

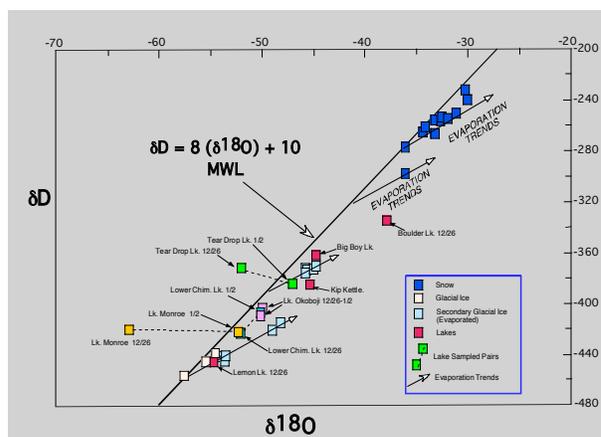
## STABLE ISOTOPE SYSTEMATICS OF CRYOGENIC EVAPORITE DEPOSITS FROM LEWIS CLIFF ICE TONGUE, ANTARCTICA: A MARS ANALOG.

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**Introduction:** Discovery of extensive evaporite deposits on the planet Mars by martian orbiter and landed rover missions suggest that water and/or cryogenic processes played a critical role in their formation during some stage of the martian past. Of particular interest within the context of this work is the recent in-situ identification of hydrated sulfate minerals [1-3]. As evaporite mineral deposits are known to form under a wide variety of different terrestrial geological and geochemical conditions, crucial to deciphering martian data is understanding how similar materials formed in terrestrial environments. In this work we report results of stable isotope analyses of a variety of samples collected from evaporite mounds and associated moraine materials from the Lewis Cliff Ice Tongue, Antarctica. These evaporite mounds consist almost entirely of two related Na-sulfate minerals, mirabilite ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) and thenardite ( $\text{Na}_2\text{SO}_4$ ). Preliminary results of our expedition to Lewis Cliff have previously been reported [4]. In addition to the sulfate minerals we also collected liquid water from several shallow moraine lakes, glacial ice, secondary glacial ice (ice lenses), and precipitation (snow). Isotope analyses of these samples include  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of precipitation, ice, and lake water, and  $\delta^{34}\text{S}$ ,  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  of the sulfates. Our data suggest that secondary glacial ice and moraine lake water influenced the growth of these evaporite minerals and mineral formation likely occurred sub-glacially.

**Results and Discussion:** O and H isotopes of water and ice were extracted by equilibration on a gas bench and analyzed via continuous flow isotope ratio mass spectrometry. All data are reported relative to V-SMOW and are plotted in figure 1.  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of precipitation (snow), glacial ice, secondary glacial ice (ice lenses) and moraine lake water range from -64.2 to -29.7‰, and -456.0 to -231.7‰, respectively. With a few exceptions all samples fall on or to the right of the Meteoric Water Line (MWL). Snow (local precipitation) is always isotopically heavier than glacial ice. We interpret this as an indication that glacial ice originated at higher latitudes or

higher altitudes and migrated to its present location, consistent with the geography of Lewis



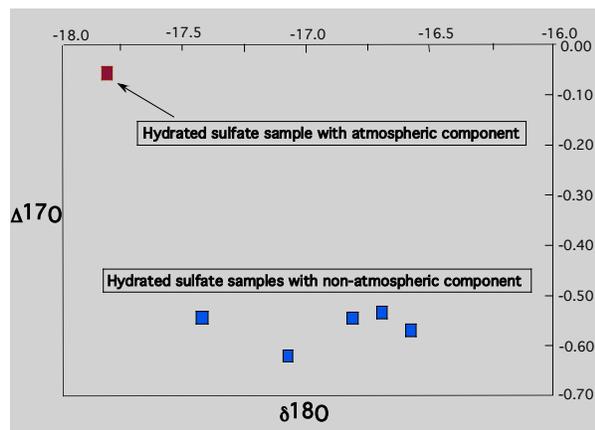
**Figure 1.**  $\delta^{18}\text{O}$  vs.  $\delta\text{D}$  of precipitation (snow), ice, and lake water from Lewis Cliff, Antarctica. The meteoric water line (MLW) follows the trend  $\delta\text{D} = 8(\delta^{18}\text{O}) + 10$ .

Cliff Ice Tongue, whereas snow originated from more coastal sources. Glacial ice tends to fall on the MWL, while secondary glacial ices (ice lenses) tend to fall to the right of the MWL, indicating an evaporation trend for these ices. The secondary ices (ice lenses) occur beneath the large evaporite mounds where the sulfate minerals are concentrated. Likewise, our data suggest that moraine lake water is derived from the glacial ice with some local mixing of a snow component and also underwent evaporation. This mixing with local precipitation is most pronounced in Boulder Lake and Big Boy Lake.

Na-sulfate minerals collected from the evaporite mounds at Lewis Cliff were analyzed for oxygen isotopes. Samples were prepared as  $\text{BaSO}_4$  and analyzed for  $\delta^{18}\text{O}$  using TCEA via continuous flow mode and for  $\Delta^{17}\text{O}$  using laser fluorination via dual inlet mode by isotope ratio mass spectrometry [5]. All data are reported relative to V-SMOW and are plotted in figure 2.  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values range from -16.6 to -17.1‰, and from -0.06 to -0.61‰, respectively.  $\Delta^{17}\text{O}$  values

were calculated by using the following equation:  $\Delta^{17}\text{O} = \delta^{17}\text{O} - [(1 + \delta^{18}\text{O})^{0.52} - 1] \times 1000$ . With one exception, these data tend to plot within a narrow  $\Delta^{17}\text{O}$  range between  $\sim -0.50$  and  $-0.60\text{‰}$ , labeled “Hydrated sulfate samples with non-atmospheric component” in figure 2. We interpret these negative values as indicative of sulfate oxygen derived entirely from that of Antarctic water. Glacial water is expected to have a small negative  $\Delta^{17}\text{O}$  value due to a smaller than 0.52 evaporation kinetic fractionation slope ( $\theta = 0.511$ ) [6], plus an augmentation by Rayleigh Distillation (all mass-dependent). Atmospheric sulfate components typically show positive  $\Delta^{17}\text{O}$  values. This is based on O-17 anomalies introduced during oxidation by atmospheric  $\text{O}_3$  or  $\text{H}_2\text{O}_2$  that is ultimately passed on to the oxidation products (in this case sulfate minerals). The one sample that does show an atmospheric component (labeled in figure 2) occurred in the field as a white sulfate surface coating on a boulder (Ely Ledges) adjacent to but separate from the evaporite mound where the other samples were taken and appears to have formed during subaerial exposure.

$\delta^{18}\text{O}$  values are highly negative, consistent with an oxidative weathering origin in an Antarctic setting (Lewis Cliff Ice Tongue).



**Figure 2.**  $\delta^{18}\text{O}$  vs.  $\Delta^{17}\text{O}$  of hydrated sodium sulfates with an apparent atmospheric component (red square) and non-atmospheric components (blue squares) from an evaporite mound at Lewis Cliff Ice Tongue, Antarctica.

$\delta^{34}\text{S}$  measurements were made on the Na-sulfate samples. Like oxygen, sulfur isotopes also vary within a narrow range ( $+48.8$  to  $+49.3\text{‰}$  (CDT)) and are extremely enriched in  $\delta^{34}\text{S}$ . We

interpret these extreme enrichments in  $\delta^{34}\text{S}$  as the result of oxidative weathering and subsequent reduction sub-glacially. This reduced sulfur could be derived from the surrounding terrain near Lewis Cliff where known deposits of Paleozoic shale and coals exist within the glacial till. Alternatively, the extreme sulfur values could be attributed to bacterial-mediated sulfate reduction, similar to what was observed in sulfur springs found in the Canadian High Arctic [7]. Under this scenario the parent sulfate (originally marine anhydrite or gypsum) is buried sub-glacially and is reduced to sulfide by bacteria under anaerobic conditions. The sulfide is in turn oxidized back to sulfate when it rises to the surface. However, the lack of surface expressions of sulfur springs and no apparent sulfide minerals or  $\text{H}_2\text{S}$  within the moraine lakes at Lewis Cliff makes this a less attractive model. Nevertheless, it is possible that all bacterial activity occurs well beneath the evaporite mounds sub-glacially.

**Conclusions:** The O and H isotope composition of water and ice from the Lewis Cliff Ice Tongue, Antarctica, and the multiple O isotope compositions of Na-sulfate minerals suggest that the source of the evaporite fluids that formed the sulfate minerals originated from the moraine lakes and/or secondary glacial ice lenses. The O isotope composition of Na-sulfate minerals suggest they formed mostly from oxidative weathering except for one sample of a surface sulfate that has a minor atmospheric secondary sulfate component. S isotopes suggest that sulfate minerals associated with the evaporite mounds formed from oxidation of local sulfide-bearing rocks (glacial till), however extreme isotope enrichments could indicate that bacterial-mediated sulfate reduction may have played a role in their formation. Recent discoveries of sulfate-rich evaporite deposits on the planet Mars means that understanding the processes of cryogenic sulfate formation in terrestrial settings, like the Lewis Cliff Ice Tongue, will be of significant value when interpreting martian data.

**References:** [1] Wang, A., et al, *GCA*, **70** (2006), 6118-6135. [2] Bibring, J., et al, *Science*, **307** (2005), 1576-1581. [3] Gendrin, A., et al, *Science*, **307** (2005), 1587-1591. [4] Harvey, R. P., et al, *LPSC XXXVII* (2006), Abstr.1044. [5] Bao, H. M., et al, *JGR* **111** (2006), D16301. [6] Angert, A., et al, *GCA*, **68** (2004), 3487-3495. [7] Grasby, S. E., et al, *Astrobiology*, **3** (2003), 583-596.