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Titanium stable isotope fractionation in synthetic TiO_2-rich lunar melts

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Titanium-rich oxides as ilmenite and armalcolite are known to significantly fractionate Ti stable isotopes in lunar and terrestrial settings [1,2,3,4] where Ti-oxides are generally isotopically light and coexisting silicates are isotopically heavy. At fO_2 relevant to lunar magmatism (~ IW-1), 10% of the overall Ti consists of trivalent Ti [5], which might additionally influence Ti stable isotope fractionation. In this study, the effect of fO_2 on Ti stable isotope fractionation was investigated by carrying out experiments, where TiO_2-rich compositions were equilibrated at different fO_2 in gas mixing furnaces. Experiments with different bulk compositions yielded Ti-bearing oxides like armalcolite and ilmenite and silicates like orthopyroxene, clinopyroxene, as well as silicate melt. Phases were separated via careful hand-picking, and an aliquot of each phase was mixed and equilibrated with a ^{47}Ti-^{49}Ti double-spike. Subsequently, Ti was purified using a highly modified HFSE chemistry [6,3] before Ti stable isotopes were analysed using MC-ICP-MS.

Our results show fO_2-dependent Ti stable isotope fractionation from oxidised to reduced conditions (air to IW-1), phase equilibria associated with Ti-oxides show the largest isotopic differences ($\Delta^{49}Ti_{armalcolite-melt}$: -0.092 to -0.200 ‰; $\Delta^{49}Ti_{armalcolite-orthopyroxene}$: -0.089 to -0.250 ‰, $\Delta^{49}Ti_{ilmenite-melt}$: -0.089 to -0.461 ‰ and $\Delta^{49}Ti_{ilmenite-clinopyroxene}$: -0.213 to -0.426 ‰) while other phase equilibria show smaller isotopic differences ($\Delta^{49}Ti_{orthopyroxene-melt}$: -0.002 to +0.050 ‰ and $\Delta^{49}Ti_{clinopyroxene-melt}$: +0.123 to -0.035 ‰). Our results confirm the strong influence of Ti-oxide formation on the Ti stable isotope composition of natural rocks [1,2,3,4,7] and indicate that Ti stable isotope fractionation during lunar mare basalt petrogenesis is strongly redox dependent. Therefore, mineral-melt fractionation factors determined from terrestrial samples are not necessarily applicable to lunar basalt petrogenesis. Using our data, we modelled the fractional crystallization of the lunar magma ocean, and the petrogenesis of low- and high-Ti lunar basalts.

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