TRANSMISSION ELECTRON MICROSCOPY OF SILICO-APATITE IN D'ORBIGNY.

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Introduction: Quenched angrites are one of the oldest known igneous rocks in the solar system and commonly contain small Ca silico-phosphates associated with late-crystallization phases [1,2]. The characterization of these silico-phosphates is important to better interpret chronological data using the U-Pb isotopic system of phosphates [3,4]. In this study we performed an FIB-TEM investigation of Ca silico-phosphates in the D'Orbigny quenched angrite to confirm its crystal structure.

Methods: We first observed D'Orbigny thin sections by optical microscope and FEG-SEM to look for appropriate areas for FIB samples and analyzed chemical compositions of silico-phosphates by electron microprobe (JEOL JXA-8900L). The FIB sectioning was performed by JEOL JIB-4000 and then FIB sections were observed by FEG-TEM (JEOL JEM-2100F).

Results: Ca silico-phosphates in D'Orbigny are present as small (up to ~10 x 30 μm in size) elongated euhedral grains associated with Al-Ti-rich clinopyroxene ("fassaite"), Ca-Fe olivine, spinel and troilite. Electron microprobe analysis gives a homogeneous composition (CaO: 48.7, P_2O_5: 29.5, SiO_2: 12.2, FeO: 5.0, TiO_2: 1.5, all in wt%) with small amounts of Cl (~0.2 wt%) for silico-phosphates. It is nearly F-free and there is no significant amount (<0.1 wt%) of REEs. Silico-phosphates in other quenched angrites (Asuka-881371 and Sahara 99555) have a very similar composition [1,2]. STEM mapping analysis of the FIB sections confirmed that Ca silico-phosphate is homogeneous in composition and no inclusions were found. The obtained SAED patterns are consistent with the apatite structure.

Discussion and Conclusion: In our previous study using SEM-EBSD and Raman spectroscopy we found that silico-phosphates in quenched angrites have a graserite structure such as apatite [1,2]. This study using TEM confirmed that Ca silico-phosphate in D'Orbigny is apatite rather than merrillite or whitlockite, and thus it should be called silico-apatite. Si-rich (~9 wt% SiO_2) Ca phosphate in NWA 4590 (slowly-cooled angrite) is also known to be silico-apatite [5]. Thus, this study suggests that Ca silico-phosphates in all angrites are silico-apatite. The chemical composition of silico-apatite lacks Ca relative to (P+Si) in the apatite stoichiometry even if we consider the presence of Fe and Ti (Ca+Fe+Ti=4.65 for P+Si=3.00). This may be due to the presence of vacancy or oxy-component to compensate charge valance caused by partial replacement of $(SiO_4)^{4-}$ tetrahedra by $(PO_4)^{3-}$ tetrahedra in the apatite structure [5].

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