

DETECTING REDUCED ZONES IN OXIDIZED FE-RICH SEDIMENTARY ROCKS: SPECTRAL CLUES TO ORGANIC MATTER CONCENTRATIONS? J. K. Crowley¹, J. S. Kargel², G. M. Marion³, S. J. Hook⁴, B. J. Thomson⁴, C. R. de Souza Filho⁵, N. T. Bridges⁴, and A. J. Brown⁶,¹ U. S. Geological Survey, MS 954, Reston, VA 20192, jcrowley@usgs.gov, ² University of Arizona, Tucson, AZ, jkargel1054@earthlink.net, ³ Desert Research Institute, NV, giles.marion@dri.edu, ⁴ Jet Propulsion Laboratory, Caltech, CA, simon.j.hook, bradley.j.thomson, nathan.t.bridges@jpl.nasa.gov, ⁵ U. of Campinas, S.P., Brazil, beto@ige.unicamp.br, ⁶ Ames Research Center, CA, abrown@arc.nasa.gov

Synopsis: This paper outlines the characteristics of terrestrial red bed sedimentary rocks and considers their possible utility as an analog for Martian sedimentary deposits. Spectral reflectance measurements of several samples of reduced and oxidized facies of terrestrial red beds are discussed, including the possible use of such spectra as bio-indicators.

Introduction: The term "red beds" refers to sedimentary rocks, mainly clastic, having characteristic deep red coloration associated with hematitic grain coatings and cements. Such rocks are formed in continental or marginal marine settings under arid climatic conditions (i.e. low weathering intensity), and usually are composed of first-cycle sediments rich in feldspars and ferro-magnesian minerals, such as biotite and hornblende. The red coloration stems from the release of ferrous iron during the early diagenetic breakdown of the ferro-magnesian mineral grains, followed by *in situ* oxidation to form amorphous iron oxides, and ultimately, hematite. Thus, red beds do not begin as red sediments, but do eventually acquire their coloration as a result of their initial mineralogy [1].

A characteristic of practically all terrestrial red bed sequences is the existence of restricted zones or layers that are not red—places where iron oxides either did not precipitate, or have been removed (Figure 1).



Figure 1. Red bed unit showing lateral color change, Pintada mining district, New Mexico.

In some cases such zones are directly associated with detrital organic matter and/or pyritic rock layers that caused local reducing conditions, inhibiting iron oxide formation [2]. In other cases changes in coloration on scales ranging from cm to dm have more complex explanations. For example, trapping of anoxic water derived from organic-rich lacustrine or lagoonal de-

posits may occur following their burial by coarser (proto-red bed) sediments. This scenario may account for the common observation of non-red strata at the top and bottom of many fining-upward red bed sequences [3].

Methods: Samples were collected from red beds of Permian and Triassic age at the Eureka, Nacimiento, Pintada, Rayo and Scholle localities in northern and central New Mexico [2]. Ultraviolet to short-wave infrared (UV-SWIR; 0.25-2.5 μm) and thermal infrared (TIR; 6.0-22.5 μm) directional hemispherical reflectance spectra of several representative samples are shown in Figures 2 and 3, respectively.

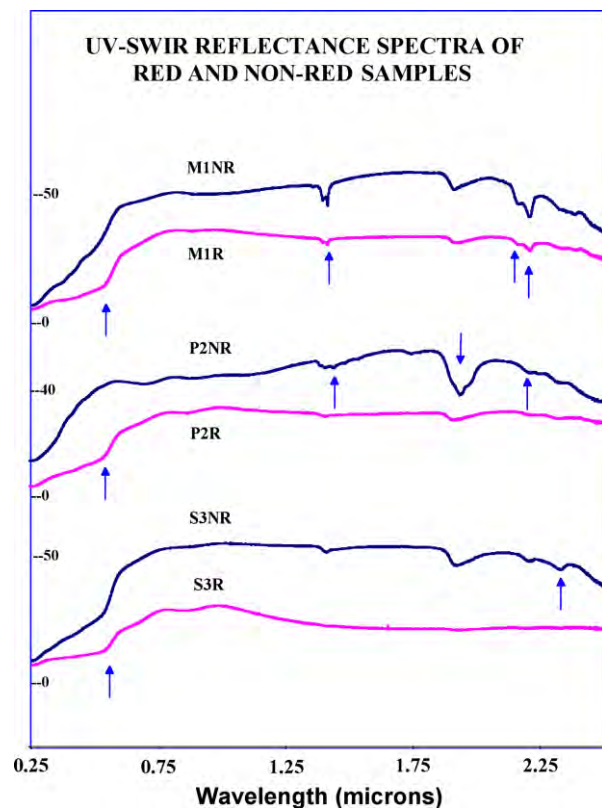


Figure 2. Laboratory UV-SWIR spectra of red and non-red samples. Reflectance (%) scales for each spectral pair shown at left. Arrows mark absorption features mentioned in text.

Results: The UV-SWIR spectra of red and non-red units display several notable features: 1) A deep inflection in the spectral curves of red samples is evi-

dent at 0.54 μm related to electronic absorption by Fe^{3+} in hematite [4]; this inflection is commonly absent or less pronounced in the spectra of non-red samples; 2) Various authigenic clay, carbonate, or sulfate minerals are present in the samples, as illustrated by diagnostic spectral absorption features of kaolinite (arrowed features at 1.41, 2.17 and 2.21 μm ; sample M1), gypsum (arrowed features at 1.44, 1.94, 2.20 μm ; sample P2), and calcite (arrowed feature at 2.34 μm ; sample S3) [4]. In all cases the band depths of the authigenic mineral absorption features are greater in the non-red samples compared to the corresponding red samples. This indicates masking of the authigenic mineral spectral features by the iron oxide; 3) The non-red samples have higher overall albedos (avg. ~45%) compared to the equivalent red samples (avg. ~28%).

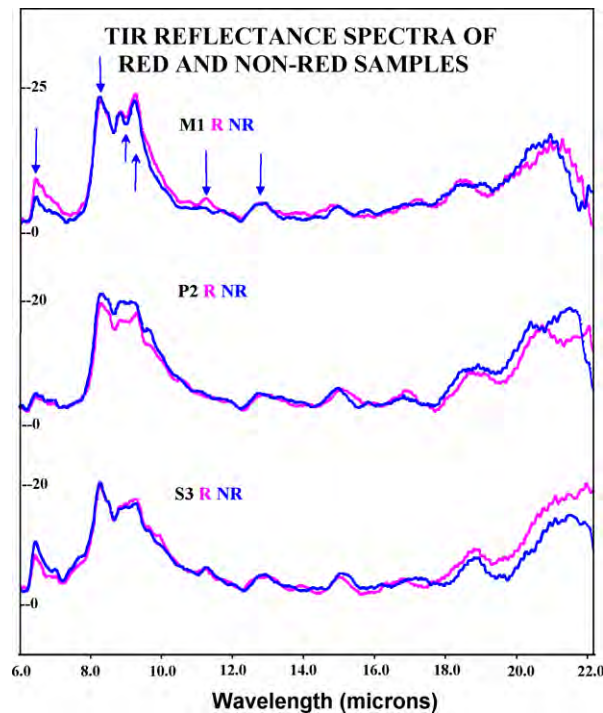


Figure 3. Laboratory TIR spectra of red and non-red samples. Reflectance (%) scales for each spectral pair shown at left. Arrows mark spectral features mentioned in text.

The TIR spectra show characteristic reflectance maxima related to stretching modes of C-O in calcite (arrowed features at 6.5 μm and 11.4 μm , sample M1), and Si-O in quartz (arrowed features at 8.3, 9.2, and 12.7 μm , sample M1) [5, 6]. Clay minerals also produce an Si-O stretching feature near 9.0 μm that commonly is superimposed as a reflectance minimum on the 9.2 μm feature of quartz (e.g. sample M1) [6]. Red and non-red samples show similar TIR spectral shapes and, in general, the spectral contrast variations are not

as pronounced as those seen in the UV-SWIR. This indicates that there are no important mineralogical differences between the red and non-red samples in each spectral pair, aside from the presence of minor amounts of iron oxide in red samples. Masking of quartz, calcite, and clay spectral features by iron oxide does not occur due to the relative transparency of iron oxide over most of the TIR wavelength range. Reflectance features of iron oxides occur between 18-22 μm but are superimposed on stronger Si-O bending features that occur in this same wavelength interval [7]. This serves to impede the TIR detection of small amounts of iron oxides in siliceous red beds.

Discussion: The spectral data indicate that red and non-red units within terrestrial red beds can be distinguished by their UV-SWIR spectral properties, whereas TIR properties do not permit ready discrimination. If similar rocks occur on Mars, UV-SWIR remote sensing data should enable their detection.

Are terrestrial red beds a useful analog for oxidized Martian sediments and the Martian regolith? The answer to this question remains uncertain. Both terrestrial and Martian rocks contain ferro-magnesian minerals that upon weathering and oxidation may impart a red coloration. Lacking abundant atmospheric oxygen on Mars, we surmise that red bed type oxidation there may be a slower UV-driven process, in which oxidants formed at the surface [8, 9] are gradually mixed into the shallow subsurface. Deeper ground waters on Mars that have equilibrated with fresh mafic volcanic materials (either rocks or detrital grains) would be reducing and would be capable of forming non-red zones in otherwise oxidized sedimentary rocks. Reduced facies in terrestrial red beds commonly are associated with organic matter, but importantly, also can preserve organic matter. If such reduced sedimentary strata exist on Mars, they would be favorable sites for organic matter preservation and would be worth examining for signs of Martian biologic activity.

References:

- [1] Walker, T. R. (1976) *GAC Sp. Pap.* 36, 85-96.
- [2] LaPoint, D. J. (1976) *GAC Sp. Pap.* 36, 357-370.
- [3] Van Houton, F. B. (1973) *Ann. Rev. Earth Plan. Sci. 1*, 39-59. [4] Hunt, G. R., and Salisbury, J. W. (1976) *Modern Geology* 5, 211-217. [5] Salisbury, J. W. and Wald, A. (1992) *Icarus* 96, 121-128. [6] Salisbury J. W. et al. (1994) *JGR* 99, 11897-11911. [7] Fallacaro, A. and Calvin, W. M. (2006) *Astrobiology* 6, 563-580. [8] Burns, R. G. and Fisher, D. S. (1993) *JGR* 98 E2, 3365-3372. [9] Bullock, M. A. et al. (1994) *Icarus* 107, 142-154.