

MINERALOGICAL COMPOSITIONS OF THE EVAPORITES AT LEWIS CLIFF ICE TONGUE, ANTARCTICA: A POTENTIAL MARTIAN ANALOG T. Liu and D. L. Bish, Department of Geological Sciences, Indiana University, 1001 E. 10th St., Bloomington, IN 47405, USA email: tingliu@indiana.edu.

Introduction: Numerous recent orbital and rover studies of Mars have documented the occurrence of a variety of hydrated minerals commonly associated with evaporite deposits, e.g., hydrated varieties of Mg-, Ca- and Fe- sulfates such as gypsum, epsomite, and jarosite. Evaporite minerals are often used to document the evolution of natural waters resulting from past water-rock interactions, but these minerals form on Earth under a wide range of conditions. Formation environments include a wide range in water:rock ratios and temperatures. As emphasized by [1], the formation of evaporite minerals under low-temperature conditions at low water:rock ratios is one of the least understood scenarios but is perhaps most applicable to evaporite formation on Mars. We have continued study of deposits from the Lewis Cliff Ice Tongue (LCIT, 84°34'161°39'E, elev. 1837m), Antarctica, originally begun by [2] and greatly expanded by [1]. These deposits are potential analogs to evaporite mineral formation in a cold, comparatively dry environment. Harvey et al. [1] suggested that the LCIT evaporite deposits may have formed through a combination of evaporation, sublimation, and freezing, and, in particular, evaporative wicking can proceed with only small quantities of water and at low temperatures. More recently, Socki et al. [3] measured anomalously high $\delta^{34}\text{S}$ values in Na-sulfate minerals (mirabilite, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and thenardite, Na_2SO_4) from LCIT evaporite mounds. These very high sulfur isotopic values suggested involvement of bacterial sulfate reduction, whereas oxygen isotopic compositions were consistent with contributions from adjacent brine lake waters. They concluded that these results were consistent with evaporation of concentrated brines (possibly by evaporative wicking) following bacterial sulfate reduction, perhaps at the bottoms of the brine lakes. In order to refine these models of low-temperature evaporite mineral formation in Antarctica, we have continued mineralogical analyses of a variety of evaporite deposits on the LCIT.

Materials and Methodology: Evaporite samples were collected on the Lewis Cliff Ice Tongue [1] from both evaporite mounds and surface efflorescences during the 2005-06 field season. In addition, alteration products on the mound surfaces were collected; these minerals document an ongoing process of mineral alteration, dissolution, and precipitation. All samples were stored in a -20°C

freezer until time of analysis, and sample preparation was done in a cold room at 4°C, using pre-cooled preparation equipment (i.e., mortar and pestle, spatulas, specimen mount, etc.). X-ray powder diffraction (XRD) measurements used a Bruker D8 Advance diffractometer with Cu K α radiation and a SolX energy-dispersive detector, and measurements were done under ambient room temperature immediately after mounting the specimens. Relative humidity (RH) at the time of field collection was ~50%, so the environment surrounding samples during XRD data measurement was maintained at 50%. Specimens were measured using rapid scan rates to minimize the possibility of modification at room temperature, and repeated measurements were made to assess the progress of any phase changes.

Results: Samples collected from three areas within the LCIT showed distinct mineralogies. Based on location and mineralogy, they fall into three categories, namely (1) Na-sulfate (mirabilite and thenardite); (2) Na-borate (borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and qilianshanite, $\text{NaHCO}_3 \cdot \text{H}_3\text{BO}_3 \cdot 2\text{H}_2\text{O}$); and (3) Na- bicarbonate (nahcolite, NaHCO_3).

Sample Description: Samples collected from the core of the evaporite mounds were composed entirely of mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), with lesser amounts of thenardite (Na_2SO_4). Based on repeated XRD measurements made at 50% RH, it appears that the core of the mounds is mirabilite and that thenardite forms as a result of dehydration at 50%RH. Further research on the stability of mirabilite indicates that the mineral begins to dehydrate at room temperature at RH values <85-89%. Mirabilite dehydration is not readily reversible and, once dehydrated to thenardite, it was usually not possible to rehydrate the material to mirabilite, even at RH values up to 95%. Given ambient conditions at the LCIT, it appears that mirabilite will only be stable when "armored" in the center of mounds. Materials on the surface of the mounds contain these two Na-sulfate minerals, along with minor nahcolite. Nahcolite apparently formed as a low-temperature product of mirabilite dehydration into thenardite. The dehydration reaction involves a large volume decrease, breaking apart mirabilite crystals and generating thenardite powder with greatly increased surface area. Subsequent hydration of thenardite by snow involves a very large heat of hydration, which has the potential to create liquid water. In this process, nahcolite is formed from

dissolved Na^+ and HCO_3^- . Indeed, nahcolite is very common on the altered mound surfaces. The morphology of many of the nahcolite occurrences, as water-clear very fine needles on the surfaces of mounds, suggests that they are neoformed.

The primary evaporite minerals at Site C include nahcolite and borate minerals (borax and euhedral qilianshanite). All of these minerals occurred only on the exterior of the mounds and were not yet identified in mound interiors. The coexistence of bicarbonate and borate minerals at Site C demonstrates that the cores of some mounds *must* contain borate minerals in addition to mirabilite. The existence of borate minerals alters our interpretation of evaporite mineral formation at LCIT but it also has the potential to shed insight into concentration and formation processes. The source of B and the Na, S, and B concentration mechanisms require further study.

Samples from Site F all contain nahcolite, occurring in a pockmarked surface. As the assemblage is composed of only a single phase, nahcolite, these evaporites may have evaporated and crystallized directly from Na-rich saline water. Alternatively, these pockmarked mounds may represent complete alteration of pre-existing Na-sulfate mounds. Figure 1 outlines the stability fields of five sodium carbonate/bicarbonate species in terms of fugacity of CO_2 and H_2O activity. This figure shows that nahcolite can form over a wide range of $a(\text{H}_2\text{O})$ as long as $P(\text{CO}_2)$ is greater than $\sim 10^{-3.8}$ at lower activities of H_2O (atmospheric $P(\text{CO}_2) = 10^{-3.5}$). The diagram also illustrates that nahcolite has a wide

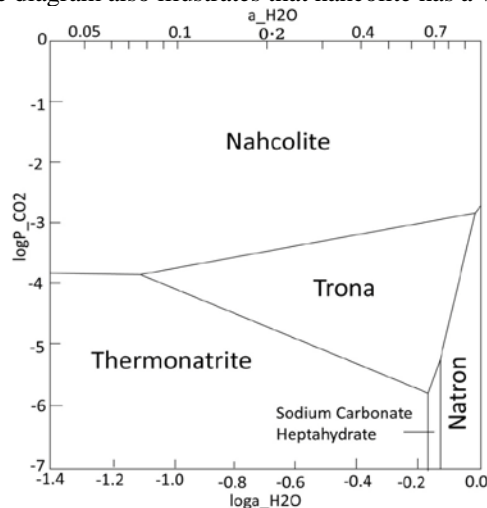


Fig. 1 Relationships in the Na_2CO_3 - NaHCO_3 - H_2O system at $T=25^\circ\text{C}$ and $P=1$ bar (trona: $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$; Natron: $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$; Thermonatrite: $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$; Sodium Carbonate Heptahydrate: $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$) (from [4])

stability range at elevated $P(\text{CO}_2)$ values. Of the phases on this figure, Nahcolite was typically observed in the evaporite mounds, and trona and natron were occasionally observed in surface efflorescences.

Origin of LCIT evaporite deposits: Oxygen isotope studies of sulfate minerals in the Antarctic Dry Valleys clarify the origins of sulfate as from both sea salt and biogenic sulfur aerosols [5]. Dort and Dort [6-8] also suggested that mirabilite deposits in Antarctica are concentrates from the transportation of sea spray and saline snow. Similarly, isotopic data reported by [3] were consistent with a genesis related to microbial sulfate reduction and evaporative concentration. The occurrence of B-containing minerals illustrates that the process(es) involved in mound formation are probably more complex. In addition to the identification of nahcolite and borax as in [9], the discovery of qilianshanite in the mounds is noteworthy. Qilianshanite was first discovered in the Juhongtu boron deposit, China, and was presumed to form in paleo-spring waters rich in B and Na or by metasomatism of Na-carbonate minerals [10]. This assemblage of B-containing minerals represents the typical natural assemblage [11]. The entire assemblage is consistent with evaporative concentration by capillary action, possibly involving freezing and subsequent sublimation, a process that could also occur on Mars, given sufficient liquid water to concentrate solutes. However, geothermal water is often involved in formation of brines that produce borate minerals [11], and borate deposits typically include Na-sulfate/carbonate/bicarbonate minerals, suggesting that the evaporate deposits at LCIT are not the products of simple evaporative concentration of groundwater but also involved input(s) from other waters.

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