

Beyond Henry's Law: Interpreting element signatures in oxide minerals at high concentrations

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The compositions of minerals are frequently used to estimate the compositions of the fluids and melts from which they formed. For major elements, concentrations in a coexisting melt or aqueous solution are readily estimated from mineral solubility data, and partition coefficients enable calculation of trace element contents. Intermediate concentrations are more difficult to constrain, however, because the impact of minor elements on solubility is commonly poorly known, and such concentrations exceed Henry's Law behaviour required for a partitioning approach. This is a problem, as this concentration range is of key interest, especially in ore formation, where it traces enrichment of the ore element. Moreover, knowledge of the changing element content in the fluid can reveal clues about the mechanisms of enrichment and ore formation.

Here, we experimentally explored the distribution of a suite of trace elements between mineral and melt at increasing concentrations of a dopant. We used perovskite (CaTiO₃) as our model mineral and doped with either La, Nd or Yb from 500 ppm to 5 wt%. The other REE + Mg, Sr, Ba, Li and Na were added at ~100 ppm to act as passive tracers of the impact of the dopant. Experiments were run in a 1 atm furnace, cooling a Ca-Ti-Si-O melt suspended from Pt wire from 1450°C to 1370°C at 1°C/hr, followed by 80hr equilibration.

Results show an abrupt change in REE distribution behaviour as a "Henrian limit" is encountered in agreement with earlier work [1]. Below this limit, a characteristic partition coefficient (D) describes the mineral-melt REE distribution, and the mineral concentration can be directly translated to a REE content in the melt. In contrast, above this limit, the REE distribution depends on the dopant concentration, and the REE content of the melt is strongly underestimated when using the Henrian D value. This change in behaviour is due to exhausting the inherently available vacancies in the perovskite structure. The change in REE behaviour is mirrored by the 1+ trace elements, which show an *increase* in D value with increasing dopant level beyond the "Henrian limit". We link this increased incorporation of the 1+ elements in perovskite to charge compensation for 3+ dopant uptake. In contrast, the 2+ trace elements can substitute isovalently, and, as therefore expected, are unaffected by increasing dopant concentration. Moreover, the systematics in element distribution among isovalent trace elements remain unchanged.

We conclude that mineral-fluid/mineral-melt distribution of elements at elevated concentrations differs strongly from that at low concentrations, even for elements that are at trace levels, which can lead to both under- and overestimation of fluid concentrations. However, the systematics among an isovalent suite of elements, such as the REE, are preserved and minerals therefore remain an accurate tracer of the REE pattern of their host fluid.

[1] Corgne & Wood (2005) *Contrib Mineral Petrol* **149** 85-97

Speciation of Nickel in Workplace Aerosols Using X-Ray Near Edge Structure Spectroscopy

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X-ray absorption near-edge structure (XANES) spectroscopy provides new interpretations of Ni speciation in sulfidic Ni processing, particularly with respect to soluble Ni in workplace aerosol samples collected at the Copper Cliff nickel smelter and refinery. Typically, Ni speciation is identified using a sequential extraction developed by the Ni industry for determining workplace exposures. However, as this technique and its variants become more widely applied, there is evidence that the method may not always accurately report soluble and metallic Ni. Because of the importance of exposure reconstruction to the determination of carcinogenicity classification of Ni compounds, we have begun to evaluate alternative speciation methodologies for Ni. Here we present the results of a study comparing Ni speciation results obtained using XANES spectroscopy and sequential extraction along with complementary SEM, EDX, and XRD results.