Intramolecular fractionation of hydrogen isotopes in silicate quenched melts

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Abstract

The interplay between the chemical composition and the molecular structure of silicate melts was central to the evolution of the Earth's crust, mantle and core. This interplay also affects geochemical records such as the partitioning of isotopes between minerals, melts and fluids in the Earth's interior. For instance, large ²H/³H fractionations between silicate melts and aqueous fluids have been observed at high temperature and pressure. Such behaviour may be promoted by the occurrence of ³H/²H intramolecular fractionation within the molecular structure of silicate melts. New Raman spectroscopy and ¹H and ³H Nuclear Magnetic Resonance (NMR) spectroscopy data reveal the source of such ³H/²H intramolecular isotopic fractionation, showing that ¹H and ³H fractionate between the silicate tetrahedral units. Such a process might affect other isotopic systems (e.g., N, C, or S) where the isotopes interact with the melt silicate network.

Introduction

Silicate melts played a determining role in the segregation and evolution of the Earth's crust, mantle and core (e.g., Wood et al., 2006; Labrosse et al., 2007). Characterisation of their structure is central to understanding those processes. The silicate melt structure comprises network forming ions (Si⁴⁺, Al³⁺, Fe³⁺,...) in interconnected oxygen polyhedra, forming a network that can be disrupted by network modifiers ions, e.g., Mg²⁺, Ca²⁺, K⁺, Na⁺. The latter may also act as charge compensators of the O²⁻ bonded to network forming trivalent cations. Additional complexity arises from large variations in Si-O-Si / Si-O-Al bond angles and cationic coordination numbers, and non-random mixing and partitioning of the cations (Mysen and Richet, 2005; Greaves and Sen, 2007).

Results

¹H and ³H isotopic NMR spectra of the hydrous alkali quenched melts present three main peaks near 16, 5 and 1.8 ppm in three frequency regions, HF, MF and LF (Fig. 1, Supplementary Information). The ¹H signal is systematically more intense in the HF region and less intense in the MF region relative to that...
H isotropic NMR spectra indicate that \(^2\)H and \(^1\)H fractionate between different environments in the silicate melt structure, with \(^2\)H preferentially populating environments with small O-O distances (Fig. 1). This effect can be quantified by calculating the fractionation factor between the HF and MF spectral regions, \(\alpha_{HF,MF}\) (Fig. 2). \(\alpha_{HF,MF}\) depends primarily on the alkali ionic radius, as shown by a ~65 % variation between the Li and K glasses, and secondarily on the glass water content. The latter influence probably originates from the fact that increasing the water content increases the fraction of molecular water, which gives a weak signal in the MF portion of \(^2\)H and \(^1\)H NMR spectra.

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The contributions between 850 and 1300 cm\(^{-1}\) of the Raman spectra of glasses with comparable composition and water content, but containing either pure \(^3\)H\(^2\)O or pure \(^2\)H\(^2\)O, systematically differ from each other (Fig. 3). The intensity of the signal assigned to Si-O stretching in Q\(^2\) units (~950 cm\(^{-1}\)) is enhanced by the presence of \(^2\)H\(^2\)O, whereas that assigned to Si-O stretching in Q\(^4\) units (~1100 cm\(^{-1}\)) is lowered (Supplementary Information for additional detail). This observation is confirmed by subtraction of the Raman spectra of the \(^1\)H\(^2\)O-bearing glasses from those of the \(^2\)H\(^2\)O-bearing glasses (Fig. 3b). The variations of the intensity near 1150-1200 cm\(^{-1}\), where the signal from Si-O stretching in Q\(^2\) units occurs, are negligible compared with those of the ~950 and ~1100 cm\(^{-1}\) signals.

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Discussion

The decrease of the $Q^2$ abundance and the increase of the $Q^3$ abundance by substitution of $\text{H}^+$ for $\text{H}^-$ in the Raman spectra of the glasses explain the fractionations of $\text{H}^+$ and $\text{H}^-$ between the melts and aqueous fluids. Therefore, these structural features can control the isotopic fractionation of $\text{H}^+$ and $\text{H}^-$ between the melts and fluids. This theory may explain the large fractionation of $\text{H}^+$ and $\text{H}^-$ between those substances (Mysen, 2013a,b; Dalou et al., 2015).

Such phenomena may affect the differences in O-H bond strength between silicate melts and aqueous fluids. Therefore, these structural features can control the isotopic fractionation of $\text{H}^+$ and $\text{H}^-$ between the melts and fluids. This theory may explain the large fractionation of $\text{H}^+$ and $\text{H}^-$ between those substances (Mysen, 2013a,b; Dalou et al., 2015).

The link between the chemical composition and the speciation of $Q^4$ units (e.g., Mysen and Richet, 2005) implies that the intramolecular fractionation of $\text{H}^+$ and $\text{H}^-$ depends on the melt composition (Fig. 2). This may result in compositionally-dependent $\alpha_{\text{fluid-melt}}$, $\alpha_{\text{vapour-melt}}$ and $\alpha_{\text{mineral-melt}}$ fractionation factors, correlated with magmatic differentiation. Moreover, the intramolecular fractionation effect affects the fraction of water that interacts structurally with the silicate network, i.e. the so-called hydroxyl groups. Therefore, the influence of this effect on the $\alpha_{\text{fluid-melt}}$, $\alpha_{\text{vapour-melt}}$ and $\alpha_{\text{mineral-melt}}$ fractionation factors can also depend on water speciation. This may not be crucial at high temperatures where most of the water resides as OH groups in the melt, but it might play a determining role at temperatures corresponding to superficial volcanism, where magma degassing occurs. Such an idea agrees with an $\alpha_{\text{vapour-melt}}$ that depends on water speciation (De Hoog et al., 2009 and references therein).

The discussion above emphasises the centrally important principles that affect $\text{H}^+/\text{H}^-$ fractionation with implications for a range of geochemical problems. However, quantitative characterisation of how intramolecular fractionation of $\text{H}^+$ and $\text{H}^-$ in silicate melts governs hydrogen isotope fractionation processes in nature remain to be assessed. This fractionation of $\text{H}^+$ and $\text{H}^-$ between the $Q^4$ units of silicate melts likely reflects different extents of steric hindrance. This is analogous to the different distribution of alkali metals among structural units, for example (Maekawa et al., 1991). Such structural complexity, in turn, may affect other isotopic systems for which the isotopes interact with the $Q^4$ units as reported, for example, for $^{15}$N/$^{14}$N (Mysen and Fogel, 2010), for $^{13}$C/$^{12}$C (Mysen et al., 2009), or for the isotopes of S (Labidi et al., 2016). Therefore, it might have played an important influence on the geochemical isotopic record used to reconstruct the history of the Earth and other silicate planets.

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