

SPECTRAL PROPERTIES OF ALUNITE-KAOLINITE MIXTURES AND DETECTION OF THESE MINERALS AT MAWRTH VALLIS. J. K. Miura¹, J. L. Bishop², J. M. Danielsen^{2,3}, A. M. Sessa⁴, Y. Itoh⁵, M. Parente⁵, J. J. Wray⁴, and G. A. Swayze⁶. ¹Brown University (Providence, RI: jasper_miura@brown.edu), ²SETI Institute (Mountain View, CA: jbishop@seti.org), ³San Jose State University (San Jose, CA), ⁴Georgia Institute of Technology (Atlanta, GA), ⁵University of Massachusetts (Amherst, MA), ⁶US Geological Survey (Denver, CO).

Introduction: The Al-sulfate mineral alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) has been identified on Mars at Mawrth Vallis [1], Columbus Crater [2], and Cross Crater [3] and is often associated with the phyllosilicate mineral kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$). Laboratory mixtures of alunite and kaolinite were prepared and visible/near infrared (VNIR) spectra were measured to facilitate identification of these minerals on Mars and constrain their detection limits. VNIR hyperspectral images acquired by the Observatoire pour la Minéralogie, L'Eau, les Glaces et l'Activité (OMEGA) instrument [4] and the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) [5] have detected a diversity of sulfate and phyllosilicate minerals, and more occurrences of alunite and kaolinite may be identified using these new mixture spectra. Our mixture results indicate that spectral features characteristic of both alunite and kaolinite are identifiable when these minerals occur in binary mixtures. We analyzed several CRISM images at Mawrth Vallis and characterized 3 regions in detail from image FRT00003BFB where alunite and kaolinite are present.

Methods - Samples: The K-bearing alunite sample used in our mixtures is a coarse vein alunite from a hydrothermal deposit in Marysvale, Utah, USA, and was ground and sieved to a size fraction of 45-125 μm . The kaolinite, from the Clay Minerals Society, Source Clays Repository, is a low-defect clay from Washington County, Georgia, USA, and was also ground and sieved to a size fraction of 45-125 μm . An Na-bearing alunite spectrum, formed at low temperatures and collected in Sadler, Texas, USA, is also used for comparison to CRISM spectra. Binary mixtures were prepared by weighing the desired abundances and gently stirring the particles together, then shaking them through a sieve to homogenize the mixture. VNIR reflectance spectra were collected using an ASD spectrometer from 0.35-2.5 μm relative to halon. These particulate samples were placed in a black teflon dish for measurement.

Methods - CRISM: A modified TRR3 calibration image was processed using a new atmospheric separation and denoising model to enhance spectral signatures [6]. Parameter maps of three spectrally cleaned and georeferenced TRR3-IP (Itoh-Parente) images were created using appropriate spectral parameters [7] to visually aid in identifying potential alunite in the Mawrth Vallis region of Mars. The spectral parameters were

most helpful in identifying alunite outcrops. CRISM image FRT00003BFB was selected for this study because it exhibited the best alunite and kaolinite outcrops. Spectra of regions of interest (ROIs) were collected by using a band depth threshold for the BD2165 parameter to create ROIs identifying pixels with possible alunite.

Analysis of Lab Mixtures: The VNIR spectra of both alunite and kaolinite include doublets near 1.4 and 2.2 μm , and the spectrum for alunite includes additional bands near 1.76 and 2.3 μm [8,9]. The spectra of the mixtures are shown in Fig. 1. The kaolinite spectrum includes a doublet at 1.397 and 1.412 μm (Al-OH stretch overtone) and a doublet at 2.166 and 2.208 μm (Al-OH bend and stretch combination band). The alunite spectrum includes a doublet at 1.427 and 1.477 μm (Al-OH stretch overtone), an absorption at 1.765 μm , a doublet at 2.166 and 2.208 μm , and an absorption at 2.321 μm (Al-OH bend and stretch combination bands).

All mixture spectra demonstrate identifiable signatures of both components. The kaolinite doublet at 1.4 μm remains present even at 75 wt.% alunite, although it is influenced by the alunite absorption at 1.427 μm . Conversely, the 1.427 μm alunite absorption readily disappears with decreasing alunite abundance, becoming a shoulder at 50 wt. % alunite, and disappearing

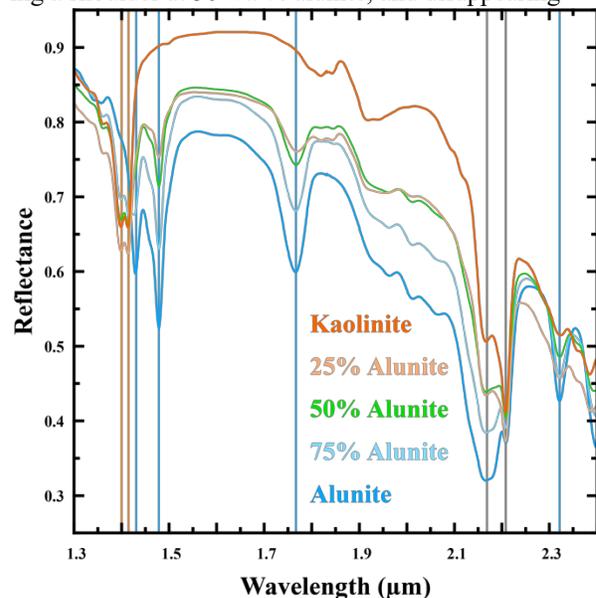


Fig. 1: VNIR reflectance spectra of alunite (blue) and kaolinite (orange) binary mixtures. Prominent spectral features are indicated with vertical lines.

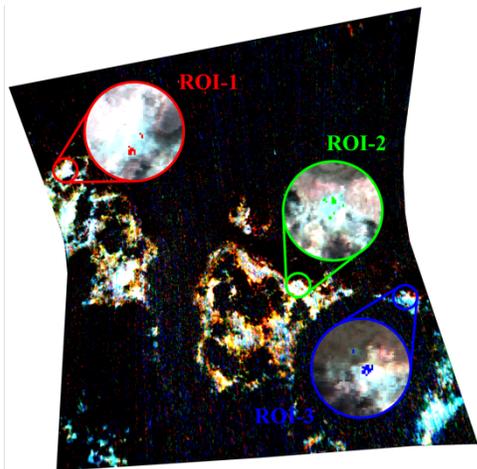


Fig. 2: Parameter map (R:BD2210_2, G:BD2190, B:BD2165) of spectrally cleaned, georeferenced modified TRR3 image FRT00003BFB. The circled areas highlight pixels used to derive spectra in Fig. 3.

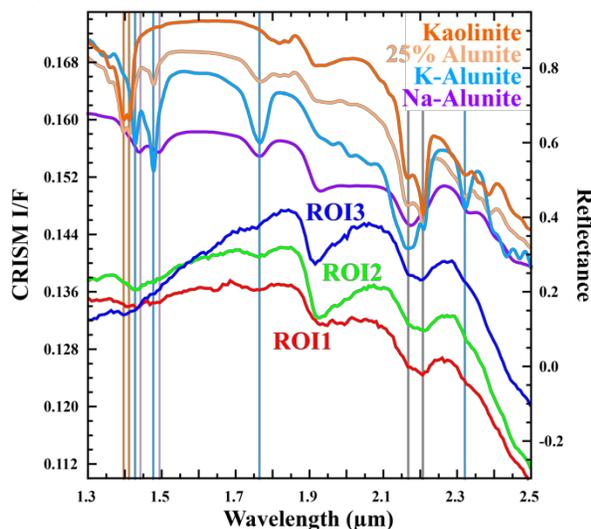


Fig. 3: Average VNIR reflectance spectra of ROI pixels in Fig. 2 compared to laboratory mixture spectra. Prominent spectral features are indicated with vertical lines.

completely with 25 wt. % alunite. In contrast, the 1.477 μm alunite absorption is readily identifiable in all mixture spectra, suggesting that this is a good alunite indicator.

Al-OH absorptions at 2.166 and 2.208 μm are present in both alunite and kaolinite, so the primary difference observed in the mixtures appears as a change in presentation. The 2.166 μm absorption is much broader and deeper in alunite. However, at an alunite abundance of 75 wt. %, the two absorptions are almost equal in strength. In addition, the 1.765 μm alunite Al-OH absorption is present in all mixtures, decreasing in strength as the alunite content decreases.

Application to Mawrth Vallis: Mawrth Vallis is a Martian outflow channel located between the southern

highlands and northern lowlands. This region contains a great abundance and diversity of aqueous hydration products [10,11], which were deposited during the Noachian period (4.1-3.7 billion years ago) [12]. The presence of alunite was suggested as one of many aqueous alteration products in image FRT00003BFB [13] and then confirmed recently in this image and another in the southern part of Mawrth Vallis [1]. For this study, CRISM spectra from three ROIs in image FRT00003BFB (Fig. 2) were examined and compared to laboratory spectra (Fig. 3). Each of these ROIs contain spectral features consistent with a mixture of kaolinite and alunite. The stronger 2.208 μm absorption relative to the 2.166 μm absorption is consistent with a mixture dominated by kaolinite, as are the weaker 1.765 μm alunite absorption and weaker 1.427 μm , 1.477 μm , and 1.765 μm alunite absorptions.

Previous work on image FRT00003BFB suggested that the alunite in this region is more Na-rich, based on a comparison to alunites from the USGS spectral library [1]. The results presented here support this possibility, particularly in ROI-1, which has absorption features at the longer wavelength position in the 1.47-1.49 μm region. This is in contrast to the alunite detection at Cross Crater, which was more potassium-rich [3].

The presence of alunite in Mawrth Vallis suggests an acidic environment, as the precipitation of Al-bearing phases (such as kaolinite and alunite) is favored at low pH conditions, which promotes the mobilization of Al^{3+} in solution. For alunite to preferentially form over other sulfates, Al must be many times more concentrated than Fe [3]. Acid alteration of feldspar could play a role in the mobilization of Al and precipitation of alunite in this region. We are investigating the stratigraphy of the alunite and kaolinite outcrops in relation to other phyllosilicates and sulfates present at Mawrth Vallis to provide insights into the aqueous geochemical history.

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References: [1] Sessa A. et al. (2018) LPSC, #2983. [2] Wray J. J. et al. (2011) *JGR*, 116, E01001. [3] Ehlmann B. L. et al. (2016) *Am.Min.*, 101, 1527-1542. [4] Bibring J.-P. et al. (2005) *Science*, 307, 1576-1581. [5] Murchie S. et al. (2009) *JGR*, 114, E00D06. [6] Itoh Y. & Parente M. (2019) LPSC, #2025. [7] Viviano-Beck, C. et al. (2014) *JGR*, 119, 1403-1431. [8] Bishop J. & Murad E. (2005) *Am.Min.*, 90, 1100-1107. [9] Bishop J. L. et al. (2008) *Clay Miner.*, 43, 35-54. [10] Bishop J. L. et al. (2013) *PSS*, 86, 130-149. [11] Poulet F. et al. (2014) *Icarus*, 231, 65-76. [12] Loizeau D. et al. (2012) *Icarus*, 219, 476-497. [13] Horgan B. et al. (2014) *8th Int'l Mars Conf.*, #1276.