

Thermodynamic controls on the partitioning of divalent cations between magnetite and silicate melts

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There is increasing interest in the use of magnetite as a geochemical proxy to interpret ore forming processes in magmatic systems. However, in order to utilise magnetite as a petrogenetic indicator, a comprehensive understanding of how different factors affect magnetite chemistry is required. Magnetite-melt partitioning of a large number of elements has been investigated experimentally as a function of oxygen fugacity (fO_2) and temperature (T) in an andesitic bulk-chemical composition. In this bulk system, at constant T, there are strong increases in the magnetite-melt partitioning of the divalent cations (Mg^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} and Cu^{2+}) with increasing fO_2 between 0 and 3 log units above the fayalite-magnetite-quartz (FMQ) buffer. This is attributed to a coupling between magnetite crystallisation and melt composition.

Traditionally, melt structure has been invoked to explain the partitioning of divalent cations [1]. At constant T, with increasing fO_2 the proportion of magnetite increases, which results in a decrease in FeO_{melt} . This leads to an increase in the degree of melt polymerisation. It has been suggested that more polymerised melts contain fewer potential sites onto which divalent cations can partition [2], offering a possible explanation for the magnetite-melt partitioning behaviour.

However, a more rigorous justification of magnetite-melt partitioning with increasing fO_2 can be derived in terms of thermodynamic principles, without the need to call upon an explanation in terms of melt structure. The presence of magnetite-rich spinel in equilibrium with melt over a range of fO_2 implies a reciprocal relationship between $a(Fe^{2+}O)$ and $a(Fe^{3+}O_{1.5})$ in the melt. We show that this relationship accounts for the observed dependence of magnetite-melt partitioning of divalent cations with fO_2 .

[1] Kohn & Schofield (1994) *Chem. Geol.* **117**, 73-87. [2] Toplis & Corgne (2002) *CMP* **144**, 22-37.