SIGNATURES OF IRON CYCLING IN A TERRESTRIAL REDOX-STRATIFIED LAKE AND IMPLICATIONS FOR GALE CRATER, MARS.

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Introduction Iron and other redox-sensitive elements can encode information pertaining to past climate and water-rock interactions, and mineral assemblages containing these elements can constrain lake bottom water conditions and potentially the relative position of the oxycline and/or shoreline through a stratigraphic section. Multiple oxidation states in a given assemblage may also indicate a potential energy source for microbes.

The mudstones in Gale crater being examined by the Curiosity rover have been interpreted to have been deposited in a lacustrine-fluvial/alluvial environment [1,2]. Sediments contain a range of ferric and ferrous minerals with a potential increase in oxidation state upsection [2-5] that may indicate drying of the lake environment. All samples also exhibit a high abundance (15-40 w%) of X-ray amorphous material [4]. These characteristics may reflect the existence of a redox stratified lake and/or variations through time in the interactions of UV, anoxic groundwater, oxic lake waters, and the ancient martian atmosphere [4].

To better understand the chemical and mineralogical trends that may occur in sediments in a mafic, redox-stratified lake system, we examine samples collected from Lake Towuti in Indonesia, a system that possesses these traits. We present results from sediment analyses from the Lake Towuti catchment, inlet rivers, surface sediment, and one 150 m long core representing ~1 Myr of lake history. The goal of this source-to-sink examination is to link observed trends in Fe mineralogy to processes within the lake and its catchment (e.g. weathering in the source region, transport, settling and transformation in the water column, or post-deposition diagenesis).

Methods: Reflectance spectra (0.35-25 μm) were collected using an ASD FieldSpec3 and FTIR spectrometer and were used for band depth calculations to identify clay minerals, carbonate, and Fe-bearing phases. X-ray diffraction (XRD) patterns were collected for all bulk powdered samples using a Bruker D2 Phaser for mineral identification. Major and minor elemental abundances were measured using ICP-AES.

Sequential Fe extractions [6] were used to separate samples into Hy-HCl-extractable (inferred amorphous) and Na-dithionite-extractable (inferred crystalline; non-

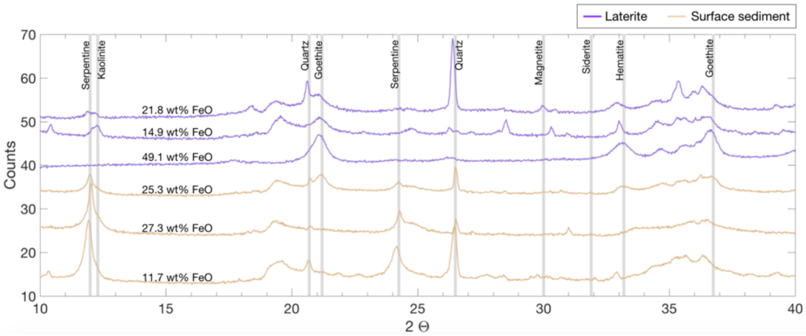

Fig. 1: XRD patterns (Cu source) of a subset of laterite samples (purple) and surface sediment samples (tan), with relevant phases highlighted and each pattern labeled with the sample's FeO wt% abundance. Crystalline Fe oxide peaks are well-defined in laterites and greatly reduced in surface samples.

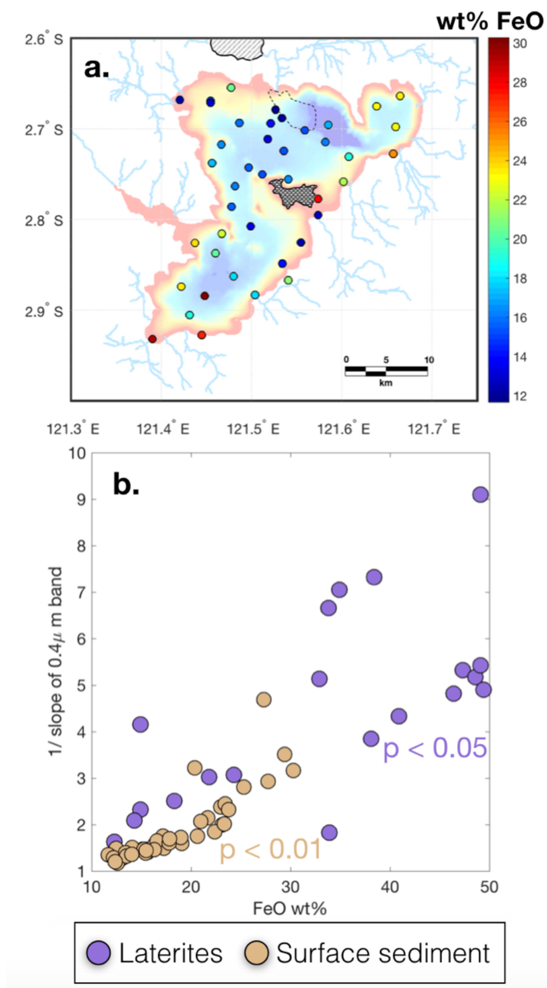

*Fig. 2: **a.** FeO abundance of surface sediment samples. **b.** Correlation of FeO abundance and Fe spectral parameter for laterites (purple) and surface samples (tan).*

silicate) Fe phases. Fe content of the supernatant was measured via ICP-AES and XRD data were collected for select samples after the extractions.

Results: XRD patterns (Fig. 1) show that the soils contain high abundances of crystalline Fe-oxides (e.g. magnetite, goethite, hematite), while samples from the lake sediment surface maintain high Fe abundance (Fig. 2a) but not in crystalline form. Spectral parameters are well-correlated with elemental abundances for Mg and Al (not pictured) as well as Fe (Fig. 2b). In this system, reflectance spectra can thus provide a rapid way to estimate changes in sediment mineralogy and chemistry.

Sequential Fe extractions indicate that as sediment moves through the system from source (laterites) to sink (lake surface and buried sediment), there is an increase in the proportion of Fe in amorphous phases relative to crystalline oxides (e.g. goethite) (Fig. 3).

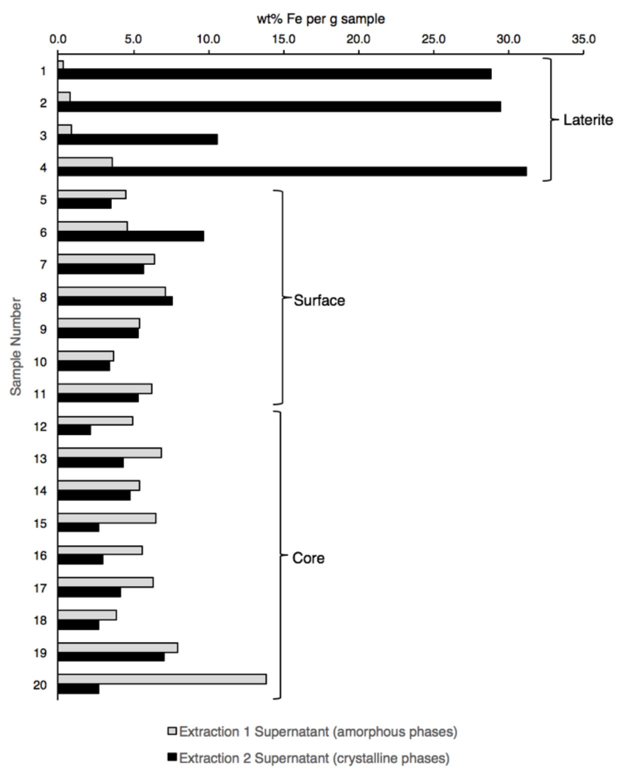

Fig. 3: *Sequential Fe extraction results showing an increase in the proportion of Fe in easily extractable (inferred amorphous, e.g. ferrihydrite) phases relative to crystalline phases (e.g. goethite, hematite).*

Iron cycling in the lake. Sequential Fe extractions indicate that as sediment moves through the system from source (laterites) to sink (lake sediment), there is an increase in the proportion of Fe in amorphous phases relative to crystalline oxides (e.g. goethite) (Fig. 3). From these observations, we infer that rapid Fe cycling [7] in the water column or shortly after deposition (early diagenesis) liberates Fe from crystalline oxides and promotes incorporation of Fe into X-ray amorphous phases.

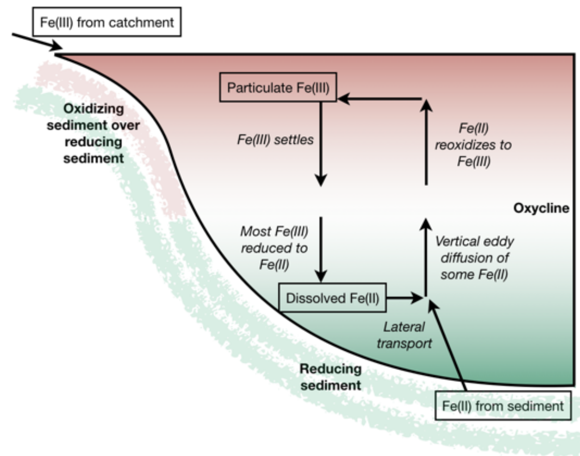

Fig. 4: *Model of Fe cycling in Lake Towuti during times of redox-stratification.*

A model for Fe cycling in the sulfur-poor lake begins with crystalline Fe^{3+} oxides carried from the catchment into the lake (Fig. 4). During periods of redox-stratification, particulate Fe sinks through the water column, crossing the oxycline and being reduced. Dissolved Fe^{2+} can be incorporated in sediment or diffuse upward to be re-oxidized. Fe^{2+} also enters the lake water through diffusion from the reducing sediment. During periods of deep mixing, the water column is oxidized and reactive, poorly crystalline Fe^{3+} minerals are delivered to the sediment where they can be reduced near the sediment-water interface. The frequency and duration of these deep mixing events and the role that biology plays in determining rates of iron cycling are unknown and are an area of future study.

Understanding the conditions that result in ferrous vs. ferric iron formation, as well as conditions that allow amorphous material and crystalline clays to coexist for long time periods, may help constrain how to interpret lake sediment chemistry and mineralogy in terms of climate on Earth and Mars. Variations in the Fe oxidation state inferred from mineralogy [4] as Curiosity moves up Mt. Sharp in Gale Crater may record changing conditions in water depth and/or intereactions between lake waters and atmospheric oxidation state. Testing the hypothesis of an ancient redox-stratified lake in Gale Crater [5] involves an understanding of how Fe mineralogy is affected by transport and diagenesis. Systems like Lake Towuti, where we can closely observe changes through time and space, can provide insight into these processes in the modern.

References: [1] Grotzinger et al. (2015), Science, 350, 6257. [2] Grotzinger et al. (2014) Science, 343, 1242777-1. [3] Vaniman et al. (2014), Science, 343. [4] Rampe et al. (2017), EPSL, 471. [5] Hurowitz et al. (2017), Science, 356, 922. [6] Poulton and Canfield (2005) Chemical Geology. [7] Crowe et al. (2008). Limn. & Oceanography.