

SCG009-01

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Time:May 23 14:15-14:45

## Speciation of P in and partitioning between aqueous fluids and silicate melts to upper mantle temperatures and pressures

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Evidence from high-grade metarphic terranes suggest that phosphorus solubility and solution mechanisms in silicate melts and aqueous fluids depend on composition resulting from a range of possible P-bearing structural complexes. The structure of phosphorus-bearing, H<sub>2</sub>O-saturated silicate melts, silicate-saturated aqueous fluids, and silicate-rich single phase (supercritical) liquids has been characterized, therefore, via in-situ experiments from ambient temperatures and pressures to 800°C/1486 MPa. The solution mechanisms and partitioning of structural species between fluids and melts were determined with the aid of confocal microRaman and with FTIR spectroscopy backed up with published phosphorus-31 MAS NMR data [1]. The experiments were conducted in an Ir-gasketed hydrothermal diamond anvil cell. Temperature and pressure were recorded with thermocouples (1°C uncertainty) and pressure- and temperature-dependent Raman shift of <sup>13</sup>C diamonds (40 MPa uncertainty). Starting materials were aluminum-free Na<sub>2</sub>O·4SiO<sub>2</sub> (NS4) and with 10 mol % Al<sub>2</sub>O<sub>3</sub> (NA10) substituting for SiO<sub>2</sub>, both with 5 mol % P<sub>2</sub>O<sub>5</sub>. These compositions enabled characterization of phosphorus behavior with coexisting haploandesite melt and aluminosilicate-saturated aqueous fluids with variable Al-content.

Aluminosilicate species of Q<sub>0</sub>, Q<sub>1</sub>, Q<sub>2</sub>, and Q<sub>3</sub> type exist in coexisting fluid and melt and in single phase liquid together with phosphate species, PO<sub>4</sub>, P<sub>2</sub>O<sub>7</sub>, and Q<sub>n</sub>P. In the Q<sub>n</sub>P notation, the n-value denotes the number of oxygen in the structural species shared with P and Si. Al substitutes for Si predominantly in the Q<sub>n</sub>P species. In melts, the abundance of the most depolymerized silicate species, Q<sub>0</sub>, is positively correlated with temperature and pressure, whereas that of the most polymerized species, Q<sub>3</sub>, decreases with temperature and pressure. In the silicate solute in aqueous fluids, the opposite relationship exists with Q<sub>0</sub> abundance decreasing and Q<sub>3</sub> (and Q<sub>1</sub> and Q<sub>2</sub>) abundance increasing with increasing temperature and pressure. The silicate melts, therefore, become increasingly depolymerized and the silicate solute in aqueous fluids decreasingly depolymerized. The P<sub>2</sub>O<sub>7</sub> and Q<sub>n</sub>P are the dominant phosphate species in fluid, melt, and single phase liquid with orthophosphate, PO<sub>4</sub>, playing a subordinate role. The fluid/melt partition coefficients for P<sub>2</sub>O<sub>7</sub> and Q<sub>n</sub>P species are in the 0.15-0.7 range with that of Q<sub>n</sub>P being greater than that of P<sub>2</sub>O<sub>7</sub>. The PO<sub>4</sub> fluid/melt partition coefficients are <0.2. In all cases, the partition coefficients increase with increasing temperature and pressure. There is no clear influence of Al<sub>2</sub>O<sub>3</sub>. Hence, it appears that P-bearing complexes in fluids and melts are associated with Na<sup>+</sup>. Mobility of phosphorus during metamorphic processes likely is principally governed by availability of alkali metals (and perhaps alkaline earths), whereas Al/Si-ratio may be a less important composition parameter. The P-partitioning between fluids and melts likely are significantly pressure-dependent because fluid and melt speciation is sensitive to pressure.

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Keywords: melt structure, aqueous fluid, phosphorus species, species partitioning, spectroscopy

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## X-ray diffraction studies on the structure of aluminosilicate melt under pressure

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The physical properties of silicate magma, such as density and viscosity, are important to understand migration of magma within the planetary interior as well as evolution of magma ocean. As these properties are related to the structure of magma, the structural studies of silicate magma at high pressures are fundamental to understand the magma related processes within the planetary interior. Therefore, we studied the structure of aluminosilicate melts at high pressures. Here we report the results of X-ray diffraction analysis on  $\text{Ca}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ ,  $\text{Mg}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ , and  $\text{NaAlSi}_2\text{O}_6$  composition melts up to 7 GPa.

Static structure of aluminosilicate melts under pressure has been studied by in situ x-ray diffraction experiments using synchrotron radiation at Photon Factory, KEK, Japan. X-ray diffraction patterns were acquired just above the melting temperature to about 7 GPa by energy-dispersive x-ray diffraction method and were analyzed by Fourier method.

Radial distribution functions of aluminosilicate melts show the increase of T-O distance as pressure increases. The T-O distance is an indicator of the coordination number of the network-forming cation, Si and Al. The higher the coordination number is, the longer the T-O distance is. In these melts, it is expected that the coordination number of Al increases in these pressure range. The first sharp diffraction peak (FSDP) of interference function shifts higher Q-side with increasing pressure, indicating the shrinkage of intermediate range structure in these melts.

The changes in the structure are related strongly to density and viscosity in these melts. These results are important to understand how these properties changes with pressure.

SCG009-03

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## Viscosity of CaMgSi<sub>2</sub>O<sub>6</sub> liquid at high pressure revisited

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The knowledge of the viscosity of silicate melts under high pressure is of importance to understand magmatic processes in the Earth's interior. It is known that the pressure dependence of viscosity is strongly related to the structure of melt. The diopside (CaMgSi<sub>2</sub>O<sub>6</sub>) composition melt is characterized as a depolymerized melt, and a positive pressure dependence of viscosity has been reported. However, there is a discrepancy in a curvature in previous studies. Scarfe et al. (1979) and Brearley et al. (1986) reported three times increase from 1 atm to 1.5 GPa. In contrast, Taniguchi (1992) showed that the positive pressure dependence was half of the previous studies. The viscosity of CaMgSi<sub>2</sub>O<sub>6</sub> liquid was measured by Reid, Suzuki et al. (2003) up to 13 GPa. However, the data at the low-pressure range between 3.5 and 7.0 GPa were scarce. In the present study, high-pressure viscosities of the diopside (CaMgSi<sub>2</sub>O<sub>6</sub>) composition melt were measured between 1 and 4 GPa. X-ray radiography technique was used to observe falling spheres in situ. We conducted experiments using the Kawai type multianvil apparatus loaded in the MAX-III press on the PF-AR NE7A station at the High Energy Acceleration Research Organization (KEK). The measured viscosities between 1 and 2 GPa were consistent with Taniguchi (1992) and inconsistent with Scarfe et al. (1979) and Brearley et al. (1986). A positive correlation to pressure was observed up to 4 GPa.

Keywords: viscosity, magma, mantle, high pressure, X-ray radiography

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## Simultaneous measurements of the elastic wave velocities and the volume for amorphous materials under pressures

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Combined ultrasonic and microtomographic measurements were conducted for simultaneous determination of elastic property and density of noncrystalline materials at high pressures. A Paris-Edinburgh anvil cell was placed in a rotation apparatus, which enabled us to take a series of x-ray radiography images under pressure over a 180° angle range and construct accurately the three-dimensional sample volume using microtomography. In addition, ultrasonic elastic wave velocity measurements were carried out simultaneously using the pulse reflection method with a 10° Y-cut LiNbO<sub>3</sub> transducer attached to the end of the lower anvil. Combined ultrasonic and microtomographic measurements were carried out for SiO<sub>2</sub> glass up to 2.6 GPa and room temperature. A decrease in elastic wave velocities of the SiO<sub>2</sub> glass was observed with increasing pressure, in agreement with previous studies. The simultaneous measurements on elastic wave velocities and density allowed us to derive bulk (Ks) and shear (G) moduli as a function of pressure. Ks and G of the SiO<sub>2</sub> glass also decreased with increasing pressure. The negative pressure dependence of Ks is stronger than that of G, and as a result the value of Ks became similar to G at 2.0-2.6 GPa. There is no reason why we cannot apply this new technique to high temperatures as well. Hence the results demonstrate that the combined ultrasonic and microtomography technique is a powerful tool to derive advanced (accurate) P-V-Ks-G(T) equations of state for noncrystalline materials.

Keywords: x-ray tomography, ultrasonic, high pressure, glass

SCG009-05

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## Universal behavior in pressure-induced melt-polymerization in primordial magmatic reservoirs

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Pressure-induced changes in melt-composition, viscosity, entropy, and solubility of elements in silicate melts in magma oceans provided a unique situation in which significant chemical differentiation of the silicate earth could have occurred and formed unrecycled partial by forming a hidden reservoir in Earth's mantle. Although the structures of silicate melts have been linked to these key properties, the melt structures at high pressure remained largely unknown. Even more challenging is to unveil the structure of natural silicate magmas in the Earth's mantle because any experimental effort to reveal the complex structure tends to be hampered by inhomogeneous broadening in experimental data associated with such complexity. Therefore, chemical constraints such as the non-bridging oxygen (NBO) content at 1 atm, rather than the real structural parameters for melt polymerization at high pressure, are commonly used to account for pressure-induced changes in the melt properties in Earth's interior. Here, we show that the pressure-induced NBO fraction in diverse silicate melts show a universal behavior where all the reported experimental NBO fractions at high pressure can be simplified into a single decaying function, regardless of melt composition. This simplicity in the pressure-induced changes in melt polymerization enables us to account for the non-linear variations in thermodynamic and the transport properties of multi-component and thus natural silicate melts at high pressure. The current results with universality in melt polymerization thus provide atomistic insights into the density crossover between melts and crystals and a formation of hidden reservoir with distinct chemical composition.

Keywords: silicate melts, high pressure, melt polymerization, mantle reservoirs

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## Pressure effect on excess molar volume of liquid Fe-S

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The excess molar volume of liquid Fe-light element alloys at high pressure represents non-ideality for mixing of end-member components and, therefore, it is very important to estimate the light element contents in the outer core based on the density deficit in the core. Sulfur is considered to be a major candidate of light elements, because it can dissolve into liquid Fe even at low pressure and it is depleted in the crust and mantle relative to the other volatile elements. Previous works (e.g. Poirier, 1994) estimated the light element contents in the core assuming ideal-mixing behavior between iron and light elements, i.e., neglecting their excess volumes. The excess molar volume of liquid Fe-S at 4 GPa was reported to be large and to have a negative value (Nishida et al., 2008). Therefore, if this excess molar volume can be applied at the core condition, the outer core may contain more light elements than the previous estimates. However, pressure effect on the excess molar volume of liquid Fe-S has never been reported.

In this study, we measured the density of liquid Fe-S at 0.5 GPa and 1650 °C using sink/float method. We fitted the present molar volume assuming Fe-S liquid can be treated as the regular solution. Derived negative excess molar volume of Fe-S at 0.5 GPa and 1650 °C is larger than that at 4 GPa. The negative excess molar volume of liquid Fe-S decreases with increasing pressure. This result may suggest the excess molar volume of liquid Fe-S at the pressure of the Earth's outer core might be small and negligible.

Keywords: Fe-S, liquid, density, excess molar volume, high pressure

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## Alkali effect in silicate melts ? A new vision on an old hypothesis

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Rheological properties of silicate melts govern both magma ascension from the mantle to the surface of the earth and volcanological eruptions styles and behaviors. In this mind, it is very important to understand what parameters influence these properties. Up to now, we know for example that viscosity of silicate melts is dependent of temperature, pressure and chemical composition (Bottinga and Weill, 1972; Urbain et al, 1982). In this work, we will focus on the Na<sub>2</sub>O-K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system, which is of a prime importance because it deals with a non-negligible part of natural melts, like for instance Vesuvius (Italy) or Erebus (Antartica) magmas. We will first present our viscosity data, and then the Adam and Gibbs theory that allows theoretically modeling Na-K mixing in aluminosilicate melts using the so-called mixed alkali effect. On the basis of these rheological results, the Na-K mixing cannot be explained with this mixed alkali effect. To go further and as rheological properties are directly linked with structural properties, we will present our first results obtained by Raman and NMR spectroscopy. These last ones provide important structural informations on the polymerization of glasses and melts, and also on the environment of tetrahedral coordinated cations. These structural results are directly linked with viscosity measurements and shown that substituting Na by K in aluminosilicate melts induces structural changes in both alkali environment and aluminosilicate network. This implies that Na and K atoms are non-randomly distributed in the aluminosilicate network. Na melts present a network with some channels and a random distribution of Al and Si. K networks are different, they present a non-random distribution of Al and Si, with two sub-networks: one rich in Si and fully polymerized, the other containing Al and K. On this view, mixing Na and K melts returns to change these configurations and induces complicated and non-linear effects.

Keywords: glass, melt, aluminosilicate

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## Probing the effect of composition on structural disorder of basaltic and slab-driven melts using solid state NMR

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Whereas the structure of multi-component silicate melts has strong implication for the properties of natural silicate melts and relevant magmatic processes in mantle and crust of the Earth, little is known about their atomic structures due to lack of suitable experimental probes of multi-component amorphous oxides. Whereas most of the progress in melt structure has been made for relatively simple binary and ternary silicate glasses, recent advances in high-resolution solid-state NMR unveil previously unknown structural details of multi-component silicate melts. Here, we report the experimental results of the effect of composition on the atomic structure and disorder in quaternary [CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (CMAS)] using multi-nuclear high-resolution 1D and 2D solid-state NMR. We also report the first NMR results for the diverse glasses with compositions of natural silicate melts. The Al-27 NMR results for diopside- Ca-Tschermakite pseudobinary join, suggest a increases in topological and configurational disorder with increasing diopside content. While the glasses with basaltic compositions show that <sup>4</sup>Al is dominant, non-negligible fraction of <sup>5</sup>Al were observed for basaltic composition melts while negligible fraction of <sup>5</sup>Al was observed for the slab-driven melts . The high-resolution O-17 3QMAS NMR spectra of diopside-Ca-Tschermakite pseudobinary join show that three types of bridging oxygens (BO; Si-O-Si, Al-O-Al, and Si-O-Al) and two types of NBO (Ca-NBO, and mixed?NBO) are partially resolved. Previously unknown structural details in Ca-Mg aluminosilicate glasses include nonrandom distributions of Ca<sup>2+</sup> and Mg<sup>2+</sup> around NBO and BO and significant fraction of Al-O-Al in natural basaltic magmas. The preferential partitioning of Ca<sup>2+</sup> and Mg<sup>2+</sup> between NBO and BO may results in a variation of activity coefficient of CaO and MgO, thus controlling composition of melts generated at the mid-ocean ridge and subduction zone.

Keywords: basaltic melt, multi-component glass, NMR, atomic structure

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## Oxidation state and coordination structure of Fe in silicate glasses and melts

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In both magmatic and industrial systems, Fe is the most abundant transition element. Due to its heterovalent nature and the different crystal- chemical behavior of the reduced and oxidized species, Fe affects a wide number of physical and chemical properties of magmas or final glass products, such as density, viscosity, stability of phases, and nucleation during crystallization. Particularly, the viscosity of Fe-bearing silicate melts decreases with decreasing Fe<sup>3+</sup> content of the melt, which provides clear but indirect evidence for differences in the structural role of Fe<sup>3+</sup> and Fe<sup>2+</sup>. Many studies have addressed the structural role of Fe in melts using glasses as structural analog (Calas and Petiau, 1983). In most cases, Fe<sup>3+</sup> in silicate melts was assigned to tetrahedral site geometry, although evidence for higher coordination was also found. On the other hand Fe<sup>2+</sup> was found distributed over sixfold-, fivefold- and fourfold-coordinated sites in melts, with the last two dominating (Rossano et al., 2000).

In the work presented here, in-situ X-ray absorption spectroscopy at the Fe K-edge was used to characterize the local structural environment of Fe<sup>3+</sup> and Fe<sup>2+</sup> in alumino-boro-silicate melts at high temperature (up to 2000K) in comparison to their quenched glassy analog at room temperature. Changes in the structural environment of Fe were evaluated by analyzing the pre-edge feature of the EXAFS spectra. The most useful characteristics of the Fe-K pre-edge for determining Fe oxidation state and coordination number are the position of its centroid and its integrated intensity. To plot these pre-edge parameters in the variogram after Wilke et al. (2001) allow determining the oxidation state and the coordination of iron. In an effort to complete this variogram, a serie of Fe-bearing minerals, with of Fe<sup>3+</sup> and Fe<sup>2+</sup> coordination ranging from 4 to 6 O atoms, has also been analysed by X-ray diffraction and Fe K-edge EXAFS techniques. The coordination structure of Fe and Fe-O distances in minerals were thus determined. The characteristics of the pre-edge features of the EXAFS spectra are now related with oxidation state, local coordination environment of Fe atoms but also with Fe-O distances.

In this study, new information about incorporation of Fe<sup>3+</sup> and Fe<sup>2+</sup> into a variety of alumino-boro-silicate glasses and melts will be presented. These results on the coordination structure of iron in silicate glasses and melts will be also discussed in regards to the kinetics of iron redox reactions in silicate melts (Magnien et al., 2008; Cochain et al., 2010).

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Keywords: XAS (XANES, EXAFS), Fe- K-edge, Fe in silicate melts, Fe in minerals, Fe coordination and redox state

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## Structural change of hydrous sodium silicate glass under high pressure using Brillouin and Raman spectroscopies

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The structure and physical properties of silicate melt are important to understand the Earth's mantle. However, it is technically difficult to conduct experiments of the melt at high pressure and high temperature. The glass is important for analog materials of the melt and one of the plausible approaches to understand its structure and density changes. It is important for melt to understand the glass which contains SiO<sub>2</sub> as a basic component of melt. Elastic velocities of glass consist of the bulk modulus, shear modulus and density. Elastic velocities enable us to discuss the structure and density changes of melt. Brillouin scattering with DAC enables us to discuss about the glass structure and density changes under high pressure indirectly based on pressure effect on trend elastic velocities. Additionally, water owes its importance to the dramatic influence which it exerts even at very low concentrations on variety of physical properties. In this study, we measured the elastic velocity of Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> glass, which is a binary system of SiO<sub>2</sub>-Na<sub>2</sub>O glass, under high pressures up to 50 GPa based on Brillouin scattering together with diamond anvil cell. The other starting material is hydrous Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> glass. I synthesized it based on hydrothermal experiment. I observed the sample using a polarization microscope and analyzed it using FT-IR to estimate the content of water in the sample. I observed the peak derived from Si-O bond of the glass using Raman spectroscopy. To expect the structure and density changes of the hydrous glass based on the elastic velocities, I measured hydrous Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> glass elastic velocity up to 50 GPa based on Brillouin scattering together with a diamond anvil cell at SPring-8. We observed the apparent elastic velocity profile change around 35 GPa. Below 35 GPa, the relatively steeper gradient ( $V_p$ ;  $dV/dP=0.11$ ,  $V_s$ ;  $dV/dP=0.043$ ) of the elastic velocity profile was observed. Above 35 GPa, the relatively gentle gradient ( $V_p$ ;  $dV/dP=0.05$ ,  $V_s$ ;  $dV/dP=0.024$ ) was observed. Based on these results, the relatively steeper gradient suggests that the structure of Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> glass changes from 10 to 35 GPa. This tendency is consistent with the result of previous Raman spectroscopy (Wolf et al., 1990) which shows that the coordination number of silica changes from 4 to 6 between 20 and 33 GPa and above 33 GPa, the coordination number of silica is constant of 6 coordination. Density vs. pressure relationship was also calculated from 35 to 50 GPa based on the observed values of  $V_p$  and  $V_s$ . The relationship possibly helps to construct the precise equation of state of sodium silicate glass under high pressure, although it requires quantitative values of glass density of ambient conditions. The measurement of elastic sound velocities using Brillouin scattering could be one of the most favorable approaches to understand the structure and density changes of glass. Combined measurement with the other spectroscopic methods like Raman scattering or X-ray diffraction and absorption would lead farther understanding of density and structure change of glass. We will present about details of the result and discussion of hydrous glass experiments.

Keywords: glass, melt, structural change, Brillouin scattering, Raman spectroscopy