Speciation and solubility of reduced C-O-H fluids in coexisting fluids and silicate melts determined *in situ* to 1.45 GPa and 800˚C

BJORN O. MYSEN[1]*, S. YAMASHITA[2]
AND MARILYN FOGEL[1]

[1]Geophysical Laboratory, Carnegie Instn. Washington, 5251 Broad Branch Rd., NW, Washington DC 20015, USA (*correspondence: bmysen@ciw.edu)
[2]ISEI, Univ. Okayama at Misasa, Misasa, JAPAN (shigeru@misasa.okayama-u.ac.jp)

The speciation of fluids and in the C-O-H system and the solubility and solution mechanism of C-O-H components in Na_2O-SiO_2 silicate melts have been determined from ambient temperature and pressure conditions to 800°C and 1435 MPa. The melt polymerization range, expressed in terms of NBO/Si (NBO/Si=Na/Si of melts in the Na_2O-SiO_2 system), was chosen to model that from haploandesite (NBO/Si=0.4) to haplobasalt (NBO/Si~1.2).

In situ experiments were conducted with an an Ir-gasketed, hydrothermal diamond anvil cell (HDAC) with confocal microRaman and FTIR spectroscopy as structural probes. The oxygen fugacity was controlled at ~1 order of magnitude above that of the IW buffer by means of the buffer reaction, $Mo+O_2=MoO_2$. H_2O served as the oxidant of Mo. Pressure in the HDAC was monitored with the pressure- and temperature-dependent Raman shift of synthetic ^{13}C diamond. This Raman shift of the ^{13}C diamond was calibrated in the HDAC with the diamond submerged in H_2O and using the equation-of-state of pure H_2O [1] to obtain pressure with the temperature controlled to within ±1°C with chromel-alumel thermocouples. By referencing the ^{13}C diamond Raman shift to the 584.72 nm Ne line, the pressure uncertainty is about ±40 MPa.

The C-solubility in melt, expressed as CH_4, is between between 0.2 and 0.5 wt % [2]. The solubility increases with increasingly depolymerized melt (NBO/Si increases). The speciation of C-O-H volatile components in silicate melts is dominated by OCH_3 functional groups bonded to Si^{4+} (to form $Si-O-CH_3$ groups) and molecular CH_4. A schematic solution mechanism is, $Si-O-Si+CH_4=Si-O-CH_3+H-O-Si$. In coexisting C-O-H fluid, the main C-bearing species are CH_4 and C_2H_6. This speciation is pressure-/temperature-dependent. In the 500°-800°C and 860-1435 MPa temperature and pressure range, the fluid is nearly pure CH_4, whereas at lower temperature and pressure, C_2H_6 becomes increasingly important. In addition to H_2O, minor fluid species are molecular H_2 and an undersaturated (C+H)-species. The abundance ratio, $(OCH_3)^{melt}/CH_4^{fluid}$ ranges from 0.01 to 0.07. Speciation changes in melt as a function of silicate composition can be correlated with changes of carbon isotope fractionation between melt and coexisting fluid.

[1] Wagner & Pruss (2002) *J Phys Chem Ref Data* **31**, 387–535. [2] Mysen *et al*. (2009) *GCA* **73**, 1696–1710.

Quantify nanoscale surface properties using advanced scanning probe microscopy

CHONGZHENG NA* AND QIANG YU

Department of Civil Engineering and Geological Sciences, 156 Fitzpatrick Hall, Notre Dame, IN 46556 (*correspondence: cna@nd.edu)

Over the past two decades, scanning probe microscopy (SPM) has evolved into a powerful set of techniques for examining surface structures and dynamics with great precision. Compared to other surface-sensitive techniques, SPM has many unique advantages that are important to the study of environmental reactions and interactions. The advantages include providing quantification in all three dimensions, acquiring physochemical information beyond topography, and performing *in situ* measurements in aqueous and gaseous environments. With these advantages, SPM has revolutionized the understanding of surfaces and interfaces from a 'collective' viewpoint emphasizing repetitive units to an 'atomistic' one stressing heterogeneity and complexity [1].

While the expeimental applicaiton of SPM has been steadily increasing, the interpretation of SPM results remains elusive to researchers outside of the cognoscenti of the field. In this talk, we will share with the audience our own experience on acquiring nanoscale surface properties using advanced SPM techniques.

Emphasis will be given to force volume microscopy [2, 3], Kelvin probe force microscopy [4], and scanning polarization force microscopy [5]. Imaging examples in aqueous and gaseous environments will be presented. Mathmatical models will be used to extract the density, potential, and mobility of the surface charges that minerals often possess in aqueous solution or humid air. These properties are important regulators of surface reactivity in mineral dissolution/growth, contaminant transport/ transformation, and mineral-bacteria interaction [6].

[1] Kubby & Boland (1999) *Surf. Sci. Rep.* **26**, 61–204. [2] Na & Martin (2008) *Environ. Sci. Technol.* **42**, 6883–6889. [3] Na & Martin (2009) *Environ. Sci. Technol.* **43**, 4967–4972. [4] Na *et al*. (2007) *Environ. Sci. Technol.* **41**, 6491–6497. [5] Kendall *et al*. (2008) *Langmuir* **24**, 2519–2524. [6] Brown *et al*. (1999) *Proc. Natl. Acad. Sci.* **96**, 3388–3395.