Phase diagrams for Nominally Anhydrous Minerals

PADRÓN-NAVARTA, J.A.[1]

[1]Géosciences Montpellier, CNRS & U. Montpellier (France)

Since the discovery of small amounts of hydrogen in Nominally Anhydrous Minerals (NAMs), there has been a considerable effort to expand the PT range experimentally investigated. Robust extrapolation to unexplored regions requires a thermodynamic treatment of hydrogen incorporation through coupled substitutions. However the thermodynamic treatment of hydrogen in NAMs - inherited from the point-defect chemistry - remains the same since early works[1]. In this formulation hydrogen concentration 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: (1) several incorporation mechanisms are known to be present – implying different power constants[2] with different PT sensitivity[3] 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 is presented here. Hydrogen incorporation is modeled as part of a solid solution between a fictive hydrous and a real anhydrous end-members (e.g. $Mg_2H_4O_4$ and Mg_2SiO_4 respectively for forsterite with hydrated Si-vacancies) 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) 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) and other oxides (controlled by the buffering assemblage) is found then by Gibbs-energy minimization techniques[4]. An example of application is presented in the MgO-SiO_2-H_2O system, at fluid-undersaturated conditions where other hydrous phases are stable and below and above the solidus to highlight the advantages of the new formulation.

[1] Bai, Q. & Kohlstedt, D. L. Nature 357, 672-674 (1992). [2] Tollan, P. M. E., Smith, R., O'Neill, H. S. C. & Hermann, J. Progress in Earth and Planetary Science 4, 14 (2017). [3] Padrón-Navarta, J. A. & Hermann, J. Journal of Geophysical Research: Solid Earth (2017). [4] Connolly, J. A. D. Geochem. Geophys. Geosyst. 10 (2009).