

IMPACT GLASS ALTERATION AND ASSOCIATED CLAY MINERALOGY PRESERVED IN THE CHICXULUB PEAK-RING: COMPARING IN-SITU AND POWDER X-RAY DIFFRACTION DATASETS

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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 peak-ring [1,2]. The main impact lithology, Unit 2, comprises a gradational sequence of a fining upward melt-bearing breccia that formed from molten-fuel coolant interaction (MFCI) [3], a process akin to phreatomagmatic volcanism. This process resulted in formation of high amounts of silicate glass that was subsequently altered by the impact-generated hydrothermal system [1-4]. This material overlies a thin sequence of impact melt rock (Unit 3) and crystalline basement (lowermost, Unit 4). The structure was rapidly buried under post-impact sediments (uppermost, Unit 1), which contributed to the exceptional preservation of various secondary hydrated silicates (i.e. zeolites, clays) including a nanocrystalline, glassy material commonly referred to palagonite, or hydrated glass [5]. This poorly characterized, heterogeneous material is thought to represent an intermediate phase of alteration between pristine silicate glass and the end products of alteration, such as clays, zeolites and carbonates [5,6]. Clays and clay-like, poorly-crystalline to amorphous materials remain poorly characterized in impact settings on both Earth and Mars, due, in part, to the wide range of conditions under which they formed, as well as a general paucity of detailed terrestrial analogue studies. Clay-bearing planetary surfaces are prime targets for exploration landing sites as they indicate previous or present aqueous environments [7,8]. Hence, additional geochemical datasets are needed to provide environmental constraints for formation of these materials, particularly for such phases present on the surface of other terrestrial bodies (e.g., Mars), for which there is minimal to no geologic context.

Here we present the results of our study focused on characterizing the stages of impact glass alteration preserved in the Chicxulub peak-ring melt-bearing breccias. In particular we focus on determining the crystallinity and geochemical composition of the glassy 'palagonite' material and its associated clay mineralogy. The excellent preservation state of the peak-ring lithologies has permitted us to document the diverse clay mineral textures, geochemistry, crystal structure and their lithologic context using a combination of electron microprobe, powder X-ray diffraction (XRD) and *in-situ* micro-XRD datasets. Additional clay mineral isotopic data ($\delta^2\text{H}$ and $\delta^{18}\text{O}$) presented in Simpson et al.

(2020, *this conference*) help to provide paleoenvironmental constraints (e.g., fluid sources, temperatures) for the formation of these clays and clay-like materials, and contribute to a more robust model for phyllosilicate formation in impact-hydrothermal environments.

Methods: All analyses were performed using facilities at The University of Western Ontario. Carbon coated, polished thin sections were examined using a JEOL JXA-8900 L electron microprobe (EPMA) with beam operating conditions of 15 kV. Rough samples (~0.5 cm diameter) 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 microprobe/SEM characterization, 28 samples of melt-bearing breccias and impact melt rocks from across the upper peak-ring (Units 2, 3 and the upper intervals of 4) were selected for clay mineral separation and powder XRD (pXRD), performed at the Laboratory for Stable Isotope Science (LSIS). The <0.2 μm size fraction was separated by centrifugation and then examined using a series of XRD scans in preferred and random orientations to identify the clay minerals [10, 11]. The pXRD was performed using a high-brilliance Rigaku Rotaflex RU-200B series diffractometer, equipped with a rotating anode (Co $K\alpha$ source); scans were performed from 2-82° 2 θ . Micro-XRD (μXRD) was performed on uncoated polished thin sections using a Bruker D8 Discover μXRD (Co $K\alpha$ source); the parallel beam had a nominal diameter of 300 μm and scans were performed from 14-105° 2 θ . 2D diffraction data were collected using a Vantec-500 Area detector, and integrated to produce conventional diffraction patterns.

Results and Discussion: *Microprobe:* Backscattered electron imaging shows that the clays are predominantly Mg-Fe rich and as derived from the altered glass. The size of the clays is highly variable, but their textures are usually well-defined by the flaky, void-filling aggregates, typical of smectites (Fig. 1). Former glass clasts vary in color in transmitted light from green to dark brown (Fig. 2A); their texture is commonly too fine-grained to resolve using EPMA (Fig. 1), but this material generally has a composition similar to the better crystallized smectites formed from it. In addition to Fe-Mg clays, some glasses contain localized zones of K-Al rich smectite. All lithologies contain significant quantities of other secondary phases, most commonly analcime, mordenite, dachiardite, calcite, Ti and Fe-oxides, sulphates and Fe-sulphides.

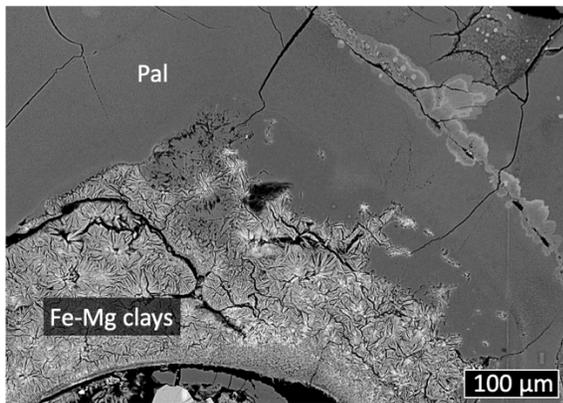


Fig. 1: Back-scattered electron image of glass clast in Unit 2A (~658 meters below seafloor, mbsf) showing Fe-Mg smectite (Fe-Mg clays) and texturally non-descript, hydrated glass (Pal).

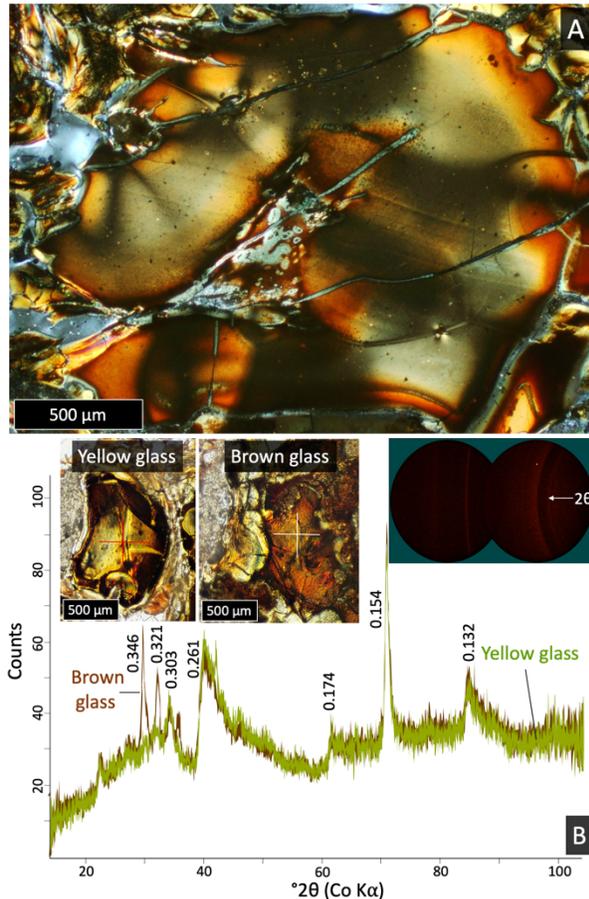


Fig. 2: (A) Transmitted light microscope image of altered glass clast from Unit 2A (~658 mbsf), and (B) μ XRD data for clast of similar material, labeled brown and green glass, also in Unit 2A. The μ XRD data indicate the presence of poorly-crystalline trioctahedral clay, zeolites and calcite.

XRD: pXRD shows that smectite is the dominant clay group present throughout the peak-ring; the smectite ranges from mostly trioctahedral (06l: $d=0.153-0.154$ nm) in Unit 2A, to mixed di- and trioctahedral (06l: $d=0.149-0.154$ nm) through parts of 2B, and back to trioctahedral through Units 2C-4. This shift is gradual and correlates well with the host rock porosity and oxygen isotope datasets [9, 12]. Throughout most of Unit 2, pXRD results for hydrated (54% relative humidity) samples have produced basal diffractions that are unusually high for smectite and various heat-treated (0% relative humidity) samples show incomplete collapse to 1.0 nm, in contrast to that expected for smectite. Ethylene glycol solvated samples, however, consistently show a well-defined ~ 1.7 nm basal diffraction, typical of smectite. These results may suggest that a corrensite-like component or hydroxy-interlayered material is associated with the smectite. μ XRD data focusing on glass clasts from Unit 2A show a poorly crystalline material mixed with tri-octahedral smectite, zeolites and carbonates (Fig. 2B); this is consistent with the microprobe and pXRD data.

Conclusions: Both XRD datasets can be linked to the textural and geochemical observations made using EPMA. The changes in octahedral cation occupancy suggested by pXRD correlate well with the oxygen isotope data presented in Simpson et al. (2020, this conference), indicating a change in formation conditions through these intervals. The pXRD for the <0.2 μ m clay size fraction indicates the presence of an additional clay component similar to corrensite but which remains uncharacterized, and the μ XRD shows a poorly-crystalline smectite mixed with additional alteration products throughout the peak-ring. The other clay component observed in pXRD may be linked to the poorly crystalline, glassy material observed in thin section.

Further work (e.g., transmission electron microscopy) is planned to determine the exact nature of the interlayering of the smectite and corrensite-like clays, as well as the glassy material itself.

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References: [1] Morgan, J. V. et al. (2016) *Science*, 354, 878–882. [2] Gulick, S. P. S. et al. (2018) *Proceedings Of the IODP Vol. 364*. [3] Osinski et al. (2019) *Geology*, v48. [4] Kring, D. A. et al. (2017) *LPSC XLVIII*, #1212. [5] Seligman, A. N. et al. (2016) *GCA*, 191, 216–238. [6] Fisk, M. & McLoughlin, M. (2013) *Geosphere*, 9, 317–341. [7] Grant et al. (2018) *PSS*, 164, 106–126. [8] Gainey et al. (2017) *Nature Communications*, 8, 1230. [9] Simpson, S. L. et al. (2020) *LPSC LI*, this conference. [10] Brindley, G.W. and Brown, G., Eds., *Crystal Structures of Clay Minerals and Their X-Ray Identification*, *Mineralogical Society*, 305–356. [11] Libbey, R. et al. (2013) *Clays and Clay Minerals*, 61, 204–217. [12] Christeson, G. L. et al. (2018) *EPSL*, 495, 1–11.