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1 An alternative to alteration and melting processes in the Earth: Reaction between
2 hydrogen (H₂) and oxide components in the Earth in space and time

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7 ABSTRACT

8 Hydrogen-rich and water-rich fluids exert different control on dissolution mechanism of
9 oxide and silicate minerals in the Earth's interior. With Mg-silicate-H₂ fluids, dissolution
10 tends to be incongruent with the $(\text{Mg}/\text{Si})^{\text{fluid}} < (\text{Mg}/\text{Si})^{\text{Mg-silicate}}$ with formation of SiOH and
11 SiH₄ complexes in the fluid (Shinozaki et al., 2013, 2014). In contrast, in Mg-silicate-H₂O
12 systems, Mg-silicate minerals in the mantle (pyroxene and forsterite) dissolve
13 stoichiometrically (congruently) in aqueous fluids to at least 10 GPa pressure. Metasomatic
14 alteration by H₂-rich fluids enriches, therefore, the mantle in SiO₂ compared with alteration
15 by H₂O fluid. This difference becomes increasingly important with mantle depth because
16 the environment becomes more reducing, which results in an increase of H₂/H₂O fluids
17 (Shinozaki et al., 2014). Chemical gradients with depth of the Earth could be affected by
18 increased H₂/H₂O of mantle fluids whereby Mg/Si ratios, for example, will become
19 variable. Silicate-H₂ alteration processes likely also played major roles during the early,
20 core-forming stages of the Earth. Such a process could be responsible for Mg/Si changes in
21 the early silicate Earth.

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23 KEY WORDS: Silicate dissolution, fluid, spectroscopy, mantle, metasomatism

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25 BODY TEXT

26 Characterization of the processes that govern the budget and recycling of H-O-C-N volatiles
27 is central to our understanding of the formation and evolution of the solid Earth, its oceans
28 and atmosphere (Kasting et al., 1993; Holland, 2009). Understanding mass and energy
29 transfer is at the core of these processes where fluid species in the H-O-C-N system

30 govern chemical compositions, physical properties and phase relations of the solid
31 Earth and space and time.

32 The uppermost mantle of the present Earth is so oxidizing that the dominant fluid
33 species is H₂O (Wood et al., 1990). However, with a decrease in oxygen fugacity the
34 H₂/H₂O ratio of a fluid will increase. In fact, the H₂/H₂O ratio would approach unity at
35 deep upper mantle pressure and temperature conditions (≥ 200 km depth) if redox
36 conditions approach those of the Fe/FeO (IW buffer) oxygen buffer. The present
37 upper mantle apparently does become increasingly reduced with depth (Frost and
38 McCammon, 2008), which, therefore, implies increasing H₂/H₂O ratio of mantle fluids.
39 During the early stages of Earth formation, the environment was also more reducing
40 even than that defined with the IW oxygen buffer (O'Neill, 1991). Therefore, H₂ might
41 have been a dominant fluid component in the early Earth.

42 The Mg-silicate solubility in aqueous fluids can reach several mol % under upper
43 mantle conditions (Kawamoto et al., 2004; Mysen et al., 2013). Indeed, second critical
44 endpoints in peridotite-H₂O, where complete miscibility exists between mantle
45 silicate and aqueous fluid, are encountered at depths between 150 and 200 km in the
46 Earth (Mibe *et al.*, 2007). Miscibility is reached when the structure of the silicate in
47 solution and that of coexisting condensed silicate is similar (Mysen, 2012).

48 Even though H₂ is compositionally important and might exert major influence of
49 silicate solution equilibria at mantle temperature and pressures, solubility data for
50 H₂-rich fluids at high pressure and temperature are not common. For example,
51 Mg₂SiO₄ (forsterite) dissolves stoichiometrically (congruently) in aqueous fluids in
52 the Mg₂SiO₄-H₂O system $[(\text{Mg}/\text{Si})^{\text{fluid}} = (\text{Mg}/\text{Si})^{\text{forsterite}}]$ to at least 10 GPa at mantle
53 temperatures (Mibe *et al.*, 2002), whereas in the Mg₂SiO₄-H₂ system periclase (MgO)

54 and an SiO₂-rich fluid are formed $[(\text{Mg}/\text{Si})^{\text{fluid}} < (\text{Mg}/\text{Si})^{\text{forsterite}}]$ at pressures as low as
55 2.5 GPa (Shinozaki *et al.*, 2013).

56 In order to determine why silicate dissolution in H₂ differs from that in H₂O fluid
57 and in order to further our understanding of how H₂ interacts with oxides in the Earth'
58 s interior, Shinozaki *et al.* (2014) employed vibrational spectroscopy to characterize
59 fluid and solid speciation in the system SiO₂-H₂ to 3.0 GPa quenched isobarically from
60 1500 K. The samples (fluid and quartz) were characterized after quenching. Shinozaki
61 *et al.* (2014) observed SiH vibrational modes in the Raman spectra, which they
62 interpreted to reflect SiH₄ species in the fluid. HH vibrational modes assigned to H₂
63 molecules were also reported. The H₂/SiH₄ in the fluid likely exceeded 5. In addition,
64 infrared spectra revealed OH vibrational frequencies consistent with ice VII (2.1 and
65 3.0- GPa) and ice VI (1.1 and 1.4 GPa). In silicate glass and melts equilibrated with H₂
66 gas, SiOH bonding has been reported at the *f*₀₂ of the IW oxygen buffer (Luth *et al.*,
67 1987).

68 The experimental observations (Shinozaki *et al.*, 2013, 2014) imply that the Mg/Si
69 ratio of H₂-rich fluid in the mantle is lower than that in pure H₂O-fluid. Consequently,
70 metasomatic alteration of the Earth' s interior by (H₂O+H₂)-fluids may lower Mg/Si
71 of peridotite mantle compared with alteration by H₂O alone. Such processes can be
72 explained as a consequence of formation of OH-groups via interaction H₂ and SiO₂,
73 whether as ice or as SiOH. This reaction can be written as SiO₂+4H₂=SiH₄+2H₂O. This
74 reaction generates not only unusual silicon hydride species, but also enhances activity
75 of H₂O in the fluid. It also provides another means by which to increase the enhanced
76 H₂O activity and elevates the oxidation state of the mantle. It also promotes changes
77 in metasomatic alteration processes so that residual mantle after alteration and rocks
78 metasomatized by such a fluid will have their Mg/Si ratio changed. Enhanced activity

79 of H₂O also exerts control of the temperature of melting and the chemical composition
80 of partial melts in the Earth's interior (Kushiro *et al.*, 1968). Melting temperature
81 decreases and melts become more silica-rich than at lower activity of H₂O.

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