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EXPERIMENTAL CONSTRAINTS ON THE CHEMICAL EVOLUTION OF ICY SATELLITES.

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Introduction: The inferred internal structure of large icy satellites hinges on the degree to which their rock component has been hydrated: this is due to the low density of hydrated silicates relative to anhydrous silicates. Accordingly, interior models of icy satellites have varied greatly in their estimates of ice thickness due to uncertainties in the density of the underlying rock. Furthermore, as both H_2O (potentially liquid) and organic materials are likely to be present, icy moons have been postulated to be possible hosts for extraterrestrial life; therefore, the stability of organic material under relevant hydrothermal conditions is an important issue.

Background: For example, Ganymede, Titan, and Triton are similar in that high pressure hydrothermal processing of silicates has likely been important in their chemical evolution. With mean densities between 1.8 and 2.1 g/cm^3, compositional models of these bodies incorporate approximately 50-80% silicate minerals by weight, with ices constituting the remaining mass. Moment of inertia constraints on the internal structure of Ganymede demonstrate that differentiation between rock and ice has occurred: such differentiation has also likely occurred in Titan and Triton. During accretion and differentiation (which could be ongoing), the silicate fraction of their interiors would have interacted with aqueous fluids at moderate to high temperatures and pressures. Indeed, a strong magnetic field appears to be generated by Ganymede implying that interior temperatures are high enough (in excess of 1000 K) to maintain a liquid iron alloy in this satellite. High temperature/pressure hydrothermal processing at rock-water interfaces would profoundly influence the bulk mineralogy and internal structure of these bodies: the degree of hydration of the rocky fraction of these bodies has been a source of ongoing uncertainty. Surprisingly few phase equilibria data exist for compositions of relevance to hydrothermal interactions on icy satellites, and thermodynamic calculations have provided the best insights into the interiors of these bodies thus far.

Interestingly, the ~~relevant~~ conditions for hydrothermal interactions on these satellites actually lie at higher pressures than those of hydrothermal flow through terrestrial oceanic crust. This is simply because while gravitational acceleration is considerably lower on icy satellites than on Earth, the extreme thickness of ice on these bodies (up to 1000 km) results in correspondingly higher H_2O pressures.

Experiments: We have conducted a series of experiments designed to simulate hydrothermal processing within icy satellite interiors. We synthesized a model carbonaceous chondrite and allowed it to react with excess H_2O at a variety of temperatures and elevated pressures within a piston-cylinder apparatus. As a model for our starting material, we followed a bulk analysis of the C1 carbonaceous chondrite, Orgueil A, including the relatively large (by terrestrial rock standards) concentrations of sulfur, and organic species of carbon.

Since oxidation state is likely to play an important role in these experiments, we have constructed sample assemblies which allow us to control the fugacity of oxygen, fO_2, and thus oxidation state within our samples. We typically use a buffer assemblage such as Ni:NiO (with an fO_2 close to the self-imposed fO_2 of the solid starting material) or Fe_3O_4:Fe_2O_3 (with an fO_2 elevated by several log units from Ni:NiO).

Our run products are characterized by x-ray diffraction, infrared spectroscopy and electron microprobe results. X-ray diffraction analysis constrains the bulk mineralogy of the sample, infrared spectroscopy is used to determine the structural state of carbon and volatiles within the sample, and the electron microprobe is used to provide compositional information that can be correlated with the textures of our samples.

Results: Our current experiments primarily address three families of reactions which are likely to occur within icy satellites: 1) Formation of hydrated ferromagnesian silicate minerals; 2) Formation of iron-sulfur alloys; and 3) Oxidation of organic materials to carbonate minerals. A summary of our results is illustrated in Figure 1. At low temperatures (below 450°C) reactions may be kinetically hindered and experimental runs under these conditions result in metastable unreacted oxides.

Hydrated Ferromagnesian Silicates: Observable hydration of silicates does not occur in our experiments until approximately 350 °C, at which point a serpentine-structured mineral begins to form in our samples: this is most likely antigorite ($Mg_3Si_2O_5(OH)_4$). We observe little or no dependence on oxygen fugacity in these low temperature runs (at 300 – 350 °C) between samples run with Ni:NiO or Fe_2O_3:Fe_3O_4 fO_2 buffers. The degree of hydration of our samples increases with temperature, and by 400 °C we observe both antigorite and trace amounts of talc ($Mg_3Si_4O_{10}(OH)_2$). At 400 °C, we observe a slight sensitivity to fO_2 in hydrous phase stability: by increasing the oxidation state it appears that the formation of talc is enhanced.

Above 500 °C, complete hydration/reaction of the ferromagnesian silicates occurs as demonstrated by total loss of the x-ray diffraction lines of the starting material oxides from the run products. Also, above 500 °C, we do not observe any evidence for the presence of serpentine minerals, but instead a chlorite mineral, clinochlore ($(Mg,Fe,Al)_6(Si,Al)_4O_{10}(OH)_4$), is evident, as is abundant talc. By 600 °C clinochlore is the dominant hydrous phase for experiments run on the Ni:NiO buffer; however, for experiments run on the Fe_2O_3:Fe_3O_4 buffer, talc is the dominant phase.

Our highest temperature experiments (800 °C) on the Ni:NiO buffer show almost complete disappearance of clinochlore, with talc as the predominant hydrous phase.

Indeed, it appears that increasing the oxidation state of the experiments at lower temperature produces an effect on mineralogy that is analogous to increases in temperature.

Iron-Sulfur Alloys: A rather abrupt change in the chemistry of sulfur in our experiments occurs between 400 and 515 °C. At temperatures below 400°C, no sulfur minerals are observed: indeed, after opening sample capsules synthesized below this temperature, the distinct odor of a sulfur-bearing volatile species was readily detected. However, by 515 °C, our x-ray diffraction patterns unequivocally show the presence of pyrrhotite ($Fe_{1-x}S$, with close to equimolar quantities of Fe and S) .

Carbonate Minerals from Organic Material: As with the formation of pyrrhotite, we observe a drastic shift in the stable form of carbon above 400 °C. At lower temperatures, organic material appears to be largely unaffected by hydrothermal processing: even on the Fe_2O_3:Fe_3O_4 buffer, oxidation does not occur. However, between 400 and 515 °C there is a dramatic shift in stability, as all of the organic material is oxidized and carbonate minerals form. Specifically, our x-ray diffraction patterns show strong evidence for breunnerite $(Mg,Fe)CO_3$, and electron microprobe images reveal cores of essentially pure calcite ($CaCO_3$) in the carbonate crystals (Figure 2).

The carbonate stability field shifts to lower temperatures by a remarkably small amount with changes in fO_2. It may be possible that the stability of organic material can be extended to higher temperatures by buffering at more reducing conditions.

Conclusions: Our results show that at even low temperatures (300 °C), partial hydration of the silicate fraction of icy satellites occurs in the form of serpentine. Above 500 °C, the hydrated silicates are in the form of talc and chlorite, with the fraction of talc increasing with both temperature and oxidation state, until approximately 850 °C, at which point dehydration to enstatite occurs.

We observe strong evidence that iron and sulfur alloy readily (and result in nearly complete alloying of sulfur) from a carbonaceous assemblage to form pyrrhotite. We therefore conclude that icy satellites are likely to possess pyrrhotite-rich cores.

Furthermore, we observe the oxidation of organic materials to form carbonate minerals at high temperatures. This would imply that any deep cycling of organic molecules during differentiation or accretion of icy satellites would oxidize these compounds if sufficiently high temperatures are present. Therefore, the organic fraction of icy satellites could be processed into carbonate-rich zones within the silicate interiors or at the base of icy mantles.

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