



Challenges and (thermodynamic) solutions in modeling hydrogen solubility in Nominally Anhydrous Minerals

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The discovery of small amounts of hydrous component (from 10's to 1,000's $\mu\text{g/g}$ of equivalent H_2O) in most nominally anhydrous minerals – NAMs (notably in mantle minerals [1]) permitted the potential existence of vast 'water' reservoirs in the deep Earth interior. The disproportionate effect of hydrogen – considering its low concentration – on many physical properties has been used since then to map out these potential reservoirs based on geophysical observations. Nevertheless there is not a current consensus in the location or in the extent of hydration of such reservoirs.

Whereas there has been a considerable effort in measuring most precisely these trace to minor quantities in both natural and synthetic NAMs, the thermodynamic treatment of hydrogen solubility in NAMs remains the same since early works [2], a treatment that it is inherited from point-defect chemistry. In this formulation water concentration in the NAM is primary a function of water fugacity to the power of a constant that depends on the incorporation mechanism. Two major challenges arise in the application of this formulation to complex systems using computational thermodynamic methods: (1) several incorporation mechanisms are known to be present – thus different power water fugacity dependencies [3] – with different pressure and temperature sensitivity [4] and more importantly (2) abrupt variation in water fugacity occurs under water-undersaturated conditions – believed to be prevailing at mantle depths.

To overcome these issues an alternative thermodynamic treatment will be presented. Hydrogen solubility will be modeled as part of a solid solution between the fictive hydrous and a real anhydrous end-members (e.g. $\text{Mg}_2\text{H}_4\text{O}_4$ and Mg_2SiO_4 respectively for forsterite) having regular solution properties in the Henry's law limit. The free energy of the fictive hydrous end-member in the anhydrous structure is found from known end-member thermodynamic properties and modified by a DQF parameter (Darken's quadratic formalism [5]) based on calibrated experiments for the particular hydrous point defect involved. The chemical potential of H_2O of the system (that formally controls hydrogen incorporation in NAMs) is found then by free-energy minimization techniques of the NAM solid solution [6]. An example of application is presented in the $\text{MgO-SiO}_2\text{-H}_2\text{O}$ system at conditions below and above solidus to highlight the advantages of the new formulation.

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