

MICROSTRUCTURAL CHARACTERIZATION OF TiO₂-II IN THE CHICXULUB PEAK RING.

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Introduction: The peak ring of the ~180 km-diameter Chicxulub impact crater on the Yucatán Peninsula, Mexico, was recently drilled during IODP-ICDP Expedition 364, producing core M0077A [1]. The new core provides insights into the anatomy, composition, tectonic deformation, shock metamorphism, and post-impact overprint of crater-filling impactites and crystalline basement rocks [2]. The basement rocks were shocked to ~12.5–17.5 GPa [3], uplifted, and hydrothermally altered [4]. This study presents a combined Raman spectroscopic and electron backscatter diffraction (EBSD) study of TiO₂-II, a high-pressure polymorph of TiO₂ with an α -PbO₂ structure (orthorhombic; space group *Pbcn*; density 4.34 g/cm³ [5,6]), in shocked granitoid rock of the Chicxulub peak ring.

Sample and Analytical Methods: We selected shocked granitoid sample 174-2 (core depth 949 m below seafloor [1,2,7]) from the Chicxulub peak ring for high-resolution analyses. The granitoid rock contains mm-sized aggregates of TiO₂ crystals replacing altered euhedral titanite. The sample was analyzed using a Leica DMLP optical microscope; a 7600f JEOL field emission gun scanning electron microscope (FEG-SEM); a CAMECA SX 100 electron microprobe; a Jobin–Yvon Horiba LabRAM HR 800 μ -Raman spectrometer (514 nm Ar laser; ~1 μ m spot diameter); and an Oxford Instruments Symmetry EBSD detector on the JEOL FEG-SEM (20 kV, 16 nA, 100 nm step size for phase and orientation mapping).

Results: Individual TiO₂ crystals in sample 174-2 are up to ~70 μ m in length and appear brown-translucent under the optical microscope. The TiO₂ grains commonly occur as euhedral to subhedral crystals. Micro-Raman analysis of TiO₂ crystals produced spectra with distinct bands at *ca.* 149, 173, 287, 315, 340, 356, and 532 wavenumbers (cm⁻¹) [7], in close agreement with Raman spectra for the high-pressure polymorph TiO₂-II [5,8] (Fig. 1). Some spectra reveal additional bands at 442 and 610 cm⁻¹, indicating the presence of rutile. No Raman peaks typical of anatase or brookite were obtained in sample 174-2. Backscattered-electron (BSE) imaging reveals lamellar and locally granular microtextures, as well as subparallel and intersecting sets of fractures within individual TiO₂ crystals (Fig. 2). Electron microprobe results show the

TiO₂ crystals contain ≤ 2.5 wt% Fe₂O₃, ≤ 1.5 wt% Nb₂O₃, ≤ 0.4 wt% SiO₂, and ≤ 0.3 wt% Ta₂O₅.

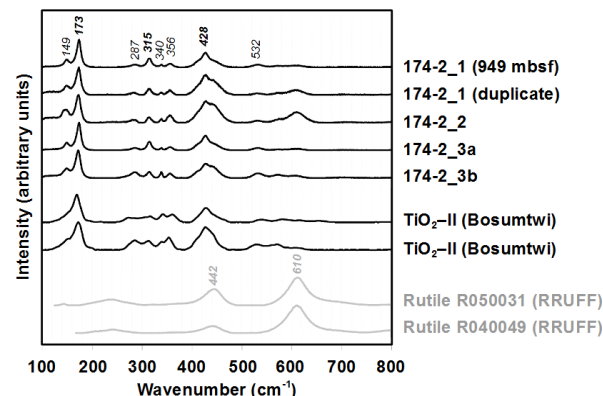


Fig. 1: Raman spectra for TiO₂-II in granitoid rock of the Chicxulub peak ring (sample 174-2), TiO₂-II from the Bosumtwi impact crater, Ghana [8], and reference spectra for rutile (RRUFF database [20]). Reference spectra for anatase and brookite are not shown. The position of laser spots in the Chicxulub sample is indicated in Fig. 2.

High-resolution EBSD mapping of individual TiO₂ crystals (Fig. 2), calibrated for rutile, anatase, brookite, and TiO₂-II (i.e., orthorhombic TiO₂ of Laue group *mmm* [9]), show a complex arrangement of locally cross-cutting lamellar and granular subdomains within each crystal investigated. EBSD phase maps reveal that the grains are composed of different TiO₂ polymorphs: (1) TiO₂-II, which forms larger, coherent, and commonly elongated lamellar domains that make up ~30 to 90% of the crystals; (2) rutile, in the form of microcrystalline granules and lamellae that locally occur between coarser-crystalline TiO₂-II; and (3) minor anatase not detected in Raman spectra, found along the margins of the TiO₂ crystals and within the surrounding matrix. The TiO₂-II correlates with slightly brighter domains in high-contrast BSE images (Fig. 2). Internal cross-cutting relationships suggest the microcrystalline-granular rutile overprints shock-produced TiO₂-II. EBSD orientation maps and pole figures show that individual TiO₂-II lamellae are related to one another by rational twin orientations, which likely formed by transformation twinning. Interphase misorientations between shock-produced TiO₂-II and neocrystalline rutile granules are systematically aligned, indicating that the solid-state reversion to rutile is crystallographically controlled.

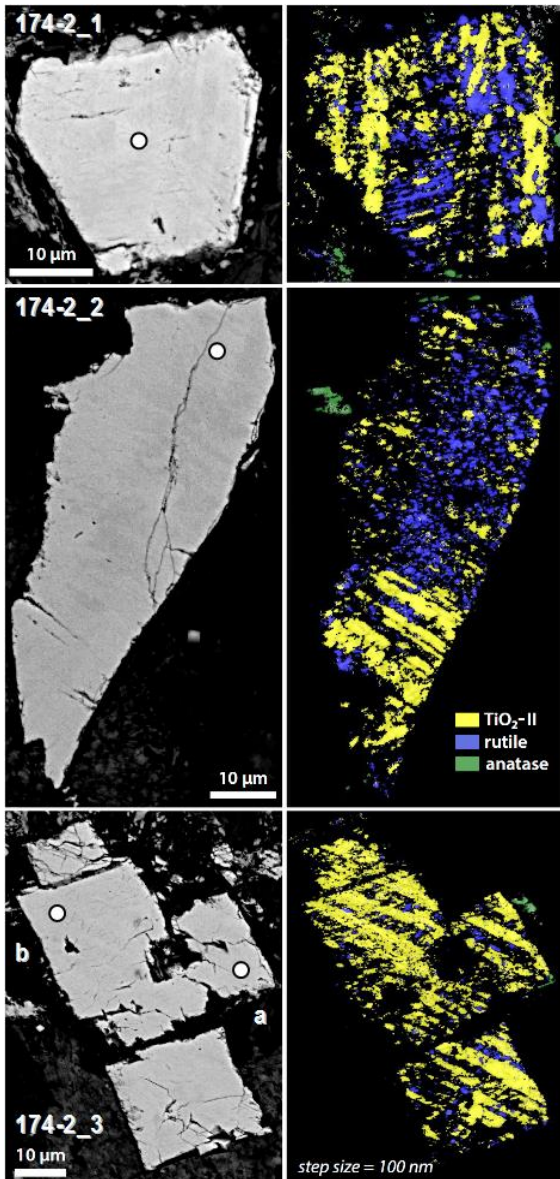


Fig. 2: Backscattered electron images (left) and corresponding EBSD phase maps (right) of TiO_2 crystals in Chicxulub peak-ring sample 174-2. White spots and labels indicate positions where Raman spectra (see Fig. 1) were collected.

Discussion and Conclusions: The discovery of $\text{TiO}_2\text{-II}$ in rocks from the Chicxulub crater is the latest addition to a short list of terrestrial impact structures and distal ejecta layers where this shock-produced high-pressure polymorph is found [5,8,10-13]. Notably, peak-ring sample 174-2 hosts an outstanding natural occurrence of $\text{TiO}_2\text{-II}$, both in terms of crystal abundance and the size of individual crystals. The $\text{TiO}_2\text{-II}$ in this and other Expedition 364 core samples [1,2] is the product of a long and complex pre-, syn-, and post-impact history recorded in Chicxulub's peak-ring lithologies. Based on our petrologic and microstructural observations of TiO_2 grains, we propose the

following sequence of geologic events: (1) Around 340 Ma, granitoid plutons crystallized in the Maya Block [14], as indicated by U-Pb ages for magmatic titanite [7]. (2) Between ~340 Ma and 66 Ma, titanite in the granitoid rock was altered to rutile and/or anatase (+calcite, +quartz), likely during a pre-impact regional magmatic and/or hydrothermal event, and presumably under high CO_2 activity [15]. (3) During the 66 Ma Chicxulub impact, rutile and/or anatase partially to fully transformed to the high-pressure polymorph $\text{TiO}_2\text{-II}$ at shock pressures ~12.5–17.5 GPa [3] (consistent with experimental transformation pressure constraints of ~13–20 GPa [16,17]). The shock-induced transformation to $\text{TiO}_2\text{-II}$ may have been facilitated by pre-impact heating of the peak ring lithologies at ~8–10 km depth [1] to ~200–250 °C (at a typical geothermal gradient of ~25 °C/km); shock metamorphic overprint of the granitoid rock contributed some additional ~100–150 °C [18]. Finally, (4) the newly formed Chicxulub crater, including shocked and uplifted rocks in its peak ring, hosted a long-lived post-impact hydrothermal system [4,19]. As the peak ring cooled, $\text{TiO}_2\text{-II}$ incompletely back-transformed to neoblastic granules of rutile (Fig. 2).

$\text{TiO}_2\text{-II}$ is stable below 340°C, but rapidly (within minutes to weeks) reverts to rutile at >440–500°C [13,16]. The formation and preservation of $\text{TiO}_2\text{-II}$ in the Chicxulub peak ring, thus, places new petrologic constraints on shock conditions and post-impact temperatures inside the peak ring during crater cooling. Chicxulub's peak-ring lithologies must have cooled below 340°C relatively quickly (or did not significantly exceed those temperatures in the first place), so as to preserve much of the shock-produced $\text{TiO}_2\text{-II}$. Furthermore, these results suggest that $\text{TiO}_2\text{-II}$ may be a common shock indicator at terrestrial impact structures, including those that experienced vigorous and long-lived post-impact hydrothermal alteration.

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