CARBONATES IN THE PROXIMAL EJECTA DEPOSITS OF THE K/T CHICXULUB IMPACT CRATER.
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Introduction: 65.5 million years ago (Ma) a ~10 km-sized asteroid hit Earth, triggering the Cretaceous-Tertiary (K/T – now Cretaceous-Paleogene K-Pg) mass extinction – one of the largest biotic turnovers in the last 500 Ma. The devastating effect of the Chicxulub impact event is caused not only by the size of the projectile, yet primarily by the characteristics of the target, that included a huge volume of volatile-rich carbonate and sulfate platform sediments [1]. Geophysical surveys and exploration drillings from the Yucatan peninsula, Mexico, and from wells in the Gulf of Mexico provide estimates for the thickness of this sedimentary complex on top of the crystalline basement from ~3 (in the West) to ~4.5 km (Gulf area) [2].

The fate of carbonates and sulfates during impact events – current state of knowledge: Petrographical and geochemical observations on natural samples [3], experimental results, and numerical modeling show a range of impact effects on carbonate and sulfate target lithologies. These effects are depending on pressure (and hence, post-shock temperatures). Increasing pressure results in the formation of pressure twins and planar features, followed by melting, dissolution in silicate melts, up to complete dissociation [3-5], i.e., release of vast quantities of CO_2, sulfur and sulfur oxides. In the Chicxulub impact event, ~100 to 500 Gt of sulfur were released nearly instantaneously [1]; and silicate melts with high CaO contents have been reported to occur, for example, as spherules in the K-Pg event bed at Haiti [6] or in melt lithologies from drill cores (e.g., Y-6, C-1, Yaxcopoil-1).

Carbonate spherules in Chicxulub ejecta deposits – altered silicate impact spherules? In addition to the CaO-rich silicic melts, the Chicxulub ejecta deposits in the Gulf of Mexico area is usually very rich in carbonates (up to 80 wt%) [7]. So far, the carbonate has commonly been considered as precipitation product during diagenesis, and has been dissolved by acid treatment in search for silicic spherules. Consequently, spherules consisting of a µm-thick outer silicate shell and a core of sparry calcite (Cc) (Fig. 1) that are very abundant in the Chicxulub ejecta deposit (e.g., at Shell Creek, AL [8]) have been interpreted as altered silicate glass spherules, with a diagenetic wall of smectite that formed after an early palagonite shell while Cc in the inner part should represent a secondary filling after total dissolution of the original silicate glass [8-10].

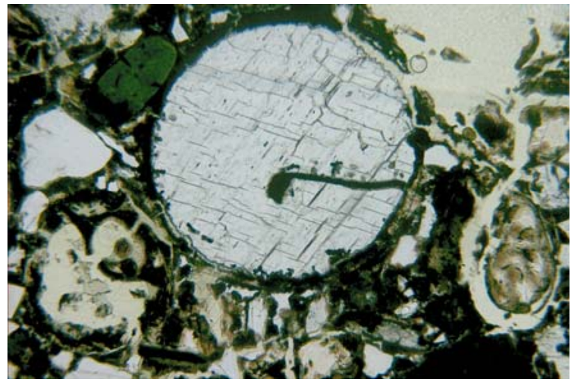

Fig. 1. (opposite column) Photomicrograph of a Cc spherule with silicic rim (Ø ~ 600 µm). Shell Creek, AL. X nicols.

Carbonate spherules as primary component in Chicxulub ejecta deposits: The proposed process [8-10], outlined above, is ad odds with observations and theoretical considerations. In volcaniclastic deposits, distinct alteration rinds form from glass reaction with water, a process termed palagonitization for basaltic glass. Further transformation of glass to secondary alteration phases is depending on chemical composition, temperature, and pH of the fluid, with higher dissolution rates in acidic environment [11]. The process is best explained by the detachment of framework cations (i.e., Al and Si) from the solid surface, causing also an increase in porosity. This transformation process necessarily progresses from the outer shell and/or cracks to the inner parts of the individual volcanic clasts. Subsequently, the early, mostly amorphous alteration rims are transformed into more stable phyllosilicates and oxides/hydroxides [11]. Yet a complete pseudomorphic replacement of silicic volcanic clasts by carbonates is extremely rare and has been observed to occur only by specific depositional conditions (e.g., at methane seeps [12]). Moreover, the glass replacement scenario would imply that the considerable decrease and increase in density (ρ) from fresh glass ($\rho \leq 2.75$ g cm^{-3}, depending on the Si content), over palagonite (ρ of 1.90 to 2.10 g cm^{-3}), to Cc ($\rho = 2.71$ g cm^{-3}) does not harm the delicate internal textures of the spherules (Fig. 1).

Supporting evidence: Other arguments contradicting a secondary origin of Cc in the impact spherules are: (i) calcite spherules contain smaller Cc spherules, separated by a few tens of µm-thin smectite (Fig. 2); (ii) glass spheroids contain voids and bubbles filled with radially grown Cc (Fig. 3); (iii) considerable compositional differences (Fe-Mg- vs Si-Al-K-rich) co-occur with sharp contacts within one spherule –

dissolution of these different types of "glass" would require very different pH/eH conditions; (iv) the K-Pg event bed in NE Mexico, Texas [7], and Alabama contain spherules showing evidence of silicate-carbonate liquid immiscibility, spherules consisting of sparry Cc or numerous accreted µm-sized Cc crystals as well as silicic spherules rimmed by sparry Cc; (v) the cathodoluminescence of Cc spherules differs drastically from that of diagenetic Cc (Fig. 4); (v) foraminifera shells that occur together with the carbonate spherules lack totally alteration or diagenetic effects; and finally, (vi) preservation of silicic glass in certain K-Pg event beds [6, 7], implies that dissolution of glass and precipitation of smectite did NOT occur over a long period of time – obviously, weathering and not diagenesis plays the major role in the alteration of the spherules.

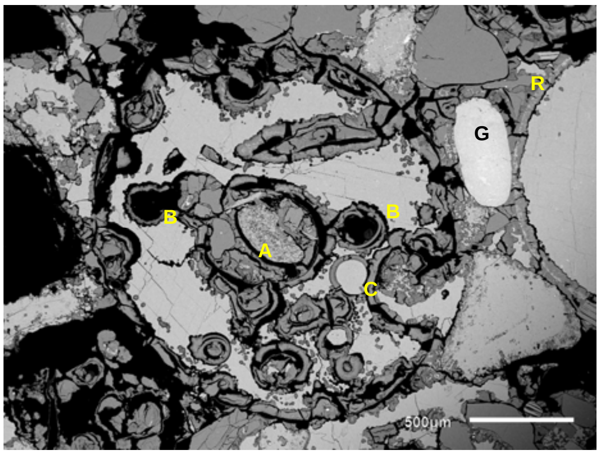

Fig. 2. BSE image of a complex carbonate spherule with silicic rim, containing a Cc-bubble (**C**), hollow bubbles (**B**), and an accretionary lapilli (**A**), all separated by thin layers of smectite. **G** = glaucony; **R** = laminated clay rim giving evidence for dissolution – precipitation during alteration of the silicic glass shell around the Cc spherule. Shell Creek, AL.

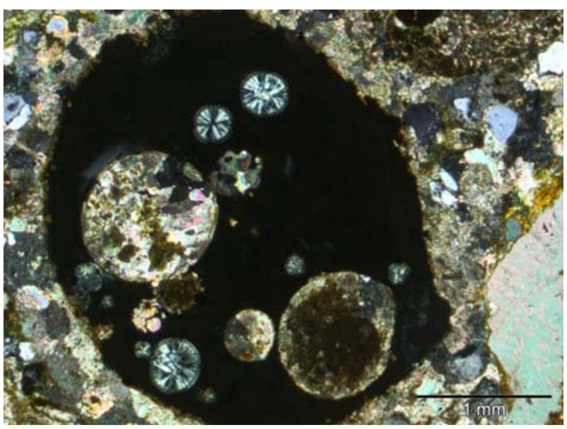

Fig. 3. Photomicrograph of a silicic glass spherule with Cc-bubbles with different textures. La Lajilla, Mexico. X nicols.

One fundamental supporting argument comes from models of cratering events: They indicate that the ejecta blanket contains material of the upper target layers; in the Chicxulub case, therefore, carbonates and sulfates shocked to a different degree are expected to occur in the K-Pg event bed (e.g., [13]). Undisputed carbonate ejecta in K-Pg event beds is present in the form of accretionary lapilli (e.g., Brazos River TX section [14]), and clasts with shock-specific textures (e.g., ODP 207, Demerara Rise [15]).

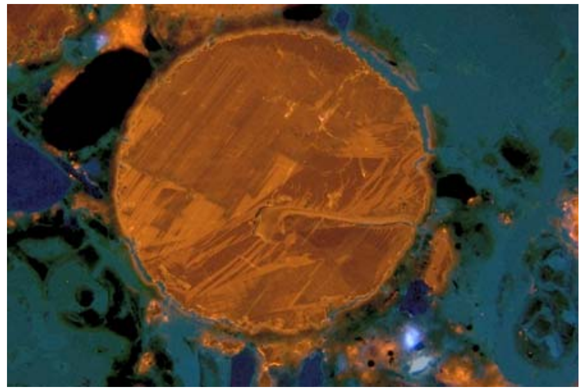

Fig. 4. Cathodoluminescence image of the carbonate spherule (Ø ~ 600 µm) shown in Fig. 1. Note the very low, dark ("brick") red to dull brown luminescence which may be related to enhanced Fe and Mg contens, and absence of concentric zoning. Shell Creek, AL.

Conclusions: Our petrographic observations suggest that considerable amounts of carbonate melt were generated and ejected by the Chicxulub impact, and deposited in the Gulf of Mexico region. The amount of carbonate ejecta frequently exceeds that one of silicic melt lithologies in K-Pg event beds. Carbonate and silicic melts were dispersed concurrent but as distinct melt batches that, in part, were mixed as evidenced by emulsion-like bubbly textures and Cc spherules with thin shells of silicic melt.

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