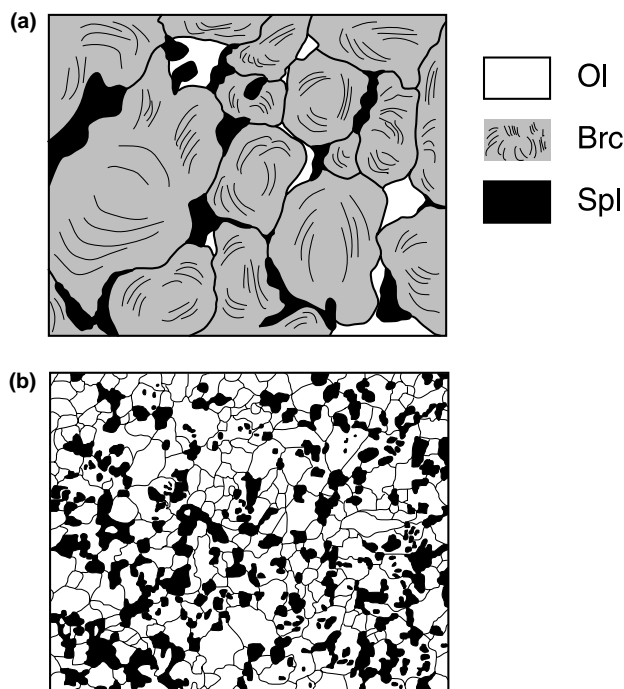


Fig. 3 Textural characteristics of periclase skarns in the core of Mg-skarns (a) and of olivine-spinel skarns forming the rim (b). The length of each figure is 2 mm.

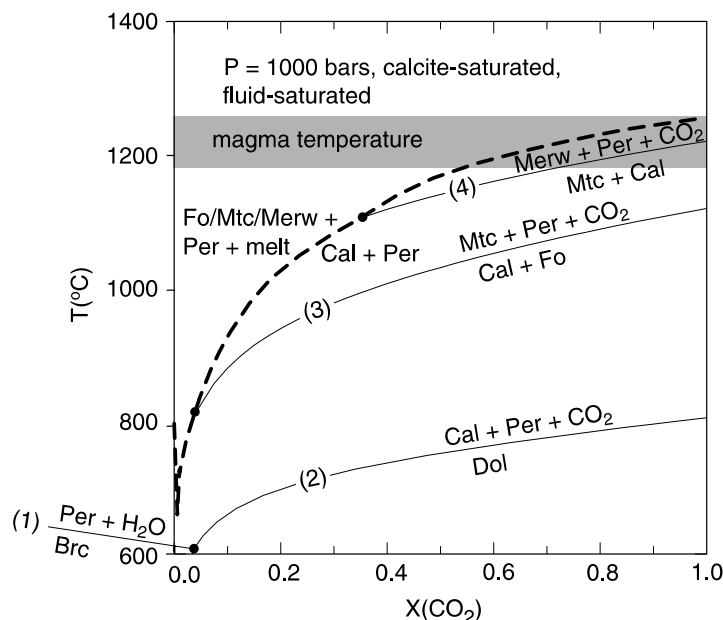


Fig. 4 A T-X (CO₂) diagram was calculated for the system MgO–CaO–SiO₂–H₂O–CO₂, P = 1 kbar and fluid-saturation with the PerPleX software package (Connolly, 1990) using the Holland and Powell (1998) mineral data. Reactions were calculated for calcite saturation of a dolomite poor in SiO₂, similar to the dolomitic country rocks of the Ioko-Dovyren intrusion. The melting curve of calcite is adapted from experimental results of Wyllie. Based on modelling results using the program MELTS (Ghiorso *et al.*, 1994) we conclude that the dunitic cumulates of the Ioko-Dovyren intrusion crystallized from a mafic magma in the temperature interval of 1260 and 1180 °C (Wenzel *et al.*, unpubl. obs.). Brc – brucite; Cal – calcite; Dol – dolomite; Fo – forsterite; Merw – merwinite; Mtc – monticellite; Per – periclase.

mafic magma. There is a strong increase in the CaO content of olivine (up to 1wt%) in and above the skarn horizons (Fig. 2). The CaO concentration of olivine depends on its Fo content and on melt composition (Libourel, 1999). It is particularly sensitive to the amount of calcium, aluminium, alkali and ferrous iron of the coexisting melt, but not to the temperature of crystallization. We find a restricted range in the Fo content of olivine of about 86–91 and no clear indication for an elevated concentration of aluminium, the alkalis and ferrous iron of the magma. Hence, we infer that the increase in CaO of olivine is related to an increase of the CaO activity in the melt. Preliminary modelling results using MELTS (Ghiorso *et al.*, 1994) show that addition of 4wt% of CaO to the parental mafic magma would increase CaO in olivine to 0.59wt% at 1230 °C and 1 kbar. Assuming a lower pressure of 0.3 kbar, addition of 4wt% CaO to the magma causes an even higher content of 0.64wt% CaO in olivine, with an Fo content of 82–83. Addition of more than 4wt% CaO changed the crystallization path, inducing abundant precipitation of clinopyroxene. The clinopyroxene is characterized by a high Al₂O₃ content (> 5.65wt%) similar to the concentrations observed in the intercumulus clinopyroxene of the zones above the skarn-rich horizons.

Overall, the observed changes in mineral composition of the skarn-bearing dunites are consistent with contamination of the mafic magma with CaO. The source of the CaO is the skarn xenoliths described above. Additional support of melt contamination around xenoliths comes from preliminary oxygen isotope analysis (Krivoplyasov *et al.*, 1982). The δ¹⁸O values of cumulus olivine (+ 12 to + 19‰ SMOW) are elevated towards the sedimentary carbonate protolith (+ 22 to + 24‰). Preliminary melt inclusion studies indicate inclusions with up to 95wt% CaO, consistent with the presence of a CaO-rich melt.

Summary and conclusions

Based on the mineralogical and geochemical results and the comparison with published experimental data dis-

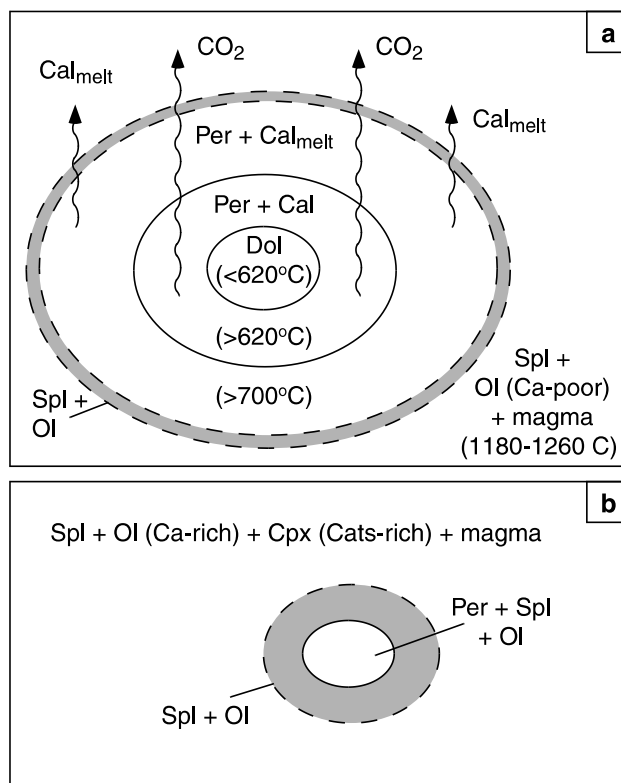


Fig. 5 The model summarizes the metamorphic evolution of Si-poor dolomitic precursors to Mg-rich skarns: Rapid heating of the xenoliths after incorporation into the mafic melt causes decomposition of dolomite to calcite + periclase, and melting of calcite. The calcite melt is squeezed out of the xenolith. Mixing of mafic magma and calcite melt results in cumulus olivine with elevated CaO content and in massive crystallization of intercumulus clinopyroxene rich in Cats molecule.

cussed above, we propose the following model for the formation of the Mg-skarns (Fig. 5):

1 Rapid heating of the xenoliths after incorporation into the mafic melt causes decomposition of dolomite to calcite + periclase, and, eventually, melting of calcite.

2 The calcite melt is squeezed out of the xenolith. This is readily achieved since the melt has a low viscosity and a remarkably small density. Xenoliths are reduced by 70% in volume. Fine-grained rims of forsterite and spinel crystallize from the mafic magma at elevated fO_2 .

3 Mixing of mafic magma and calcite melt results in cumulus olivine with elevated CaO content. Mixing of mafic magma and calcite melt also results in massive crystallization of intercumulus clinopyroxene rich in $CaAl_2SiO_6$ instead of plagioclase.

Our investigations demonstrate the possibility to generate carbonatite-like

melts (e.g. Green and Wallace, 1988; Wallace and Green, 1988) in the continental crust. Such a carbonate melt can readily mix with and impose its chemical signatures on large volumes of mafic magma due to its low viscosity. Carbonate contamination will dramatically affect the redox state of the crystallizing magma (Wenzel *et al.*, unpubl. obs.). The modification of the chemical signatures of mafic magmas by carbonate contamination may be more important than previously assumed, since the content of carbonates among the present continental sedimentary rock volume is estimated to be as high as 15% (Taylor and McLennan, 1985). Carbonate contamination would be expected in continental areas, such as in intracontinental rift zones and at continental margins. Detailed geological and mineralogical investigations are necessary to exclude such process if one attempts to reconstruct potential mantle

source characteristics of the mafic magma.

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