

## Vibrational constraints on Hydrogen isotopic fractionation between Mg-Chlorite and gaseous water

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Kieffer-type [1] statistical mechanics calculations can be used to estimate the D/H reduced isotopic partition function ratio (RIPFR) for hydrous minerals [2]. By combining this RIPFR with the RIPFR for gaseous water [3], the equilibrium hydrogen isotopic fractionation (EHIF) factors between minerals and water at low pressures can be calculated. For many common minerals not all Raman and infra-red (IR) frequencies have been assigned to different vibrational modes, making it necessary to apply Kieffer's simplifying rules [4] to the density of states function.

For Mg-chlorite the simplest model, which is consistent with Raman and IR vibrational mode assignments [5,6] and which can roughly reproduce natural and experimentally observed D/H EHIF data [7,8,9] requires: 1. separate OH-librational modes between approximately 100-800 cm<sup>-1</sup> with a frequency shift of 0.73 upon deuteration [6] and 2. two times more OH-librational modes than there are OH-vibrational stretches (between 3400 – 3700 cm<sup>-1</sup>). These features cause a minimum at intermediate temperatures and an upwards curvature when plotted against 1000/T of the EHIF curve at low temperatures.

Recent hydrogen isotope fractionation experiments [10] between Mg-chlorite and hydrogen using the methods of Vennemann & O'Neil [11] yield an EHIF curve that is much steeper than what this simple vibrational model and previous data suggest [7,8,9].

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## The role of volatile exsolution and sub-solidus fluid/rock interactions in producing high <sup>56</sup>Fe/<sup>54</sup>Fe ratios in siliceous igneous rocks

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Highly differentiated igneous rocks can, in some cases, have <sup>56</sup>Fe/<sup>54</sup>Fe ratios that are up to 0.3 ‰ higher than those of mafic- to intermediate-composition igneous rocks. The highest δ<sup>56</sup>Fe<sub>IGR</sub> values are restricted to rocks that have high Rb (> 100 ppm) and SiO<sub>2</sub> (> 70 wt.%) and low Fe<sub>2</sub>O<sub>3</sub> (< 2 wt.%, total Fe) contents. Although in principle crystal fractionation might explain the high δ<sup>56</sup>Fe values, this is inconsistent with the anomalously low Zr/Hf ratios (< 26) of high-δ<sup>56</sup>Fe igneous rocks. The highest δ<sup>56</sup>Fe values occur in volcanic and plutonic rocks that contain independent evidence for fluid exsolution, consistent with the low Zr/Hf ratios, suggesting that loss of a low-δ<sup>56</sup>Fe chloride fluid is the most likely explanation for the high δ<sup>56</sup>Fe values in the bulk rocks. The isotopic effects of fluid loss are most pronounced in the evolved rocks that lost Cl-bearing fluids at low magmatic or sub-solidus temperatures. High-δ<sup>56</sup>Fe igneous rocks are not likely to have formed through fractional crystallization but by complexation of Fe with Cl in volatile-rich, high-silica magmatic systems, followed by fluid loss. Based on mineral solubility and predicted Fe isotope fractionations among silicates, magnetite, and ferrous chloride fluids, the increase in δ<sup>56</sup>Fe values of bulk rocks is probably controlled by isotopic exchange between magnetite and FeCl<sub>2</sub>, which predicts an increase in the δ<sup>56</sup>Fe values of magnetite upon fluid exsolution. This is consistent with the δ<sup>56</sup>Fe values measured in this study for bulk rocks, magnetite, and Fe silicates. Our results have implications for transition-metal stable isotope studies of hydrothermal ore deposits. Fluids exsolved from siliceous hydrous magmas may represent precursors to mineralizing fluids that sometimes produce porphyry-style Cu or Cu-Au mineralization. These types of deposits, as well as hydrothermal Fe deposits, may have anomalous Fe isotope compositions, and our results suggest that superposition of sub-solidus re-equilibration and precipitation of sulfides from a Cl-bearing fluid may control the Fe isotope composition of such deposits. Further detailed studies of Fe (and possibly Cu and Zn) isotopes in ore deposits may provide a unique identification of magmatic fluid contribution to hydrothermal ore deposits.