

**REAL-TIME XRD-XRF AT A MARS-ANALOG SULFATE SITE IN LEADVILLE, COLORADO, USING A CHEMIN-HERITAGE INSTRUMENT.** S. J. Chipera<sup>1</sup>, P. Sarrazin<sup>2</sup>, L. Alcantar-Lopez<sup>1</sup>, D. T. Vaniman<sup>3</sup>, D. L. Bish<sup>4</sup>, D. Blake<sup>5</sup>, & G. Chiari<sup>6</sup>. <sup>1</sup>Chesapeake Energy Corporation, 6100 N. Western Ave, Oklahoma City, OK, 73118, Steve.Chipera@CHK.com, <sup>2</sup>inXitu Inc., Mountain View, CA, <sup>3</sup>Earth & Env. Sciences, Los Alamos National Laboratory, Los Alamos, NM 87545, <sup>4</sup>Dept. of Geological Sciences, Indiana University, Bloomington, IN 47405, <sup>5</sup>NASA Ames Research Center, Moffett Field, CA, <sup>6</sup>Getty Conservation Institute, Los Angeles CA 90049

**Introduction:** Terrestrial sulfide alteration localities hold considerable interest for Mars-analog mineralogy studies (e.g., [1,2]). Leadville Colorado, located at 3094 m elevation in the Rocky Mountains, provides a sulfide alteration setting with a unique and diverse source of sulfate minerals [3]. Extensive mine spoil piles contain pyrite that has been oxidizing for over a century. The resultant sulfates are highly soluble and were leached from the spoil piles to reprecipitate upon evaporation. In particular, sulfates are found thickly deposited on wooden structures where the wood wicks the sulfate solutions to exposed surfaces that are protected from the elements beneath old mine structures.

The sulfate minerals identified have been diverse, consisting of many of the hydrates of Mg- and Fe<sup>+2</sup>-sulfates (4, 5, 6, 7 H<sub>2</sub>O), Fe<sup>+3</sup>-sulfates such as copiapite and fibroferrite, gypsum, and various other sulfates containing Mn, Zn, and Al [3]. Other hydrates of the common sulfates may be present seasonally as alteration products, in response to changing ambient relative humidity and temperature [3].

**Methods:** The sulfate mineralogy observed at Leadville was reexamined using a real-time portable X-ray diffraction (XRD)-X-ray fluorescence (XRF) instrument based on the MSL CheMin concept. Terra (Fig. 1) is a commercially available, self-contained field-portable instrument. Samples were lightly ground (<150µm) and loaded into a piezoelectric cell that vibrates the sample to move the particles within the X-ray beam (Fig. 2). This CheMin-heritage instrument allows for rapid (minutes) identification of minerals, although longer data-collection times are required for complicated mixtures.

**Results:** Figure 3 shows the XRD pattern of a mineral identified on-site as melanterite (FeSO<sub>4</sub>•7H<sub>2</sub>O). When returned for analysis on a laboratory XRD instrument, the sample had already altered to >50% siderotil (FeSO<sub>4</sub>•5H<sub>2</sub>O) even though it was stored in sealed, double Ziploc bags. Sulfate minerals show considerable variability in their hydration states, with many of the more-hydrated phases responding rapidly to changes in relative humidity [4]. Several samples identified by Terra as epsomite had complete-

ly altered to starkeyite and hexahydrite by the time they were returned to the laboratory.

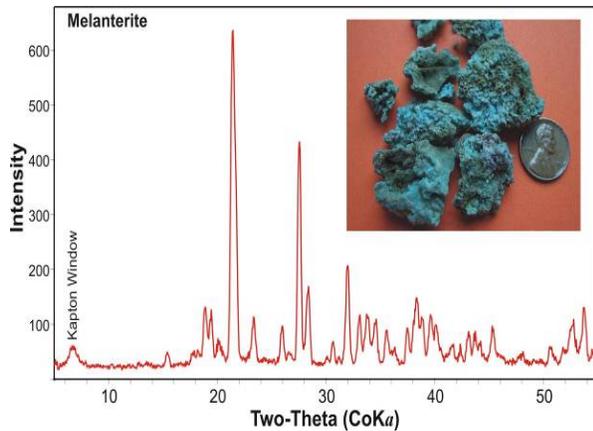


**Figure 1: Terra deployed on site in Leadville, CO.**



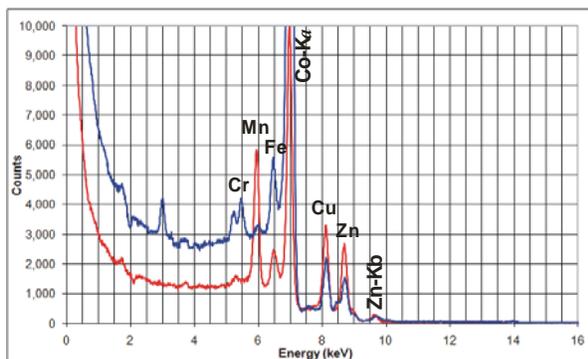
**Figure 2: Loading sample into the piezoelectric-actuated cell.**

The Terra instrument is capable of obtaining XRF information in addition to diffraction data. However, the XRF capability of the instrument has not yet been optimized and a significant background contamination of Fe, Cu, and Zn originating from hardware components must be subtracted from the collected data. As analyses were conducted in atmosphere, air absorption of the lighter, and geologically important elements, such as Na, Mg, Al, and Si, is significant. However, the additional chemical capability proved to be extremely important in distinguishing the chemical species of isostructural sulfate minerals.

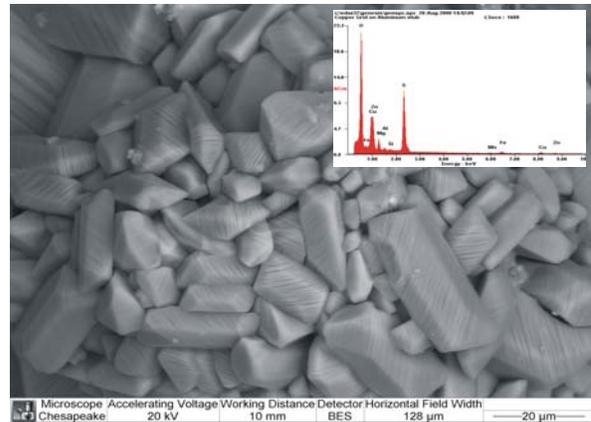


**Figure 3: XRD pattern of melanterite collected on site at Leadville, CO.**

Common cations composing the sulfate minerals at Leadville are Mg, Fe, Zn, Cu, and Mn. The sulfate deposits are seldom single minerals and are normally polyphase mixtures. Even individual minerals are not isochemical but may contain several coexisting cations. For example, a sample consisting mineralogically of hexahydrite and starkeyite, was found to contain the cations Mg (43%), Zn (32%), Mn (18.7%), and Fe (5.9%) after being dissolved in DI water and analyzed for cation content. The XRF capability of the Terra instrument showed that the melanterite sample in Figure 3 contained significant Cu, Zn, and Mn in addition to the normal Fe (Fig 4). Analysis of this sample using a scanning electron microscope (SEM) (Fig. 5) showed marked compositional variations (striped appearance in the backscattered-electron image), and energy-dispersive X-ray analysis confirmed the Fe-Cu-Zn-Mn composition shown by the Terra instrument.

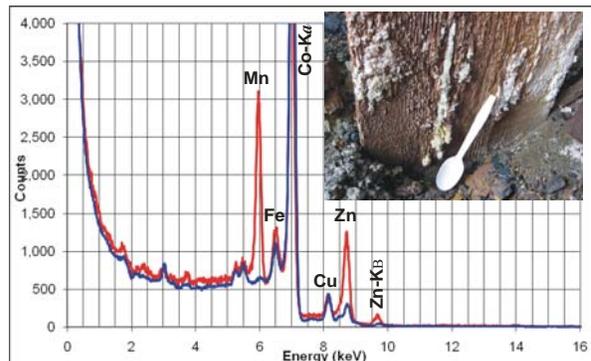


**Figure 4: XRF signal from the melanterite collected simultaneously as the XRD data in Figure 3 (red pattern). Blue pattern: background signal from hardware/collimator of an empty sample cell.**



**Figure 5: SEM backscattered-electron image of Leadville melanterite showing compositional variability.**

Figure 6 shows the XRF signal from a white sulfate precipitate on a mill beam; Terra XRD analysis identified this sample as a mixture of hexahydrite and epsomite ( $\text{MgSO}_4 \cdot 6,7\text{H}_2\text{O}$ ). The XRF data show that, the sample also contains significant Zn (e.g., goslarite  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) and Mn (e.g., mallardite  $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$ ).



**Figure 6: XRF signal from a white sulfate (epsomite + hexahydrite) showing strong Zn and Mn substitution (Red pattern). Blue pattern as in Figure 4.**

These examples demonstrate the value of *in situ* XRD/XRF analysis in the study of ephemeral minerals and hydrates with narrow stability ranges. Similar concerns exist when one considers hydrous sulfates and hydrated minerals in extraterrestrial settings.

**References:** [1] Fernández-Remolar D. C. et al. (2005) *Earth Planet. Sci. Let.* 240, 149-167. [2] Alpers C. H. (2006) In *Martian Sulfates as Recorders of Atmospheric-Fluid-Rock Interactions*, LPI #7064. [3] Chipera S.J. et al., (2008) LPSC XXXVIII, #1462. [4] Chipera S. J. and Vaniman D. T. (2007) *Geoch. Cosmoch. Acta.* 71, 241-250.