

Application of Ge/Si ratios to ultramafic alkaline rocks using a novel LA-ICP-QQQ-MS method

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Germanium has, until recently, found limited interest in igneous and metamorphic rock studies due to analytical limitations, specifically low concentrations and many interferences in ICP-MS analyses. However, Ge and Ge/Si ratios have shown potential as tracers of magmatic fractionation and to distinguish between magma sources based on preferential substitution of Ge for Si in amphibole, mica, and garnet [1].

Here, we present a novel LA-ICP-QQQ-MS method that employs N₂O as a reaction gas to analyse Ge as an oxide. We compare this method to previously used techniques (LA-ICP-MS and H-mode LA-ICP-MS [2]), and document improvements in precision, and a substantial reduction of interferences when measuring the ⁷⁴Ge isotope as an oxide: ⁹⁰Ge (⁷⁴Ge¹⁶O).

Application of this novel method to the hydrous minerals phlogopite and richterite as well as diopside with varying aegirine contents in alkaline intrusive complexes at Bilibin and Inagli (Aldan Shield, Siberia) show different results for Ge/Si to those previously acquired for non-alkaline intermediate rocks [3]. Ge/Si ratios are lower in amphibole ($13.3 \pm 0.88 \times 10^{-6}$) and mica ($7.10\text{-}9.72 \times 10^{-6}$), and higher in clinopyroxene ($11\text{-}12.7 \times 10^{-6}$) in these alkaline complexes compared to similar minerals in basaltic and intermediate compositions.

We investigated a range of parameters to further understand the behaviour of Ge with comparisons to the limited published data and show that Ge/Si ratios seem to be controlled largely by mineral chemistry. In particular, Ge/Si decreases with increasing MgO contents for all minerals, and with Mg# and alkalis for amphibole and mica. MnO contents, however, increase with Ge/Si for all minerals. Mineral trace element patterns for Bilibin and Inagli support the Ge/Si ratio results in showing distinct behaviour of trace elements between minerals in peralkaline and subalkaline melts. With an increase in the quantity and quality of Ge and Ge/Si data, we suggest that Ge/Si may become a viable tracer for identifying the mineralogy of melt sources.

[1] De Argollo, R., Schilling, J.-G. (1978) *Nature* 276, 24-28.

[2] Veter, M., Alard, O., Foley, S.F. (2021) Goldschmidt Conference 2021, Lyon, France.

[3] He, D., Lee, C.-T.A., Farner, M. (2019) *Geochem. Geophys. Geosys.* 20, 4472-4486