

Methane under pressure: Dissociation reactions from *ab initio* simulation

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Using *ab initio* molecular dynamics [1], we have investigated the stability of methane under pressure up to 24 GPa and in the temperature range 2-4000 K, studied in recent diamond anvil cell experiments [2]. In particular, we have explored the possible formation of alkanes from methane dissociation.

We have calculated structural and vibrational properties, and compared the relative stability of several hydrocarbons mixtures.

Our results show that the temperature is the main driving force for methane dissociation, with pressure enhancing the formation of higher hydrocarbons, at temperatures where dissociation is observed.

[1] Qbox code, <http://eslab.ucsvais.edu> [2] Kolesnikov, Kutcherov & Goncharov (2009) *Nature Geoscience* **8**, 566–570.

Ab initio molecular dynamics study of single phase SiO₂-H₂O fluids at supercritical conditions

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It is well known that the miscibility of aqueous fluids and silicate melts increases with pressure, P , and temperature, T . For the system SiO₂-H₂O, experimental studies suggest that a wet solidus, i.e. fluid-melt immiscibility, only exists up to pressures of about 1 to 2 GPa (see e.g. [1] and references therein). The upper P - T conditions of the immiscibility region (present at pressures lower than 1 to 2 GPa) is not well defined, but at 0.4 GPa hydrous melt and aqueous fluid seem to coexist at least between 1100 °C and 1600 °C. We are interested in how the molecular structure and dynamics change between the two-phase and the single-phase regions. Since experimental approaches to study this problem require *in situ* measurements and are technically very challenging, we employ molecular modelling to address this issue.

Ab initio molecular dynamics (AIMD) simulations are computationally expensive but they do not depend on empirical parameters and can reliably predict the molecular structure of liquids at extreme conditions. While previous AIMD studies of the SiO₂-H₂O system concentrated on hydrous melts with 3.8 wt-% H₂O [2] and aqueous fluids with 5 and 16 wt-% SiO₂ [3], we focus here on an intermediate composition with 23 wt-% (50 mol %) H₂O. We study a system of 32 H₂O and 32 SiO₂ molecules as a function of pressure up to about 5 GPa and temperature between 1500 °C and 2700 °C. Although the concentration of the H₂O component is relatively high, the structure of the fluid is dominated by hydroxyl groups instead of free H₂O molecules. With increasing pressure, coordination numbers generally increase and five-fold coordinated silicon atoms are observed. Besides the structural analysis of the simulated fluids, we will also discuss dynamical properties, such as life times of O-H and Si-O bonds and ionic diffusivities.

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[1] Hack *et al.* (2007) *Rev. Mineral. Geochem.* **65**, 129–185.
[2] Pöhlmann *et al.* (2004) *Phys. Rev. B* **70**, 184209.
[3] Doltsinis *et al.* (2007) *J. Theor. Comput. Chem.* **6**, 49–62