

Solubilities of H-O-C-S-Cl volatiles in fluids and silicate melts and their control on magmatic processes

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The fluid-driven ascent of buoyant magma, explosive volcanic eruptions, and mineralizing hydrothermal processes are controlled by the abundances and solubilities of the dominant magmatic volatile components H₂O, CO₂, H₂S/SO₂/SO₃, and Cl in melts and in coexisting fluids and/or sulfide liquids. The efficacy of these processes depends on the presence, quantity, and composition of fluids that are dominantly aqueous; their presence in magma is the cause of excess magmatic and volcanic degassing. The solubilities of these volatiles in melts and fluids are constrained by experimental observations and thermodynamic and empirical modelling, but until recently the experimental constraints have been largely limited to simple binary volatile systems: H₂O-CO₂, H₂O-Cl, H₂O-S.

Recent and emerging experimentally derived solubility data on H-O-C-S-Cl volatile components in basaltic to rhyolitic melts provide fundamentally important constraints and new insights on volatile behavior in complex natural systems. It is well established that trace quantities of CO₂ and/or Cl dramatically reduce the concentrations of H₂O in melt required to force exsolution of one or more fluid phases from volatile-bearing melts. Recent research further demonstrates that the addition of S reduces Cl solubility by 25-30 percent relative in rhyodacitic, trachytic, phonolitic, and a variety of basaltic melts for oxygen fugacities at and above NNO ([1]; see summary in [2]). Hence, the overall influence of adding relatively oxidizing S is to reduce Cl and H₂O solubilities in melts and to enhance the stability of fluid(s) which fosters excess magmatic degassing. Other experimental work shows reduced CO₂ solubilities in various melts and increased solubilities in coexisting fluid at shallow crustal pressures. The (fluid/melt) partition coefficient for CO₂ in haplogranitic melts increases by nearly a factor of ten with the addition of geologically relevant abundances of reduced S²⁻ to silicate melt at oxygen fugacities of NNO-0.4 to NNO+0.3 [3]. Other research [4] at more reducing conditions (NNO-1.6 to NNO-3.2) observed decreased CO₂ solubility in basaltic melt due to dilution of CO₂ in the coexisting fluid by the presence of comparatively reduced C species. Moreover, ongoing research shows that the addition of Cl to a CO₂-H₂O vapor reduces the solubility of CO₂ in a coexisting phonolitic melt by 80 relative percent; this apparently results from the condensation of saline brine from the vapor phase and the formation of two fluid phases [5]. These new experimental observations will be interpreted in light of and applied to processes of fluid exsolution and excess magmatic degassing for subduction-related and other magmas.

[1] Botcharnikov *et al.* (2004) *Chem. Geol.* **213**, 207-225. [2] Webster & Botcharnikov (2011) *Rev. Mineral. Geochem.* **73**, 247-283. [3] Webster *et al.* (2011) *Contrib. Mineral. Petrol.* **162**, 849-865. [4] Morizet *et al.* (2010) *Chem. Geol.* **279**, 1-16. [5] Webster *et al.* (in preparation).

Glacially derived iron as the key driver for biogeochemical processes in Arctic fjord sediments (West Svalbard)

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Glaciers deliver an important fraction of bioavailable iron to the high latitude oceans. This iron is produced by mechanical and microbially enhanced chemical weathering, e.g., oxidation of iron-sulfide minerals in proglacial and supraglacial environments, and may enter the marine system in aqueous form, as (nannoparticulate) Fe-(hydr)oxides, or more stable Fe mineral phases [1]. A fraction of glacial iron is delivered directly to the open ocean by icebergs [1]. However, little is known about the fate of the large iron pool that enters high latitude coastal marine waters, particularly fjord systems, by glacial meltwater runoff.

In two comprehensive sampling campaigns along the Western Svalbard coast in 2010 and 2011, sediment cores were collected at Smeerenburgfjorden, Kongsfjorden, and Van Keulenfjorden along transects from the mouth of the fjords to the tidewater glaciers at the terminal end of the fjords. Results of pore water and solid phase analyses show that the input of glacially derived iron plays an important role in biogeochemical processes in the fjord sediments by controlling the cycling of sulfur and manganese and by providing a large Fe-oxide pool for dissimilatory iron reducers. High solid phase reactive iron concentrations and high dissolved Fe concentrations in the pore water prevail in Kongsfjorden and Van Keulenfjorden, and suggest a benthic flux of dissolved iron from the sediment to the water column. Correspondingly, the concentration and sulfur isotope composition of chromium reducible sulfur (CRS) in the iron-dominated fjord sediments largely reflect the delivery rate and isotope composition of detrital pyrite originating from the adjacent glaciers. These values deviate strongly from the sulfur isotope composition of sedimentary acid volatile sulfur (AVS), which presumably formed from hydrogen sulfide production during organoclastic sulfate reduction, although nearly constant pore water sulfate concentrations with depth in Kongsfjorden and Van Keulenfjorden sediments argue for low production.

Overall, our data point to extensive benthic iron cycling in Svalbard fjord sediments, probably coupled to considerable oxidative sulfur cycling promoted by sediment bioirrigation by the benthic macrofauna. Our findings contribute to the hypothesis that benthic recycling of glacially derived iron in high latitude fjord sediments facilitates the transport of this micronutrient across the fjords while maintaining its bioavailability for fertilization of primary productivity on the adjacent continental shelf.

[1] Raiswell (2011) *Elements* **7**, 101-106.