Melt compositional controls on trace element partitioning: An experimental study of titanite/melt partitioning

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The aim of this study is to systematically investigate the influence of melt composition on the partitioning of trace elements between titanite and a range of different silicate melts. Titanite was chosen because of its important role as an accessory mineral, particulary with regard to intermediate to silicic alkaline and calc-alkaline magmas. Experiments were performed isobarically at constant temperature. One compositional series was prepared to investigate the effect of the Na/Al ratio in melts on the partitioning between titanite and melts. The molar SiO_2, K_2O, CaO and MgO content are kept constant in this series. Additionally three natural bulk compositions were choosen, representative of basaltic andesite, dacite, and rhyolite.

The partition coefficients for the REE (including Y^{3+}) show a convex-upward shape when plotted against ionic radius. That is because titanite accommodates the middle REE (Sm, Gd) more readily than the LREE (La, Ce^{3+}, Pr) and HREE and Y. With increasing AS-index (Alumina Saturation Index: $Al_2O_3/(CaO+Na_2O+K_2O)$) or increasing NBO/T ratio the D-values for all REE increase by orders of magnitude. It is surprising, however, that the mono-, di- and tetravalent elements (with the exception of Th) show no significant variation with changing melt composition.

We conclude that the bulk composition (and consequently also melt composition) exerts a major influence on the partitioning of some trace elements (e.g., REE). This is may be caused by two major mechanisms: Firstly, melt composition influences the shape of coordination polyeder in which the REE are located. Distortion of coordination polyhedra in melts increases with decreasing NBO/T. With increasing distortion of the coordination polyeder (and decreasing NBO/T) partition coefficients increase. Secondly, the bulk composition controls the Al and Na content in titanite. We suggest, however, that these minor contents of Al and Na (Al :0.005 to 0.027 apfu and Na 0.019 to 0.001 apfu) have no significant effect on the crystal structure of titanite. However, we speculate that the REE^{3+} ions require Al and Na ions for charge balance according to the following exchange reaction: $REE^{3+} + Al^{3+} = Si^{4+} + Ca^{2+}$.

Th^{4+} exhibits a similar trend like the REE, Nb and Ta. It is interesting to note that the behaviour of U^{4+} differs from that of Th^{4+}. The D_{Th}/D_U ratio changes quite drastically with increasing AS-Index. D values vary between <1 to >>1. The reason for this is unclear (Note that all experiments were performed under controlled atmosphere which should prevent the formation of U^{6+}).

Uranium biosorption by the lichen *Trapelia involuta* at a uranium mine

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In a preliminary study McLean et al. (1998) reported an association of U with dark coloured apothecial tissues in *Trapelia involuta* growing on uraniferous minerals at an uranium mine and suggested melanin pigments were involved in fixation. The study was limited to investigating a single sample and neither methods nor results were fully described. A TEM/SEM study was carried out on another sample collected from the same locality (Kasama et al., 2001).

X-ray element mapping and probe traverses across the lichen-rock interface identify the highest U, Fe and Cu concentrations in the outer parts of melanised apothecia. The accumulation of mineral particulates and complexing with lichen acids are not considered responsible for this since element ratios in the traverses do not correspond with those of likely mineral phases and lichen substances are localised in different tissues. Biosorption of metals by melanin-like pigments are considered to be responsible for the observed metal fixation. No detectable U or Cu was observed in control samples although Fe showed a similar localisation in some specimens. High concentrations of mucopolysaccharides and P recorded inside apothecia suggests that the formation of melanised tissues may be an adaptive response to adsorb metals and protect vital reproductive tissues from the toxic effects of U and other metals, since the uranyl ion complexes strongly with phosphate species.

The ability of lichens to tolerate and accumulate high concentrations of metals (including radionuclides), possibly involving the diverse secondary metabolites produced by these organisms may provide natural solutions for the remediation of metal contaminated sites and assist in our understanding of the biogeochemical cycling of elements.

References

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