

**DISCOVERY OF A SHOCK-INDUCED POLYMORPH OF RUTILE WITH  $\alpha$ -PbO<sub>2</sub> STRUCTURE (TiO<sub>2</sub>II) IN FOUR NEOARCHEAN SPHERULE LAYERS FROM WESTERN AUSTRALIA AND SOUTH AFRICA**

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**Introduction:** Over a dozen Precambrian spherule layers (SLs) older than ~2.4 Ga have been found in South Africa (SA) and Western Australia (WA) [1]. Geochemical evidence (e.g., Ir, Cr isotopic ratios) supports an impact origin for the layers (e.g., [2]). However, only a single shock-metamorphosed grain has previously been found in these SLs [3]. We present the results of a study of heavy mineral (HM) separates from samples of the Carawine, the Jeerinah, and the Bee Gorge SLs (CSL, JSL, BGSL, respectively) from WA, and the Monteville SL (MSL) from SA.

**Samples and Methods:** We dissolved nine dolomite/dolomixtite SL samples (~8.4 kg), and seven dolomite and carbonate lutite context samples (CS) (~1.84 kg) in warm HCl and/or HNO<sub>3</sub>. We wet sieved the residues into five size fractions, and then put the 63-125  $\mu$ m and the 125-250  $\mu$ m size fractions through heavy liquid (>2.96 g/cm<sup>3</sup>) separation. Single-grain X-ray diffraction (XRD) using Gandolfi and Debye-Scherrer (D-S) cameras was initially done on ~200 grains from seven samples of the CSL, the JSL, and the BGSL. Micro-Raman spectroscopy was then done on ~2100 grains from the 16 samples.

**Results:** The HM assemblages typically include abundant (>50%) anatase, and minor (~1%-10%) rutile, zircon, and tourmaline, and trace (<1%) actinolite, anglesite, clinopyroxene, clinozoisite, magnesiochromite, monazite, and xenotime. Using micro-Raman spectroscopy, we identified the  $\alpha$ -PbO<sub>2</sub>-structured TiO<sub>2</sub> phase (TiO<sub>2</sub>II) in 23 rutile grains in four samples, one from each of the SLs. In addition to the rutile bands, many spectra show strong bands indicative of the TiO<sub>2</sub>II phase at wavenumbers (cm<sup>-1</sup>) 150, 174, 285, 314, 339, 356, 428, 532, and 571 [4]. For the four SLs, there are ~0.02 of these grains/g of SL, and these grains average ~1.8% of the total rutile grains/SL.

**Interpretations and Conclusions:** We interpret the TiO<sub>2</sub>II-bearing rutiles in the four SLs as shocked grains on the basis of their geologic and petrologic contexts. The presence of 23 shocked rutiles in the four SLs and their absence in the CS suggest a genetic association of the grains with the SLs. The shocked rutiles provide physical evidence that confirms an impact origin for the four SLs. To our knowledge, this is the first report of a shock-induced, high-pressure polymorph in any Precambrian SL/distal impact-ejecta layer.

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