Mg/Si Ratios of Aqueous Fluids in Earth's Upper Mantle

Water influences most physicochemical characteristics of earth-forming materials: melting temperature, partial melt chemistry, density and viscosity, electric conductivity, melt extraction, phase transition boundaries and element distribution. Aqueous fluids can dissolve significant amounts of silicate components under high pressure and high temperature conditions. Such fluids can act, therefore, as transfer agents during metamorphism, magmatism, and volcanism. Therefore, knowledge of the chemical compositions of silicates dissolved in aqueous fluids is essential to the understanding of the effects of H_2O on the physicochemical properties of rocks.

A direct observation of aqueous fluids coexisting with $MgSiO_3$ enstatite and/or Mg_2SiO_4 forsterite is performed at 0.5 - 5.8 GPa and 800 - 1000°C with a Bassett-modified externally heated diamond anvil cell [1] and synchrotron X-rays at beamline **BL04B2** [2]. Rigorous temperature control maintains the temperature of each diamond to be within a few °C. Pressure was determined from the measured unit-cell volume of gold foils using the P-V-T equation of state for gold. Use of this synchrotron X-ray system enables the mineral coexisting with aqueous fluids under high pressure and high temperature conditions to be identified and the Mg/Si ratios of aqueous fluids coexisting with $MgSiO_3$ enstatite and Mg_2SiO_4

forsterite, which are the main mineral constituents of Earth's upper mantle, to be estimated.

Possible Mg/Si ratios of aqueous fluids coexisting with $MgSiO_3$ enstatite and Mg_2SiO_4 forsterite are shown in Fig. 1(a) [3]. In the pressure range of 0.5 - 2.8 GPa, Mg_2SiO_4 forsterite crystallizes at 1000°C in the $MgSiO_3$-H_2O system. This indicates that the aqueous fluids can dissolve more SiO_2-rich components than MgO-rich components, resulting in Mg/Si atomic ratio of less than unity (Fig. 1 (b)). In contrast, at pressures greater than 3.9 GPa, $MgSiO_3$ enstatite dissolves congruently at 1000°C, whereas Mg_2SiO_4 forsterite dissolves congruently up to 5.0 GPa. These data suggest that the aqueous fluids coexisting with Mg_2SiO_4 enstatite and Mg_2SiO_4 forsterite can have Mg/Si ratios in the range 1 < Mg/Si < 2 under these conditions (Fig. 1(c)). In the present experimental
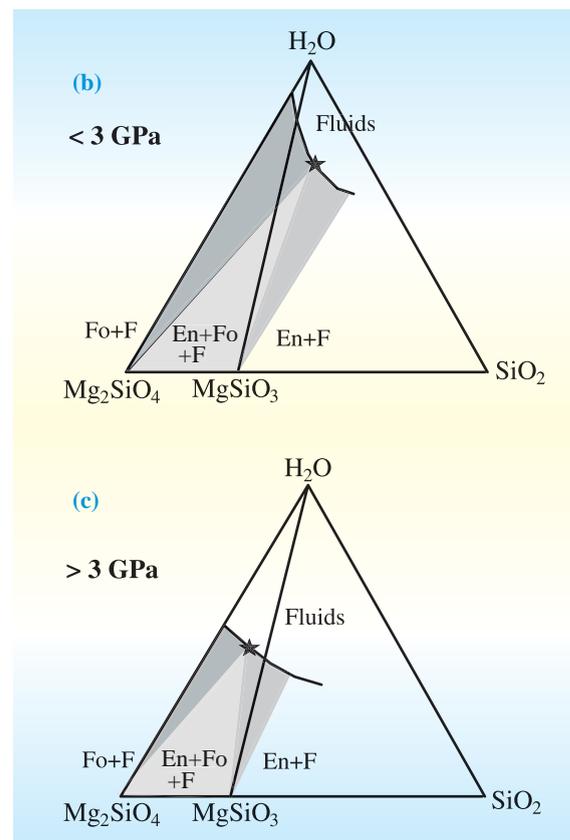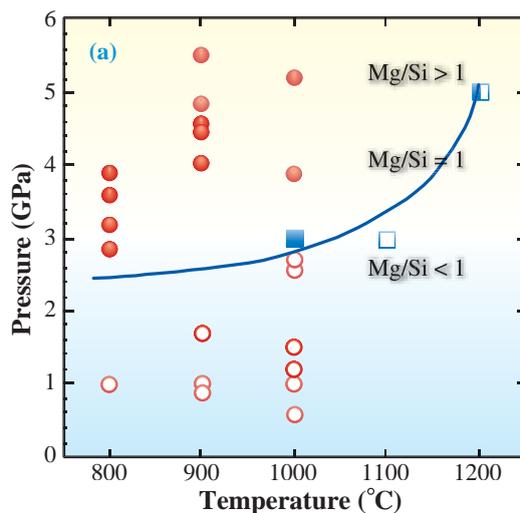
Fig. 1. **(a)** Experimental results showing Mg/Si ratios of silicate components in aqueous fluids coexisting with enstatite (En) and forsterite (Fo). The values of 1200°C at 5 GPa and 1000°C and 1100°C at 3 GPa are obtained from previous studies [4,5]. **(b, c)** Schematic isothermal sections of Mg_2SiO_4-SiO_2-H_2O system at 1000°C. Stars represent possible H_2O fluids coexisting with Fo and En. At pressures lower than 3 GPa, the aqueous fluids (F) coexisting with En and Fo have Mg/Si < 1, and at pressures higher than 3 GPa, they have 1 < Mg/Si < 2.

configurations, the Mg/Si ratios of aqueous fluids are fixed by the starting material. As we see in Fig. 1(b,c), the fluid compositions can change along the univariant curve. Therefore, in the present experiments, we cannot determine the Mg/Si ratios but can only suggest the chemical ranges of the aqueous fluids coexisting with enstatite and forsterite: Mg/Si < 1 or 1 < Mg/Si < 2.

The present experimental data and the data from previous quench experiments [4] suggest that the Mg/Si ratios of aqueous fluids can change drastically from SiO_2-rich to MgO-rich regime at around 3 GPa (Fig. 2(a)). The origin of such a drastic change remains to be investigated in the future. Liquid H_2O may change its structure under these conditions and cause the change in solution chemistry [6]. This speculation is based on the discontinuity in the pressure dependence of the Raman OH stretching frequency of water at 0.4 ±0.1 GPa at 25 C, 1.0 ±0.1 GPa at 100 C and 1.3 ± 0.1 GPa at 300 C.

The chemical compositions of partial melts of H_2O-saturated mantle peridotite were also characterized by high Mg/Si ratios [7]. The aqueous fluids that coexist with mantle minerals have Mg/Si ratios similar to those found in the partial melts of hydrous peridotite (Fig. 2(b)). Somewhere within the upper mantle these two fluids unite to form a single regime and a continuous change between these two fluids occurs. Therefore, the traditional H_2O-saturated solidus temperature may represent a temperature where the concentrations of silicate components dissolved into aqueous fluids increase drastically and may therefore justify its description as a "practical solidus."
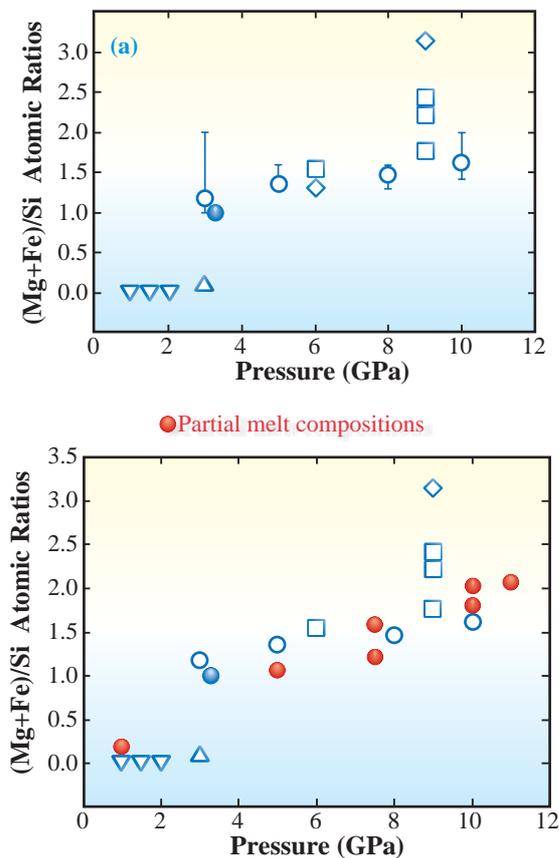
Fig. 2. **(a)** Pressure and Mg/Si ratios of aqueous fluids coexisting with forsterite and enstatite at a temperature range from 1000 to 1100 °C [4]. **(b)** Comparison of aqueous fluid chemistry with partial melt chemistry at 1050 - 1100 °C in a mantle peridotite model of 13.7 weight % H_2O [7].

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