

Tungsten residence in silicate rocks: implications for interpreting W isotopic compositions

J. LIU, D. G. PEARSON, T. CHACKO, Y. LUO

Department of Earth and Atmospheric Sciences,
University of Alberta, Edmonton, Alberta Canada
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High-precision measurements of W isotopic ratios have boosted recent exploration of early Earth processes from the small W isotope anomalies observable in some Hadean-Archean rocks. However, before applying W isotopic data to understand the geological processes responsible for the formation of these rocks, it is critical to evaluate whether the rocks' present W contents and isotopic compositions reflect that of the protolith or the effects of secondary W addition/mobilization. To investigate this issue, we have carried out in situ concentration measurements of W and other HFSEs in mineral phases and alteration assemblages within a broad spectrum of rocks using LA-ICP-MS. Isotope dilution whole-rock W concentration measurements are used along with modes calculated from mineral and bulk rock major element data to examine the mass balance for W and other elements. In general, W is positively correlated with Nb, Ta, Ti, Sn, Mo and U, indicating similar geochemical behavior. Within granitic gneisses and amphibolites, biotite, hornblende, titanite and ilmenite control the W budget, while plagioclase and k-feldspar have little effect. For granulites, pyroxenites and eclogites, titanite, rutile, ilmenite, magnetite and sulfide, as well as grain boundary alteration assemblages dominate the W budget, while garnet, clinopyroxene, orthopyroxene and plagioclase have little or no W. Within mantle harzburgites and dunites, major phases such as olivine, clinopyroxene, orthopyroxene and spinel/chromite have very low concentrations of W, Nb, Ta, Sn and Mo. Instead, these elements are concentrated along grain boundaries and within sulfide/mss. Mass balance shows that for granitic gneisses and amphibolites, the rock-forming minerals can adequately account for the whole-rock W budget, whereas for ultramafic rocks such as pyroxenites, eclogites and harzburgites and dunites, significant W is hosted along grain boundaries, indicating that metamorphism and melt/fluid metasomatism can dramatically modify W concentrations in such rocks. Therefore, for rocks that experienced subsequent W enrichments, their W isotopic compositions may not necessarily represent their mantle sources, but could predominantly reflect later inputs, for example from a crustal reservoir that has long existed on Earth.