ESRF	**Experiment title:** Single-crystal X-ray diffraction study of O_2 up to 200 GPa	**Experiment number**: HC-4883
Beamline: ID11	**Date of experiment**: from: June 3rd 2022 to: June 6th 2020	**Date of report**: 11.08.2022
Shifts: 9	**Local contact(s)**: Eleanor Lawrence Bright	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dominique Laniel* (University of Edinburgh, UK)

Timofey Fedotenko* (DESY, Germany)

Leonid Dubrovinsky (University of Bayreuth, Germany)

Report:

Objectives

As an archetypal molecular system, oxygen is one of the most studied elements at high pressures and features a surprisingly complex solid-state behavior. Stable from 10 GPa, the ε-O_2 phase is comprised of exotic $(O_2)_4$ units and transforms into the ζ-O_2 polymorph above 96 GPa. Observed up to the highest pressure attained on oxygen, 134 GPa, this molecular, metallic, and superconducting phase is of the utmost importance for fundamental condensed matter physics and earth sciences. The main objectives of this proposal were to solve the currently unknown structure of ζ-O_2—essential for the understanding its properties—employing single-crystal X-ray diffraction and extend the phase diagram of oxygen from 134 GPa to 200 GPa

Results

BX90-type diamond anvil cells (DACs) were prepared to cover the pressure domain between 120 and 200 GPa. As detailed in the proposal, the culet of the diamond anvils was coated with a thin layer of MgO, planned to act as a chemical as well as a thermal insulator from the diamond anvils, and the cells were cryogenically loaded with O_2. The DACs were precompressed to the targetted pressure of 130 GPa and laser-heated at the University of Bayreuth.

These DACs were then brought to the ID11 beamline of the ESRF for their characterization by single-crystal X-ray diffraction. A full map of the experimental chamber encouragingly revealed well-defined single-crystal X-ray diffraction spots, suggestive of the formation of a new phase that appeared to be distinctive of any known oxygen allotropes. High-quality single-crystal data was collected, and the corresponding structure was solved and refined.

Unexpectedly, the synthesized solid was found to be an orthocarbonate with the Mg_2CO_4 stoichiometry (see Figure 1), analogous to the known Ca_2CO_4[1] and Sr_2CO_4[2] compounds. Contrary to our preliminary experiments at 40 GPa (see proposal), the MgO coating reacted with both the O_2 sample as well as the diamond anvil, the latter providing the carbon atoms (*i.e.* $2MgO + O_2 + C \rightarrow Mg_2CO_4$). Although not the expected result, the synthesis of Mg_2CO_4 is potentially a very exciting result from a geological perspective, and further studies will be undertaken to determine if, as we suppose, $MgCO_3$ and MgO—both in the mantle—can also react to form Mg_2CO_4.

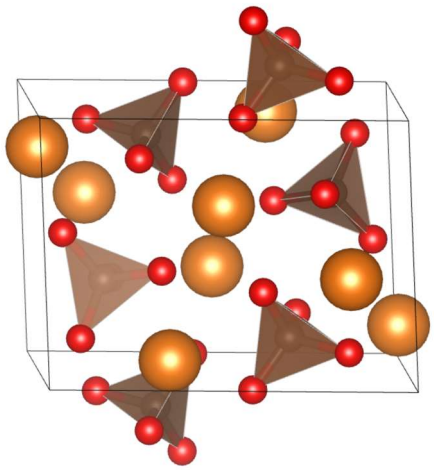

Figure 1: Crystal structure of Mg_2CO_4.

Despite our best efforts, no diffraction signal from pure oxygen could be observed. The investigation of the oxygen phase diagram and solving the crystal structure of its metallic phase will require the use of a different thermal and chemical insulator. A noble gas, such as helium, could potentially be used for this purpose. Alternatively, employing cleverly-chosen precursors that, when laser-heated, would release O_2 is another possible avenue. In any case, further experiments will be necessary.

References

1. Binck, J. *et al.* Synthesis of calcium orthocarbonate, Ca2CO4- Pnma at P-T conditions of Earth's transition zone and lower mantle. *Am. Mineral.* **107**, 336–342 (2022).
2. Laniel, D. *et al.* Synthesis, crystal structure and structure–property relations of strontium orthocarbonate, Sr2CO4. *Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater.* **77**, 131–137 (2021).