CLAY MINERAL DIVERSITY THROUGH THE CHICXULUB PEAK-RING: A COMPARISON OF MICROTEXTURAL, X-RAY DIFFRACTION AND SPECTRAL DATASETS. S. L. Simpson<sup>1</sup>, G. R. Osinski<sup>1</sup>, F. J. Longstaffe<sup>1</sup>. <sup>1</sup>Centre for Planetary Science and Exploration / Dept. of Earth Sciences. University of Western Ontario, London, Canada. (SSimps56@uwo.ca).

**Introduction:** In 2016 the joint International Ocean Discovery Program (IODP)-International Continental Scientific Drilling Program (ICDP) Expedition 364 recovered core from the Chicxulub impact crater peakring between ~506 and 1335 metres below the seafloor (mbsf) (21.45°N, 89.95°W) [1,2]. Initial petrological characterization reveals that it comprises altered granitoid basement (lowermost, Unit 4), overlain by a thin layer of impact melt rock (Unit 3) and a gradational sequence of impact melt-bearing breccias (Unit 2). The main impactite sequence (Units 2, 3) was rapidly buried under post-impact sediments (uppermost, Unit 1). This contributed to the exceptional preservation of the structure and a diverse suite of impact hydrothermal mineralization, including various mid-low temperature hydrated silicates (i.e., zeolites, clays, palagonite, opal), which are typically poorly preserved in craters on Earth due to weathering and overprinting [3,4]. Clay mineralization is especially ubiquitous throughout Unit 2 and the upper sections of Unit 3 and is associated with pervasively altered silicate glass [5].

The various lithologies that comprise the peak-ring have distinct physical properties (e.g., porosity) [6] and primary mineralogical compositions, which, when combined with their proximity to local heat sources, affected the type and duration of hydrothermal circulation present through the structure. This record may be fossilized in the clay mineralogy, which serves as an excellent paleoenvironmental indicator due to the ability of clays to preserve information on fluid composition and temperature [7,8,9]. Clay minerals remain generally poorly characterized in impact settings on both Earth and Mars due, in part, to a lack of detailed studies focusing on terrestrial analogues and the wide range of conditions under which they form. Planetary surfaces rich in clays are prime targets for current and future exploration landing sites as they indicate previously or presently hydrous environments. The forthcoming Mars 2020 and Exo-Mars 2020 mission landing sites, for example, were chosen, in part, due to their abundance of clays [10].

Here we present a subset of results from a wider study on the post-impact hydrothermal environment preserved in the Chicxulub peak-ring; in particular, we summarize our work on clay mineral characterization in Units 2 and 3. The overall excellent preservation state of the peak-ring structure and careful sample preparation has permitted us to document the diverse clay mineral textures, discrete changes in chemical composition, lithologic context and crystal structure using a combination of electron microprobe, X-ray diffraction (XRD) and spectral (UV-VNIR ranges) datasets. This work, in

conjunction with isotopic datasets presented in Simpson et al., (2019) [11], will contribute to the construction of a 3-dimensional model of the hydrothermal environment through the peak-ring, as well as determine whether these specific datasets can be correlated to accurately identify the distinct clay mineralogies preserved.

Methods: All analyses were performed using facilities at the University of Western Ontario. Polished thin sections were prepared without the use of water, carbon coated, and examined using a JEOL JXA-8900 L electron microprobe with beam operating conditions of 15 kV. Rough samples were coated with osmium and examined using a LEO (Zeiss) 1540XB Scanning Electron Microscope (SEM) with beam operating conditions between 3 and 30 kV at the Western Nanofabrication Facility. Following initial microprobe characterization, 13 samples of homogeneous melt-bearing breccias and of individual "glass" clasts were selected for clay mineral separation and powder X-ray diffraction (XRD), performed at the Laboratory for Stable Isotope Science (LSIS). Various particle sizes (i.e. <2, 2-0.2, and <0.2  $\mu$ m) were separated by centrifugation. Aliquots of each were saturated with Ca<sup>2+</sup> and K<sup>+</sup>, and then examined using a series of XRD scans in preferred orientation to identify the clay minerals [12,13,14]. XRD of randomly oriented samples was used to determine the b-parameters of the clay assemblages. XRD was performed using a high-brilliance Rigaku Rotaflex RU-200B series diffractometer, equipped with a rotating anode (Co Ka source). Spectral analysis was performed on hand samples as well as <2, 2-0.2 and <0.2  $\mu$ m particle size fraction separates using a handheld ASD FieldSpec 4 point spectrometer, with a  $\sim 0.5$  cm spot size (active detection, integrated light source) over 0.35 to 2.5  $\mu$ m (UV-VNIR) ranges; these were compared to USGS lab spectra [15].

Results: *Microprobe:* Backscattered electron imaging indicates that the clays are predominantly derived from altered silicate glass, but are also found in smaller amounts dispersed within the pore space of the groundmass throughout all subunits. These generally display a flaky "smectitic" texture and vary significantly in average grain size (Fig. 1). Quantitative data obtained using wavelength-dispersive spectroscopy (WDS) shows that the clays are rich in Fe and Mg; the Fe/Mg ratio averages ~0.86 (range, 1.13 to 0.56). The Fe/Mg ratio does not change significantly with depth through the core. Close inspection of the "glass" clasts indicate that no original, unaltered material has been preserved. Instead, all glass is replaced with a very poorly crystalline, fine clay, here referred to as palagonite (Fig. 1). In unit 2B

and C some altered glasses, in addition to the Fe-Mg clays, contain localized zones of K-rich smectitic clay (Fig. 2). Clays are almost always associated with calcite, other zeolite minerals, Ti and Fe-oxides and, more rarely, opal.

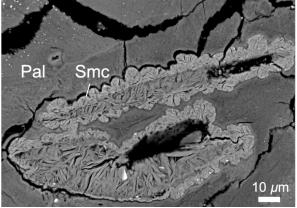


Figure 1: Backscattered electron (BSE) image of altered glass in a clast of melt-bearing breccia in Unit 2B; these clasts are pervasively altered to a mixture of Fe-Mg smectitic clay ('Smc') (var. saponite) and a chemically similar, very fine, poorly crystalline smectitic material described as palagonite ('Pal').

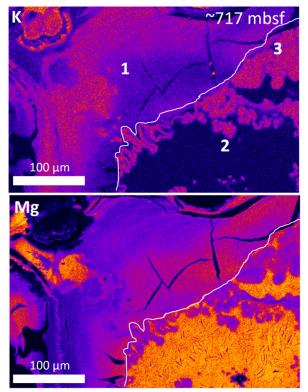


Figure 2: Wavelength-dispersive spectroscopy (WDS) element map showing K and Mg concentration in an altered glass clast from Unit 2C; warmer colors indicate higher count intensities. Labels: (1) hydrated glass (palagonite); (2) Mg-smectites (saponite) and (3) K-rich clays.

XRD: Results consistently indicate smectite to be the dominant clay group present throughout the peak-ring. and thus far the different particle size fractions (i.e. 2-0.2 and <0.2  $\mu$ m) are almost identical. Results for hydrated (54% relative humidity) and heat-treated (0% relative humidity) samples have shown incomplete peak collapse for some samples, possibly indicating the presence of hydroxy-interlayer material within the clays. Despite smectite being the most ubiquitous clay mineral group, results show a change in octahedral cation site occupancy as indicated by a shift from predominantly trioctahedral to dioctahedral, and then back to trioctahedral through Unit 2; this shift is gradual and correlates with the host rock porosity [6]. Spectral analysis: Spectral datasets obtained from individual glass clasts in hand samples indicate a mixture of opal and Fe-Mg clays, and some closely resemble hydrated basaltic glass. This result is unsurprising considering the spot size, which is not small enough to resolve multiple, individual minerals at this scale without some overlap.

Conclusions and ongoing work: BSE imaging reveals very distinct, contrasting sizes and textures of clay minerals, which – on a large scale – do not appear to change significantly in overall composition with depth through the peak-ring. This result contrasts with the XRD results, which indicate some variation in octahedral cation site occupancy that changes with depth and correlates with porosity measurements. This work will expand through the continued characterization of different particle size fractions to determine whether they are mineralogically distinct (i.e. 2-0.2 vs <0.2  $\mu$ m). These samples will also be used for forthcoming hydrogen and oxygen isotope analysis, which is explored more thoroughly in Simpson et al. (2019) [11]. Ultimately, the combination of these various datasets will contribute to a robust, cross-sectional view of the hydrothermal system and more specifically, the clay mineralogy through the peak-ring structure.

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