

Supplementary Material to the article

“The first experimental synthesis of Mg orthocarbonate by the reaction $\text{MgCO}_3 + \text{MgO} = \text{Mg}_2\text{CO}_4$ at pressures of the earth’s lower mantle”

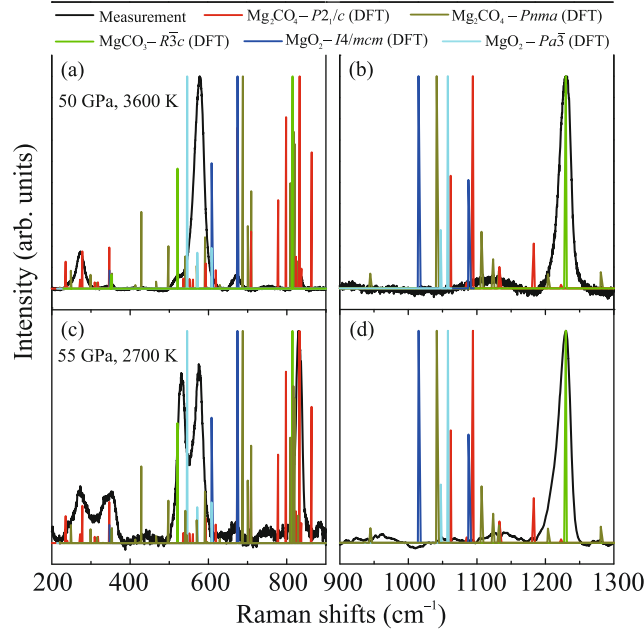


Fig. S1. Experimentally determined Raman spectra at 3600 K and 50 GPa (a), (b) and at 55 GPa and 2700 K (c), (d) in comparison to DFT-based calculations for MgCO_3 - $R\bar{3}c$, Mg_2CO_4 - $P2_1/c$, Mg_2CO_4 - $Pnma$, MgO - $I4/mcm$, and MgO - $Pa\bar{3}$ phases at 60 GPa

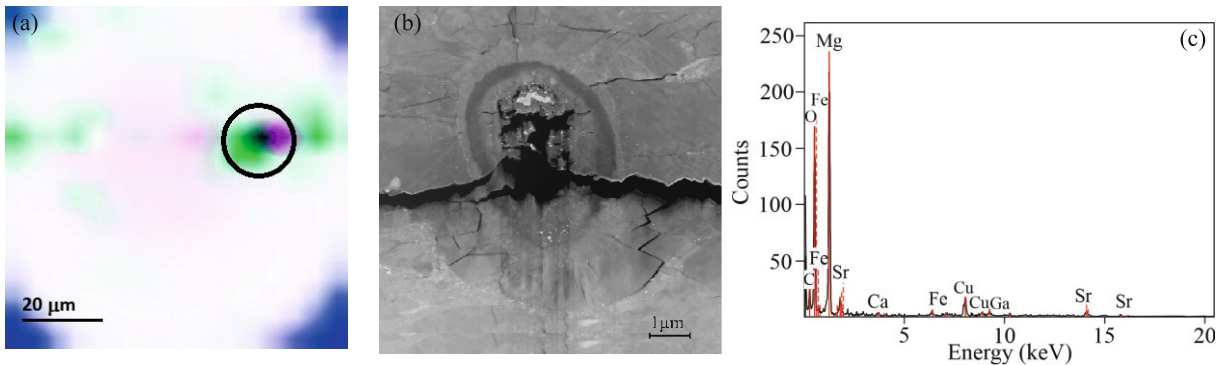


Fig. S2. (a) – A map showing the spatial distribution of the intensity of the XRD peaks from rhenium gasket (blue), platinum powder (green), newly formed phase with peak near $1.9 \text{ \AA}$ (magenta); the laser heated area is shown by a circle; (b) – TEM HAADF micrograph of the sample extracted from the DAC chamber; (c) – the EDS spectrum of the new phase, suggested as Mg-carbonate/orthocarbonate; Fe and Ca are impurities inherited from the initial sample of MgCO_3 , Ga is from FIB sample preparation, Cu – from the copper grid

High-pressure compounds in the Mg–C–O system. There are eight known stable compounds in the Mg–C–O system at pressures above 50 GPa: MgCO_3 , Mg_2CO_4 , MgO , MgO_2 , Mg_2C , C, O_2 , CO_2 . MgCO_3 and MgO were the initial reagents and were observed in all experiments as unreacted components due to the temperature gradient in the DAC chamber. Peaks of C (diamond), O_2 , CO_2 were not identified neither on the

Raman spectra, nor on X-ray diffraction patterns. The performed calculations (Fig. S2) have shown that the only Mg-carbide phase stable at 50–60 GPa is $\text{Mg}_2\text{C}-Pnma$, and we do not observe this phase in our experiments.

Stability of Mg-carbides at high pressures. According to available experimental and theoretical data, Mg_2C is the only Mg-carbide thermodynamically stable at pressures above several GPa and up to 300 GPa. Experimentally Mg_2C was synthesised at pressures of 15–30 GPa in the crystal structure of fluorite ($Fm\bar{3}m$) with the ionic character of Mg-C bond [1]. Theoretically, it was predicted that at 40 GPa Mg_2C adops anti-cottunite ($Pnma$) structure [2]. The calculations of Gibbs free energies have shown that at pressure of 25 GPa, $\text{Mg}_2\text{C}-Fm\bar{3}m$ transforms into $P4_2/mnm$ (rutile-type) and then at more than 3000 K into $P6_3/mmc$ structure [2]. Unfortunately, the energetic relations of these phases were not traced to higher pressures. Our calculations have shown that $P4_2/mnm$ and $P6_3/mmc$ are dynamically unstable at 50 GPa (Fig. S3). Assuming the ionic character of $\text{Mg}_2\text{C}-Fm\bar{3}m$ structure and as the consequence absence of sharp Raman peaks, the only carbide which can be observed in our experiments is $\text{Mg}_2\text{C}-Pnma$. Regarding this phase, we can unambiguously conclude that it was not formed in our experiments.

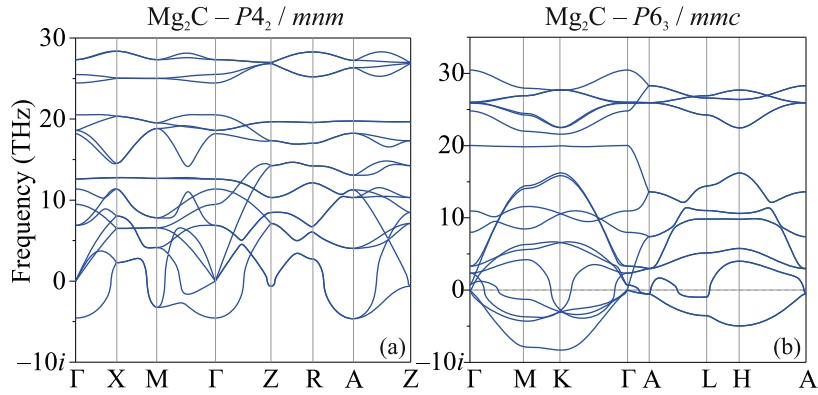


Fig. S3. Phonon dispersion curves of Mg_2C phases at 50 GPa

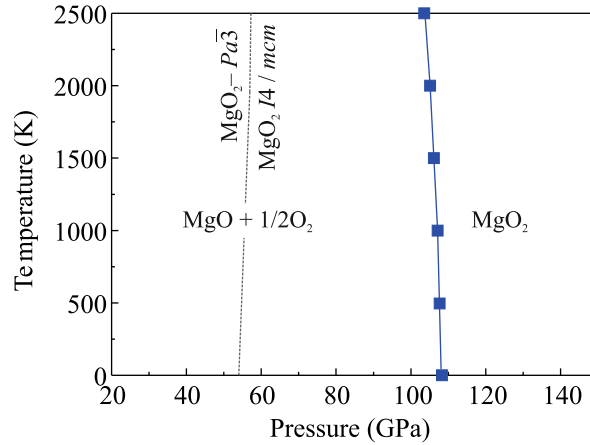


Fig. S4. Theoretical phase diagram of MgO_2

1. O. O. Kurakevych, T. A. Strobel, D. Y. Kim, and G. D. Cody, *Angewandte Chemie International Edition* **52**(34), 8930 (2013).
2. C. Fan and J. Li, *Phys. Chem. Chem. Phys.* **17**(19), 12970 (2013).