SPHENE AND TiO_2 ASSEMBLAGES IN THE CHICXULUB PEAK RING: U–Pb SYSTEMATICS AND IMPLICATIONS FOR SHOCK PRESSURES, TEMPERATURES, AND CRATER COOLING

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Introduction: Basement rocks in the peak ring of the ~180 km Chicxulub impact structure, recently probed during the IODP–ICDP Expedition 364 (Site M0077) and predominantly composed of granitoids [1], were shocked to ~12.5–17.5 GPa [2], uplifted, and hydrothermally altered [3]. One accessory mineral assemblage commonly found in the peak ring granitoids and in impact breccias is sphene (titanite; $CaTiSiO_5$) up to several mm in size and, where altered, in places associated with TiO_2 crystals. Here, we report shock-related and post-impact microstructures observed in sphene, and their significance for constraining the temperature regime in Chicxulub's peak ring.

Samples and Analytical Methods: Primary magmatic and altered sphene was studied in polished thin-sections of samples (a) 85–1–26–28 (impact melt breccia, core depth ~717 mbsf); (b) 150–3–25.5–27 (shocked granite, ~887 m); (c) 163–3–52.5–54.5 (shocked granite with impact melt breccia, ~917 m); (d) 174–2–19–20 (shocked granite, ~949 m); and (e) 237–2–60–61.5 (shocked granite, ~1133 m). The samples were analyzed using optical polarization microscopy at the LPI; a JEOL 5910LV scanning electron microscope; a Jobin–Yvon Horiba LabRAM HR 800 µ-Raman spectrometer (514 nm Ar laser; 1 µm resolution) at the Johnson Space Center; and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) using a Varian 810 quadrupole system (193 nm laser, 40–50 µm spot size, 30 s on sample after 20 s of blank; MKED1 sphene standard [4]) at the University of Houston.

Results: Sphene in the granite ranges from seemingly unaltered crystals, some of them with irregular and planar fractures [samples (b) and (e)], via grains partially replaced by brownish, semi-opaque crystals of TiO_2 along fractures [(c)], to granular aggregates that entirely consist of neoblasts (≤ 50 µm) of TiO_2 [(d) and (e)] surrounded by relict sphene, chlorite, and locally silica, calcite, and/or epidote. One sphene aggregate ~300 µm in size in (a) has a microporous texture and an irregular outline; another aggregate in (d) is microcrystalline-porous sphene, chlorite, and minor TiO_2. Raman spectra of the TiO_2 crystals in samples (d) and (e) show distinct bands at wavenumbers (cm^{-1}) 150, 173, 281, 287, 315, 340, 356, 428, 440, 532, 578, and 609, and closely resemble spectra for TiO_2–II, a high-pressure polymorph of TiO_2 with α-PbO_2 structure [5–11]. Laser ablation ICP-MS analysis of one mm-sized sphene grain in sample (b) produced a U–Pb concordia age of 341 ± 6 Ma (n=3, MSWD=0.85, P=0.36), consistent with U–Pb ages for zircon from the peak ring granite [12]. The likely hydrothermally grown microcrystalline-porous sphene aggregate in sample a); and the intensely altered, microcrystalline sphene and TiO_2–II crystals in sample (d) all yielded considerable amounts of common Pb ($^{206}Pb/^{204}Pb \leq 20$), which precluded precise U–Pb geochronology.

Discussion: Shock-produced TiO_2–II was previously reported from four terrestrial impact structures [6–9] and distal impact ejecta deposits [10,11], where it had likely been produced from rutile and/or anatase. This study is the first report of TiO_2–II from the Chicxulub crater, and probably the first recognition of this high-pressure TiO_2 polymorph associated with shocked and altered sphene. However, rutile and/or anatase may have been present in (altered) sphene crystals prior to the Chicxulub impact, i.e., the TiO_2–II may not be a direct shock-decomposition product of sphene. The apparent discrepancy between shock pressures required to produce TiO_2–II in experiments (≥ 20 GPa) [13] and estimates for the peak ring rocks (≤ 17.5 GPa) [2] may be explained by the pre-heating of basement rocks at ~10 km depth [1] prior to the Chicxulub impact. As TiO_2–II is stable below 340°C and completely reverts to rutile within minutes to hours above 500°C [5,6], the presence of this phase in the shocked granitoids, where preserved, provides new constraints on the temperature and cooling history of the Chicxulub peak ring [14].

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