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Solubility mechanisms of H_2O in silicate melts at high pressures and temperatures: a Raman spectroscopic study: reply

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Freund (1982) makes two comments on a recent paper by Mysen *et al.* (1980). (1) Substitution of D_2O for H_2O may not cause the shift of the 980 cm^{-1} band, as suggested by Mysen *et al.* (1980). (2) Arguments for the absence of H_2 made by Mysen *et al.* (1980) are inadequate. These comments will be dealt with in order.

As correctly pointed out by Freund (1982), the expected frequency shift of the 980 cm^{-1} Si–OH band depends wholly on whether or not the vibration is one of O–D domination or Si–O domination. Mysen *et al.* (1980) did not apply the D_2O substitution for H_2O as a critical test of whether or not there were OH-groups in the melt. This was simply an additional test on the influence of H_2O on aluminosilicate melts, conducted because of the poor spectroscopic resolution in this frequency region. The conclusions by Mysen *et al.* (1980) are not dependent on this assignment. The interpretation of the 980 cm^{-1} band is, therefore, unaffected, whether or not the suggestion by Mysen *et al.* (1980) for the effect of D_2O is correct.

Freund (1982) suggests that the 880 cm^{-1} band may be due to Al–OH. Mysen *et al.* (1980) considered this possibility and concluded that because the position of this band is independent of whether or not D_2O or H_2O is the solute and because of other data on the subject (as discussed on p. 904 in the original paper), vibration involving H or D together with Al were considered unlikely. More importantly, however, Mysen *et al.* (1980) on p. 905 pointed out that the frequency of the band near 880 cm^{-1} depends on H_2O content of the melt and on the Al-content of the solvent. If this band were due to Al–H, Si–H, Al–OH or Si–OH, the relationship noted by Mysen *et al.* (1980) is not likely to be observed. In addition, it should be reiterated that the frequency changes in this region coincide with frequency changes due to altered (Si,Al)-coupling in the frequency range between 1000 and 1200 cm^{-1}, as also discussed through the paper by Mysen *et al.* (1980). The latter effects would not be likely if both Al–OH and Si–OH were formed in equal proportion to their original abundance. The D_2O solution experiments have little bearing on this conclusion.

Freund (1982) finally suggests that Mysen *et al.* (1980) did not document a case for absence of H_2 in the quenched glasses. It does not matter which reference is chosen in this context. Studies by, for example, Van der Steen and Van den Bloom (1977) involving both H_2 and D_2, and by Faile and Roy (1970) and by Hartwig (1977) in samples that demonstrably contained H_2 or D_2, or both, prove the existence of the main H_2 band near 4100 cm^{-1}, and the analogous D_2 band near 2900 cm^{-1}. Mysen *et al.* (1980) observed neither.

In summary, the H_2O-solution model derived from interpretation of spectroscopic data by Mysen *et al.* (1980) and by references therein is internally consistent. The model is also consistent with published thermodynamic, phase equilibrium and other chemical data on H_2O-bearing systems in the upper mantle (for summary of such data, see Mysen, 1977; and references therein).

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