

WATER-SILICATE INTERACTIONS IN ICY WORLD INTERIORS: FATE OF ANTIFREEZES, RADIONUCLIDES, CARBON, NITROGEN, AND SULFUR. M. Neveu¹, S. J. Desch², J. C. Castillo-Rogez³. ¹NASA Postdoctoral Management Program Fellow, NASA HQ, Washington, DC, United States, marc.f.neveu@nasa.gov. ²Arizona State University, Tempe, AZ, United States. ³Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, United States.

Introduction: 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 [1], we explore two ways by which water-rock interaction can feed back on the persistence of oceans: the production or consumption of antifreeze compounds (volatiles and salts), and the potential leaching into the fluid of lithophile radionuclides, a long-term heat source. We also quantify how water-silicate interaction influences the partitioning between fluid and rock of the bioessential elements C, N, and S, as well as their chemical forms.

Methods: We use the *PHREEQC* code [2] to model the interaction of chondritic rock (ordinary [3,4] or carbonaceous [3,5]) with pure water and with C, N, S-bearing fluid [6], thought to be the materials initially accreted by ocean worlds. Simulations are carried out at temperatures, pressures, and water-to-rock ratios of 0–200°C, 1–1000 bar, and 0.1–10 by mass, respectively. Model outputs are solid, aqueous, and gas compositions at chemical equilibrium.

Results: Mineral assemblages are dominated by serpentines (40–75 mass% solids), but also chlorite and saponite clays. Magnetite and sulfides (e.g. pyrite) are also common (≤ 30 mass%). fO_2 is a few log units below the fayalite-magnetite-quartz (FMQ) buffer value if starting with ordinary chondrite, and a few units above FMQ otherwise. This is much more reducing than in much of Earth's oceans today. Solutions are dominated by NH_3 , CH_4 , HCO_3^- , H_2 , Na^+ , and Cl^- , with a pH of 8–12. Outgassing, if any, occurs at a few moles per kg of rock and comprises CH_4 and H_2 .

Fate of Antifreezes: NH_3 is conserved in fluids, unless equilibrium is achieved below 50°C, in which case N is incorporated into clays as ammonium, which substitutes for fully leached potassium. CH_3OH , while a strong antifreeze [7], is too scarce to play a major role. The other prominent antifreezes are chloride salts. Concentrations of dissolved Cl seem to hinge on its primordial supply in ices, which is unconstrained by the meteoritical record. Other salts (e.g. sulfates) have comparatively negligible antifreeze effects [1].

Fate of Radionuclides: Silicates retain Th and U. U leaching would require much higher fO_2 . Crucially, ^{40}K can be leached at high water:rock ratio and/or low T at which potassium is exchanged with ammonium in minerals.

Fates of C, N, and S: A few percent carbonates and/or graphite form, but most C is reduced to methane

if not inhibited by kinetics. Otherwise, metastable organic solutes are the dominant C reservoir [8].

Partial oxidation of the initial NH_3 and organic N to N_2 can occur only if some H_2 escapes the system. Limited protonation of NH_3 to NH_4^+ can occur. NH_4^+ -minerals form at low T . Low-temperature NH_4^+ - K^+ exchange does not seem to be impeded by kinetic effects, but the release of N and S from organics could [9]. The other reactions significantly affected by kinetics involve the reduction of N_2 and sulfate [10,11], but these compounds are not expected to be abundant, as much of N and S should be reduced initially [6,12].

Match to Observations: Our simulation products match reports of chloride salts on Europa and Enceladus [13,14]; CI chondrites mineralogies; the observation of serpentines, NH_4 -phyllosilicates, and carbonates on Ceres' surface [15]; and of Na and NH_4 -carbonate and chloride in Ceres' bright spots [16]. They also match results from previous modeling studies with similar assumptions [8,17–20], and expand them to heretofore unexplored physicochemical conditions.

Database: This work involved the compilation and careful validation of a comprehensive thermodynamic database, distributed with *PHREEQC* at https://www.brr.cr.usgs.gov/projects/GWC_coupled/phreeqc.

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