

CHARACTERIZATION OF IMPACT GLASS ALTERATION AND ASSOCIATED SECONDARY CLAY MINERALOGY THROUGH THE UPPER CHICXULUB PEAK RING

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Introduction: Preliminary characterization of secondary alteration within the Chicxulub peak ring has revealed a spatially extensive, long-lived system that could have been favorable for the development of microbial communities [1-3]. Clay and zeolite mineralization is especially pervasive throughout the upper impact breccias and impact melt rock sequence and is associated with the remnants of silicate glasses. The conditions under which clay minerals, and related mineraloids (e.g., palagonite), form is arguably one of the most enigmatic subjects plaguing mineralogists studying both Earth and extraterrestrial materials. These phases form under such a wide range of conditions and are ubiquitous in previously or presently hydrous environments [4]. Silicate glass (diaplectic and quenched normal melt varieties) alteration is a complex process, the sequence of which has not been fully characterized in impact-hydrothermal settings. The formation and subsequent preservation of clays with high surface to volume ratio, namely the smectitic varieties, are also of interest within the astrobiology community as they have the potential to act as templates for prebiotic organic materials synthesis [5, 6].

In 2016 the joint International Ocean Discovery Program (IODP)-International Continental Scientific Drilling Program (ICDP) Expedition 364 recovered core from the Chicxulub peak-ring between ~506 and 1335 metres below the seafloor (mbsf) at Site M0077A, located at 21.45°N, 89.95°W [3]. The uppermost part of the sequence contains a layer of impact melt-bearing breccia overlying clast-poor impact melt rock, above highly fractured and altered crystalline basement. Here we present the results of a study on secondary clay mineralization within the upper impact melt-bearing breccia sequence, analyzing bulk-rock materials and focusing on silicate glass alteration. We have employed a variety of techniques to accomplish the following: (1) characterize the samples petrologically and texturally at the microscale, focusing on impact melt glasses and associated alteration products; and (2) separate and characterize the clay minerals to determine whether any zonation or transitions are preserved throughout the suevites and impact melt rocks.

Methods: All analyses were performed using facilities at the University of Western Ontario. Polished thin sections were 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 characterization, 5 samples of relatively homogeneous melt-bearing breccias at depths of ~629, ~635, ~639, ~663 and ~714 mbsf were selected for clay mineral separation and powder X-ray diffraction (pXRD), performed at the Laboratory for Stable Isotope Science (LSIS). The <2 μm size-fraction was separated from whole-rock drill cuttings following the techniques of Libbey et al. [7]. Samples were saturated with Ca^{2+} and K^{+} solutions, and samples of each were dispersed in deionized water and pipetted onto glass slides to achieve a preferred basal orientation of the clay minerals. A series of pXRD patterns were obtained for each sample in order to identify its clay minerals [7-9]. Scans were performed using a high-brilliance Rigaku Rotaflex RU-200B series diffractometer, equipped with a rotating anode (Co $K\alpha$ source operated at 160 mA and 45kV) and a graphite monochromator, at 2° 2 θ /min at a step size of 0.02° 2 θ .

Results: pXRD patterns of the <2 μm size-fractions of 5 whole-rock samples indicate smectite to be the dominant clay mineral group, with other minor unidentified phases. EPMA results reveal that it is Fe-Mg rich (*var.* saponite or nontronite) and ubiquitous as a secondary phase in the altered silicate glass clasts, but also exists within the matrices in lesser amounts (Figs. 1, 2). The smectite generally occurs along fractures within glass clasts and also forms alteration fronts; some has completely replaced smaller spherulitic clasts, forming a budding, globular texture.

Detailed wavelength-dispersive X-ray spectroscopy (WDS) maps and microimaging of the vesicular, altered remnant glassy clasts indicate a second phase that is finer-grained and less crystalline than the smectites (Fig. 1); it can be divided into two chemically distinct zones within a clast, one richer in Mg, Fe, and Ca and the other richer in Na, Al, and Si. Other minor accompanying mineral groups are Fe-Ti oxides, zeolites, carbonates, and minor barite and sulphides [1, 2].

Discussion: Fe-Mg smectite is arguably the most omnipresent clay throughout the impact breccias and melt lithologies in the Chicxulub peak ring, and it appears to be largely a byproduct of impact melt and

glass alteration; however, pXRD results for hydrated (54% relative humidity) and heat-treated (0% relative humidity) slides have shown incomplete peak collapse for some samples, possibly indicating the presence of hydroxy-interlayer material within the clays.

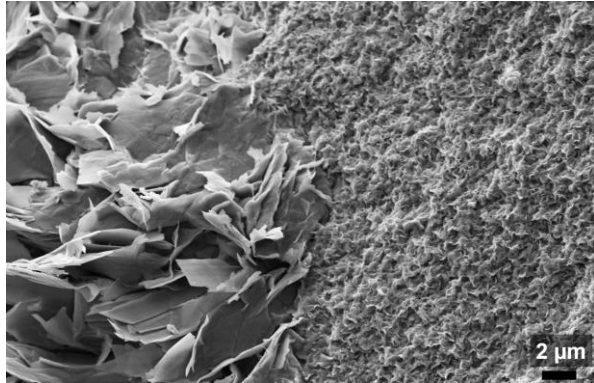


Figure 1: Secondary electron image of crystalline Fe-Mg smectite, and a poorly crystalline palagonite-like phase that has pervasively replaced a clast of impact glass in core 61, ~680 mbsf.

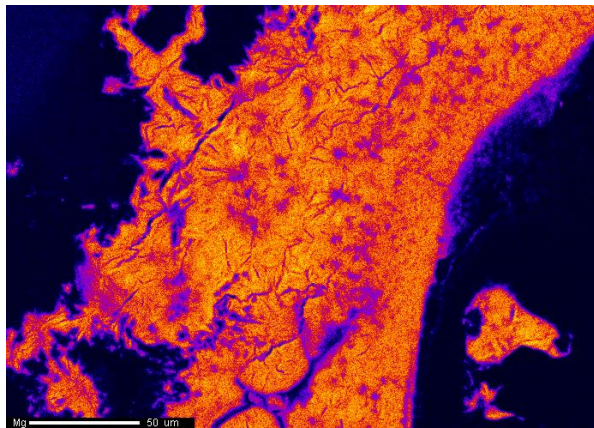


Figure 2: WDS map showing Mg concentration in secondary smectites within an altered glass clast in core 53, ~656 mbsf. Warmer colors indicate higher count intensity.

Elemental partitioning within individual altered glass clasts revealed by WDS mapping shows two distinct zones; one is more felsic (high Na, Si, Al, low Fe, Mg) and the other more mafic (enriched in Ca, Fe, Mg, and depleted of Si). Petrographic and microprobe imaging of both thin sections and rough samples indicates that these zones are composed of a poorly crystalline, palagonite-like mineraloid similar to that observed in volcanic rocks [10,11]. This second phase is easily distinguished from the larger, better crystallized smectite (Fig 1). Palagonitization is thought to be an early-stage devitrification process in hydrated glasses and is generally followed by clay mineral formation. It is possible that the smectite and palagonitic phases preserved

in situ in these glassy clasts represent two separate stages of alteration.

Previous work focusing on the hydrothermal system preserved in the Yaxcopoil-1 drill core uncovered similar secondary Mg- and Fe-rich smectites, as well as ‘amorphous mineral mixtures’, within impact melt-bearing breccias. The mafic composition of these clays was attributed to an Mg-rich precursor silicate glass that is thought to have formed as a later-stage hydrothermal phase below 300°C but before weathering and diagenesis [12-14]. Similar clay mineralogy, textures and alteration patterns are observed within the upper peak ring breccias described in the present study.

Forthcoming work: Additional clay separations are underway focusing specifically on the altered silicate glasses. Clay fractions will also be isolated from other bulk samples within the core, and smaller size fractions (<0.2 μm) will be collected from these and earlier separates. pXRD scans focusing on the 060 basal reflections will be performed in order to determine whether the smectites are predominantly tri- or dioctahedral varieties. Quantitative spot analysis will be performed on these phases (smectite + palagonite) to better understand their compositions and water content; this work may also reveal information on the initial sources of melt within the Chicxulub peak-ring breccias, and can be compared to the ‘microtektite’ glass spherules described by Belza et al. (2015) and altered glasses uncovered in the Yaxcopoil-1 core [12-15]. Lastly, these phases will also be examined spectrally (Raman, SWIR/VNIR). The clay separates will subsequently be used for $\delta^{18}\text{O}$ analysis.

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