Water speciation in silicate melts investigated by Raman spectroscopy: Implication for volcanic process

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In addition to temperature, pressure and main chemical components, volatiles exert a strong influence on the physical properties of magmas. In particular, water plays a fundamental role in the dynamics and evolution of magmas in the deep interior and during volcano eruptions. However, water speciation in silicate melts is not fully understood. Infrared and NMR spectroscopy had provided some valuable informations about the H_2O/OH^- speciation. Nevertheless, some issues still remain unsolved about the OH^-/H_2O linkage to the silicate network.

Raman spectroscopy already allows quantifying the proportion of water dissolved in an aluminosilicate melt. Raman spectra are composed of i) a low wave number region that corresponds to vibrations of the silicate network (0-1500 cm^{-1}), and ii) a high wave-number region, which corresponds to the OH^- stretching vibrations and H_2O molecular vibrations (3100-3750 cm^{-1}). We have performed a first set of *in situ* experiments using a micro-furnace at ambient atmosphere. An evolution of the high wave-number region in function of the time and temperature is observed. New Raman peaks can be distinguished, particularly near 3650-3700 cm^{-1}. In this communication, we will present and discuss these observations between water and the silicate network in melts. Raman spectroscopy provides valuable informations to build a general model of water speciation, distinguishing the OH bonds between tetrahedral species and network modifiers for example. Results from this new model confirmed the amphoteric behavior of the water previously reported from polymeric modelling for instance, and opens new ways to study water in melts.

Near neutral seawater pH 3.45 billion years ago

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Many if not most known metabolic pathways had evolved by 3.5 Ga. The environmental conditions under which early evolution took place remain highly controversial and speculative, however. In particular, coeval ocean chemistry has been proposed to range anywhere from slightly acidic or modern like (NaCl type, pH<8.5) to strongly alkaline (Na_2CO_3 type, pH>10). Seawater pH is a key geochemical variable, which is tightly coupled to the composition of the atmosphere, and the nature and intensity of interactions between atmosphere, hydrosphere and lithosphere. Here, we extend the classical paleo-pH proxy method of boron isotopes in marine carbonates to a suite of well-preserved and extensively documented marine ferruginous cherts deposited 3.5 billion years ago. Like with carbonates, the approach is based on the large pH-dependent boron and boron isotope incorporation into solid phases, in particular Fe-(hydr)oxides. The samples are from the Pilbara craton (Western Ausltralia) that inlcude low metamorphic grade deposits showing alternation bands of pure and ferruginous silica, which are interpreted as resulting from chemical precipitation from silicon-rich seawater variably mixed with iron-rich hydrothermal fluids under quiet and probably deep water conditions.

We developed a mathematical model using Monte Carlo simulations coupled with a minimization routine to provide a set of self-consistent pH values of the hydrothermal-seawater mixture corresponding to each analyzed ferruginous band. Despite the large range of initial conditions tested and the methodological uncertainties involved, the simulations robustly converge to pH values ranging from 3.4 to 6.6. Mixing model combined with trace elements (REE) analyses imply circumneutral seawater (pH 7-9) and acidic hydrothermal fluids (pH ~3) discharging at the seafloor.

Altogether, the boron distribution and isotopic signatures of the Pilbara craton cherts are consistent with active buffering of the 3.5 Ga oceans by atmosphere-water-rock interactions not unlike those that have prevented dramatic shifts in seawater pH during the more recent geological past.