



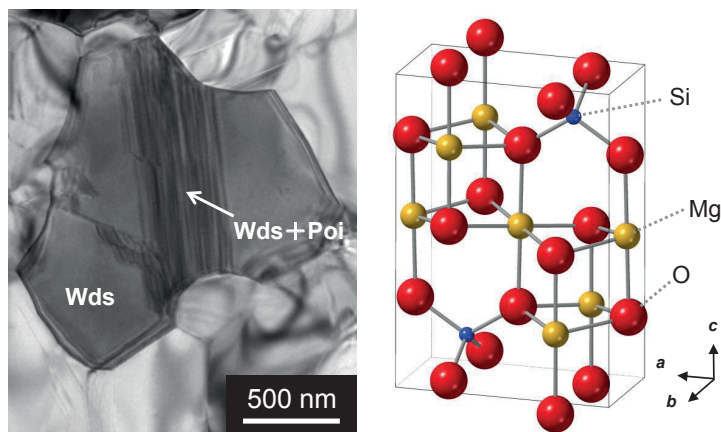
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The Fourth Polymorph of Mg_2SiO_4 : Poirierite in Shocked Meteorites

Mineral physicists, using high-temperature and high-pressure experiments, have been trying to clarify the structural changes and phase equilibrium of minerals inferred to exist in Earth's deep interior. A variety of high-pressure phases of silicates and oxides have now been synthesized. In nature, such phases have been found mainly in shocked materials from terrestrial impact craters and stony meteorites, because high-velocity collisions effectively simulate the high-pressure and high-temperature conditions in Earth's deep mantle. Mineralogists have been enthusiastically using transmission electron microscopy (TEM) to hunt down high-pressure minerals after the discoveries of $MgSiO_3$ -ilmenite (akimotoite) and $MgSiO_3$ -perovskite (bridgmanite) in shocked chondritic meteorites during the late 1990s (Sharp et al. 1997; Tomioka and Fujino 1997, 1999). Currently, over 30 high-pressure minerals have been discovered in natural rocks.

Olivine [$(Mg,Fe)_2SiO_4$] is the most common constituent mineral in the Earth's upper mantle. It transforms into a spinelloid structure (wadsleyite) and a spinel structure (ringwoodite) with increasing pressure. These high-pressure minerals are considered dominant in the mantle transition zone at depths of 410–660 km. Meteoritic wadsleyite and ringwoodite often show nanometre-scale planar defects observable only under a TEM. Based on the observations of the defect structures, combined with the topological analyses of the crystal structures of the olivine polymorphs, shear mechanisms without long-range ionic diffusion are posited to promote polymorphic transformations. The transformation model also predicts the possible occurrence of an intermediate spinelloid structure (ϵ phase) (Madon and Poirier 1983). This hypothetical phase remained undiscovered in high-pressure syntheses products and natural samples for more than three decades. Our high-resolution TEM studies, however, have recently clarified that the ϵ phase is present in shocked chondrites (Tomioka et al. 2021). The phase has been approved as a new mineral species by the International Mineralogical Association's Commission on New Minerals, Nomenclature and Classification and named "poirierite" in honour of Jean-Paul Poirier, who greatly contributed to mineral physics, including the theoretical prediction of ϵ - Mg_2SiO_4 .

In the Miami and Tenham chondrites, wadsleyite and ringwoodite occur as monomineralic aggregates entrapped in shock-induced melt veins. These occurrences suggest that the olivine grains in the host rock were



(LEFT) Transmission electron micrograph of a wadsleyite (Wds) grain intergrown with poirierite (Poi) in the Miami chondrite. (RIGHT) The crystal structure of poirierite refined by single-crystal X-ray diffraction data.

initially transformed into stable high-pressure phases by nucleation and growth mechanisms in prograde shock metamorphism without melting. The nanoscale lamellar poirierite is topotactically intergrown within the wadsleyite and ringwoodite grains (FIG. 1). Single-crystal X-ray diffraction analysis of poirierite coexisting with ringwoodite in the Suizhou chondrite, as well as the results from first-principles calculations, confirmed that poirierite has an orthorhombic unit cell having the smallest dimensions of any of the pre-existing spinelloid structures (FIG. 1). Rapid cooling and decompression during retrograde shock metamorphism would have hindered the direct back-transformations from wadsleyite/ringwoodite to olivine but would have promoted the metastable formation of poirierite by a shear mechanism.

The formation processes of high-pressure minerals, including poirierite, are closely related to the pressure–temperature–time histories of impact events. The pressure values deduced from phase equilibria of meteoritic components provide mutual collision velocities of their parent bodies. Shock pressure durations, estimated from phase transformation kinetics and element diffusion in meteoritic high-pressure minerals, provide the sizes of impactors. The mineral formation process when combined with the radiometric ages of shock events of meteorites provides more robust constraints for the theoretical models of the evolution of the early Solar System. Such knowledge also potentially contributes to a better understanding of the dynamics of the deep Earth.

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