



# Spectral masking of goethite in abandoned mine drainage systems: Implications for Mars



Selby Cull<sup>a,\*</sup>, Charles A. Cravotta III<sup>b</sup>, Julia Grace Klinges<sup>c</sup>, Chloe Weeks<sup>a</sup>

<sup>a</sup> Department of Geology, Bryn Mawr College, 101 Merion Avenue, Bryn Mawr, PA 19010, United States

<sup>b</sup> U.S. Geological Survey, Pennsylvania Water Science Center, New Cumberland, PA 17070, United States

<sup>c</sup> Haverford College, Haverford, PA 19041, United States

## ARTICLE INFO

### Article history:

Received 15 January 2014

Received in revised form 18 June 2014

Accepted 26 June 2014

Available online 24 July 2014

Editor: C. Sotin

### Keywords:

Mars  
remote sensing  
acid mine drainage

## ABSTRACT

Remote sensing studies of the surface of Mars use visible- to near-infrared (VNIR) spectroscopy to identify hydrated and hydroxylated minerals, which can be used to constrain past environmental conditions on the surface of Mars. However, due to differences in optical properties, some hydrated phases can mask others in VNIR spectra, complicating environmental interpretations. Here, we examine the role of masking in VNIR spectra of natural precipitates of ferrihydrite, schwertmannite, and goethite from abandoned mine drainage (AMD) systems in southeastern Pennsylvania. Mixtures of ferrihydrite, schwertmannite, and goethite were identified in four AMD sites by using X-ray diffractometry (XRD), and their XRD patterns compared to their VNIR spectra. We find that both ferrihydrite and schwertmannite can mask goethite in VNIR spectra of natural AMD precipitates. These findings suggest that care should be taken in interpreting environments on Mars where ferrihydrite, schwertmannite, or goethite are found, as the former two may be masking the latter. Additionally, our findings suggest that outcrops on Mars with both goethite and ferrihydrite/schwertmannite VNIR signatures may have high relative abundances of goethite, or the goethite may exist in a coarsely crystalline phase.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Over the past decade, satellite and landed missions to Mars have used visible- to near-infrared (VNIR) spectroscopy to identify and map minerals across the surface. Identifying the assemblages of minerals present in individual outcrops has allowed for the interpretation of past geochemical conditions (e.g., pH, Eh, temperature, and availability of cations and anions). In this way, a wide variety of low-temperature aqueous environments have been identified in ancient Martian terrains (e.g., Murchie et al., 2007, 2009; Langevin et al., 2005).

However, one of the major limitations of using VNIR spectroscopy to interpret past environments is how it responds to mineral assemblages. In reflectance spectroscopy, minerals are identified by the positions and shapes of absorption bands. In the near-infrared region, these bands are controlled by overtones and combinations of molecular vibrations: band positions depend on the crystal structure, bond lengths, and mineral composition; and band depths depend on the optical constants of the mineral at that wavelength, and the abundance of the mineral (e.g., Hapke, 1993).

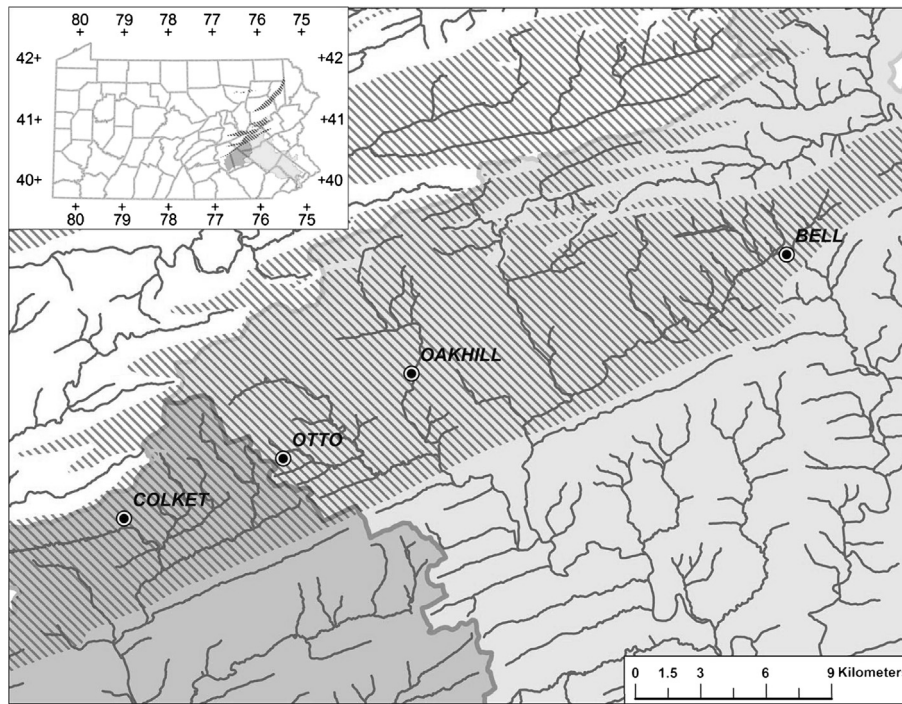
In other words: the depth of a mineral's absorption is not a direct function of the mineral's abundance.

If mixed with another mineral that has stronger optical constants at the same wavelengths, a mineral phase may be completely masked in the VNIR, even if it exists in greater abundance. For example, laboratory investigations by Chevrier et al. (2006) showed that a mixture of goethite, ferrihydrite, and siderite can mask up to 20 wt% siderite in the VNIR. Similarly, Muirhead et al. (2009) showed that hematite–magnetite–maghemite can mask ferrihydrite. This spectral masking effect can complicate the interpretation of environmental conditions on Mars, because key minerals can be obscured in the VNIR spectra.

An important set of minerals for interpreting past environmental conditions are the ferric oxyhydroxides and oxyhydroxysulfates: ferrihydrite ( $\text{Fe}_2^+\text{O}_3 \cdot 0.5\text{H}_2\text{O}$ ), goethite ( $\alpha\text{-FeOOH}$ ), schwertmannite [ $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$ ], and jarosite [ $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ]. These minerals have been identified at several locations on the Martian surface, including Mawrth Vallis (ferrihydrite, goethite, and jarosite, Farrand et al., 2009), the Mars Pathfinder landing site (ferrihydrite–schwertmannite mixtures in soil, Bishop et al., 1998), Aram Chaos (ferrihydrite–schwertmannite, Liu et al., 2012), and Meridiani Planum (schwertmannite, Farrand et al., 2007; Bibring et al., 2006; Klingelhöfer et al., 2005).

\* Corresponding author. Tel.: +1 610 526 5116; fax: +1 610 526 5086.

E-mail address: scull@brynmawr.edu (S. Cull).



**Fig. 1.** Primary drainage basins and notable acid mine drainage (AMD) sites in the Southern Anthracite Coalfield, Pennsylvania. Shaded areas show different watersheds associated with each AMD site. Hachures indicate areas underlain by coal-bearing rocks.

The ferric oxyhydroxide and oxyhydroxysulfate minerals are of particular interest to our understanding of past and present Martian environments for several reasons. First, they are markers of liquid water and oxidizing conditions. Both geochemical modeling (e.g., Tosca et al., 2005) and laboratory experiments (e.g., King and McSween, 2005; Tosca et al., 2008) have shown that these hydrous minerals can form as aqueous alteration products of basalt and volcanic ash. Second, they can serve as markers of environmental conditions at their time of formation. For example, most ferrihydrite forms at low temperatures ( $<25^{\circ}\text{C}$ ) at  $\text{pH} >3$ ; schwertmannite forms in acid–sulfate environments with a  $\text{pH} 2.8\text{--}4.5$ ; and goethite forms over a range of conditions (e.g., Bigham et al., 1996). Also, because these three minerals can be genetically linked (ferrihydrite and schwertmannite can co-precipitate in some circumstances, and both can re-crystallize into goethite), the exact assemblages and stratigraphic relationships of these minerals can provide insight into changing aqueous processes and environments at these locations on Mars. Finally, although ferric oxyhydroxide and oxyhydroxysulfate minerals can be synthesized inorganically, microbial processes commonly are associated with the oxidation of ferrous iron and the precipitation of these minerals from aqueous solutions in Earth environments (Bigham et al., 1990, 1992; Nordstrom and Alpers, 1999; Nordstrom, 2000).

Nevertheless, environmental interpretations on the basis of VNIR spectra are only useful to the extent that we can estimate mineral distributions in geologic and geographic context. Because they form in specific, but potentially diverse environments – and often are produced together or transformed from one another – iron-bearing minerals likely occur on Mars as mixtures with ferrihydrite, schwertmannite, and goethite. Interpretations about past and present environments would be hindered if an important mineral phase were spectrally masked.

Here, we analyze ferrihydrite–schwertmannite–goethite mixtures that naturally precipitate in abandoned mine drainage (AMD) systems in southeastern Pennsylvania. We use X-ray diffractometer (XRD) data to assess the presence of the three mineral phases,

and a field VNIR spectrometer to record corresponding spectra of the mixtures. Geochemical data on the aqueous and surface environment at each sampling site are presented, and the results discussed in the context of ferrihydrite–schwertmannite–goethite mixtures on Mars.

## 2. Material and methods

### 2.1. Sampling sites

Samples were obtained from selected AMD sites in Pennsylvania's Southern Anthracite Field in November 2012 (Fig. 1). The coalfield is dominated by the Pennsylvanian-Age Llewellyn and Pottsville Formations: sandstone, siltstone, and conglomerates interbedded with  $\sim 30$  coal beds, each about 1–4 m thick (e.g., Wood et al., 1968; Way, 2000). The Llewellyn and Pottsville coal beds were extensively mined during the 1800–1960s, resulting in a legacy of abandoned underground mines and waste rock piles. Pyrite and other sulfides in the exposed coal beds and host rocks oxidized during exposure to the atmosphere and, now, the oxidation products continue to leach from the flooded, abandoned mines, leading to extensive stream contamination. The contaminated streams have elevated concentrations of dissolved Fe that oxidizes along the flow path and forms ochreous precipitates, including ferrihydrite, schwertmannite, and goethite (Fig. 2). Contaminated local streams that drain the Southern Anthracite Field include Swatara Creek (Cravotta and Bilger, 2001; Cravotta et al., 2010), which is a tributary of the Susquehanna River, Wabash Creek, which feeds into the Little Schuylkill River (Cravotta, 2008b), plus the headwaters of the Schuylkill River (Cravotta and Ward, 2008), Mill Creek (Cravotta and Nantz, 2008), and the West Branch Schuylkill River (Cravotta et al., 2014), which are major tributaries of the upper Schuylkill River.

Several AMD systems that represented different aqueous environments were selected for analysis:

Download English Version:

<https://daneshyari.com/en/article/6429113>

Download Persian Version:

<https://daneshyari.com/article/6429113>

[Daneshyari.com](https://daneshyari.com)