# The trace element variations in clinopyroxenes from spinel peridotite xenoliths from Western Victoria (Australia)

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## Introduction

Geochemical studies of clinopyroxenes from peridotite xenoliths significantly improved our knowledge about upper mantle compositions and processes. Investigations of trace elements in single grain clinopyroxenes provide reliable information about chemical composition with respect to texture. Despite the rapid growth of microbeam techniques for *in situ* determination of trace elements, such as secondary ion mass spectrometry (SIMS), studies linking crystal chemistry and trace element variations have until now been scarce.

In this respect, clinopyroxenes in mantle xenoliths from Mt.Leura and Mt.Noorat (western Victoria, Australia) furnish a unique opportunity, since crystal chemical studies have demonstrated that site configurations may be related to specific suites of possible mantle residua from partial melting (Dal Negro *et al.*, 1986; Cundari *et al.*, 1986). In this paper we examine whether a relationship exists between trace element variations produced by melting and/or metasomatic processes in the upper mantle and the chemistry and crystal structure of clinopyroxenes.

### The samples studied

The selected samples are represented by a suite of mantle xenoliths associated with basanitic lavas from Mt.Leura and Mt.Noorat, in the Victorian 'Newer Volcanics'. Detailed petrographic and geochemical investigations (O'Reilly and Griffin, 1988; Chen *et al.*, 1989) showed that the upper mantle beneath the Newer Volcanics is compositionally and isotopically heterogeneous. Pieces of mantle brought to surface are composed of spinellherzolites and spinel-harzburgites which formed as ancient partial melting residues and were subsequently enriched by interaction with metasomatic agents, also including carbonatite melts (Yaxley et al., 1991).

In the selected samples texture is subequigranular and unbanded. Modal clinopyroxene in the 'dry' four-phase spinel assemblage (only sample LE8 from Mt.Leura contains accessory mica) ranges from 6.4 to 26.6 and from 5.2 to 14.8 in the Mt.Leura and Mt.Noorat xenoliths, respectively.

#### Results

Single-crystal X-ray refinements have shown that Mt.Leura clinopyroxenes have the smaller M1, M2 and T and unit cell volumes, relative to the Mt.Noorat clinopyroxenes (Dal Negro *et al.*, 1986; Cundari *et al.*, 1986). Ion microprobe



Fig. 1. Representative incompatibility diagrams for Mt. Leura and Mt. Noorat clinopyroxenes.



Fig. 2. Variations of Ce (a) Zr (b) contents (ppm) relative to M2 and M1 site volumes, respectively.

investigations allowed three main types of incompatibility diagrams in Mt.Leura clinopyroxenes to be distinguished (Fig. 1). The first one is highly LREE-enriched ( $Ce_N/Yb_N$  from 4.7 to 22.8) and it shows significant negative Sr and Ti anomalies (Sr/Sr\* and Ti/Ti\* from 0.44 to 0.82 and from < 0.1 to 0.3, respectively). The second one has concave-upward REE patterns (Sm<sub>N</sub>/  $Dy_N l$ ) and is less *LREE*-enriched (Ce<sub>N</sub>/Yb<sub>N</sub> from 3.3 to 4.5). Samples from this group are characterized by various degrees of Zr and Ti depletions relative to the adjacent REE (Zr/Zr\* and Ti/Ti\* from 0.3 to 0.7 and from 0.4 to 0.6, respectively). The third group is characterized by convex-upward patterns but less LREE-enriched than the samples from the previous groups  $(Ce_N/$  $Yb_{N}$  from 1.0 to 2.2).

Similar incompatibility diagrams have been also recognized in Mt.Noorat clinopyroxenes. However, most of the Mt.Noorat samples show slightly *LREE*-depleted patterns, with  $Ce_N/Yb_N$  ranging from 0.5 to 0.8 (Fig. 1).

## Discussion

Although M1 and M2 volumes are negatively correlated with modal cpx as expected for a simple series of residues from partial melting, the lack of correlation between cpx and clinopyroxene Mg# indicates a more complex origin. Incompatibility diagrams clearly demonstrate that clinopyroxenes have been in part modified or produced by mantle metasomatism. This is also supported by a plot of Ti/Zr versus Sm/Dy which shows a broad negative correlation trend moving from the chondritic ratio towards progressively lower Ti/Zr and higher Sm/ Nd values, in the opposite direction of partial melting trend.

When plotted relative to the site volumes, the trace elements entering M2, such as *LREE* and Sr, show a similar behaviour: in clinopyroxenes with lower Ce<sub>N</sub>/Yb<sub>N</sub> values, *LREE* and Sr decrease with the increasing site volumes, whereas the opposite is apparently observed for samples with higher Ce<sub>N</sub>/Yb<sub>N</sub> values (Fig. 2a).

As for elements entering M1, decoupling between Ti and Zr contents is important. Ti shows a broad negative correlation with M1 volumes, whereas Zr, similarly to *LREE* and Sr, decreases with increasing M1 volumes in the less *LREE*-enriched clinopyroxenes and apparently increases in the more *LREE*-enriched ones (Fig. 2b).

*LREE*, Sr, Zr and Ti are positively correlated with  $Na^+$  occupancy of M2 when clinopyroxene variations are observed within each group with distinct incompatibility diagrams.

Although the present data could be tentatively explained by assuming a crystal-chemical control for the metasomatic processes, i.e. that clinopyroxenes which survived larger degrees of melting were easily enriched by the successive interaction with metasomatic agents due to the more appropriate site volumes, we suggest that crystalchemistry and trace-element variations of clinopyroxenes from Mt. Leura and Mt. Noorat are the result of highly complex processes including: 1) partial melting at different depths, 2) crystallization from alkaline magmas, cryptic metasomatism by 3) alkaline magmas and 4) carbonatitic melts.

We suggest that during metasomatism Mt.Leura and Mt.Noorat clinopyroxenes incorporated significants amounts of *LREE* and Sr (interaction with alkaline and carbonatitic melts), Zr (interaction with alkaline melts), but not Ti. As expected, metasomatism increasing the clinopyroxene modal abundances may restore clinopyroxene to a less depleted composition. However, present data indicate that the mineral chemistry of clinopyroxenes may be also significantly modified by interaction with alkaline and, particularly, carbonatitic melts.

#### References

Chen, C.-Y., Frey, F.A., Song, Y. (1989) Earth Planet. Sci. Lett., 93, 195-209.