

REFLECTANCE SPECTRA OF LOW ATOMIC WEIGHT (“APXS-BLIND”) Na-BEARING MINERALS: NITRATES, NITRITES, BORATES, HYDROXIDES, AND PEROXIDES. E. A. Cloutis¹, ¹Department of Geography, University of Winnipeg, 515 Portage Avenue, Winnipeg, MB, Canada R3B 2E9; e.cloutis@uwinnipeg.ca.

Introduction: The Mars Exploration Rovers (MERS) are equipped with an alpha proton X-ray spectrometer (APXS) instrument that provides information on a wide range of elemental abundances, generally above Na in terms of atomic weight [1]. Consequently it is unable to provide complete characterization of many classes of rock forming minerals, including nitrates, nitrites, borates, hydroxides, peroxides, and carbonates. Detection of such minerals is possible only through indirect means, such as low overall elemental totals.

In a related application, our ability to detect the presence of various minerals on the surface of Mars via reflectance spectroscopy is critically dependent on knowledge of the spectral properties of target minerals, normally obtained through laboratory spectral studies. In order to address the spectral detectability of minerals whose presence cannot be directly detected by APXS, we are engaged in an ongoing study of the spectral reflectance properties of minerals composed of low atomic weight anionic groups, specifically borates, nitrates, nitrites, hydroxides, peroxides, carbonates, and bicarbonates. Here we describe spectral reflectance data for some of these minerals.

The presence of nitrates (or nitrites) on Mars is inferred from measurements of N isotopic ratios in the Martian atmosphere and Martian meteorites [2]. Borates are also plausible constituents of the Martian surface because of their common occurrence in evaporite (playa) deposits in terrestrial deserts [3]. Peroxides and hydroxides are plausible surface constituents on the basis of measured near-surface H abundances [4], and surface conditions [5].

Experimental Procedure: We measured 0.35-2.5 μm reflectance spectra of some nitrates, nitrites, and borates, hydroxides and peroxides, specifically: synthetic potassium nitrate (NIT002; KNO_3), synthetic sodium nitrate (NIT001; NaNO_3), synthetic sodium nitrite (NTR001; NaNO_2), borax (BOR002; $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8(\text{H}_2\text{O})$), kernite (BOR001; $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3(\text{H}_2\text{O})$), synthetic Na-hydroxide (OOH030; NaOH), and synthetic Na-peroxide (POX002; Na_2O_2). Note that the presence of these minerals could be inferred on Mars via APXS spectrometry by detection of Na or K and no other APXS-detectable elements.

Reflectance spectra were measured for <45 μm grain size fractions of NIT001 and NIT002, <500 μm

fractions of BOR001 and BOR002, and unsorted powders for the remaining samples. Spectra were measured using the University of Winnipeg’s PSF ASD FieldSpecPro HR spectrometer [6]. The spectra were measured at $i=30^\circ$ and $e=0^\circ$ relative to Spectralon[®], and corrected for irregularities in Spectralon’s[®] absolute reflectance, as well as occasional spectral offsets in the ASD data at 1000 and 1830 nm.

Results – Nitrates and Nitrites: The reflectance spectra of the two nitrates and one nitrite are shown in Figure 1. The reflectance spectra of these phases are characterized by a number of absorption bands longward of 1.8 μm . The Na- and K-nitrates (<45 μm powders) are characterized by very high overall reflectance (close to 100%). The Na- and K-nitrate spectra are very similar to each other, exhibiting five distinct absorption features. The bands in the K-nitrate are shifted to longer wavelengths relative to the Na-nitrate (Table 1). The two longest wavelength absorption features in both spectra are clearly asymmetric, indicating that they are composed of two or more absorption bands.

The Na-nitrite spectrum differs from the Na-nitrate spectrum; it exhibits absorption features near 2.01, 2.12, 2.21 and >2.5 μm (Figure 1). The shortest wavelength band displays clear asymmetry.

Results – Borates: Borates are another mineral group that could potentially occur on Mars [3], and the borate ionic group would be undetectable by APXS. Reflectance spectra of two Na-borates (Figure 2) exhibit absorption bands at different positions for each phase (Table 1). The two spectra are dominated by O+H and borate ionic group-related absorption bands. Many absorption bands are apparent because of the high reflectance (transparency) of the samples.

Results – Na-Hydroxide and Peroxide: Figure 3 shows reflectance spectra of synthetic Na-hydroxide and Na-peroxide (measured at 23° and -23° C). The Na-hydroxide exhibits a number of sharp absorption bands near 0.73, 0.96, and 1.4 μm , and broader features near 1.29, 2.00, 2.37 and 2.45 μm . These features can be attributed to both O-H stretching overtones/combinations and Na-OH combination bands (2.37 and 2.45 μm).

The room temperature and -23° C Na-peroxide spectra exhibit narrow OH absorption bands at 0.96 and 1.40 μm , and NaOH combination bands at 2.37 and 2.41 μm . These likely arise from the hygroscopic

nature of Na-peroxide. There are no significant differences between the room- and low-temperature spectra.

Discussion: The spectra of the various Na-rich materials are dominated by two main types of absorption bands: OH combinations and overtones and Na-OH combination bands. In the case of the nitrates, substitution of Na by K leads to shifts in all of the absorption bands to longer wavelengths, indicating that the type of cation affects OH band positions. When the major anionic group changes (from nitrate to nitrite), further changes in the spectral properties occur, both in terms of number of absorption bands, shapes, and wavelength positions.

The two borates differ largely in terms of number of OH and H₂O groups in each mineral, and structure. These differences lead to changes in all absorption band positions. The borate spectra are dominated by O+H absorptions and Na-OH absorptions, as expected.

The Na-hydroxide and peroxide spectra exhibit only minor differences in spectral properties. The peroxide spectra exhibit more resolvable features in the 2.4 μm region, while the Na-hydroxide spectrum exhibits more resolvable constituent absorption bands in the 1.4 μm region.

Due to the absence of transition series elements, overall reflectance of the samples is generally high. This suggests that, in the presence of additional mineral species, these phases may be difficult to detect if such identifications are based on the weaker absorption bands. At longer wavelengths (beyond $\sim 1.9 \mu\text{m}$), absorption bands fall in the region where many other minerals also exhibit absorption bands.

Table 1. Absorption band wavelength positions (in μm) in mineral spectra used in this study.

Phase	Band position (μm)
Na-nitrate:	1.80, 1.94, 2.06, 2.21, 2.41
K-nitrate:	1.82, 1.98, 2.10, 2.25, 2.47
Na-nitrite:	2.01, 2.12, 2.21, >2.5
Kernite:	0.99, 1.43, 1.50, 1.57, 1.79, 1.97, 2.29, >2.5
Borax:	0.98, 1.16, 1.42, 1.48, 1.56, 1.92, 2.15, >2.5
NaOH:	0.73, 0.96, 1.29, 1.40, ~ 2.1 , 2.37, 2.45
Na ₂ O ₂ :	0.96, 1.40, 2.37, 2.41

References: [1] Bruckner, J, et al. (2003) *J. Geophys. Res.* 108, CiteID 8066. [2] Grady M. M. et al. (1993) *LPS XXIV*, 553-554. [3] Ricardo, A. et al. (2004) *Science* 303, 196-199. [4] Feldman, W. C. et al. (2002) *Science*, 297, 75-78. [5] Zent, A. P. et al. (2008) *J. Geophys. Res.*, 113, CiteID E09001. [6] Cloutis, E. et al. (2006) *LPS XXXVII*, Abstract #2121.

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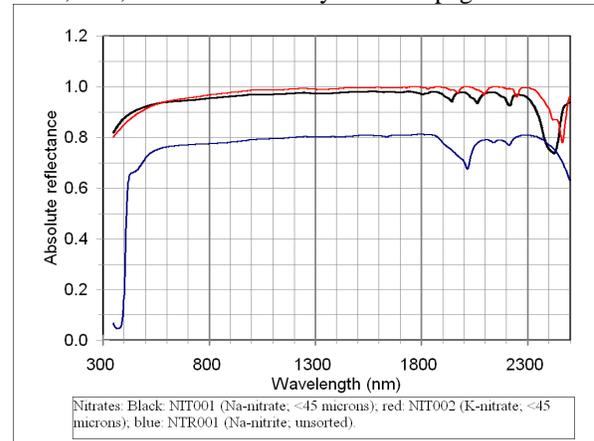


Figure 1. Reflectance spectra (0.35-2.5 μm) of Na-nitrate, K-nitrate, and Na-nitrite.

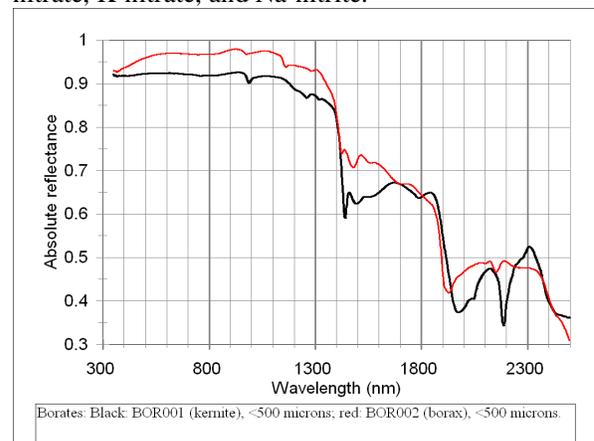


Figure 2. Reflectance spectra (0.35-2.5 μm) of Borates, borax and kernite.

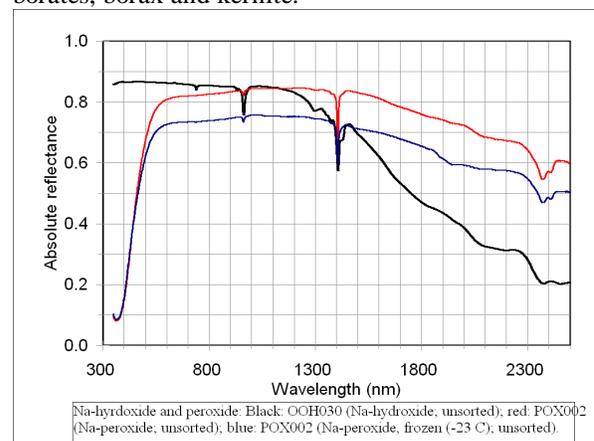


Figure 3. Reflectance spectra (0.35-2.5 μm) of Na-hydroxide and Na-peroxide.