

A NOVEL CUBIC, TRANSPARENT AND SUPER-HARD POLYMORPH OF CARBON FROM THE RIES AND POPIGAI CRATERS: IMPLICATIONS TO UNDERSTANDING DYNAMIC-INDUCED NATURAL HIGH-PRESSURE PHASE TRANSITIONS IN THE CARBON SYSTEM. A. El Goresy¹, L. S. Dubrovinsky², Ph. Gillet³, S. Mostefaoui¹, G. Graup¹, M. Drakopoulos⁴, A. S. Simionovici⁴, V. Swamy⁵ and V. L. Masaitis⁶, ¹Max-Planck-Institut für Chemie, 55128 Mainz, Germany (E-mail: goresy@mpch-mainz.mpg.de), ²Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany, ³Ecole Normale Supérieure de Lyon, 69364 Lyon, France, ⁴European Synchrotron Radiation Facility, Grenoble 38043, France, ⁵CRCT, École Polytechnique de Montréal, C.P. 6079, Montréal (Québec) H3C 3A7, Canada, ⁶Karpinsky Geological Institute, St. Petersburg, 199106, Russia.

Introduction: Cubic diamond (**space group $Fd\bar{3}m$**) and lonsdaleite (**space group $P63/mmc$**) are the only known natural high-pressure polymorphs of carbon so far. Lonsdaleite was reported from shocked rocks in several terrestrial impact craters and in nano-size grains in unequilibrated chondrites [1-4]. In terrestrial impact craters it occurs with shock-induced diamond, primary and secondary graphites in distinct petrographic setting [5]. Demineralization residues of shocked rocks from the Lappajärvi and Popigai craters contain, in addition to diamond and graphite, transparent but amorphous carbon [1-3]. Recently, transparent very hard and dense carbon platelets that are thought to be “Raman inactive” were reported in coexistence with impact diamond in shocked gneisses from the Ries crater [6]. In addition, transparent super-hard carbon with broad Raman Bands at $\sim 1390\text{ cm}^{-1}$ (sp^3 bonding) and 1600 cm^{-1} (sp^2 bonding) of unknown nature was also found in shocked gneisses from Popigai crater [5]. Here, we report the results of micro beam x-ray diffraction studies of this carbon phase using Synchrotron radiation at the ESRF Facility in Grenoble, France. The studies revealed the discovery of a new cubic, dense and super-hard polymorph of carbon.

Analytical Techniques: A Large ($70\ \mu\text{m}$) transparent flat platelet with very high relief (height up to $12\ \mu\text{m}$ above the section surface) that could be misidentified as diamond was selected for the Synchrotron study. The grain displays uneven surface with rough gouges and particles of metallic lead scraped from the lead polishing disc, due to high resistance to polishing thus indicating its extreme polishing hardness. It also shows highly variable relief indicating the presence of different transparent materials with different polishing hardness. The transparent interior part of the platelet is covered with small flakes (up to $7\ \mu\text{m}$) of secondary graphite formed by back transformation. EDAX analysis at low voltage without carbon coating with a Field Emission SEM (FESEM) indicated that the grain is pure carbon. The grain was then cored out using a high-precision micro-drilling instrument and mounted on a hole in a metal plate holder. X-ray diffraction, imaging and fluorescence studies were carried out at the ID22 beam line of the ESRF in Grenoble, France. The sample in the metallic holder was positioned in the

image plane on a high precision XYZ remote-controlled stage. A $\varnothing 100\text{ mm}$ CCD camera located behind the sample recorded WAXS diffraction images simultaneously with the fluorescence measurements. The x-ray micro beam ($2 \times 10\ \mu\text{m}$) was scanned over the whole grain and the surrounding silicate matrix. Diffraction and fluorescence data were collected for every beam spot. X-ray and fluorescence phase identification mapping was laid out on the microscopic photograph thus allowing fine-scale spatial phase separation and further delineation of the textural relations of the coexisting phases.

Results: The platelet is encompassed by a $40\ \mu\text{m}$ long cristobalite on the right side and a $15\ \mu\text{m}$ long quartz on the left (Fig. 1). The carbon phases and the surrounding low-pressure silica are enclosed in quenched wavy plagioclase. X-ray diffraction mapping of the platelet indicated the presence of three distinct crystalline carbon phases in a remarkable setting (Fig. 1). The high relief portion of the interior of the grain (Fig. 1) revealed, in addition to the (111) and (200) reflections of metallic Pb, an x-ray pattern that is different from any known carbon modification (Fig. 2) [4]. The pattern is also different from that of cristobalite, quartz, plagioclase, garnet, rutile, ilmenite or zircon, minerals that are present in the gneiss. The diffraction lines are also different from those of nontronite. Contamination from the neighboring phases can entirely be ruled out. Twenty-three diffraction lines obtained from the super-hard carbon could be unambiguously indexed in terms of a cubic cell with $a = 14.6970\ \text{\AA}$; cell volume $a^3 = 3174.58\ \text{\AA}^3$ (**space group: $Pm\bar{3}m$**). The estimated density, based on the structural model, is $\rho = 2.49\text{ gm/cm}^3$. This phase is a novel natural super-hard, polymorph of carbon. The diffraction mapping indicates that the platelet has an onionskin like structure. The new carbon phase is entirely surrounded by lonsdaleite (Figs. 1 & 2), followed by an outer most, $7\text{-}\mu\text{m}$ shell of secondary graphite, respectively (Fig. 1). Lonsdaleite occupies the portion of the interior of the grain with the lower relief than that of the new phase, thus manifesting its lower polishing hardness compared to the new phase (Fig. 1).

Discussion and Conclusions: Shock events in the Ries and Popigai craters induced the formation of a

A NOVEL NATURAL, CUBIC, SUPER-HARD, AND TRANSPARENT CARBON,..., etc.: A. El Goresy et al.

new cubic, super-hard, dense, and transparent polymorph of carbon, in addition to diamond and lonsdaleite. The new phase occurs in the Ries shocked gneisses in coexistence with cubic diamond [6]. The dense carbon grains in the shocked gneisses from Popigai consist of the new phase, lonsdaleite and secondary graphite. Raman spectra of the new phase are strongly suggestive of both sp^3 and sp^2 bonding [6]. The phase is either Raman inactive or has a weak Raman cross section. The petrographic setting of the three carbon phases is indicative of reconstructive phase transformation to the new dense phase and lonsdaleite, followed by partial back transformation of lonsdaleite to secondary polycrystalline graphite at high post-shock temperatures. The spatial arrangement of the new phase occupying the core of the dense carbon platelet with lonsdaleite completely surrounding it may reflect a sharp change in the peak-shock pressures from the interior outwards. We don't know at present if the new carbon phase is a primary species or a quench phase of an unknown metastable much denser carbon polymorph. Our estimated density ($\rho = 2.49 \text{ gm/cm}^3$) of the new phase is subject of the validity of the computed atomic arrangements in the structural model. At any case, the polishing hardness of the new carbon phase is considerably higher than that of cubic diamond (Ries) and lonsdaleite (Popigai), respectively.



Figure 1.: Fine scale textural relations of the new polymorph of carbon (colored blue), lonsdaleite (colored green) and secondary graphite (colored brown) as obtained from Synchrotron micro-beam x-ray diffraction and fluorescence mapping studies. The length of black scale bar on the lower right corner is $20\mu\text{m}$.

We don't know if this new phase is a stable polymorph with a distinct P and T stability field in the carbon phase diagram. A carbon polymorph with similar

properties or crystal structure was not synthesized at high-pressures and temperatures so far. To the best of our knowledge such polymorph was not predicted by theoretical calculations.

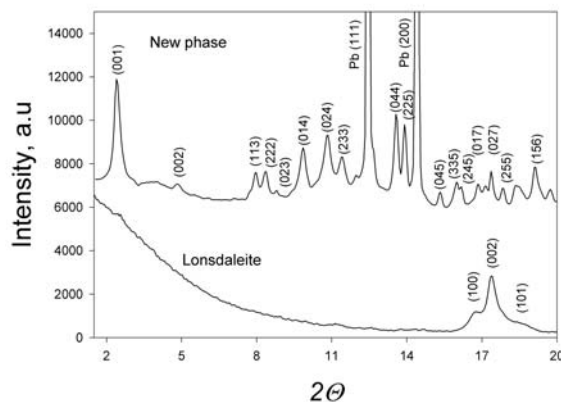


Figure 2.: X-diffraction patterns of the new super-hard carbon phase with the strongest reflections (111) and (200) of the polishing lead (upper pattern) and the pattern of lonsdaleite (lower pattern) obtained from the pertinent phases as shown in Figure 1.

References: [1] Rost R. et al. (1978) *Dokl. Akad. Nauk SSSR*, 241, 695–698. [2] Koeberl C. et al. (1997) *Geology*, 25, 967-970. [3] Langenhorst F. et al. (1998) *Meteoritics & Planet. Sciences* 33, A90-A91. [4] Daulton T. L. et al. (1996) *Geochim. Cosmochim. Acta*, 60,23,4853-4872. [5] El Goresy A. et al. (2002) *LPSC XXXIII*, No. 1031. [6] El Goresy A. et al. (2001) *Amer. Mineralogist*, 86, 611-621.