

IDENTIFYING THE EFFECTS OF SHOCK ON THE COMPOSITION OF MARTIAN PHOSPHATE MINERALS USING CORRELATIVE STRUCTURAL AND CHEMICAL TECHNIQUES.

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Introduction: Determining when and if habitable environments existed on Mars is a major focus of planetary science research, the answers to which will directly influence our understanding of life on Earth, Mars, and throughout the Solar System. While evidence from rovers and remote sensing analyses have confirmed that water was once widespread across the Martian surface, the presence of water alone is not enough to confirm if the conditions necessary for life were once present. A detailed understanding of the timing of magmatism, bombardment, water, and phosphorous availability on Mars are all essential.

As one of the only OH-bearing phases in Martian meteorites, the hydrous components of phosphate minerals such as apatite ($\text{Ca}_5[\text{PO}_4]_3[\text{Cl},\text{F},\text{OH}]$) (versus anhydrous merrillite ($\text{Ca}_9\text{NaMg}[\text{PO}_4]_7$)) have been used as indicators of fluid interactions in the Martian crust, and even to theorize the origin of water within Mars and the terrestrial planets [1,2]. The volatile compositions of Martian apatites have also been used to estimate the amount of phosphorous that was once available to potential Martian life (i.e. the Cl-rich mineral chlorapatite dissolves more rapidly than the F-rich mineral fluorapatite, and thus would release more phosphorous needed to build DNA and RNA [3]). Phosphate minerals are also important repositories of U-Th-Pb and can provide valuable information on the timing of magmatism, hydrothermal events, and impacts [4,5].

However, at this time no Martian samples have been directly retrieved from the planet's surface, restricting our analyses to shock-deformed meteorites that have undergone intense deformation during violent impact and ejection from the Martian surface [6]. These shock events can cause mineral transformations, chemical reactions, and loss of volatiles and isotope species through transient, high-diffusivity pathways. Recent experimental studies have even shown that the chemical composition of synthetic phosphate minerals can be altered by shock [7].

As the effects of shock on the composition and structure of phosphate minerals are poorly understood, here we aim to document the chemical and isotopic compositions of phosphate minerals over a range of shock states allowing for more accurate identification of pri-

mary and secondary domains, and consequent predictions of the timing of water, phosphorous, and possibly life on Mars.

Samples & Methods: In order to define the full range of shock-produced micro- and nano-structural features in Martian phosphates, we have collected structural and chemical data from 37 grains across eight Martian shergottites and almost the entire shock scale [8]. The samples are: NWA 4480 (S2), NWA 8159 (S3), Zagami (S4), NWA 10134 (S4), NWA 10593 (S4), Tissint (S5), NWA 6342 (S6), and NWA 7721 (S6).

Structural Characterization: First-order shock stage estimates for each meteorite were determined based on shock-pressure barometry of the major rock forming minerals [8,9], or from literature where available. After collecting detailed backscattered electron (BSE) imaging, at least three phosphate grains in each sample were selected for detailed structural analysis using electron backscatter diffraction (EBSD) with the goal of encompassing the shock heterogeneity within each sample. EBSD maps were collected using Oxford Instruments Nordlys-Nano EBSD detectors equipped on either the Hitachi Su6600 FEG-SEM at the University of Western Ontario, or the Zeiss EVO MA10 LaB₆-SEM at Portsmouth University.

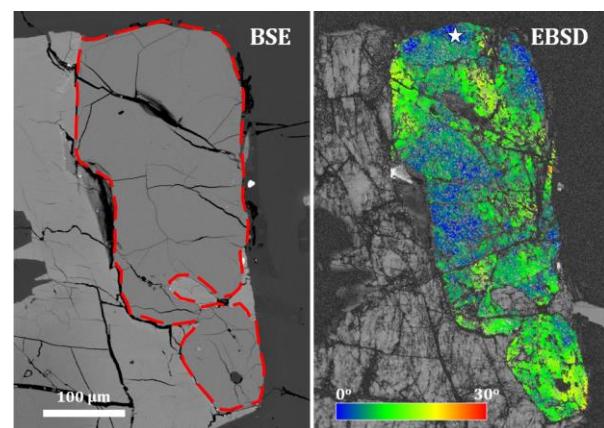


Figure 1: BSE and EBSD maps of merrillite in NWA 10593. While some fracturing is visible in the BSE image, only EBSD reveals the structural complexity caused by shock deformation. The colors correspond to misorientation relative to a defined point of reference (denoted by the white star).

Chemistry: The major element and volatile compositions of selected merrillite and apatite grains have been determined using the JEOL JXA-8230 electron microprobe at Queen's University, with the goal of correlating structural shock features to different amounts of volatile loss and composition transformations/disturbances. Using electron microprobe to analyze fluorine and chlorine in apatite is difficult as these elements are highly mobile under the electron beam (i.e. [10-13]). In order to carefully and effectively measure F and Cl, (and subsequently calculate OH in apatite [1,2]) the phosphates in this study were analysed using ideal instrument conditions based on those outlined by [12], and with the use of a LDE1 diffracting pseudocrystal in order to accurately measure F [14]. The instrument conditions were checked against well-known secondary standards Ap001-Ap023 [1].

Results: Our findings reveal a wide range of shock effects in each sample, from relatively unshocked grains, to varying amounts of crystal-plastic deformation, and even shock-recrystallization. In general, phosphate deformation increases along with each sample's shock state (from S2 to S6; Figure 2), although the amount of deformation experienced on a grain-to-grain basis was highly variable. The high-pressure polymorph tuite was not observed.

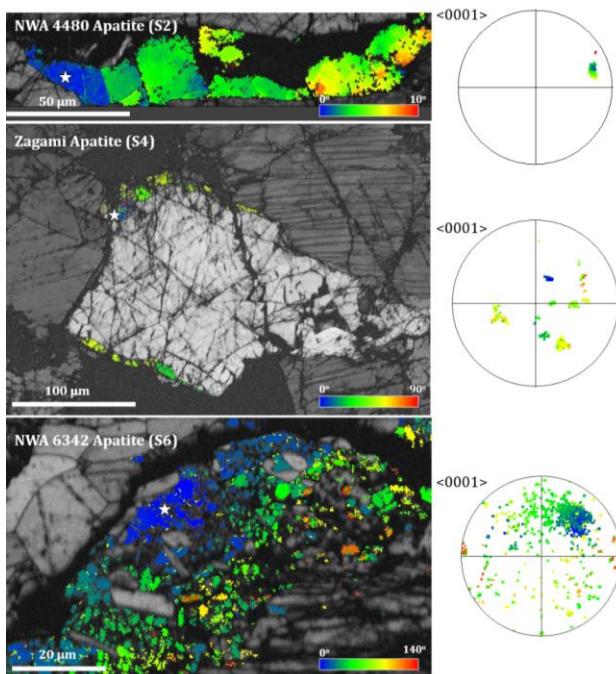


Figure 2: EBSD maps and pole figures of apatite in Martian meteorites from shock stages S2-S6. The <0001> pole figures show the orientation of the c-axis in the sample plane.

While both apatite and merrillite are found to exhibit crystal-plastic deformation, the magnitude of the deformation is far greater in merrillite (up to 50° of misorientation versus up to 25° in apatite). In the higher shock stages (S4-S6) apatite is most commonly observed as recrystallized granular domains separated by high angle sub-grain boundaries (>10°). These domains (approximately 1-5 μm in diameter) are typically randomly oriented and exhibit less than 10° of misorientation (Figure 2 – Zagami). Recrystallized merrillite is also observed, but only at shock stage S6. Unlike the randomly oriented granular apatite, the merrillite sub-domains appear to “remember” their previous structure and have recrystallized in similar, but slightly displaced configurations. Preliminary analysis also reveals that the amount of deformation observed in apatite may be linked to the mineral’s volatile composition (Figure 3). Less OH⁻ was observed with increasing crystal-plastic deformation and recrystallization. With this correlative structural and chemical technique, this study will constrain how the compositions of phosphate minerals are altered by shock, and provide new constraints on the Martian volatile record.

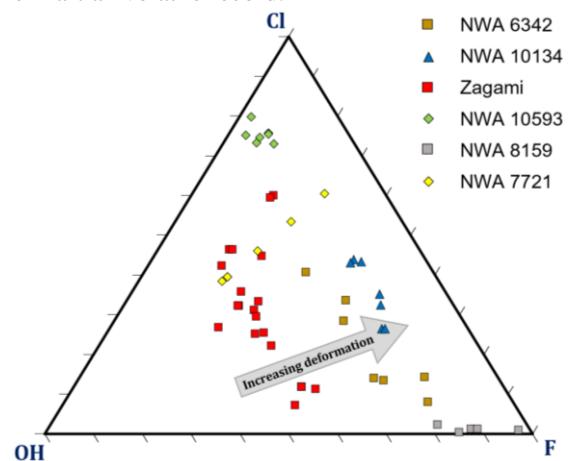


Figure 3: Ternary plot of apatite X-site occupancy.

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