

HYDROTHERMAL PROCESSING OF COMETARY VOLATILES — APPLICATION TO TRITON; Everett L. Shock and William B. McKinnon¹, Department of Earth & Planetary Sciences and ¹McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130, USA

Although Triton's density (essentially, its ice/rock ratio) is consistent with an origin as a solar orbiting planetesimal [1], its atmospheric composition (N_2 and CH_4) as well as geological inferences for the presence of NH_3 - H_2O ice [2] are not entirely consistent with a kinetically-inhibited solar composition [3]. Most simply, the latter predicts that nitrogen should appear as N_2 (not NH_3) and carbon as CO (not CH_4). The situation is more complicated, though, as comets (e.g., Halley) contain some NH_3 and CH_4 [4], so a Triton of similar composition will also get its share. However, CO is the dominant carbon-bearing cometary volatile, but is completely absent from Triton's surface and atmosphere (of similar volatility to N_2 , CO should be there).

Now, a captured Triton may have undergone substantial tidal heating as its orbit circularized, depending on the capture mechanism [5-9]. This heating is more than sufficient to melt any cometary ices, and probably results in a molten rock core as well [9]. It is highly probable that Triton underwent extensive chemical evolution during the epoch of tidal heating (which may have lasted more than 500 m.y. [9]), and in particular, dissolved species in Triton's mainly liquid-water ocean may have reacted with hot, subjacent core rocks. CO may be destroyed in such hydrothermal reactions [10]. We have examined the hydrothermal processing of cometary volatiles, and present results here relevant to Triton, and to the "missing CO" question.

The possible consequences of chemical interaction of solutions derived from the melting of cometary material with basalt or solids of other composition can be evaluated with the aid of speciation and mass transfer calculations. These calculations can be conducted for stable or metastable equilibrium states depending on what is known about kinetic barriers within the chemical system of interest. The metastable state we evaluate is based on kinetic inhibition of all reactions leading to the formation of methane and other hydrocarbons. These constraints are consistent with observations of terrestrial geochemical processes occurring at temperatures $\leq 550^\circ C$ in which light hydrocarbons are typically far from equilibrium with other species in the C-H-O-N system [11-15]. Metastable equilibrium among aqueous organic compounds and CO_2 , as well as formation of metastable assemblages which exclude methane, also have been documented in experimental studies [16,17]. Similar constraints were imposed to evaluate the possible abiotic synthesis of organic compounds from CO_2 and N_2 in seafloor hydrothermal systems [14], and the consequences of aqueous alteration of polycyclic aromatic hydrocarbons on meteorite parent bodies [18]. In the present study, the same type of metastable state is assumed to result from the hydrothermal interaction of molten cometary ices with basalt.

As an example of the redistribution of carbon and nitrogen during hydrothermal reactions involving aqueous solutions derived from the melting of cometary material, we consider the fate of formaldehyde (H_2CO) and HCN, two of the simple organic constituents of comets [4, 19]. We consider aqueous species containing 1 or 2 carbon atoms and/or 1 or 2 nitrogen atoms per molecule including: CO, CO_2 , N_2 , NH_3 , formic acid, acetic acid, oxalic acid, acetaldehyde, methanol, ethanol, methanamine, ethanamine, glycine, and urea. These compounds represent a subset of aqueous species for which thermodynamic data can be evaluated at hydrothermal conditions [20-22], but represent many types of possible products. As shown elsewhere [14], metastable equilibrium activities are systematically lower for homologues of the organic species considered here.

Molecular abundances of formaldehyde and HCN from Comet Halley (0.04 and 0.001 relative to H_2O , respectively) were adopted [4]. The value for formaldehyde is intermediate in the possible range. These values provide two mass balance constraints on the calculations. We have also assumed that the activity of H_2O is unity, and have input values of the fugacity of H_2 (f_{H_2}). Calculations were performed as functions of temperature and f_{H_2} at 2500 bars (appropriate for the base of Triton's primordial "ocean"). Variations in f_{H_2} reflect changes in the oxidation state of the system.

Isothermal calculations ($200^\circ C$) as a function of f_{H_2} are presented in Fig. 1. The vertical dashed lines indicate the fugacities of H_2 set by reactions between H_2O and three mineral assemblages: hematite-magnetite (HM), pyrite-pyrrhotite-magnetite (PPM) and fayalite-magnetite-quartz (FMQ). Activities of CO, CO_2 , N_2 and NH_3 , as well as final activities of HCN and formaldehyde are shown in Fig. 1a, and activities of the predominant organic products are shown in Fig. 1b. Note that activities of several minor aqueous organic species are not shown. It can be seen in Fig. 1a that CO_2 and N_2 are the predominant inorganic products at low fugacities of H_2 , but that CO_2 and NH_3 predominate at f_{H_2} values consistent with the PPM and FMQ buffer assemblages. Note that CO is a minor species at all values of f_{H_2} at $200^\circ C$. Comparison of Figs. 1a and 1b shows that the decrease in the activity of CO_2 with increasing f_{H_2} is accompanied by increases in the activities of several organic species, and that acetic acid becomes the predominant carbon-bearing species at f_{H_2} values at -FMQ and above.

If a mineral assemblage can buffer the f_{H_2} imposed on the aqueous solution, then the redistribution of C and N brought on by changes in temperature can be isolated. As an example, results of calculations at values of f_{H_2} set by the FMQ buffer (taken to be representative of hydrothermal alteration of basalt) over the range 200 to $400^\circ C$ are shown in Fig. 2, where it can

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be seen that CO_2 is the predominant carbon-bearing species at all temperatures, but that N_2 predominates over NH_3 only at temperatures $>350^\circ\text{C}$. With increasing temperatures at FMQ-buffered conditions, the activities of several aqueous organic species decrease dramatically, as shown in Fig. 2b. Note that formic acid becomes the predominant organic carbon-bearing species at higher temperatures. Comparison with Fig 2a shows that the activity of CO becomes greater than that of formic acid in about the same temperature range, indicating that CO is the second most abundant carbon-bearing species at higher temperatures.

A fundamental result for Triton is that CO can get largely destroyed during an epoch of tidal heating and hydrothermal alteration. If conditions are more oxidizing than FMQ, then CO_2 is the major product. This is acceptable because CO_2 is involatile under Triton's present surface conditions, and would be most likely locked up in a water-ice clathrate. If conditions are more reducing, then the production of organics may exceed that of CO_2 . Also, even without N_2 and NH_3 as starting materials, these species are important (if not dominant) nitrogen-bearing products, and should be expected on Triton. If N_2 , NH_3 , CO, and CO_2 are included in the starting materials, a picture qualitatively similar to Figs. 1 and 2 will result. Further work will consider in detail a broader range of starting materials, temperatures, and oxidation states.

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