Gas clathrate hydrate thermodynamics and kinetics: limits on near-surface volatile fluxes for cold terrestrial planetary systems through deep time.

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Gas clathrate hydrates (a gas molecule such as CO_2, CH_4, H_2S, etc. trapped within a cage of water molecules) are thermodynamically stable at low-moderate temperatures and moderate-high pressures, conditions found near the surface of many terrestrial planetary bodies in our solar system, including Earth, Mars, Europa, Titan, Enceladus, and other icy moons. While gas hydrates are often thought of as ephemeral phases in Earth's ocean and permafrost sediments, they can serve as reservoirs for water, carbon, and other volatile phases over millions to billions of years. Hydrate stability zones (HSZ- the depth at which gas hydrates are thermodynamically stable given the P-T conditions) can extend to significant depths [1]. In addition, gas hydrate formation and dissociation rates below the freezing point of water are transport limited, relying on solid-state diffusion of gas to or from the ice-hydrate interface [2]. Slow gas diffusion rates through ice and hydrate at low temperatures result in geologically long-lived metastable gas hydrate reservoirs in the near subsurface.

Geologic models of gas hydrates in planetary systems must thefore consider both thermodynamic and kinetic constraints on clathrate reservoirs to better understand long-term volatile fluxes in the near subsurface. Gas diffusion as well as hydrate formation and dissociation rates are needed to effectively model these complex systems. Using gas hydrate formation and dissociation rates measured in our laboratory, we have developed a coupled thermodynamic and kinetic model of obliquity-driven changes in HSZs on Mars. This model suggests that gas hydrates may provide a significant reservoir for carbon and water within the crust over 10s of km depth. In addition, these hydrate reservoirs may remain thermodynamically stable over geologic timescales, and even when preturbed, may persist as metastable bodies for thousands to millions of years, resulting in significant long-term volatile fluxes. Similar geologic models of gas hydrate reservoirs on Europa, Titan, and Enceladus are underway.

[1] Root and Elwood Madden (2012) *Icarus* doi:10.1016/j.icarus.2011.12.024
[2] Gainey and Elwood Madden (2012) *Icarus* doi:10.1016/j.icarus.2011.12.019

Control of aqueous Mn(II) on Mn(III, IV)-oxide mineralogy and structure

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Mn oxides are among the most reactive mineral phases found in the environment, exerting strong control on the aqueous and solid phase chemistry of soils and sediments through adsorption and redox reactions. Natural Mn oxides are believed to be of predominantly biological origin, representing either primary products of biological Mn(II) oxidation, or secondary products resulting from alteration of primary bio-oxides [1]. Oxidation of Mn(II) by bacteria and fungi has been shown to produce poorly crystalline and highly reactive hexagonal birnessite-type Mn-oxide products [2-5], which readily engage in (abiotic) secondary redox and sorption reactions that may impact their structure and reactivity.

Recent work [3,6] has shown that aqueous Mn(II) may act as a reductant of hexagonal birnessite (which typifies the phyllomanganates that dominate in natural aquatic environments), causing reductive transformation of birnessite (nominally Mn(IV)O2) into the feitknechtite and manganite polymorphs of Mn(III)OOH through interfacial electron transfer from adsorbed Mn(II) to structural Mn(IV) atoms and arrangement of product Mn(III) into Mn(III)OOH, summarized by the comproportionation reaction $Mn(II) + Mn(IV)O_2 + 2\ H_2O \rightarrow 2Mn(III)OOH + 2H^+$. The transformation reaction is time-dependent, involving formation of feitknechtite as the initial metastable transformation product which is catalytically converted into the more stable manganite polymorph during ongoing reaction with Mn(II) [6]. An important finding from this work is that thermodynamic predictions of occurring reactions and transformation have limited merit in these systems due to uncertainty in thermodynamic data of the Mn oxides involved (due to size and composition effects), which necessitates experimental work to assess the occurrence and importance of specific transformation pathways.

The work presented here focuses on the impacts of pH and Mn(II) concentration on occurring transformation reactions, reporting notable changes in system reactivity as a function of these variables. The results point to a potentially major role of aqueous Mn(II) as a control on the mineralogy and structure of environmental Mn-oxides, and as a moderator of the reductive arm of Mn-oxide redox cycling.

[1] Tebo *et al.* (2004) *Annual Rev. Earth Planet. Sci.* **32**, 287-328. [2] Villalobos *et al.* (2003) *Geochim. Cosmochim. Acta* **67**, 2649-2662. [3] Bargar *et al.* (2005) *Am. Mineral.* **90**, 143-154. [4] Webb *et al.* (2005) *Am. Mineral.* **90**, 1342-1357; [5] Santelli *et al.* (2011) *Geochim. Cosmochim. Acta* **75**, 2762-2776. [6] Elzinga (2011) *Env. Sci. Technol.* **45**, 6366-6372.