# MINERAL AND CHEMICAL CHANGES IN A 100 M LONG SEDIMENT CORE FROM LAKE TOWUTI, INDONESIA AND IMPLICATIONS FOR MAFIC LACUSTRINE SEDIMENTS IN GALE CRATER, MARS.

R. Y. Sheppard[1*], R. E. Milliken[1], J. M. Russell[1], M. D. Dyar[2,3], E. C. Sklute[3], S. Bijaksana[4], M. Melles[5], and H. Vogel[6]. [1]Dept. Earth, Environmental, and Planetary Sciences, Brown University, [2]Dept. Astronomy, Mt. Holyoke College, [3]Planetary Science Institute, [4]Institut Teknologi Bandung, [5]Institute of Geology and Mineralogy, University of Cologne, [6]Institute of Geological Sciences & Oeschger Centre for Climate Change Research, University of Bern.

**Introduction:** Lake Towuti on the island of Sulawesi in Indonesia offers a unique opportunity to study the relationships between surface weathering under warm humid conditions, fluvial transport and deposition of mafic sediment, and diagenesis in a redox-stratified lake. Previous studies have documented the changes in sediment composition induced by transport and deposition from the catchment to the modern surface of the lake floor: sediment is dominated by serpentine, clay, and complex Fe oxyhydroxides, with spatial trends broadly representing bedrock in nearby catchments [1-6]. To better understand how these chemical and mineralogical trends change through time and may be affected by diagenesis, we examine the composition, crystallinity, and visible color of sediment from a ~100 m long drill core extracted from the lake bottom in 2015. The core spans a period of continuous lacustrine deposition over the last ~1 Ma [7].

**Methods:** Powder X-ray diffraction (XRD) patterns were collected for mineral identification using a Bruker D2 Phaser. Visible-near IR (VNIR) reflectance spectra were collected using an ASD FieldSpec3 (0.35-2.5 µm) and FTIR spectrometer (1.35-28 µm) to calculate strengths (band depths) of absorptions associated with clay minerals, carbonates, and Fe-bearing phases (e.g., oxides). Major and minor elemental abundances were measured using ICP-AES. Sequential Fe extractions [8] were used to separate samples into Hy-HCl-extractable (inferred amorphous) and Na-dithionite-extractable (inferred crystalline, non-silicate) Fe phases. Mössbauer spectra were collected for select samples at 4, 130, and 295 K on a W100 spectrometer using a ~75-65 mCi $^{57}$Co source in rhodium. Low temperature Mössbauer spectra were obtained using a Janis Research Co. Model 850 closed-cycle helium compression system. The spectra were fit using the Mex_disd program. Sample color was described qualitatively as well as calculated quantitatively; calculations were based on VIS reflectance data and white-balanced images of the wet and dry sediment imaged under identical conditions.

**Results and discussion:** The upper 100 m of basin sediments are dominated alternating thinly bedded red and green clays with occasional turbidites, tephras, and diatomaceous oozes [7,9]. Analysis of the chemical and spectral data allow for division of the core into three statistically distinct zones (Fig. 1): Zone 1 (0-27 mblf) is dominated by Mg-serpentine, Zone 2 (27-62 mblf) is dominated by Al-rich clays such as kaolinite, and Zone 3 (62-97 mblf) is dominated by Al-rich clays (commonly kaolinite) and carbonate (siderite). We observe strong correlations between the spectral and chemical data: MgO abundance correlates with band depth at 2.32 µm, $Al_2O_3$ with band depth at 2.21 µm, and total inorganic carbon (TIC) with band depth at 4.0 µm. This is consistent with previous results that discussed the effectiveness of VNIR spectra as a means to rapidly estimate composition of modern sediment in the Lake Towuti system [3,5,6], and our results demonstrate this method also applies downcore.

The mineral hosts of Fe also vary between the three Zones, and Mossbauer analyses suggest that most core samples have both ferrous and ferric components. Results from the sequential Fe extractions (Fig. 2) 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 X-ray amorphous phases relative to crystalline oxides. In addition, deeper sediments are more enriched in amorphous Fe phases compared with shallower sediments. This suggests that crystalline Fe oxides (e.g., hematite and goethite observed in the laterites) continue to be converted to amorphous/nanocrystalline phases with progressive burial depth and/or time. Amorphous Fe persists even in the oldest sediments (up to 1 Ma [7]), and it is likely that this process is heavily influenced by the presence of organic matter and microbes in the sediment column.

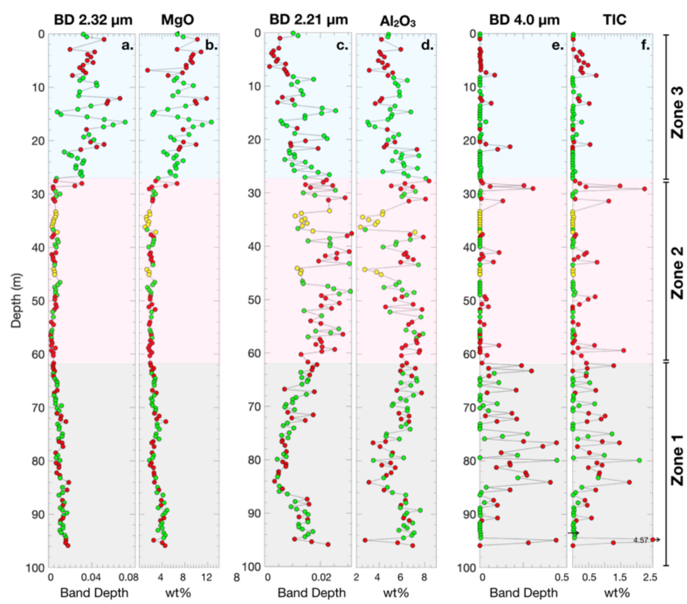



*Fig. 1: Downcore plots of spectral and chemical measurements. Depth is in meters below lake floor. The three Zones are highlighted in different colors. Zone 3 is dominated by Mg serpentine, Zone 2 by Al clay, and Zone 1 by Fe carbonate (siderite). The color of each dot is the wet sample color.*

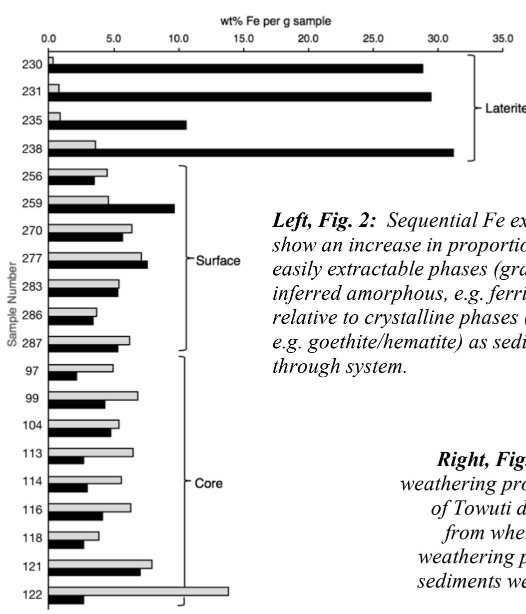
**Implications and Conclusions**: As a redox-stratified lake hosted in mafic terrain, Lake Towuti presents an interesting location to study diagenetic processes associated with mafic lacustrine sediment on Mars, including Gale and Jezero craters. Movement of Fe-rich sediment through the Lake Towuti system, coupled with reducing pore fluids and the presence of organic matter, allows for cycling of Fe between different phases. The majority of Fe enters the lake in the form of crystalline Fe oxides but then quickly begins to alter to X-ray amorphous phases once it reaches the lake bottom [3]. This process appears to continue downcore, though the Mössbauer data and observations of alternating red/green sediment layers suggests Fe continues to be present in multiple oxidation states throughout the upper ~100 m of the core.

The division of the Lake Towuti basinal sediments into three distinct mineralogical zones provides a framework for considering environmental changes through time (Fig. 3). A significant change in the erosive power of the major inlet river (sediment source) is inferred to occur between Zones 3 and 2 (at 27 mblf). This is likely due to subsidence and a change in baselevel. Diagenetic processes are prevalent and ongoing in the upper 100 m of the sediment, producing siderite in each Zone, though it is more common in Zone 1. Siderite is likely still forming from reactive Fe in the sediment, which is consistent with the identification of abundant nanophase Fe throughout the core. The boundaries between the three mineral Zones do not appear to be correlated to color, grain size, or other macroscopic properties of the core.

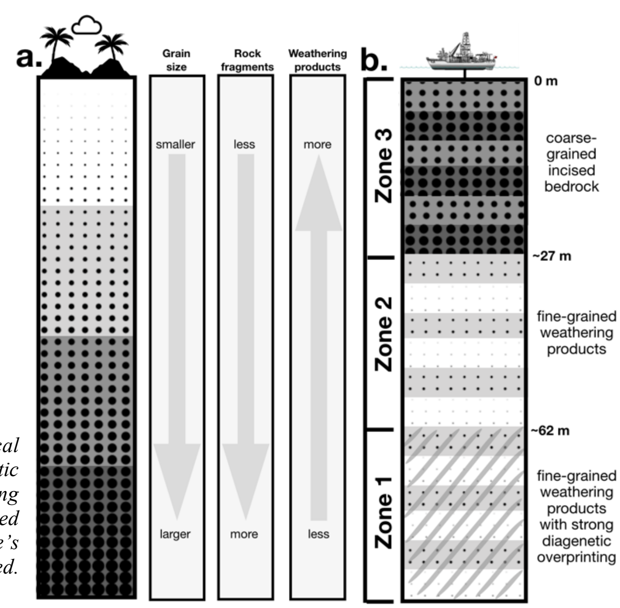
*Connections to Gale crater*. The mudstones in Gale crater being examined by the Curiosity rover are interpreted to have been deposited in a closed-basin lacustrine-fluvial/alluvial environment [10]. Sediments contain a range of ferric and ferrous minerals with a potential increase in oxidation state upsection [11-14] that may indicate a change in the redox state of the lake waters or diagenetic fluids. All samples also exhibit a high abundance (15-40 w%) of X-ray amorphous material [11]. 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 [13].

The observation that color has a complex relationship to Fe oxidation state in the Lake Towuti sediment is also relevant to Gale crater. Curiosity observed red and gray patches across its traverse of the Vera Rubin Ridge [15-16] with little discernible difference in Fe mineralogy. Given the persistence of chemically complex Fe-rich amorphous phases throughout Curiosity's entire traverse, it is possible that amorphous Fe-rich phases are also present in Gale crater. The Fe mineralogy of Lake Towuti is complex, and that much of it is poorly crystalline, and therefore more difficult to characterize using standard techniques, means that determining the abundance of oxidized versus reduced Fe requires more detailed analytical methods. The indication that sediment in Lake Towuti may retain amorphous Fe phases over 100s of thousands of years is intriguing, particularly given that water is constantly available for reactions. Further constraining the timescale and mechanisms by which this material matures to more crystalline phases may shed light on the persistence of amorphous phases on Mars as well.

**References:** [1] Morlock et al. (2018), *J. Paleolimnol*. [2] Hasberg et al. (2019), *Sedimentology* 66, 675–698. [3] Sheppard et al. (2019), *Chem. Geol.* 512, 11–30. [4] Costa et al. (2015), *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 417, 467–475. [5] Weber et al. (2015), *J. Paleolimnol.* 54 (2), 253–261. [6] Goudge et al. (2017), *GSA Bull.* 129 (7/8), 806–819. [7] Russell et al. Submitted 2020 to *Palaeogeography, Palaeoclimatology, Palaeoecology.* [8] Poulton and Canfield (2005), *Chem. Geol.* 214, 209–221. [9] Russell et al. (2016), *Sci. Drill.* 21, 29–40. [10] Grotzinger et al. (2014), *Science* 343. [11] Rampe et al. (2017), *EPSL* 471, 172–185. [12] Vaniman et al. (2014), *Mar. Sci.* 343. [13] Hurowitz et al. (2017), *Science* 356. [14] Yen et al. (2017), *EPSL* 471, 186–198. [15] Fraeman et al. Submitted 2019 to *Journal of Geophysical Research* special issue. [16] Horgan et al. Submitted 2019 to *Journal of Geophysical Research* special issue.




***Left, Fig. 2:*** *Sequential Fe extractions show an increase in proportion of Fe in easily extractable phases (gray bars, inferred amorphous, e.g. ferrihydrite) relative to crystalline phases (black bars, e.g. goethite/hematite) as sediment moves through system.*




***Right, Fig. 3: a.*** *Theoretical weathering profile.* ***b.*** *Schematic of Towuti drill core, showing from where in the idealized weathering profile that Zone's sediments were likely sourced.*