DISCOVERY OF A NEW MODULAR STRUCTURED TITANIUM OXIDE IN SHOCK MELT POCKETS OF THE EUCRITE NORTHWEST AFRICA 8003

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Introduction: In the course of mineralogical investigations on HED meteorites, we identified a new Ti oxide (abbreviated as NTO hereafter), $(Ti,Al,Fe)_2Ti_3O_9$, in shock-induced melt pockets of the eucrite Northwest Africa (NWA) 8003, a basaltic eucrite in which five high-presseure minerals have been observed [1]. This phase turned out to be isostructural with the n=5 member in the Andersson family $M^{3+}_2Ti_{n-2}O_{2n-1}$. Schreyerite $V_2Ti_3O_9$ is the first natural mineral of the Andersson-family phase with n=5. It occurs in terrestrial rocks as exsolution in rutile or is associated with titanite [2–3]. The second Andersson-family mineral with n=5 is machiite $(Al,Sc)_2(Ti,Zr)_3O_9$, a new refractory mineral closely associated with corundum in the CM2 chondrite Murchison [4–5]. The NTO in NWA 8003 is the third mineral of the Andersson-family phase with n=5. Here we report the occurrence, chemical composition, and crystal structure of NTO to understand its origin and formation mechanism.

Methods: The petrographic textures of NWA 8003 were investigated by using field emission scanning electron microscopy (FE-SEM; Zeiss Supra 55, FEI Quanta 3D). Two FIB lamellae across melt pockets were investigated using transmission electron microsopy (TEM; FEI Tecnai G^2 FEG). Bright field (BF) imaging, selected area electron diffraction (SAED), scanning transmission electron microscopy (STEM), high-resolution (HR) TEM and EDX analyses were conducted in order to identify the compositional and structural details of the phases in the melt pockets. Fe $L_{2,3}$-edge electron energy-loss spectroscopy (EELS) was used to determine the valence state of Fe.

Results and Discussion: The NTO is observed in Al-Ti-rich shock-induced melt pockets, which occurs at the ilmenite-tissintite interface. The minerals associated with NTO are corundum (Crn), Al-Ti-pyroxene (Al-Ti-px), and Al-bearing ilmenite (Ilm), troilite (Tr) (Fig. 1). The euhedral-subhedral crystals of NTO reach lengths of up to 2 μm. TEM-EDX analyses yield an average chemical composition $(Ti_{0.35}Al_{0.32}Fe_{0.31})_2Ti_3O_9$, which can be simplified as $(Ti,Al,Fe)_2Ti_3O_9$. EELS of the Fe $L_{2,3}$ edge shows that the iron is almost exclusively ferrous. Diffuse streaks and splitting of diffraction spots observed in some of the SAED patterns indicating the presence of planar defects along the **a** direction. Geometric analysis of the splitting spots shows that these planar defects occur at an average distance of 42 Å, which is in agreement with modulations observed in HR images.

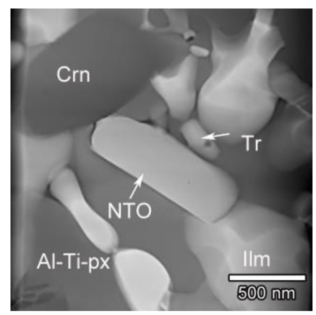

Fig.1. STEM image shows the minerals in an Al-Ti-rich melt pocket from NWA 8003.

The structures of the Andersson-family phase $M^{3+}_2Ti_{n-2}O_{2n-1}$ can either be described as ordered intergrowths of V_3O_5-type and α-PbO_2-type modular slabs or, equally, as derived from the rutile structure by introducing anion substitution and crystallographic shear planes [6–7]. Member n=5 corresponds to the maximum alternation of V_3O_5-type and α-PbO_2-type slab. Planar defects observed in NTO are due to intercalation of extra slab(s) into the normal, regularly alternating stacking of V_3O_5-type and α-PbO_2-type slabs. Chemically, the NTO in NWA 8003 is a solid solution between machiite $Al_2Ti_3O_9$ and a theoretical end-member $(TiFe^{2+})Ti_3O_9$. The end-member $(TiFe^{2+})Ti_3O_9$ dominates over the end-member $Al_2Ti_3O_9$ (machiite) in NTO. Synthetic experiments suggested that the single phase M_5O_9 in the Andersson family can only be obtained with certain cation ratio and over a narrow temperature range, indicating its metastable nature [8]. This inference is consistent with the occurrence of NTO as euhedral-subhedral grains in shock-induced melt pockets, whose cooling is usually very fast.

Summary: We find a new Ti oxide in a shocked eucrite NWA 8003 with crystal structure identical to that of Andersson-family phase $M^{3+}_2Ti_{n-2}O_{2n-1}$ with n=5. This Ti oxide has a modulated structure. Its unique occurrence indicates that this Ti oxide formed through crystallization from shock-induced melts.

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