

## Solubility mechanisms of H<sub>2</sub>O 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<sub>2</sub>O for H<sub>2</sub>O may not cause the shift of the 980 cm<sup>-1</sup> band, as suggested by Mysen *et al.* (1980). (2) Arguments for the absence of H<sub>2</sub> 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<sup>-1</sup> 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<sub>2</sub>O substitution for H<sub>2</sub>O 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<sub>2</sub>O 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<sup>-1</sup> band is, therefore, unaffected, whether or not the suggestion by Mysen *et al.* (1980) for the effect of D<sub>2</sub>O is correct.

Freund (1982) suggests that the 880 cm<sup>-1</sup> 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<sub>2</sub>O or H<sub>2</sub>O 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<sup>-1</sup> depends on H<sub>2</sub>O 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<sup>-1</sup>, 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<sub>2</sub>O 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<sub>2</sub> 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<sub>2</sub> and D<sub>2</sub>, and by Faile and Roy (1970) and by Hartwig (1977) in samples that demonstrably contained H<sub>2</sub> or D<sub>2</sub>, or both, prove the existence of the main H<sub>2</sub> band near 4100 cm<sup>-1</sup>, and the analogous D<sub>2</sub> band near 2900 cm<sup>-1</sup>. Mysen *et al.* (1980) observed neither.

In summary, the H<sub>2</sub>O-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<sub>2</sub>O-bearing systems in the upper mantle (for summary of such data, see Mysen, 1977; and references therein).

### References

- Faile, S. P. and Roy, D. M. (1970) Mechanism of color center destruction in hydrogen impregnated radiation resistant glasses. *Materials Research Bulletin*, 5, 385-390.
- Freund, F. Solubility mechanisms of H<sub>2</sub>O in silicate melts at high pressures and temperatures: discussion. *American Mineralogist*, 67, 153-154.
- Hartwig, C. M. (1977) The radiation-induced formation of hydrogen and deuterium compounds in silica as observed by Raman scattering. *Journal of Chemical Physics*, 66, 227-239.
- Mysen, B. O. (1977) The solubility of H<sub>2</sub>O and CO<sub>2</sub> in the predicted pressure and temperature range of magma genesis in the upper mantle, and some petrological and geophysical implications. *Reviews of Geophysics*, 15, 351-361.
- Mysen, B. O., Virgo, David, Harrison, W. J. and Scarfe, C. M. (1980) Solubility mechanisms of H<sub>2</sub>O in silicate melts at high pressures and temperatures: A Raman spectroscopic study. *American Mineralogist*, 65, 900-914.
- Van der Steen, G. H. A. M. and Van den Bloom, H. (1977) Raman study of hydrogen-containing vitreous silica. *Journal of Non-Crystalline Solids*, 23, 279-286.

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