



Aqueous geochemistry in icy world interiors: Equilibrium fluid, rock, and gas compositions, and fate of antifreezes and radionuclides

Marc Neveu^{a,*}, Steven J. Desch^a, Julie C. Castillo-Rogez^b

^a School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-1404, USA

^b Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA

Received 9 November 2016; accepted in revised form 15 June 2017; available online 22 June 2017

Abstract

The geophysical evolution of many icy moons and dwarf planets seems to have provided opportunities for interaction between liquid water and rock (silicate and organic solids). Here, we explore two ways by which water-rock interaction can feed back on geophysical evolution: the production or consumption of antifreeze compounds, which affect the persistence and abundance of cold liquid; and the potential leaching into the fluid of lithophile radionuclides, affecting the distribution of a long-term heat source. We compile, validate, and use a numerical model, implemented with the *PHREEQC* code, of the interaction of chondritic rock with pure water and with C, N, S-bearing cometary fluid, thought to be the materials initially accreted by icy worlds, and describe the resulting equilibrium fluid and rock assemblages at temperatures, pressures, and water-to-rock ratios of 0–200 °C, 1–1000 bar, and 0.1–10 by mass, respectively. Our findings suggest that water-rock interaction can strongly alter the nature and amount of antifreezes, resulting in solutions rich in reduced nitrogen and carbon, and sometimes dissolved H₂, with additional sodium, calcium, chlorine, and/or oxidized carbon. Such fluids can remain partially liquid down to 176 K if NH₃ is present. The prominence of Cl in solution seems to hinge on its primordial supply in ices, which is unconstrained by the meteoritical record. Equilibrium assemblages, rich in serpentine and saponite clays, retain thorium and uranium radionuclides unless U-Cl or U-HCO₃ complexing, which was not modeled, significantly enhances U solubility. However, the radionuclide ⁴⁰K can be leached at high water:rock ratio and/or low temperature at which K is exchanged with ammonium in minerals. We recommend the inclusion of these effects in future models of the geophysical evolution of ocean-bearing icy worlds. Our simulation products match observations of chloride salts on Europa and Enceladus; Cl chondrites mineralogies; the observation of serpentines, NH₄-phyllosilicates, and carbonates on Ceres' surface; and of Na and NH₄-carbonate and chloride in Ceres' bright spots. They also match results from previous modeling studies with similar assumptions, and systematically expand these results to heretofore unexplored physico-chemical conditions. This work involved the compilation and careful validation of a comprehensive *PHREEQC* database, which combines the advantages of the default databases *phreeqc.dat* (carefully vetted data, molar volumes) and *lhl.dat* (large diversity of species), and should be of broad use to anyone seeking to model aqueous geochemistry at pressures that differ from 1 bar with *PHREEQC*.

© 2017 Elsevier Ltd. All rights reserved.

Keywords: Icy worlds; Antifreezes; Radionuclides; Ammonium minerals; Potassium; Chondrites

* Corresponding author at: NASA Postdoctoral Management Fellow at NASA Headquarters, Washington, DC 20546, USA.
E-mail address: MNeveu@asu.edu (M. Neveu).

1. INTRODUCTION

The bulk densities of most known icy moons and dwarf planets larger than about 250 km in radius, estimated from measurements of their mass and size, are intermediate between those of water ice (918–935 kg m⁻³ depending on temperature; Croft et al., 1988) and chondritic rock (grain density 2800–5000 kg m⁻³, assuming 25% porosity; Britt and Consolmagno, 2003). This suggests icy worlds accreted a mixture of these materials. A plethora of thermal modeling studies, beginning with the work of Lewis (1971), have suggested that radiogenic heating alone can partially melt ice in icy world interiors, producing subsurface liquid that may have persisted over several Gyr in contact with silicates and organics. If so, substantial interaction between liquid water and “rock” (silicates and other solids found in chondrites such as metals, as well as organics of chondritic, nebular, and/or interstellar origin) is expected to have driven the chemical evolution of these objects. The extent of interaction scales with the water-rock interface area, which is higher if rocky cores are fractured or unconsolidated (Neveu et al., 2015a; Roberts, 2015) or if rock is in the form of suspended fines (Neveu and Desch, 2015; Travis et al., 2015). Observational clues of extensive water-rock interaction on icy worlds are building up. Surface salts on Europa may result from such interaction (McCord et al., 1998; Kargel et al., 2000; Zolotov and Shock, 2001; Hand and Carlson, 2015). Salts, aqueously precipitated silica, and H₂ gas seem to be ejected from an ocean inside Enceladus (Postberg et al., 2009; Postberg et al., 2011; Hsu et al., 2015; Waite et al., 2017). On Ceres’ warm surface, a lag deposit from ice sublimation reveals mineral products of aqueous alteration (Rivkin et al., 2011; Ammannito et al., 2016; De Sanctis et al., 2016). Thus, water-rock interaction may have been pervasive in icy world interiors, as predicted by Ransford et al. (1981).

The occurrence of aqueous geochemistry inside icy worlds has major implications for their habitability. The progressive oxidation of reduced mineral assemblages by aqueous fluids generates redox gradients, an energy source widely used on Earth by chemoautotrophic microorganisms (Swan et al., 2011). This energy source, together with liquid water and chondritic organics over geological timescales, may provide a habitat for such lifeforms (Kargel et al., 2000; Shock and Holland, 2007; Vance et al., 2007; Abramov and Mojzsis, 2011; Russell et al., 2014; Holm et al., 2015).

Water-rock interaction may also shape the internal evolution of icy worlds. Constrained by their thermal and geophysical state, it can feed back on their geophysical evolution in several ways (Fig. 1). First, the long-term persistence of subsurface liquid may hinge on its antifreeze content. Many geophysical models have assumed that antifreezes such as ammonia (NH₃) or methanol (CH₃OH) remain in the liquid (Grasset and Sotin, 1996; Desch et al., 2009; Deschamps et al., 2010; Malamud and Prialnik, 2015), despite geochemical model suggestions (Kargel, 1992) that NH₃ could be lost by oxidation to N₂ (Matson et al., 2007; Glein et al., 2009), formation of NH₄⁺ salts, or substitution of NH₄ for K in minerals due

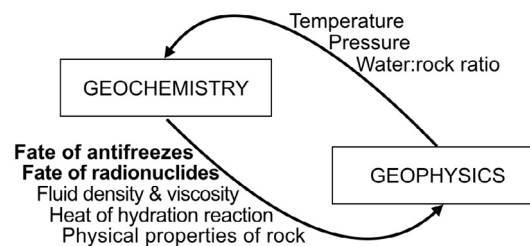


Fig. 1. Feedbacks between geophysical and geochemical processes. Current geophysical models of icy world interiors suggest and constrain settings under which aqueous geochemical reactions can take place. Although some effects of geochemistry on geophysics have been investigated, the fates of antifreezes and radionuclides (bold) and their consequences on long-term geophysical evolution have not been quantified.

to the similar ionic radii of NH₄⁺ and K⁺ (Engel et al., 1994; Fortes et al., 2007; Zolotov, 2009; Castillo-Rogez and McCord, 2010). Similarly, methanol can convert to acetic acid or other small aqueous organics (Shock and McKinnon, 1993), or perhaps even be reduced to CH₄ or oxidized to CO₂ or carbonate. Second, radionuclides such as ⁴⁰K, ²³²Th, ²³⁵U, and ²³⁸U, assumed to be present solely in rock, may be leached into the fluid, changing the internal distribution of heat sources (Kirk and Stevenson, 1987; Engel et al., 1994; Castillo-Rogez and Lunine, 2010). Third, leached minerals enrich the fluid in salts, which may not only decrease the fluid eutectic temperature, but also affect its density and viscosity and therefore its ability to convectively transport heat and mix material (Travis et al., 2012). Fourth, the hydration of mafic silicates is exothermic, and may significantly increase heat production (Cohen and Coker, 2000; Vance et al., 2007; Malamud and Prialnik, 2013; Malamud and Prialnik, 2015), although perhaps not always as hydration can be self-limiting: for example, the formation of secondary minerals of higher specific volume reduces permeability and fluid flow (Palguta et al., 2010; Neveu et al., 2015a). Finally, the alteration of mineral assemblages changes their physical properties, lowering silicate densities and thermal conductivities by 30% and several-fold, respectively (Castillo-Rogez and McCord, 2010; Neveu et al., 2015a).

A few models of water-rich bodies account for the potentially major effects of aqueous geochemistry on icy world geophysics, such as heats of serpentinization (Cohen and Coker, 2000; Vance et al., 2007; Wakita and Sekiya, 2011; Malamud and Prialnik, 2013; Malamud and Prialnik, 2015; Neveu et al., 2015a) and the changes in rock properties following hydration or dehydration (Castillo-Rogez and McCord, 2010; Abramov and Mojzsis, 2011; Neveu et al., 2015a). However, to our knowledge, no published model yet accounts for the geochemical production or consumption of antifreezes, and the possible leaching of radionuclides has been modeled only in geochemically unconstrained cases (Castillo-Rogez and Lunine, 2010). Likewise, the outcomes of water-rock interaction have largely been explored independently of any feedbacks on geophysical evolution (Shock and McKinnon, 1993; Zolotov and Shock, 2001; McKinnon and Zolensky, 2003;

Download English Version:

<https://daneshyari.com/en/article/5783182>

Download Persian Version:

<https://daneshyari.com/article/5783182>

[Daneshyari.com](https://daneshyari.com)