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Trace-element geochemistry of mantle olivine and application to mantle petrogenesis and geothermobarometry

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ABSTRACT

Trace-element compositions of olivine from 75 mantle rocks of diverse origin, including xenoliths from kimberlites, basaltic lavas and orogenic peridotites, were determined by laser ablation ICP-MS to study systematic variations between mantle lithologies, partitioning mechanisms in olivine and their potential for geothermobarometry and unravelling mantle processes. Samples were selected to cover a wide range of forsterite contents (89.1–93.4), equilibration temperatures and pressures (750–1450 °C; 15–80 kbar).

Trace elements in olivine can be divided into three groups. Group I elements (Ni, Mn, Co, Cu, Zn and Li) show small concentration ranges and olivine is the major host mineral. These are mostly divalent elements and have ionic radii close to that of Mg. Group II elements (Cr, Al, V, Sc, Ca and Na) show large concentration ranges, which are mainly controlled by the equilibration temperature of the host rock. The elements are strongly concentrated in co-existing mantle minerals (garnet, clinopyroxene and spinel) and show a narrow range of bulk rock concentrations. They fit less comfortably in the olivine lattice than Group I elements because of their charge or size. Differences between garnet and spinel-facies rocks are apparent for Al, Ca and Sc. Group III elements (Ti, Zr, Nb and Y) show large ranges of concentration in olivine as well as in co-existing minerals, and are strongly dependent on bulk rock contents. Concentration differences between olivine from garnet and spinel-facies rocks are apparent for all these elements. They are strongly incompatible in olivine and other rock-forming mantle minerals because of their charge or size.

Various mantle lithologies can be discriminated using olivine composition. Spinel, garnet and garnet–spinel peridotites can be distinguished in olivine Sc–Zr and MnO–Al_2O_3 diagrams, whereas volcanic olivine is distinguished by high Ca and Al contents (picritic olivine) or high Nb contents (kimberlitic olivine). Since concentrations of Group III elements in olivine are diagnostic of whole-rock contents they can be used to trace the petrogenetic history of the rock. For instance, Ti contents and Cr# (Cr/(Cr + Al)) of olivine correlate with the amount of melt extracted from a mantle residue, although refertilisation may subsequently have increased Ti contents in high-*T* peridotites from the base of the lithosphere.

The olivine dataset can be used to examine substitution reactions. Uptake of Al and Cr appears to be largely charge-balanced by Na in garnet-facies olivine, and olivine Cr# strongly correlates with that of co-existing minerals, in particular clinopyroxene and spinel. In spinel-facies olivine a large excess of trivalent cations is present in olivine, which can be fully attributed to excess Al. This suggests a Tschermak-style substitution, in which replacement of Mg by Al in the octahedral site is charge-balanced by replacement of Si by Al in the tetrahedral site.

Partition coefficients of Group II elements are highly temperature sensitive with most of the element variability being shown by olivine. This allows the definition of simple geothermometers based solely on the concentrations of these elements in olivine. The most widely applicable of these is Al-in-olivine for garnet peridotites, following the expression

$$T_{\mathrm{Al-ol}}(^{\circ}\mathrm{C}) = \frac{9423 + 51.4P + 1860\mathrm{Cr\#}^{\mathrm{ol}}}{(13.409 - \ln[\mathrm{Al}]^{\mathrm{ol}})} - 273$$

with *P* in kbar, $\mathrm{Al}^{\mathrm{ol}}$ the Al concentration of olivine in ppm, and $\mathrm{Cr\#}^{\mathrm{ol}}$ is Cr/(Cr + Al) in olivine. This thermometer predicts the temperature with a residual of 15 °C based on calibration with two-pyroxene and Al-in-opx geothermobarometers (Brey and Köhler, 1990). Although calibrated using lherzolites only, the thermometer

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performs well for clinopyroxene-free harzburgites and also spinel peridotites. An alternative thermometer is presented for the case where the presence of Cr^{2+} is expected, e.g., for olivine inclusions in diamonds.

The geochemical and thermobarometric information recorded by olivine can be a useful tool in studies of the petrogenesis of lithospheric mantle, olivine xenocrysts in mantle-derived magmas, the formation of diamonds and diamond exploration using detrital olivine.

1. Introduction

Olivine is the most abundant mineral in the upper mantle, as well as a common inclusion in diamond (Sobolev et al., 2008). Despite its abundance, olivine has received relatively little attention in studies of trace-element partitioning and mantle and igneous geochemistry because it contains low concentrations of incompatible trace-elements, leading to analytical difficulties. With the advance of analytical techniques many elements can now routinely be determined in olivine, but a framework within which to interpret the results is lacking. This paper presents a comprehensive study of trace element concentrations in mantle olivine from a wide variety of origins and examines the factors that control these concentrations. It explores the viability of olivine geochemistry as a petrogenetic tool and its applicability in geothermobarometry, and establishes olivine trace-element geochemistry as a useful tool for studying igneous and metamorphic processes in the crust and upper mantle. An important potential application lies in fingerprinting olivine xenocrysts, olivine inclusions in diamonds and detrital olivine.

1.1. Olivine structure and crystal chemistry

Olivine is an orthorhombic mineral with continuous solid solution between the two end-members forsterite (Mg_2SiO_4; Fo_{100}) and fayalite (Fe_2SiO4; Fa_{100} or Fo_0). In mantle rocks it shows little compositional variability compared to the other rock-forming mantle minerals (garnet, spinel, orthopyroxene and clinopyroxene), with nearly all mantle olivine falling in the range Fo_{89} to Fo_{94} (Deer et al., 1997). Small amounts of MnO and NiO are present at the 0.1–0.4 wt.% level, followed by CaO, Al_2O_3 and Cr_2O_3, other elements generally even lower.

The olivine structure consists of individual SiO_4 tetrahedra (T site) linked by six-fold coordinated divalent cations (M sites) (Birle et al., 1968; Burns, 1970). The Si–O tetrahedra point alternatively each way along the *a* axis. The M-site cations occupy two sets of lattice positions, M1 and M2, both of which are distorted from octahedral symmetry, and M1 being slightly smaller and more distorted than M2 (Birle et al., 1968). Although Fe and Mg are ordered to a high degree, significant disordering may occur for other cations (Lumpkin et al., 1983). Replacement of the main octahedral cations Mg and Fe by other cations is a function of their ionic radius and valence (Fig. 1), replacement becoming increasingly difficult with increasing mismatch in size or charge. In addition, several transition metals are influenced by crystal-field effects (Burns, 1970).

1.2. Previous work

Early trace-element data for mantle olivine determined by ion probe was presented in several comprehensive studies by Hervig et al. (1980a,b, 1986) and Hervig and Smith (1982), who investigated the crystal chemistry of olivine, attempted the use of olivine compositions to make inferences about the origin of cratonic lithosphere, and investigated the applicability of several trace elements as thermometers for garnet and spinel peridotites. They noticed the high Cr contents of diamond inclusions. In their study of the oxidation state of Cr in the mantle, Li et al. (1995) concluded that significant Cr^{2+} may be present in high-*T* (>1600 K) olivine from komatiites and diamond inclusions, but is less important in olivine from lower *T* parageneses. Kurosawa et al. (1997), who measured H_2O and several trace elements (Li, Na, Cr and Al) in mantle olivine, reported a trivalent cation deficiency to charge-balance the monovalent cations (including H^+) in garnet peridotites, which was attributed to the possible presence of Fe^{3+} (not measured). In contrast, spinel peridotites had an excess of trivalent cations, and they suggested a possible Tschermak-style (MgSi = 2Al) substitution in these rocks. Richmond and Brodholdt (2000) used atomistic computer simulations to determine the substitution behaviour of Fe^{3+} and concluded that, in the system Si–O–Mg–Fe^{3+},

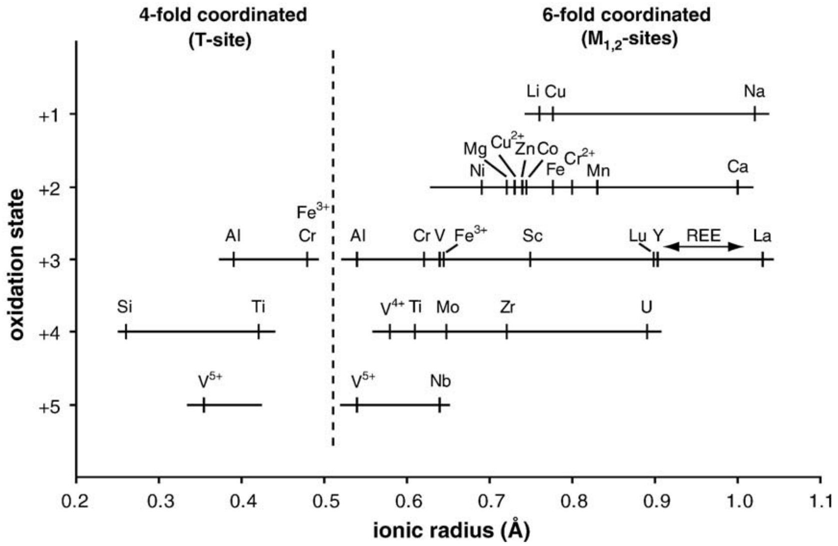

Fig. 1. Ionic radii and oxidation states of cations that partition into the olivine structure. Ionic radii after Shannon (1976) with all transition metals in high-spin state (Burns, 1970). Cation charges are only indicated for subordinate oxidation states under normal mantle conditions. The optimum size of a site depends on the charge of the cation, and is 0.72 Å for 2+ and 1+ ions in the olivine M1,2 site, 0.71 Å for 3+ ions, and slightly smaller for higher oxidation states (Wood and Blundy, 2003).