

SPINELS RENAISSANCE: THE PAST, PRESENT, AND FUTURE OF THOSE UBIQUITOUS MINERALS AND MATERIALS

## Compositional effects on the solubility of minor and trace elements in oxide spinel minerals: Insights from crystal-crystal partition coefficients in chromite exsolution

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### ABSTRACT

Chromite from Los Congos and Los Guanacos in the Eastern Pampean Ranges of Córdoba (Argentinian Central Andes) shows homogenous and exsolution textures. The composition of the exsolved phases in chromite approaches the end-members of spinel ( $\text{MgAl}_2\text{O}_4$ ; Spl) and magnetite ( $\text{Fe}^{2+}\text{Fe}_3^+\text{O}_4$ ; Mag) that define the corners of the spinel prism at relatively constant  $\text{Cr}^{3+}/\text{R}^{3+}$  ratio (where  $\text{R}^{3+}$  is  $\text{Cr}+\text{Al}+\text{Fe}^{3+}$ ). The exsolution of these phases from the original chromite is estimated to have accounted at  $\geq 600$  °C on the basis of the major element compositions of chromite with homogenous and exsolution textures that are in equilibrium with forsterite-rich olivine ( $\text{Fo}_{95}$ ). The relatively large size of the exsolved phases in chromite (up to ca. 200  $\mu\text{m}$ ) provided, for the first time, the ability to conduct in situ analysis with laser ablation-inductively coupled plasma-mass spectrometry for a suite of minor and trace elements to constrain their crystal-crystal partition coefficient between the spinel-rich and magnetite-rich phases ( $D_{\text{Spl/Mag}}^{\text{Spl/Mag}}$ ). Minor and trace elements listed in increasing order of compatibility with the spinel-rich phase are Ti, Sc, Ni, V, Ge, Mn, Cu, Sn, Co, Ga, and Zn.  $D_{\text{Spl/Mag}}^{\text{Spl/Mag}}$  values span more than an order of magnitude, from  $D_{\text{Ti}}^{\text{Spl/Mag}} = 0.30 \pm 0.06$  to  $D_{\text{Zn}}^{\text{Spl/Mag}} = 5.48 \pm 0.63$ . Our results are in remarkable agreement with data available for exsolutions of spinel-rich and magnetite-rich phases in other chromite from nature, despite their different  $\text{Cr}^{3+}/\text{R}^{3+}$  ratio. The estimated crystal-crystal partitioning coefficients reflect the effect that crystal-chemistry of the exsolved phases from chromite imposes on all investigated elements, excepting Cu and Sc (and only slightly for Mn). The observed preferential partitioning of Ti and Sc into the magnetite-rich phase is consistent with high-temperature chromite/melt experiments and suggests a significant dependence on  $\text{Fe}^{3+}$  substitution in the spinel structure. A compositional effect of major elements on Ga, Co, and Zn is observed in the exsolved phases from chromite but not in the experiments; this might be due to crystal-chemistry differences along the  $\text{MgFe}_{1-x}\text{Al}_x\text{Fe}_2^{3+}$  exchange vector, which is poorly covered experimentally. This inference is supported by the strong covariance of Ga, Co, and Zn observed only in chromite from layered intrusions where this exchange vector is important. A systematic increase of Zn and Co coupled with a net decrease in Ga during hydrous metamorphism of chromite bodies cannot be explained exclusively by compositional changes of major elements in the chromite (which are enriched in the magnetite component). The most likely explanation is that the contents of minor and trace elements in chromite from metamorphosed chromites are controlled by interactions with metamorphic fluids involved in the formation of chlorite.

**Keywords:** Chromite exsolution, spinel-magnetite, partition coefficient, minor and trace elements, hydrous metamorphism