# DETECTING REDUCED ZONES IN OXIDIZED FE-RICH SEDIMENTARY ROCKS: SPECTRAL CLUES TO ORGANIC MATTER CONCENTRATIONS?

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**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].

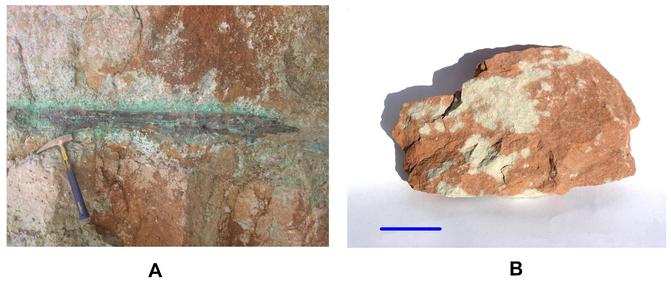
A characteristic of practically all terrestrial red bed sequences is the existence of restricted zones or layers that are not red--places where iron oxides either did not precipitate, or have been removed. (Figure 1)

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

In some cases such zones are clearly 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 deposits 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].

In addition to hematite, other authigenic minerals commonly form in the pore spaces of red beds, including various carbonates, feldspars, clays, and other silicates. These minerals provide information on diagenetic processes and fluid compositions relevant to organic matter preservation. For example, early-formed carbonate cements would indicate a lack of subsequent interaction with strongly acidic fluids; similarly, the presence of ferrous minerals, such as ferroan chlorites, would place constraints on fluid oxidation states. Many authigenic minerals have distinctive spectral characteristics, and thus, might provide a remote sensing basis for inferring diagenetic effects on red beds.

Figure 2. A) Fossilized log with copper mineralization associated with local OM-caused reducing conditions, Eureka Mine, NM. B) Small scale color variations in sandstone related to the initial distribution of microscopic OM, Pintada Canyon, NM. Scale bar is 2.5 cm in length.



A



B

**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 3 and 4, respectively. The UV-SWIR data were recorded with a Perkin Elmer Lambda 900 spectrometer. The TIR data were recorded with a Thermo-Nicolet Nexus 670 FTIR spectrometer. Both spectrometers were equipped with integrating spheres.

Bulk sample mineralogy was determined by X-ray powder diffraction analysis. Petrographic thin sections were examined to determine sample diagenetic histories and cement compositions.

**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 evident at 0.54 μm related to electronic absorption by Fe3+ in hematite [4]; this inflection is commonly absent or is less pronounced in the spectra of non-red samples; 2) Authigenic clay, carbonate, and 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, 2.22 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%)

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 significant mineralogical differences between the red and non-red samples 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 transparency of iron oxide over most of the TIR wavelength range. Reflectance features of hematite occur between 18-22 μm but are superimposed on stronger Si-O bending features that are present in this same wavelength interval [7]. This serves to impede the detection of small amounts of hematite using TIR data.

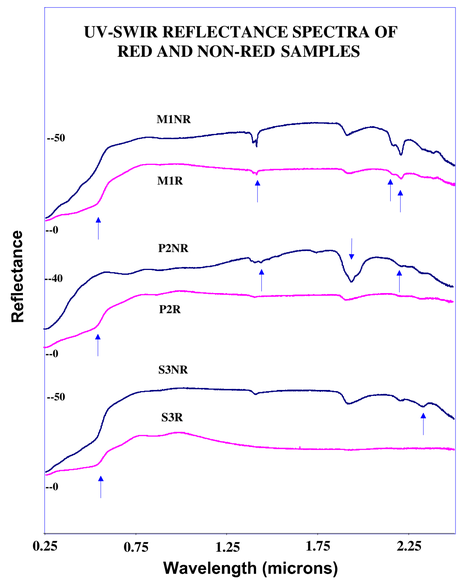



Figure 3. Laboratory UV-SWIR spectra of red (R) and non-red (NR) samples. Percent reflectance scales for each spectral pair shown at left. Arrows mark absorption features mentioned in text.

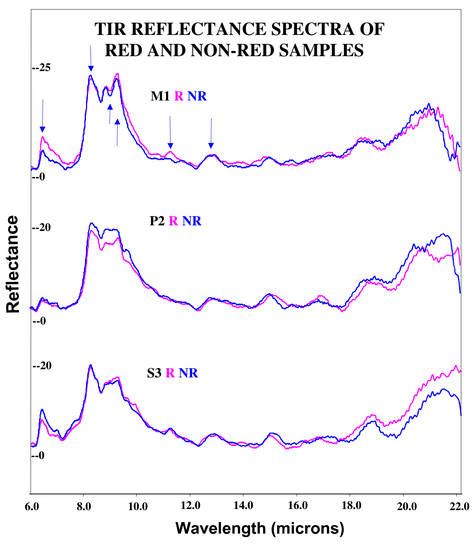



Figure 4. Laboratory TIR spectra of red (R) and non-red (NR) samples. Percent reflectance scales for each spectral pair shown at left. Arrows mark absorption features mentioned in text.

**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; both wavelength ranges may afford clues to the rocks' diagenetic histories.

Are terrestrial red beds a useful analog for oxidized Martian sediments and the Martian regolith? Both terrestrial and Martian rocks contain ferro-magnesian minerals that upon weathering and oxidation may impart a red coloration, and the processes that cause reddening may not be too dissimilar on the two planets. 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 relatively fresh mafic volcanic materials (present either as rocks or detrital grains) should be sufficiently reducing to form or preserve non-red zones in otherwise oxidized sedimentary rocks. Reduced facies in red beds commonly are associated with organic matter, but importantly, also can preserve organic matter. If such reduced strata exist, they would be favorable sites for organic matter preservation and would be worth examining for signs of Martian biologic activity.

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