ISOTOPIC AND MINERALOGICAL STRATIGRAPHY OF SECONDARY CLAYS FROM THE CHICXULUB PEAK-RING AND IMPLICATIONS FOR POST-IMPACT FLUID-ROCK INTERACTION.

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Introduction: Lithologic characterization of core material collected from the 2016 joint International Ocean Discovery Program–International Continental Scientific Drilling Program (IODP–ICDP) Expedition 364 indicates post-impact hydrothermal alteration has affected the Chicxulub peak-ring [1-4]. The impact melt-bearing breccias and melt rocks preserve a diverse suite of secondary minerals that suggest an evolving hypogene-supergene water-rock system that was alkaline-saline, comparable to seawater-basaltic glass alteration. These phases include predominantly Mg-Fe clays, zeolites, feldspars and carbonates together with lesser amounts of sulfides, sulfates and oxides [4,5]. The clays are especially pervasive through these units, likely due to the alteration of high amounts of silicate glass [6]. The conditions under which clay minerals form in impact settings on Earth and Mars, especially within the context of impact-generated hydrothermal systems, is convoluted due to their large range of possible formation conditions, as well as a general lack of detailed studies of terrestrial analogue sites. Clay minerals are commonly found in craters on Earth and across the surface of Mars, but are commonly not preserved *in situ* and lack significant geologic context. Phyllosilicates serve as excellent proxies for water-rock interaction in ancient environments due to their ability to preserve isotopic information about temperature and fluid sources; additionally, clays with high surface to volume ratios (i.e. the smectite group) can act as foundations for the synthesis of prebiotic organic materials [7,8].

Here we present the most recent δ^2H and δ^{18}O results from a detailed study of the clay mineralogy and geochemistry preserved in the Chicxulub upper peak-ring impact melt-bearing breccias and melt rocks. In particular, we present the clay isotope and mineral stratigraphy preserved throughout Units 2, 3 and part of 4, the information they reveal about hydrothermal fluid sources and temperatures, and discuss the paleoenvironmental conditions these results may indicate.

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. Following characterization, 28 samples of melt-bearing breccias and impact melt rocks from Units 2, 3 and 4 [1,2] were selected for clay mineral separation and powder X-ray diffraction (XRD), performed at the Laboratory for Stable Isotope Science (LSIS). The <0.2μm 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 [9-11]. XRD was performed using a high-brilliance Rigaku Rotaflex RU-200B series diffractometer, equipped with a rotating anode (Co Kα source). Hydrogen and oxygen isotope analysis of the clay minerals was completed using the methods most recently summarized by Huggett et al. (2017) [12] and Qi et al. (2017) [13].

Results: *Mineralogy:* Mg-Fe smectites are the most common clay mineral group comprising the <0.2μm size fraction of all lithologies. Subunits 2A, 2C, Unit 3 and the upper intervals of 4 contain a predominantly trioctahedral component (06*l* d=0.153-0.154nm; saponite), while the more porous intervals of 2B contain significant amounts of an additional dioctahedral component (06*l* d=0.149-0.150nm). The upper melt-bearing breccia intervals (2A-B and part of 2C) also show the properties of smectite interlayered with a chloritic component, but do not display all the characteristics of a typical corrensite [9]; these features, along with detailed clay XRD mineralogy through the other peak-ring units, are described more thoroughly by Simpson et al. (2020; *this conference*). *Isotope results:* δ^{18}O and δ^2H results are shown in Figure 1; our δ^{18}O data range from +10.3 to +18.6‰, similar to those obtained from the bulk silicate fraction of the Yaxcopoil-1 core [14], which sampled the annular trough surrounding the peak ring. Our δ^2H results consistently fall between –105 and –87‰ and show no apparent patterns with depth or correlation with the changes observed in the oxygen isotope data; these δ^2H results are also considerably lower than those obtained for the Yaxcopoil-1 core (–54 to –34‰) [14].

Discussion: Our isotope results plot along, or close to, the supergene-hydrothermal line [15], suggesting relatively low temperatures (30-60°C) and a fluid source unlike that proposed for the Yaxcopoil-1 core (Fig. 1). Based on the mineralogy, which suggests a Mg-Fe smectite mixed with a 'corrensitic' interlayered component, we have plotted the likely reservoir ranges for both a smectite and chlorite endmember composition, for comparison [15-17]. The data presented here indicate the fluids within the peak-ring, at least within the later, cooler stages of hydrothermal alteration, do not reflect a single unmodified end member and they certainly are not representative of seawater; instead, our results suggest a fluid source that was predominantly meteoric in origin. At first glance, this is seemingly at odds with the interpretation that seawater inundated the structure immediately post-impact.

Chicxulub had a profound effect on the regional karstic aquifer throughout the northern Yucatán peninsula; this is evident today in the unusual hydrogeological properties throughout this region, notably the high density of cenotes concentrated along the outer rim of the structure. They exhibit elevated groundwater flow and anomalously high freshwater discharge where they intersect the coast [18-20]. It is possible that meteoric fluids, during the later stages of the hydrothermal system, affected the peak-ring in a similar way and the hydrogeology of Chicxulub, and by extension large meteorite impacts, is more complex than previously thought.

There is a significant difference in the oxygen isotope composition of clays within the more porous region of 2B (~689 to 706 mbsf) (+14.2 to +18.6‰) when compared to the rest of the upper peak-ring impactites (+10.3 to +14‰). The mineralogy of these intervals is also different as they contain a significant dioctahedral component not observed elsewhere, indicating different formation conditions of the clay minerals. These differences could be attributed to the primary depositional environment of the breccias, which currently exhibit higher porosity and permeability [3]. Due to their physical properties, this region of the core likely experienced higher fluid flow for a longer period of time than other parts of the peak-ring (i.e. a higher W/R ratio) and, therefore, was also more susceptible to prolonged isotopic exchange between the fluids and rocks. It is possible that this region also records lower alteration temperatures compared to the surrounding impactites.

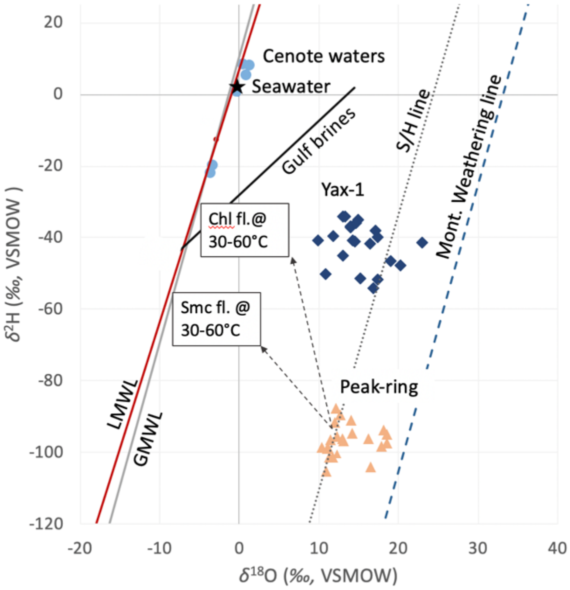

Figure 1: Summary of δ^{18}O and δ^2H results obtained for the <0.2μm size fraction (Peak-ring) and their respective calculated fluid compositions from 30-60°C for both chlorite (Chl fl @30-60°C) and smectite (Smc fl @30-60°C). These are compared to the results for bulk silicate analysis in Yaxcopoil-1 (Yax-1) [14]. Also shown are Local and Global Meteoric Water Lines (LMWL and GMWL, respectively), modern Xcolac cenote waters, Mexico [20], Gulf brines [21, 22], the supergene-hydrothermal line (S/H) after Sheppard and Gilg (1996) [14] and the montmorillonite weathering line (Mont.) after Savin and Epstein (1970) [23].

Conclusions: Integration of the mineralogical and isotopic datasets presented here provide a description of the possible fluid chemistry and temperatures that led to clay formation in the Chicxulub peak-ring. Changes in host rock porosity and permeability are reflected in the clay mineralogy and oxygen isotope results. Hydrogen isotope data are consistent through all units and suggest a modified, primarily meteoric water endmember. Local meteoric fluids are thought to not have changed significantly in this region over time, so it is difficult to know whether these data reflect modern or ancient sources. Temperature calculations, however, based on both oxygen and hydrogen isotope datasets (30-60°C) are consistent with smectite formation. That said, the possibility of post-formational clay-water isotopic exchange in the event that a later fluid episode affected the peak-ring cannot be ruled out, especially for hydrogen, which is much more susceptible to such effects than oxygen [24]. Nevertheless, these results emphasize the need for consideration of both regional and local geologic histories when trying to understand fluid-rock interaction, especially in a feature as large as Chicxulub. Clays are a complex group of minerals; additional detailed studies similar to this one on terrestrial analogue sites would provide further insight into how they might form on other hydrous, terrestrial bodies in our Solar System such as Mars, where they are also widespread.

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