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TEM Analyses of Carbonates from CM Chondrites - Possible Impact Events Revealed by Pervasive Microstructural Features

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Recently it has been shown that shock metamorphism can have significant effects on chemical and chlorine isotopic records in calcium phosphates, principally as a result of chlorine mobilization during shock melting and recrystallization [1]. Similarly, shock events could potentially disturb or completely reset the isotope chronometers measured in carbonate minerals [e.g., 2]. Therefore, it is important to characterize and understand the shock metamorphic effects before interpreting the isotopic measurements related to age dating, as discussed by [3]. Considering that carbonates are susceptible to shock metamorphism because the bonding between Ca cations and CO_3 groups is relatively weak [4], they could be used as recorders of the shock metamorphic environment and help interpret metamorphic conditions on asteroids. In this study, we examine carbonate microstructures from two CM2s with two different shock metamorphic stages (Boriskino − ~S3-S4 according to the pressure values from [5] and Murchison − S1 [6]). Our detailed transmission electron microscopy (TEM) observations will help assess if impact events are recorded in these minerals. As a consequence, a new shock metamorphism classification scheme based on carbonates instead of silicates could be considered in future studies, especially for chondrites that lack the shock indicator minerals typically used in the shock classification scheme of meteorites (olivine, pyroxenes, and feldspars, [7-9]).

Two polished sections of Boriskino and Murchison (on loan from the Field Museum of Natural History and the UH meteorite collection, respectively) were first characterized by scanning electron microscopy (SEM) using backscattered electron imaging on a Helios 660 dual-beam focused ion beam SEM (FIB-SEM) instrument at the Advanced Electron Microscopy Center (AEMC) at the University of Hawaiʻi at Mānoa. Six electron transparent sections of carbonates and the surrounding fine-grained matrix were prepared by the conventional *in situ* FIB technique (five FIB sections in Boriskino and one in Murchison). Each FIB section was studied using a variety of TEM techniques, including scanning transmission electron microscopy (STEM) imaging, nanodiffraction, and energy-dispersive X-ray spectroscopy (EDS). The images and analysis were carried out at 200 kV and 300 kV using the Titan G2 analytical (S)TEM at AEMC, TitanX at the Molecular Foundry, Lawrence Berkeley National Laboratory, and the JEOL NEOARM aberration-corrected STEM/TEM instrument at the Center for Micro-Engineered Materials, at UNM. Nanodiffraction was carried out using a camera length of 190 mm, and a convergence angle of 0.3 mrad.

TEM observations show the occurrence of complex microstructures in the carbonates from Boriskino (Fig. 1). The most pervasive microstructural features are dislocations that appear in all investigated carbonates (Ca carbonate, and dolomite). These dislocations are accompanied by twinning in three out of the four Ca carbonates analyzed from Boriskino. Most of these microstructural features are visible only in the STEM micrographs taken using a convergent beam (0.3 mrad) that provides better contrast, especially in deformed crystals. Additionally, we identified a large number of anhedral pores with sizes up to ~ 400 nm in one of the dolomite crystals from Boriskino. Multiple Mg-, Fe-rich silicate inclusions (~20 nm in diameter) and Ni-rich sulfides were observed in a Ca carbonate from Boriskino (Fig. 1); however, the exact mineralogy of these inclusions was not yet obtained due to the large thickness of the FIB section.

Furthermore, we analyzed one Ca carbonate (~20 x 25 µm) crystal from Murchison (Fig. 1). Twinning is the dominant microstructural feature identified in this mineral. However, Ca carbonates from CM chondrites are often twinned and may show zoning in cathodoluminescence (CL) [10]. No other deformation features such as dislocations are present to any significant degree.

Our TEM study shows that the microstructures of carbonates in shocked meteorites (Fig. 1, Boriskino, ~S3-S4) record very distinct microstructures compared to unshocked samples (Murchison, S1), which we interpret as being the result of shock metamorphism (Fig. 1). Additionally, the presence of shock features in different generations of carbonates indicates that shock deformation event/(s) occurred after the precipitation of all the carbonates. Future studies will assess if carbonates show similar increasing microstructural changes as the shock pressure increases. The effects of shock events on the isotopic systematics of carbonates (e.g., Mn-Cr) remain to be determined [11].

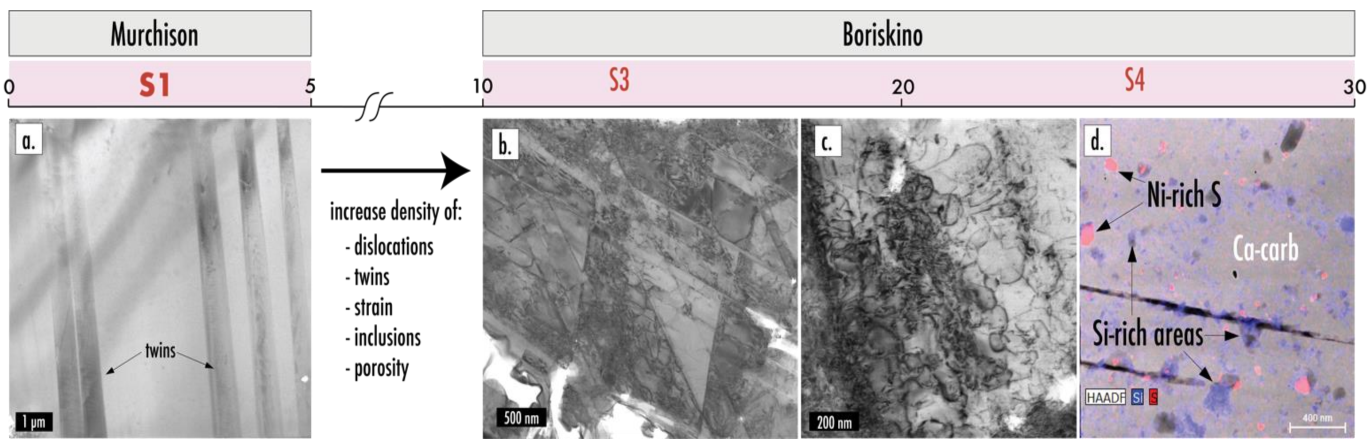

Figure 1. Bright-field (BF) STEM micrographs of Ca carbonates (Ca-carb) from Murchison (a, S1) showing simple twinning and a low dislocation density compared with Ca carbonates (b-c) from Boriskino (~S3-S4), displaying the occurrence of complex microstructural features, such as twins, high density of dislocation loops, and strain. d) EDS maps and a high-angle annular dark field (HAADF) micrograph showing the distribution of numerous Si- (blue) and S-rich (red) inclusions inside a Ca carbonate from Boriskino.

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