

Structures of Astromaterials Revealed by EBSD

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Introduction: Groups at the Johnson Space Center and the University of Tokyo have been using electron back-scattered diffraction (EBSD) to reveal the crystal structures of extraterrestrial minerals for many years. Even though we also routinely use transmission electron microscopy, synchrotron X-ray diffraction (SXRD), and conventional electron diffraction, we find that EBSD is the most powerful technique for crystal structure elucidation in many instances. In this talk I describe a few of the cases where we have found EBSD to provide crucial, unique information.

Asteroid 2008TC3 -Almahata Sitta: The Almahata Sitta meteorite (Alma) is the first example of a recovered asteroidal sample that fell to earth after detection while still in solar orbit (asteroid 2008TC3), and thus is critical to understanding the relationship between meteorites and their asteroidal parent bodies [1&2]. Alma is an anomalous polymict ureilite, and the structures of the low-calcium pyroxenes have been particularly instructive.

The pyroxene crystal structure gives important information on thermal history when coupled with chemical composition. Thus we employed EBSD to study the crystallography of Alma pyroxenes. Although the Ca contents of these low-Ca pyroxenes are as low as W_{O_2} , the obtained Kikuchi bands show that all Alma low-Ca pyroxenes have the pigeonite ($P21/c$) crystal. This is consistent with the observation that (100) twinning is common in these low-Ca pyroxenes. Alma pigeonites in the same pyroxene areas show generally similar orientation as suggested by optical microscopy. The Kikuchi bands from augite in Alma can be indexed by the $C2/c$ augite structure, but it is usually difficult to distinguish between the $P21/c$ and $C2/c$ pyroxene structures on EBSD patterns. The absence of orthopyroxene ($Pbca$) in Alma indicates that the pyroxene equilibration temperature was high, probably higher than 1300°C [3&4].

In our EBSD study of grain boundary metals in Alma fragment 44 we found unique features never seen in any natural sample. In order to further characterize these metal grains, we also performed a detailed TEM study on a FIB section prepared from one of the Alma 44 grain boundary metals and here discuss its thermal history. The metal is composed of compositionally homogeneous Fe metal (93 Fe, 5 Ni, and 2 Si in wt%). However, BF-STEM images exhibited clear contrast composed of elongated laths ($\sim 2 \mu\text{m}$ long) embedded in an interstitial matrix. The EBSD and SAED patterns showed that these laths are $\alpha\text{-Fe}$ (bcc) while interstitial areas are $\gamma\text{-Fe}$ (fcc), suggesting the formation of two iron phases by the martensite transformation. High resolution images of the $\alpha\text{-Fe}$ laths further revealed a tweed-like texture, and the obtained EBSD and SAED patterns show the coexistence of both $\alpha\text{-Fe}$ and $\gamma\text{-Fe}$ with the $K\text{-S}$ crystallographic orientation relationship of martensite. The formation of lath martensite from the Fe-Ni metal is clearly due to rapid cooling from high temperature where $\gamma\text{-Fe}$ was stable. The presence of C and Si decreases the martensite transformation temperature in the Fe-Ni system [e.g., 5], and may have also enhanced its stability. We tried to estimate a cooling rate using this unique metal texture, but its complex composition with an unknown C amount does not permit us to simply employ a T-T-T diagram of the Fe-Ni-C system. The C abundance is known to significantly control the formation of martensite. However, since we did not see any Fe carbides and C could not be detected by EPMA, the C abundance must be low. Fe metals in Alma show textures and phase assemblages that are not seen in any other natural samples. These features may be due to shock-reheating of various original grain boundary assemblages having

different amounts of graphite, phosphide, silicide and troilite in an event that did not affect most main group ureilites but occurred on the Alma/2008TC3 asteroid.

Dmitryivanovite: The empirical formula for dmitryivanovite is $\text{Ca}_{1.000}(\text{Al}_{1.993}\text{Si}_{0.003}\text{Ti}_{0.002})_{1.998}\text{O}_4$ which is close to the theoretical value CaAl_2O_4 [6&7]. Our attempts to obtain diffraction data from this phase by SXRDR failed, but we successfully analyzed several different areas of CaAl_2O_4 in the meteorite NWA470 by EBSD. The EBSD patterns of the new mineral matched only the high-pressure polymorph of CaAl_2O_4 rather than that from low-pressure CaAl_2O_4 .

The binary system of $\text{CaO-Al}_2\text{O}_3$ includes two important minerals found in meteorites: hibonite ($\text{CaAl}_{12}\text{O}_{19}$) and grossite (CaAl_4O_7). The discovery of dmitryivanovite presents us with the third calcium aluminum oxide to be described from nature. The most likely scenario for producing dmitryivanovite involves either nebular condensation or evaporation, or a combination of both. Calculations by a diversity of investigators suggest that the condensation of CaAl_2O_4 from a nebular system requires considerable enrichment in dust relative to gas [8]. Therefore, the presence of CaAl_2O_4 in this CH3 chondrite suggests that there was just such a region in the solar nebula where dust was suitably abundant. The EBSD analysis in this study reveals that CaAl_2O_4 in NWA470 is a high-pressure polymorph.

The phase boundary between low-pressure CaAl_2O_4 and the high-pressure polymorph lies from 1 GPa and 700°C to 2.5 GPa and 1500°C [9]. High pressure (~2 GPa) is required to stabilize the high-pressure CaAl_2O_4 polymorph at 1600K, above which CaAl_2O_4 condenses from the solar nebula [6]. It is unlikely that the solar nebula ever had such a high total gas pressure, and thus dmitryivanovite probably originally formed with a low-pressure crystal structure. NWA470 shows weakly developed shock features with estimated shock pressure and peak temperatures of ~2 GPa and <50°C, respectively [10]. Under these pressure-temperature conditions, the high-pressure polymorph of CaAl_2O_4 should be stable because of the large stability field of this phase at low temperatures. Therefore, we believe that the high-pressure polymorph of CaAl_2O_4 (dmitryivanovite) was produced during shock metamorphism of the NWA470 parent asteroid.

Andreyivanovite (ideally FeCrP) is a new phosphide species from the Kaidun meteorite, which fell in South Yemen in 1980 [11]. Kaidun is a unique breccia containing an unprecedented variety of fragments of different chondritic as well as achondritic lithologies. Andreyivanovite was found as individual grains and linear arrays of grains with a maximum dimension of 8µm within two masses of Fe-rich serpentine. In one sample it is associated with Fe-Ni-Cr sulfides and florenskyite (FeTiP). The average of nine electron microprobe analyses yielded the formula $\text{Fe}(\text{Cr}_{0.587}\text{Fe}_{0.150}\text{V}_{0.109}\text{Ti}_{0.081}\text{Ni}_{0.060}\text{Co}_{0.002})\text{P}$. Examination of single grains of andreyivanovite using Laue patterns collected by in-situ SXRDR, and more definitively by EBSD revealed that it is isostructural with florenskyite. Andreyivanovite could have formed as a result of cooling and crystallization of a melted precursor consisting mainly of Fe-Ni metal enriched in P, Ti, and Cr. Serpentine associated with andreyivanovite would then have formed during aqueous alteration on the parent asteroid. It is also possible that the andreyivanovite could have formed during aqueous alteration, however, artificial FeTiP has been synthesized only during melting experiments, at low oxygen fugacity, and there is no evidence that a hydrothermal genesis is reasonable.

Aid to Synchrotron X-ray diffraction Studies. In the past decade our groups have made numerous attempts to determine the crystal structures of chondrite sulfides by SXRDR, but with only a few

exceptions we have found them to be apparently amorphous by this technique. This has always been rather perplexing since these sulfides frequently exhibit euhedral crystal morphologies. We were beginning to conclude that the chondrite sulfides had generally been rendered amorphous by shock. However, we have learned that practically all of our chondrite thin sections have very thin amorphous surfaces, a common polishing side effect of which we were unaware. We have learned that use of a Vibramet polisher can remove this coating, finally permitting elucidation of the crystal structure by EBSD and SXR. We tested this idea by reanalyzing (by EBSD and SXR) previously “amorphous” sulfides in the Orgueil and Kaidun meteorites following Vibramet polishing. In both chondrites we have found abundant very crystalline sulfides. We now routinely use EBSD to identify the most well-crystalline sulfides in meteorite samples before taking the much more onerous step of performing SXR – a fantastic savings in beam time.

References

- [1] Jenniskens et al. (2009) *Nature* **458**, 485-488.
- [2] Zolensky et al. Submitted to *Meteoritics and Planetary Science*.
- [3] Takeda et al. (2009) *Meteoritics and Planetary Science* **44**, 5117.
- [4] Tribaudino (2006) *Meteoritics and Planetary Science* **41**, 979-988.
- [5] Sverdlin and Ness (1997) *Chapter 2, Steel Heat Treatment Handbook*, ed. by Tlitten & Howes, Marcel Dekker Inc. NY.
- [6] Mikouchi et al., (2009) *American Mineralogist* **94**, 746-750.
- [7] Ivanova et al. (2002) *Meteoritics and Planetary Science* **37**, 1337-1345.
- [8] Ebel and Grossman (2000) *Geochimica et Cosmochimica Acta* **64**, 339-366.
- [9] Ito et al. (1980) *Materials Research Bulletin* **15**, 925-932.
- [10] Stöffler et al. (1991) *Geochimica et Cosmochimica Acta* **55**, 3845-3867.
- [11] Zolensky et al. (2008) *American Mineralogist* **93**, 1295-1299.