

**PHYSICAL ALTERATION OF MARTIAN DUST GRAINS, ITS INFLUENCE ON DETECTION OF CLAYS AND IDENTIFICATION OF AQUEOUS PROCESSES ON MARS.** Janice L. Bishop<sup>1</sup>, Ahmed Drief<sup>2</sup>, and M. Darby Dyar<sup>3</sup>, <sup>1</sup>SETI Institute/NASA-ARC, Mail Stop 239-4, Moffett Field, CA 94035, <sup>2</sup>Dept. of Geology, Univ. of Calif., Davis, CA, 95616, <sup>3</sup>Dept. of Earth and Environment, Mount Holyoke College, South Hadley, MA 01075. (contact: jbishop@mail.arc.nasa.gov)

**Introduction:** Clays, if present on Mars, have been illusive. Determining whether or not clay minerals and other aqueous alteration species are present on Mars provides key information about the extent and duration of aqueous processes on Mars. The purpose of this study is to characterize in detail changes in the mineral grains resulting from grinding and to assess the influence of physical processes on clay minerals on the surface of Mars. Physical alteration through grinding was shown to greatly affect the structure and a number of properties of antigorite [1] and kaolinite [2]. This project builds on an initial study [3] and includes a combination of SEM, HRTEM, reflectance and Mössbauer spectroscopies. Grain size was found to decrease, as expected, with grinding. In addition, nanophase carbonate, Si-OH and iron oxide species were formed.

**Methods and Results:** The antigorite sample in this study is a weathering product of an olivine rock with magnetite inclusions from Mulhacen, Spain, and was freshly prepared following procedures outlined in [1]. This antigorite,  $\text{Si}_{2.01}\text{Al}_{0.12}\text{Fe}_{0.08}\text{Mg}_{2.70}\text{O}_5(\text{OH})_4$ , sample (including a few% magnetite) was initially ground in a vibration grinder for 30 sec. to produce sufficient particulate material for the study and was termed An-0. Subsequent samples are labeled according to the number of minutes ground, i.e. An-1 was ground for 1 min. and An-30 for 30 min. Samples were dry sieved to <45 and <125  $\mu\text{m}$  particle size.

Reflectance spectra measured in this study indicate that grinding has a profound influence on both the shape of the spectral features and the spectral continuum in the visible/near-infrared (NIR) and mid-IR regions. Biconical, off-axis FTIR data were scaled to bidirectional data at 1.2  $\mu\text{m}$  and corrected for absolute reflectance [4]. High resolution HRTEM was performed at UC Berkeley and shows aggregates of ultrafine grains in the ground samples. Mössbauer data were measured at room temperature as in [5] and show reductions in the amount of antigorite and magnetite in these samples with grinding.

**HRTEM:** The image of antigorite particles ground for 30 minutes in Fig. 1 illustrates the ultrafine particle sizes produced by grinding. The antigorite grains are on the order of 50-100 nm in size and are surrounded by grains only a few nm across. These tend to adhere to each other and form larger aggregates. The in-

creased surface energy due to the mechanical stress caused by grinding plays an important role in their adhesion.

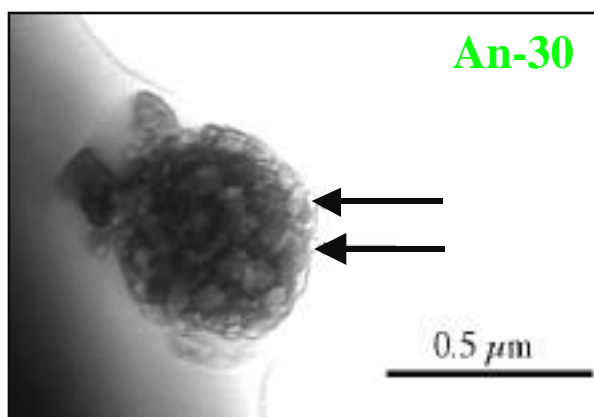


Fig. 1 HRTEM image of antigorite (ground for 30 min.) showing aggregates of ultrafine particles.

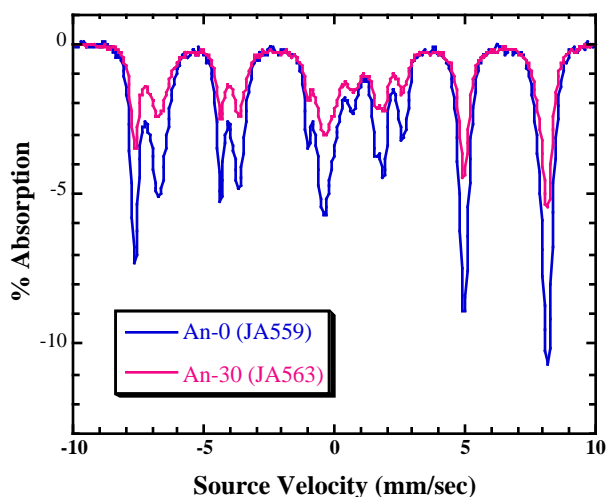


Fig. 2 Mössbauer spectra (278 K) of ground antigorites. The peaks are characteristic of antigorite and magnetite.

**Mössbauer Spectra:** The room temperature spectra shown in Fig. 2 are characteristic of a mixture of antigorite and magnetite. The antigorite  $\text{Fe}^{2+}$  peaks (which lie at roughly -0.2 and 2.45 mm/s) decrease in intensity with grinding, but there is no related increase in the region where  $\text{Fe}^{3+}$  peaks should occur in antigorite (0.10 and 0.75 mm/s). All the magnetite peaks decrease with increased grinding, and there is no apparent change in peak intensity/line asymmetry that

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would signal significant changes in grain size or the creation of nonstoichiometric magnetite or maghemite. Thus, the observed changes in both antigorite and magnetite spectra suggest that neither phase is becoming more oxidized; rather, the decreasing intensities suggest a change to an amorphous material. Low temperature Mössbauer measurements are underway to characterize the nanophase/amorphous iron oxide species.

**Reflectance Spectra:** Visible/NIR reflectance spectra are shown in Fig. 3, where the color varies from dark blue for the freshest samples to pink for the most altered. These spectra show that grinding of antigorite grains induces a spectral slope, darkens the spectra, reduces the intensity of the OH features (marked with orange arrows in Fig. 3), and changes the character of the iron bands (marked by green arrows in Fig. 3) from 0.6 to 1.0  $\mu\text{m}$ . The NIR OH bands for serpentine clays depend on the abundance of Mg, Fe and Al in the octahedral sites [6]; for this antigorite sample these bands are primarily due to combinations and overtones of the Mg-OH vibrations and occur at 1.38, 1.40, 2.32, 2.52, 2.56, and 2.73  $\mu\text{m}$ . Spectra of the <45 and <125  $\mu\text{m}$  dry sieved aggregates appear the same, suggesting that any spectrally relevant particle sizes are much smaller.

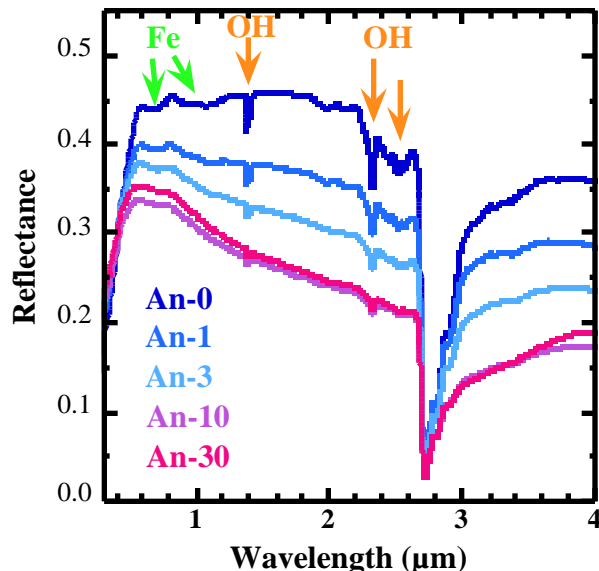


Fig. 3 Visible/NIR reflectance spectra of the ground antigorite samples (dry sieved <45  $\mu\text{m}$ ).

Mid-IR reflectance spectra of the ground antigorite samples are shown in Fig. 4 following the color scheme above. These spectra show a decrease in the intensity of the silicate bands near 490, 675, 890, and 1050  $\text{cm}^{-1}$ , shifts in some band centers, creation of new

features near 820, 870, 1350, 1480 and 1600  $\text{cm}^{-1}$ , and a reduction in the spectral contrast above 1200  $\text{cm}^{-1}$  with increased grinding. Arrows in Fig. 4 indicate the position of the new bands formed with grinding; these are most obvious in the pink spectrum (An-30, ground for 30 min.). The new bands from 1350-1600  $\text{cm}^{-1}$  are attributed to nanophase carbonate grains formed during the physical alteration process via oxidation of carbide supplied by the grinder. These are similar to carbonate features [7] observed in an average martian dust spectrum measured by the thermal emission spectrometer (TES) [8].

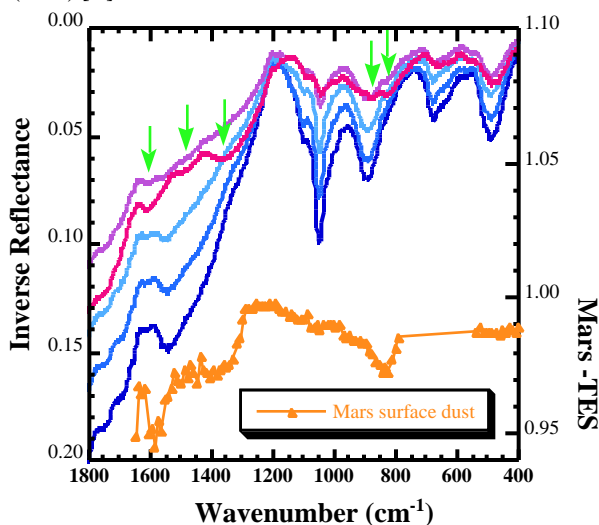


Fig. 4 Mid-IR reflectance spectra of the ground antigorite samples and TES spectra of Mars. The average surface dust spectrum is from Bandfield and Smith [8]. The arrows indicate new bands that appear after grinding.

**Applications to Mars:** NIR spectral studies of Mars have shown evidence for weak features near 2.2-2.3  $\mu\text{m}$  in some regions (e.g. Lunae Planum) that are attributed to octahedrally bound OH in clays or other minerals [9], although the features are too weak for mineral identification in existing spectral datasets of Mars. Upcoming OMEGA and CRISM spectrometers will measure NIR spectra at higher spatial and spectral resolution and will be able to provide closer inspection of any putative OH features present in the alteration products on the surface of Mars. Previous studies have suggested chemical alteration as a mechanism for reducing the ~2.2-2.3  $\mu\text{m}$  OH species in layer silicates on Mars [10, 11, 12]. This study shows that physical alteration can reduce the intensity of these metal-OH bands, but does not appear to shift the band centers. Additional experiments are needed in order to better quantify the effects of physical alteration on antigorite and other clay minerals. Abrasion of dust and soil particles due to dust storms, dust devils, and impacts

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on Mars is likely to have an effect on the mineral and glass grains and may diminish this OH spectral feature making it harder to detect layer silicates on Mars.

Extended visible region spectra of the ground antigorites are shown in Fig. 5 along with selected rock and soil spectra measured by the Imager for Mars Pathfinder (IMP). Both antigorite and magnetite have  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in their mineral structures. The Mössbauer spectra suggest that grinding reduces the total number of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  sites in the antigorite and magnetite structures and that some nanophase/amorphous iron oxides are produced. The extended visible region spectra also indicate a weakening in the iron absorption bands near 0.7 and 1  $\mu\text{m}$ . The spectral changes observed due to grinding of the antigorite (plus magnetite) samples are on a scale similar to the spectral changes observed on Mars (Fig. 5). In addition to the influence of physical alteration on the iron features, the formation of amorphous/nanophase particles produces a downward NIR slope that is seen in some of the IMP spectra (Fig. 5 and [13, 14]).

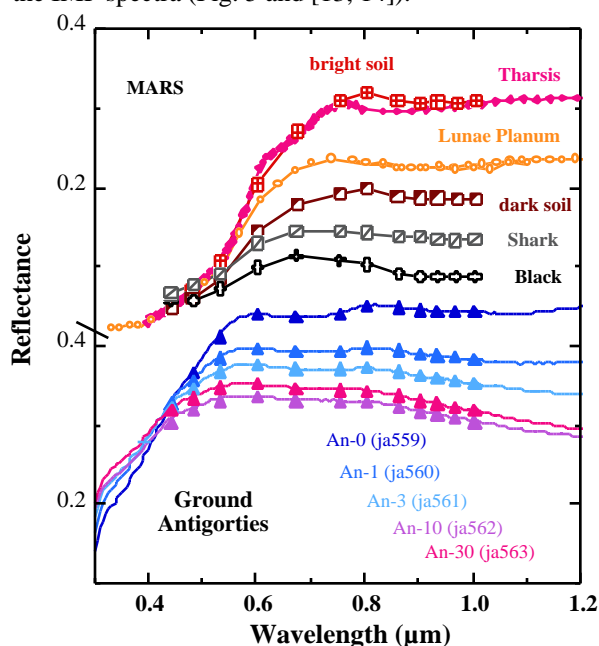


Figure 5 Extended visible region reflectance spectra of the ground antigorites (re-samples to IMP band passes) and Mars. The Tharsis telescopic/ISM spectrum is from Mustard & Bell [15], the Lunae Planum telescopic and ISM spectrum are from McCord et al [16] and Murchie et al. [9]. The Pathfinder rock and soil spectra are from Barnouin-Jha et al. [17] and Yingst et al. [18].

The changes in the mid-IR spectra of antigorite and other layer silicates due to physical alteration may have important applications to the TES and mini-TES data of Mars. A decrease in the intensity of the silicate and OH bands in layer silicates due to abrasion may

indicate that this component is being under-represented in the mixing models. Also the creation of new carbonate features through physical alteration may provide a mechanism to explain the carbonate identified by Bandfield et al. [7]. Atmospheric  $\text{CO}_2$  molecules adsorbed on the martian dust and soil grains may be oxidized during abrasion on Mars to form nanophase carbonate grains imbedded in the dust and soil particles. The formation of a new band near 820  $\text{cm}^{-1}$  in the antigorite spectra with increased grinding is attributed to nanophase and/or surface Si-OH species. This could be occurring on Mars also as the silicate components of the martian dust and soil particles are abraded.

Further characterization of the amorphous species is underway. Continued work on the influence of physical alteration on potential Mars analogue materials will be helpful for interpretation of the data the MERs will measure with mini-TES, Pancam and the mini Mössbauer. A better understanding of the influence of physical alteration on volcanic glass and its alteration products will also be needed in order to characterize any alteration products in the TES, OMEGA and CRISM datasets. Identification of clay minerals and other chemical alteration products, if present, is important for understanding the aqueous history on Mars. This study suggests that the presence of carbonates in the dust may be a result of inorganic processes, rather than aqueous processes, and needs to be studied in more detail.

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