HYDROGEN CHLORIDE AS A SOURCE OF ACID FLUIDS IN PARENT BODIES OF CHONDRITES.

M. Yu. Zolotov[1] and M. V. Mironenko[2]. [1]School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-1404; [2]Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 19 Kosygin Str., Moscow 119991, Russia. E-mails: zolotov@asu.edu, mironenko@geokhi.ru.

Introduction: Chondrites reveal signs of aqueous alteration on their parent bodies [1-4] that occurred under a broad range of pH. The dominance of secondary Mg-phyllosilicates (saponite, serpentine, chlorite) in pervasively altered CI and CM chondrites [1-4] suggests alkaline conditions during deposition [5,6]. However, localized occurrences of phosphates and carbonates in CM carbonaceous chondrites [7] and several other types of chondrites [e.g., 8] may indicate local aqueous processes at low pH [7]. These data show that acidic conditions might have existed inside chondrules, while alkaline environments could have characterized matrices [7]. Here, we argue that early low-pH fluids in asteroids were present as HCl-rich aqueous solutions that formed through eutectic (~186 K) melting of HCl hydrate(s).

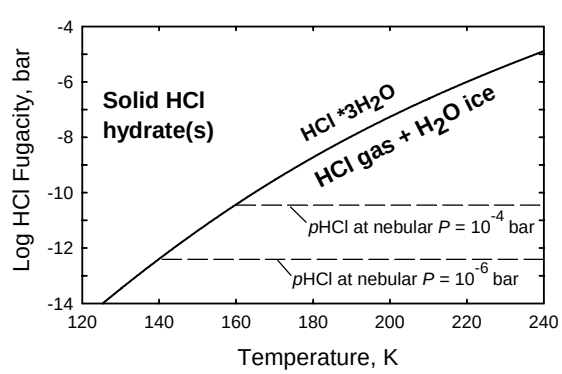
Incorporation of chlorine in chondrites: Chlorine in chondrites is present in sodalite, chlorapatite, halite, sylvite, scapolite, lawrencite, and as an admixture in other phases [2,9]. Although sodalite has been modeled as a high-temperature condensate from nebular gas [10,11], Cl-bearing phases in chondrites exist in minerals formed on parent bodies. In particular, a parent body origin of sodalite in Ca-Al rich inclusions (CAIs), amoeboid olivine aggregates, and matrices from CV chondrites is supported by several studies [2,4,12]. Isotopic (Rb/Sr, Cl/Cl, I/Xe) data indicate a young age for sodalite in CAIs [13-16]. Likewise, apatite and halite in chondrites are products of parent body processes [2]. In the Semarkona (LL3.0) matrix, elevated concentrations of Cl in smectite indicate an asteroidal incorporation of Cl [9]. Therefore, Cl could have been incorporated in parent bodies in a simple condensed form. A delivery of Cl as a component of water ice is consistent with the positive correlation between Cl content in chondrites and the degree of aqueous alteration, which reflects the ice/rock ratio in the primordial composition of parent asteroids. In fact, heavily hydrated CI chondrites have the highest Cl content among chondrites.

In the solar nebula, Cl probably existed mainly as HCl gas, especially after water ice condensed at ~180K [e.g., 11]. Although HCl-grain interactions could have produced chlorides, this process was limited by the low partial pressure (p) of nebular HCl ($p_{HCl} = 10^{-12.4}$ bar, at total nebular pressure 10^{-6} bar, nebular $HCl/H_2 = 10^{-6.4}$, and solar $Cl/H = 10^{-6.7}$ [11]). High temperatures prevented the adsorption of HCl onto mineral grains, and low temperatures led slow reaction rates. No observations in chondrites favor HCl-grain interactions in the solar nebula.

Most nebular HCl gas probably survived the condensation of water ice, although some HCl might have been trapped in water ice. When the temperature reached ~160-140 K, HCl gas condensed as solid $HCl{\cdot}3H_2O$ (Fig. 1). The hydrate may have condensed on nebular mineral grains and water ice particles. The low-temperature adsorption of HCl onto ice surfaces induced the formation of $HCl{\cdot}3H_2O$. An efficient low-temperature interaction of HCl gas with water ice has been demonstrated experimentally with applications to stratospheric processes [17]. It follows that peripheral parts of water ice grains were enriched in the HCl hydrate. Inside ice grains, previously trapped HCl molecules could have been hydrated as well. Further decreases in temperature facilitated $HCl{\cdot}6H_2O$ formation.

Fate of HCl in parent bodies; acid alteration of chondritic materials: Solid grains accreted on parent bodies in a mixture with water ice particles [e.g., 19]. The release of heat from short-lived radionuclides [20]

Fig. 1. The stability of solid $HCl{\cdot}3H_2O$ in equilibrium with water ice as a function of temperature and fugacity of HCl. The solid line corresponds to the equilibrium $HCl{\bullet}3H_2O(cr) = HCl(gas) + 3H_2O(ice, I)$. The horizontal dashed lines depict a range of pHCl in the solar nebula. $HCl{\cdot}3H_2O$ can form at temperatures below ~160K. HCl condensation at ~140K is more likely because of low total P in a low-T nebula. It is assumed that water ice condensed at higher temperatures (180K-160K at nebular pressures of 10^4-10^{-6} bar, respectively) and controlled pH_2O at temperatures of HCl condensation. Thermodynamic data from the FREZCHEM database [18] were used.



increased the temperature of mineral grains and ice particles that were in close contact with minerals. Once the temperature reached ~186 K, which is the temperature of the H_2O-HCl binary eutectic (see [18] for references), a low-pH solution formed. Despite its low bulk content in ice, near-eutectic solutions were concentrated, and thus, reactive.

The non-uniform release of heat in mineral-ice mixtures produced a patchy pattern of melting of HCl hydrates. The slow transfer of heat generated in large rocky objects (e.g., chondrules) generated early eutectic solutions in those objects, followed by low-pH alteration. Likewise, the melting of HCl-rich parts of ice particles in contact with large objects facilitated early alteration. In addition, pockets of eutectic brines could have migrated towards local heat sources (chondrules) and accumulated in them. These inferences are consistent with the preferential alteration of chondrules at low pH [7]. The interaction of chondrules with Cl-rich fluids is also consistent with ubiquitous Cl-bearing phases observed on grain boundaries of olivine in Allende chondrules [21]. Note that the mesostases of most chondrules in Allende indicates a net gain of Cl [2].

Fine-grained particles in matrices altered faster than chondrules owing to their larger surface area. This caused faster neutralization of solutions in matrices [7]. Rapid low-pH dissolution of amorphous material in matrix, as well as kamacite, favored neutralization. Low rates of alteration at sub-zero temperatures would have been compensated by high activities of H^+ in near-eutectic solutions. As the temperature increased, the pH increased because of dilution caused by ice melting, and the release of cations (Fe^{2+}, Mg^{2+}, Ca^{2+}, Al^{3+}) during dissolution of minerals and glasses.

The formation of silica in many chondrites could be related to early low-pH alteration. Amorphous silica marks early stages of acid weathering (pH < ~3) of mafic silicate rocks and dissolves as pH increases [e.g., 22,23]. These observations are consistent with the low solubility and slow dissolution of amorphous silica in acids [24,25]. The presence of silica in several mildly aqueously altered ordinary chondrites (Sharps, Mezö-Madaras, Bishunpur [2]) may indicate an early cessation of aqueous alteration that began at low pH. The absence of silica in heavily altered CM and CI chondrites may reveal its dissolution in neutral to alkaline fluids that developed at advanced stages of alteration.

Summary: A parent body origin of Cl-bearing minerals and Cl-H_2O correlation in chondrites imply incorporation of Cl in a non-mineral form, such as HCl hydrates. Heating in parent bodies led to the formation of acidic HCl-H_2O eutectic solutions that altered chondritic materials in patchy patterns. The formation of amorphous silica and mobility of P and Al observed in chondrites signify early alteration at low-pH and low-temperature. Subsequent ice melting, dilution, and neutralization of solution led to the dissolution of silica and formation of phyllosilicates at alkaline conditions.

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