

D/H intramolecular partitioning in alkali silicate melts: with implications for tracing subduction processes

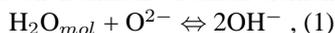
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The D/H ratio is an important probe for studying the cycle of water in the Earth interior in general, and in subduction zones in particular. Indeed, D/H ratios in melt inclusions (MIs) of arc magmas for instance indicate that the δD of subduction fluids is high, near -30 ‰, compared to the δD of the mantle that is near -80 ‰. A possible explanation for these different values is that D/H fractionation during dehydration of the slab in subduction zones enriches the subduction fluids in D, leading to high δD values in subduction magmas. This might be accomplished with hydrogen exchange between the melt and another source enriched in D before entrapment of MIs or a diffusive loss of H from within the inclusion leading to D/H fractionation. However, chemical effects affecting the δD ratio have not been considered because it is usually assumed that D and H have the same chemical and structural properties in silicate melts and glasses.

However, recent results from ²H and ¹H MAS NMR of Na₂Si₄O₉ glasses quenched from melt (equilibrated with fluid at 1400°C and 1.5 GPa) with various amounts of (D_xH_(1-x))₂O (x = D/[D+H]) lead to the conclusion that D and H isotopes occupy different structural positions in the network. From the ¹H MAS NMR spectra OH⁻ groups are distributed in two environments with mean O...O distances close to 0.26 and 0.29 nm in the Na₂Si₄O₉ glass. These environments give rise to two strong NMR lines at 16 and 5 ppm respectively. By contrary, ²H MAS NMR spectra of the same glasses display a strong line at 16 ppm accompanied by a small band near 5 ppm regardless of D/H ratio and total water concentration. This observation leads to the suggestion that OD⁻ groups are mainly present in an environment with small O...O distances. In other words, the structural behavior of OH⁻ and OD⁻ groups in the quenched silicate melts (glasses) differs.

In M₂Si₄O₉ glasses, (M = Li, Na or K) with different concentrations of pure H₂O or D₂O (from 3.3 up to 17.6 mol%), ²H and ¹H MAS NMR spectra confirm that by exchanging H with D the intensity of the 16 ppm NMR line increases greatly, whereas the intensity of the 5 ppm line decreases drastically. Interestingly, such a spectral evolution is also observed when increasing the size of the alkali element in the network of hydrous alkali silicate glass. These effects are attributed to steric and electronic effects in the environment of alkali elements, which cause shifts in the equilibrium between H₂O and O²⁻ of the silicate network:



The specific preference of OD⁻ groups for small O...O sites is in this mind intriguing, but is not in conflict with previous observations. Indeed, increasing the ionic size of alkali elements lead to promote OH⁻ in the small O...O environment. Similarly, it appears that increasing the size of the proton (by substituting H by D) promotes their existence in this small O...O environment. On this basis, we propose that those two observations have a common origin, maybe related to the probability of interaction between H/D and alkali elements depending of their ionic size and/or to molar volume effects related to those ionic sizes.

This large structural-controlled partitioning of D and H in melts, which depends on the melt composition, might be another fractionation process affecting the δD of subduction melts. Consequently, δD values recorded in MIs might be the result of such a structural process and might not reflect the δD of released fluids in the mantle wedge during slab subduction.

Keywords: D/H isotopes, silicate glass, NMR spectroscopy, Raman spectroscopy, Subduction fluids