

# Distribution of trace elements in minerals from anhydrous spinel peridotites and websterites from the Ronda Peridotite: implications for the nature of LILE, REE and HFSE reservoirs in the subcontinental lithospheric mantle

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**Intermineral distribution coefficients ( $D^{x/cpx}$ ).** We report dissolution ICP-MS analyses of Rb, Ba, Th, U, Nb, Ta, REE, Sr, Zr, Hf and Sc in leached separates of clinopyroxene, orthopyroxene, olivine and spinel in anhydrous spinel peridotites (12 samples) and websterites (6 samples) from the Ronda peridotite (S. Spain). None of the selected samples display evidence of cryptic metasomatism. This data-set provides a good example of the distribution of a large group of trace elements in anhydrous minerals from the subcontinental lithospheric mantle, as exemplified by orogenic massifs.

The average partition coefficients (relative to clinopyroxene:  $D^{x/cpx}$ ) of the studied trace elements are shown in Fig. 1. For most elements, there are no statistical differences in the  $D^{opx/cpx}$  between spinel peridotites and websterites. For the REE, Zr and Hf, the small standard deviation is suggestive of the lack of an important compositional effect in the partitioning of the studied compositions ('fertiles' to 'depleted'). As previously suggested, clinopyroxene is the main host of REE and other incompatible elements in anhydrous spinel mantle rocks. The  $D^{opx/cpx}$  for Zr and Hf is a factor 10 higher than for MREE, indicating the potential of orthopyroxene to fractionate these High Field Strength Elements (HFSE= Zr, Hf, Nb, Ta) relative to REE<sup>1</sup>.

When plotted in increasing order of compatibility in a melt/peridotite system (Fig. 1), the  $D^{x/cpx}$  of the Highly Incompatible trace Elements (HIE = Rb, Ba, Th, U, Nb, Ta) systematically increases from the MREE (Fig. 1). This feature is more marked in the olivine/cpx and spinel/cpx partitioning (Fig.1). Although the distribution of MREE, HREE, Zr and Hf in clinopyroxenes, orthopyroxenes and, partly, in olivines might be accounted for by crystallographic control in these minerals. However, the distribution of the HIE is inconsistent with a crystallographic control, especially in the case of spinels and olivines. The fact

that the relative increase of the  $D^{x/cpx}$  of the HIE is correlated with their degree of incompatibility in a melt/peridotite system, and that olivines and spinels from different samples display similar normalized trace element patterns and abundances of HIE, indicates that an important part of their budget may be hosted in melt/fluid inclusions within these minerals.

In Ronda minerals, two-phase fluid/(melt?) inclusions (~1µm) typically occur as inclusions trails similar to secondary fluid/melt inclusions documented in peridotite xenoliths worldwide<sup>2</sup>.

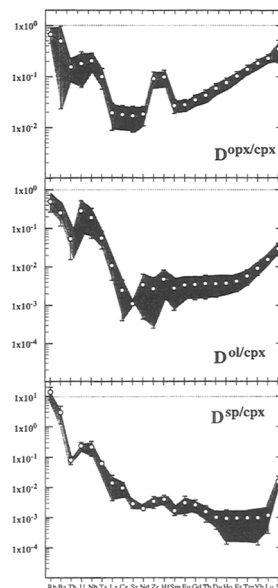


FIG. 1. Average and one standard deviation of inter-mineral partition coefficients (relative to clinopyroxene) in minerals from anhydrous spinel peridotites and websterites [cpx = clinopyroxene; opx = orthopyroxene; ol = olivine; sp = spinel].

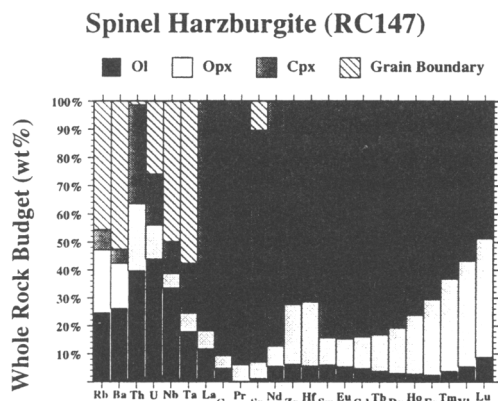


FIG. 2. Distribution of trace element in the mineral phases of a spinel harzburgite sample. The grain boundary component is the difference between the whole rock and the reconstructed whole rock composition using silicate mineral composition and modes.

These trails of fluid inclusions are cut and transposed during high-temperature recrystallization of olivine ( $> 900^{\circ}\text{C}$ ), indicating that are of mantle origin, and could therefore represent trapped metasomatic melts in the subcontinental lithosphere.

Assuming that the concentration of the highly incompatible elements in olivines and spinels is dominated by fluid inclusions, some inferences about the composition of these melt/fluids inclusions can be inferred from the ratio of incompatible elements in these minerals. These melt/fluids would be characterized by a strong fractionation of incompatible elements, similar to that expected in small melt fractions (SMF) migrating throughout the conductive lithospheric mantle<sup>3</sup>. Furthermore, these fluid/melts inclusions would have geochemical characteristics akin to the continental crust and arc lavas. Their low Th/U ratios ( $\sim 1$ ) might indicate a high activity of volatiles, probably as a result of progressive crystal fractionation of SMF during cooling and decompression in the conductive continental lithosphere. However, their unusually high Ta/La and Nb/La ratios ( $\sim 4$ ) might imply that they are mixtures of melts/fluids and a Nb-(Ta)-rich phase (rutile?), which might have been precipitated during cooling (and increasing silica activity) of the metasomatic SMF.

**Trace elements reservoirs in lithospheric spinel peridotites: results of mass balance calculations.**

To characterize the reservoirs of trace elements in spinel peridotites, we have conducted a mass balance calculation in a fresh ( $< 2\%$  serpentine) spinel harzburgite from Ronda (Fig. 2). The mass balance calculation indicates that the whole rock budget of

trace elements in anhydrous spinel peridotites is dominated by several different reservoirs. The REE, Zr and Hf budget is controlled by the crystallographic contribution of clinopyroxene and, to a lesser extent, orthopyroxene. Conversely, about 50% of the Rb, Ba, Nb and Ta budget is hosted by a 'grain boundary component'. Contrarily to recent findings<sup>5</sup>, this grain boundary component cannot be accounted for by amphibole, since neither this phase nor their breakdown products are present in our samples. Most likely, the grain boundary component consists of a Ti-oxide  $\mu\text{m}$ -layer of metasomatic origin coating spinel grain surfaces that has been previously identified in xenoliths samples<sup>4</sup>. The rest of Rb, Ba, Nb and Ta, and over 70% of the U and Th budget, is likely hosted in fluid inclusions in silicates, especially in olivine (Fig. 2).

**Differences between the normalized patterns of whole rock and clinopyroxene.**

Previous studies have demonstrated that the REE normalized pattern of clinopyroxene mimic that of the whole rock. This finding has been used to characterize the trace element ratios of mantle peridotites and draw conclusions about whole rock composition through analyses of clinopyroxenes. We find that clinopyroxene patterns, and to a lesser extent Zr/Sm and Hf/Sm ratios, are similar to the whole rock and have not been masked by later subsolidus re-equilibration. However, the Nb/La and Ta/La ratios in clinopyroxene are not comparable to those of the whole rock. Clinopyroxenes display a markedly negative Nb and Ta anomaly, which is not present in the whole rock patterns. The negative Nb-Ta anomaly in the clinopyroxene it is not counterbalanced by positive anomalies of Nb and Ta, relative to U and La, in the rest of the minerals. This observation further suggests the equilibration of clinopyroxene with a  $\mu\text{m}$ -Nb-Ta bearing phase. As a consequence, the use of these elements in clinopyroxene to infer the Nb and Ta in the equilibrium melts would result in 'artificial' negative Nb and Ta anomalies in the calculated liquids.

**References**

1. Rampone *et al.* (1991) *Nature*, **354**, 518–20.
2. Schiano, P. and Clochiatti, R. (1994) *Nature*, **368**, 621–3.
3. McKenzie, D (1989) *Earth Planet. Sci. Lett.*, **95**, 53–72.
4. Bodinier, J.L. *et al.* (1996) *Geochim. Cosmochim. Acta*, **60**, 545–50.
5. Eggins, S. *et al.*, (1998) *Earth Planet. Sci. Lett.*, **15**, 53–71.