HIGH-TEMPERATURE HYDROGEN CHLORIDE RELEASES FROM MIXTURES OF SODIUM CHLORIDE WITH SULFATES: IMPLICATIONS FOR THE CHLORINE-MINERALOGY AS DETERMINED BY THE SAMPLE ANALYSIS AT MARS INSTRUMENT ON THE CURIOSITY ROVER IN GALE CRATER, MARS.

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Introduction: Hydrogen chloride releases above 500 °C occurred in several samples analyzed by the Sample Analysis at Mars (SAM) evolved gas analyzer on the Curiosity rover in Gale crater. These have been attributed to reactions between chlorides (original or from oxychlorine decomposition) and water [1]. Some of these HCl releases that peaked below the melting temperature of common chlorides did not co-evolve with oxygen or water, and were not explained by laboratory analog work (Figure 1) [1]. Therefore, these HCl releases were not caused by $MgCl_2$ or soley due to reactions between water and melting chlorides. The goal of this work was to explain the HCl releases that did not co-evolve with oxygen or water and occurred below the melting point of common chlorides, which have not been explained by previous laboratory analog work. This work specifically evaluates the role of evolved SO_2 in the production of HCl.

Materials and Methods:

NaCl was chosen as a martian analog chloride as NaCl was detected in soil and rock samples in Gale crater [2]. Sulfates examined in this work included synthetic Mg sulfate hydrate (EMD), kieserite, epsomite, melanterite/rozenite, and gypsum. Not all sulfate phases were detected by the Chemistry and Mineralogy X-ray diffractometer (XRD), but Fe-, Mg- and Ca-sulfates were detected by SAM in Gale crater samples [3].

A sodium chloride solution was added to each powdered sulfate (50:50 by weight) in a 150 µL alumina crucible. The sample crucible and an identical empty reference crucible were analyzed in a Labsys EVO differenetial scanning calorimeter/thermal gravimeter connected to a ThermoStar quadrupole mass spectrometer configured to run similarly to the SAM instrument. The furnace was set to a pressure of 30 mbar with a flow rate of 3 sccm helium. Samples were heated from 30 °C to 1000 °C at a rate of 35 K/min.

Results and Discussion:

Laboratory experiments:

NaCl analyzed by itself did not release SO_2 or HCl and had a DSC endotherm indicative of melting at 790 °C. The sulfates also did not produce HCl when analyzed by themselves (Figure 2).

The NaCl mixture with synthetic Mg sulfate hydrate produced an HCl release with a peak at 640 °C, and did not co-evolve water or SO_2 from Mg sulfate (Figure 2). The HCl release in this mixture occurred at the same temperature as a DSC endotherm, indicating NaCl melting, catalyzed by the presence of Mg sulfate. Mg sulfate decreased the NaCl melting point and made it more reactive with water in the system (rxn 1).

NaCl mixed with kieserite produced HCl release peaks at 635 °C and 909 °C (Figure 2). The first HCl release co-occured with an endotherm, indicating increased reactivity of NaCl with water due to melting. The second HCl peak occurred at approximately the same temperature as a SO_2 release (peak at 961 °C). This HCl release was caused by a reaction between Na_2O and SO_2 (rxn 2) [4, 5], which increases HCl production by consuming the product of rxn 1 and shifting it to the right.

$$H_2O_{(g)} + 2NaCl_{(s,\,l)} \rightarrow 2HCl_{(g)} + Na_2O \qquad [1]$$

$$SO_2 + 1/2O_2 + Na_2O + NaCl_{(s,\,l)} \rightarrow Na_2SO_{4(s,\,l)} \qquad [2]$$

Evolved SO_2 and O_2 can be sourced from sulfate decomposition. The O_2 is then consumed via rxn 2.

NaCl mixed with epsomite produced broad HCl releases with peaks at 648 °C and 833 °C (Figure 2). The first peak co-occurred with a DSC endotherm and was attributed to increased NaCl reactivity with water due to melting. The second peak occurred at a similar temperature as an SO_2 release (peak at 864 °C; rxns 1-2). Melanterite/rozenite mixed with NaCl produced an HCl release peak at 642 °C (Figure 2). This release co-occurred with a small, broad endotherm and also co-evolved with an SO_2 release. In this case, the HCl release was likely caused by reactions 1-2.

NaCl mixed with gypsum did not produce an HCl release. This could be caused by two scenarios: 1) Ca sulfate does not significantly depress the melting point of NaCl or, 2) the SO_2 release from Ca sulfate occurs at too high a temperature for reactions 1-2 to take place.

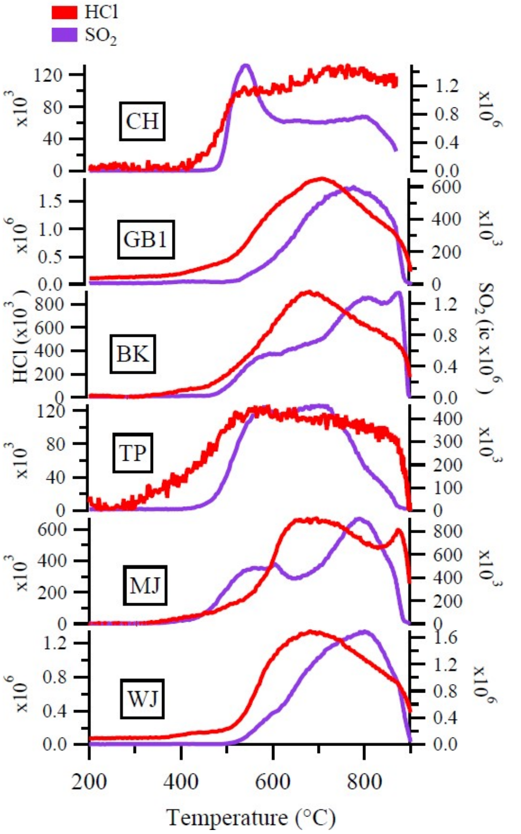
Laboratory mixtures will be analyzed using heated XRD in order to fully understand reactions taking place during heating.

Comparison to SAM data:

Several SAM samples produced HCl releases that peaked below the melting point of common chlorides and did not co-evolve with water or oxygen (Figure 1). These HCl releases occured at similar temperatures as SO_2 releases, suggesting that reactions 1-2 might be taking place or sulfates depressed the melting point of chlorides, making them more reactive with water.

Conclusion: NaCl was mixed with various sulfates and analyzed in a SAM-like laboratory analog instrument in order to better understand the cause of the high temperature HCl releases observed in SAM data. The results from this work suggest that sulfates present in SAM samples 1) depress the melting point of common chlorides, making them more reactive with water, and/or 2) SO_2 from sulfate decomposition reacts with Na_2O via reactions 1-2, increasing HCl production.

Understanding the reaction between chlorides and sulfates is especially important as Curiosity approaches the sulfate-bearing unit, which contains Mg sulfates as indicated by orbital spectral data [6]. This work also reinfornces the idea that chlorides are present in Gale crater samples. The presence of chlorides, in addition to oxychlorines, in Gale crater samples can provide information about the Cl cycle on Mars. Constraints on the type of chloride present in these samples can provide information about past aqueous and diagenetic conditions due to their different solubilities and formation conditions.



[1]

Fig. 1. HCl and SO_2 releases from samples analyzed by the SAM instrument. CH=Confidence Hills, GB1=Gobabeb 1, BK=Buckskin, TP=Telegraph Peak, MJ=Mojave, WJ=Windjana.

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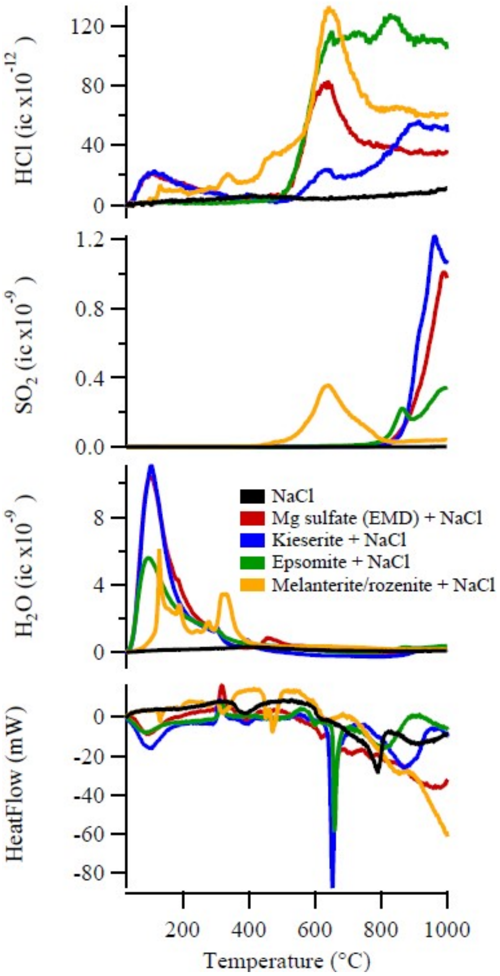

Fig. 2. HCl, SO_2, H_2O, and DSC Heatflow from mixtures of NaCl with sulfates.