

# Compositional dependencies of the partition coefficients for Zr, Nb, Ta, Hf and selected transition elements between spinel and melt

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## Introduction

Partition coefficients for the elements Ta, Nb, Hf, Zr, Sc, V, Ga, Zn and Co have been determined by Laser Ablation ICP-MS and/or electron microprobe between spinel and melt using an alkali olivine basalt and a picrite basalt at 1 atmosphere. Trace element spinel-melt partitioning is of particular interest because, for many elements, spinel gives a better indication than other minerals of the magma chemistry from which it is crystallised (Arai, 1992). However, there is an extremely limited set of partition coefficients for spinel/liquid pairs ( $D^{sp/liq}$ ), although they are important for partial melting and fractional crystallisation calculations. There are often significant discrepancies between experimental determinations and those derived from natural phenocryst/matrix pairs (Lemarchand *et al.*, 1987), often covering more than one order of magnitude. Structural parameters like lattice constants, degree of inversion and temperature were found to be significant factors controlling the partitioning behaviour.

## Experiments

Experiments were conducted in vertical 1 atm. quench furnaces using Pt-wire loop technique. Oxygen fugacity was controlled by conventional gas mixing ( $H_2$  and  $CO_2$ ) and simultaneously measured by solid state  $f_{O_2}$  sensors. Temperature was measured with Pt/Pt<sub>90</sub>Rh<sub>10</sub> thermocouples immediately adjacent to the sample with an extra thermocouple for the  $f_{O_2}$  sensor. Temperature was calibrated against the melting point of Au and is accurate to 3°C. To ensure equilibrium and provide a check for Henry's law behaviour experiments were conducted with different levels of trace element addition and long run durations between 1 and 7 days.

## Results

The investigated spinels span almost the entire range in Cr and Fe of spinel compositions found in mafic extrusive rocks (Roeder & Reynolds, 1991). The chemical coherence of the behaviour of high field strength elements (HFSE) Zr, Nb, Ta and Hf is evident in the measured partition coefficients of 0.06 for Ta, 0.08 for Nb, 0.06 for Zr and 0.05 for Hf. These are uniform across the range of major element compositions, particularly Fe and Cr, represented by the spinels. This is also true for Al or Ti rich compositions but with a difference in the level of the partition coefficient, varying between 0.02–2.0 for Ta, Nb, Zr, Hf (Nielsen *et al.*, 1994).  $D^{HFSE}$  thus varies with structural parameter, such as the degree of inversion (Fig. 1). These results indicate that only titanomagnetite- or ulvospinel-rich spinels (and thus not mantle spinels) will take up significant amounts of HFSE and Sc. Vanadium partitioning shows a strong dependence on  $f_{O_2}$ , varying from  $D^{sp/liq} = 0.09$  (air) to 68 at  $\log f_{O_2} = IW$ . Under oxidized conditions vanadium is predominantly in the 5+ valence state and should therefore show very low  $D^{sp/liq}$  similar to that of Ta and Nb. In contrast to the

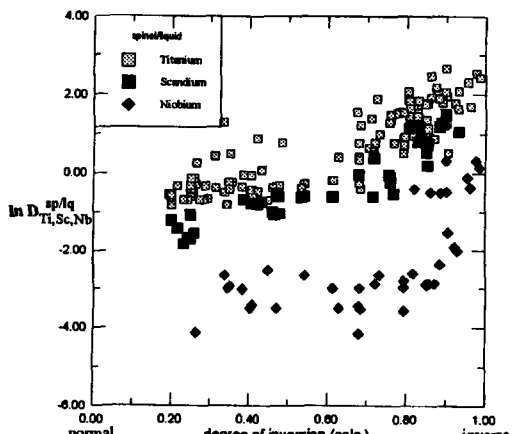


FIG. 1. Compositional dependence of trace element partitioning behaviour.

TABLE 1. Partition coefficients for spinel, olivine, opx, cpx and garnet

	Spinel	Olivine	Opx	Cpx	Garnet
Zr	0.06 <sup>8</sup> -1.3 <sup>7</sup>	0.01 <sup>2</sup>	0.03 <sup>2</sup>	0.10 <sup>2</sup> -0.1234 <sup>5</sup>	0.32 <sup>2</sup> -0.7 <sup>1</sup>
Nb	0.08 <sup>8</sup> -1.38 <sup>7</sup>	≤0.01 <sup>2</sup>	0.01 <sup>2</sup>	0.005 <sup>1</sup> -0.0077 <sup>5</sup>	0.02 <sup>1</sup> -0.07 <sup>2</sup>
Ta	0.06 <sup>8</sup> -1.95 <sup>7</sup>	≤0.01 <sup>2</sup>	≤0.01 <sup>2</sup>	0.013 <sup>1</sup> -0.02 <sup>2</sup>	0.04 <sup>2</sup> -0.06 <sup>1</sup>
Hf	0.05 <sup>8</sup> -1.77 <sup>7</sup>	≤0.01 <sup>2</sup>	0.14 <sup>2</sup>	0.22 <sup>2</sup> -0.256 <sup>5</sup>	0.44 <sup>2</sup> -0.53 <sup>3</sup>
V	0.09 <sup>8</sup> -68 <sup>4</sup>	0.04 <sup>3</sup> -1.3 <sup>3</sup>	0.90 <sup>2</sup>	1.31 <sup>2</sup> -3.1 <sup>5</sup>	1.57 <sup>2</sup>
Sc	0.24 <sup>8</sup> -4.45 <sup>7</sup>	0.16 <sup>8</sup> -0.26 <sup>8</sup>	0.33 <sup>2</sup>	0.51 <sup>2</sup> -1.31 <sup>5</sup>	2.27 <sup>2</sup>
Co	5.0 <sup>8</sup> -8.3 <sup>8</sup>	1.4 <sup>3</sup> -6.7 <sup>3</sup>	0.9-1.3 <sup>6</sup>		9.0 <sup>3</sup>
Ga	3.2 <sup>8</sup>	0.024 <sup>6</sup>	0.19 <sup>6</sup>	0.74 <sup>5</sup>	
Zn	3.6 <sup>8</sup> -4.5 <sup>8</sup>				

<sup>1</sup> Green *et al.* (1989), <sup>2</sup> Ulmer (1989), <sup>3</sup> Irving (1978), <sup>4</sup> Lindstrom (1976), <sup>5</sup> Hart and Dunn (1993), <sup>6</sup> Beattie *et al.* (1991), <sup>7</sup> Nielsen *et al.* (1994); <sup>8</sup> Horn *et al.* (1994).

incompatibility of the V<sup>5+</sup> ion in spinels, V<sup>3+</sup> should be compatible due to equivalent charge and similar ionic radius to that of Cr<sup>3+</sup>. The compatibility of V<sup>3+</sup> can be expected to be guided by the crystal field stabilization energy which increases in the order Sc<sup>3+</sup> > V<sup>3+</sup> > Cr<sup>3+</sup> (Blum, 1982). Vanadium compatibility in spinel is thus a strong function of V<sub>2</sub>O<sub>5</sub>/V<sub>2</sub>O<sub>3</sub> in the melt from which it crystallizes. Primitive volcanic rocks have often experienced early fractionation of spinel as shown by non-primitive chromium contents and by the presence of chrome-spinel inclusions in olivine phenocrysts (Foley, 1985). The partitioning relations suggest that fractionation of chrome-spinel should be confirmed by reduced vanadium contents provided that fractionation occur at f<sub>O<sub>2</sub></sub> ≤ NNO. Other determined D-values are shown in comparison with olivine, cpx, opx and garnet.

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