

A New Natural Dense Polymorph of Rutile with the α -PbO₂ Structure in Shocked Gneisses from the Ries Meteorite Crater, Germany

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TiO₂ occurs in the Earth's crust, chondritic and differentiated meteorites in the low-pressure polymorphs rutile (P42/mnm), anatase (I41/amd), and brookite (Pbca). The behaviour of TiO₂ under high-pressure has attracted the attention of experimentalists due to the analogy of its behaviour to that of silica (Liu, 1978, Gerward and Olsen, 1997). Static DAC experiments on TiO₂ produced two post-rutile polymorphs: the baddeleyite-structured type phase (P21/c) $\rho=4.728\text{gm/cm}^3$, and α -PbO₂ structured phase, (Pbcn); $\rho=4.336\text{ gm/cm}^3$. The rutile/baddeleyite phase transition commences at 12GPa and is complete at 20GPa (Gerward and Olsen, 1997). The α PbO₂ polymorph forms upon decompression of the baddeleyite-structured phase at 7GPa (Gerward and Olsen, 1997). Dynamic experiments indicate that a phase transformation begins below 20GPa and is complete below 40GPa (McQueen et al., 1967, Linde and DeCarli, 1969). The baddeleyite-structured phase was never recovered in any shock-wave experiment. Dynamic sample recovery experiments revealed only α -PbO₂-structured Titania (McQueen et al., 1967, Linde and DeCarli, 1969). It was suggested that the recovered orthorhombic (Pbcn) polymorph formed upon decompression of the much denser baddeleyite polymorph.

Rutile grains in shocked gneiss fragments whose silicates experienced peak-shock-pressures between 30 and 35GPa (El Goresy et al., 2000) were investigated in reflected light microscopy. The gneisses were collected from the suevite fall out ejecta in the Ries meteorite crater in Germany. Grains with signs of densification evidenced from high reflectivity were selected for detailed microscopic and fine-scale laser micro-Raman investigations. Reflected light survey of the shocked rutiles revealed the occurrence finely-spaced lamellae with a prominent tweed pattern and higher reflectance at the rutile grain boundaries. These zones also depict pale blue internal reflections not typical of rutile, anatase or brookite. Detailed fine-scale laser micro-Raman mapping were conducted on a large number of these grains depicting the evidence of

densification. A rutile grain experimentally shocked at P>15 GPa in which the α PbO₂ polymorph was confirmed by X-ray diffraction was used for comparison.

The Raman spectrum of the interior of the shocked grains showed the characteristic Raman bands of rutile at the wave numbers 240, 446, and 610cm⁻¹. The outer rims with the higher reflectance revealed a distinct Raman spectrum with the characteristic Raman bands: 152, 285, 315, 340, 358, 428, 532cm⁻¹ in addition to the subdued bands of rutile. The Raman spectrum is identical to that of the α PbO₂-structured phase in the experimentally shocked sample. However, the Raman bands of the natural sample are better resolved than those of the experimentally produced phase indicating a higher degree of crystallinity. None of the analysed areas revealed the spectral signature of the baddeleyite polymorph, anatase or brookite. Probably the natural α PbO₂-structured phase was formed upon decompression from a high shock state of the much denser baddeleyite polymorph. This is the first natural occurrence of a post-rutile polymorph.

The occurrence of the dense α PbO₂-structured TiO₂-polymorph at the outer rims of the rutile grains is strongly suggestive that phase transformation was most efficient at their grain boundaries. The survival of this phase in the naturally shocked gneisses also sets an upper bound for the post-shock temperature at 550 C. X-ray diffraction and Transmission Electron Microscopy data will also be presented.

Liu G-L, *Science*, **199**, 422-424, (1978).

Gerward L & Olsen JS, *J. Appl. Cryst.*, **30**, 319-325, (1997).

McQueen RG, Jamieson JC & Marsh SP, *Science*, **155**, 1401-1404, (1967).

Linde RK & DeCarli PS, *J. Chem. Phys.*, **50**, 319-325, (1969).

El Goresy A, Gillet PH, Chen M, Künstler F, Graup G & Stähle V, *Am. Mineral.*, **85**, Submitted, (2000).