

# THE SILICO-PHOSPHATE TSANGPOITE AND MATHYITE PROVIDE NEW CONSTRAINTS TO THE METASOMATIC PROCESS IN THE ANGRITE D'ORBIGNY.

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**Introduction:** Tsangpoite, ideally  $\text{Ca}_5(\text{PO}_4)_2\text{SiO}_4$ , the hexagonal polymorph of silicocarnotite (IMA 2014-110, [1]), and matyhite, ideally  $(\text{Ca}_{18}(\text{Ca}_1\Box_1)\text{Fe}_2\text{P}_{14}\text{O}_{56})$ , the Fe-analogue of Ca-merrillite (IMA 2015-121, [2]), were identified in the D'Orbigny angrite meteorite. The study of these two new phosphates -previously described as silica-phosphate in the angrite D'Orbigny [3-4]- help to advance in the comprehension of the metasomatic processes which led to enrichments in FeO and MnO that highly modify the Mg-rich composition of the olivines to the one seen now [5].

**Samples and analytical techniques:** Two polished slab samples: D'Orbigny C-N1172-NH and M1173 (Naturhistorisches Museum Wien, Austria.) belong to the porous part and the dense part of the angrite D'Orbigny, respectively. Samples were studied by optical microscopy and SEM-BEI imaging and energy-dispersive X-ray (SEM-EDX) techniques. Analyses were done using a JEOL JSM-7000F field emission scanning electron microscope. TEM samples were prepared by the FIB technique (using a SEIKO SMI-3050) for selected area electron diffraction (SAED) using a JEOL 3010 AEM.

**Textural setting:** Tsangpoite and matyhite specifically occur in well-defined but separated domains.

Tsangpoite crystals either occur within "intact" Fe-sulfide (Fig. 1 a-b) or Fa-Kir symplectite after Fe-sulfide, or are currently embedded within the hedenbergite domain close to resorbed Fe-sulfide (Fig. 1c). In the "intact" Fe-sulfide not in direct contact with hedenbergite, tsangpoite crystals with hexagonal cross-section occur exclusively in the local domain subjected to metasomatic replacement of Fe-sulfide by Mag + wüstite + Tsa ± celsian ± Al-Ti-Fe Spl (Fig. 1 a-b).

Matyhite was not found in the "intact" Fe-sulfide but are frequently nucleated/grew within the Fe-sulfide-mediated Fa-Kir symplectite (Fig. 2a-d), yielding the occurrences of dendritic matyhite enclosed within Fa-Kir symplectite (Fig. 2b). Matyhite with high abundance of tiny Fe-sulfide droplets frequently occurs at the areas of contact between Fa-Kir symplectite and hedenbergite (Fig. 2e-f), or between Fa-Kir overgrowth and hedenbergite.

The tsangpoite crystals that nucleated from Fe-sulfide frequently possess a central tube filled with opaque minerals (e.g. Fig. 3).

**Discussion:** Based on detailed petrographic studies

these new minerals likely represent metasomatic products of an external Ca-Ti-Al-P-O rich source [6]. Accordingly and based on the petrogenetic relationships, the formation sequence likely is tsangpoite→matyhite→kuratite→Fa+Kir symplectite (over resorbed Fe-sulfide)→hedenbergite, with a crystallization temperatures >1000°C. Tsangpoite is the quenched product of the high-temperature hexagonal silicocarnotite form above 1450°C in  $\text{Ca}_2\text{SiO}_4$  -  $\text{Ca}_3(\text{PO}_4)_2$  system [2]. Such high temperatures are higher than the 1250°C at which a rock with the bulk composition of D'Orbigny is completely melt. Therefore, the hexagonal structure of tsangpoite could have been stabilized by vacancies (~ 7% cationic vacancy in the M-site) and impurities and grow at temperatures not lower than 1200°C [6]. A recent study of the silicophosphates in D'Orbigny [7] showed that the water content estimated from raw counts on <sup>1</sup>H range from 85 to 1892 µg g<sup>-1</sup>. Although these water contents are considered as approximation [7] they seem to be at odd with the lack of Raman peak at ~2000, ~3000 or ~3500 cm<sup>-1</sup>, characteristic of OH vibrations, and therefore indicative that tsangpoite and matyhite are OH-free [6]. While further thermochemical and kinetics evidences are required to clarify the exact formation mechanisms/conditions of the euhedral tsangpoite, matyhite and kuratite at the grain boundary of angrite D'Orbigny, we favor formation via off-eutectic solidification of the P-rich partial melts/fluids over Fe-sulfide upon cooling. These processes took place at T >1000°C, considering the 900-1100°C stability field of rhönites (kuratite), and/or the formation of merrillite (matyhite) without whitlockite component, i.e. hydroxyl, at T > 1050°C [e.g. 8]. This metasomatic event must only last for a short time, as shown by the Pb isotopic (<sup>207</sup>Pb–<sup>206</sup>Pb) age of the silicophosphates (4568 ± 20 Ma [7]) akin to the ages of the whole rock and mineral phases in D'Orbigny dated with <sup>53</sup>Mn–<sup>53</sup>Cr and <sup>207</sup>Pb/<sup>206</sup>Pb methods (4562 ± 0.6 Ma and 4564.42 ± 0.12 Ma), respectively [9-10].

**References:** [1] Hwang et al. (2015) *Min. Mag.* **79**, 529-535; [2] Hwang et al. (2016) *Min. Mag.* **80**, 691-697; [3] Mittlefehldt et al. (2002) *Meteoritics & Planetary Sci.* **37**, 345-369; [4] Kurat et al., (2004) *GCA* **68**, 1901-1921; [5] Varela et al., (2017) *GCA* **217**, 349-364; [6] Hwang et al. (2017) *Min. Mag.* (in press); [7]

Sarfian et al., (2017) *Phil. Trans. Roy. Soc. A* 375, 1-27; [8] Hughes et al. (2008) *Am. Mineral.* **93**, 1300-1305.

[9] Glavin et al., (2004) *MAPS* **39**, 693-700; [10] Amelin, (2008) *GCA* **71**, 221-232.

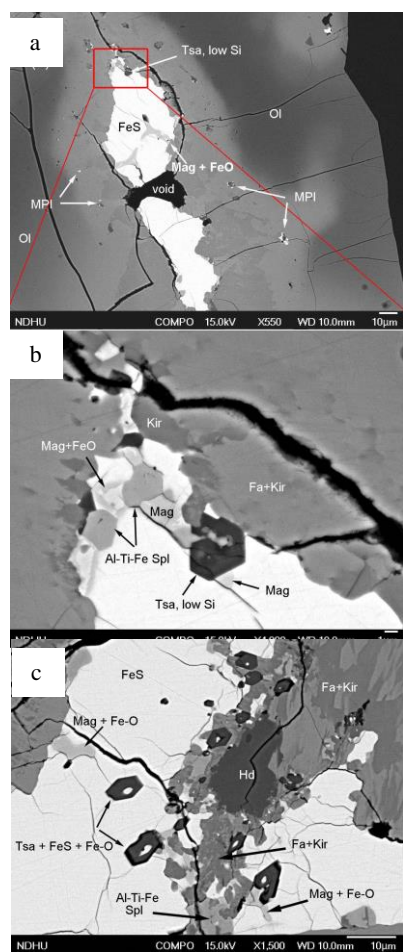


Figure 1: SEM-BE-TOPO micrographs showing the “intact” FeS at the impinging Fa-Kir overgrowths (a-b). Tsangpoite crystals in residue FeS (c).

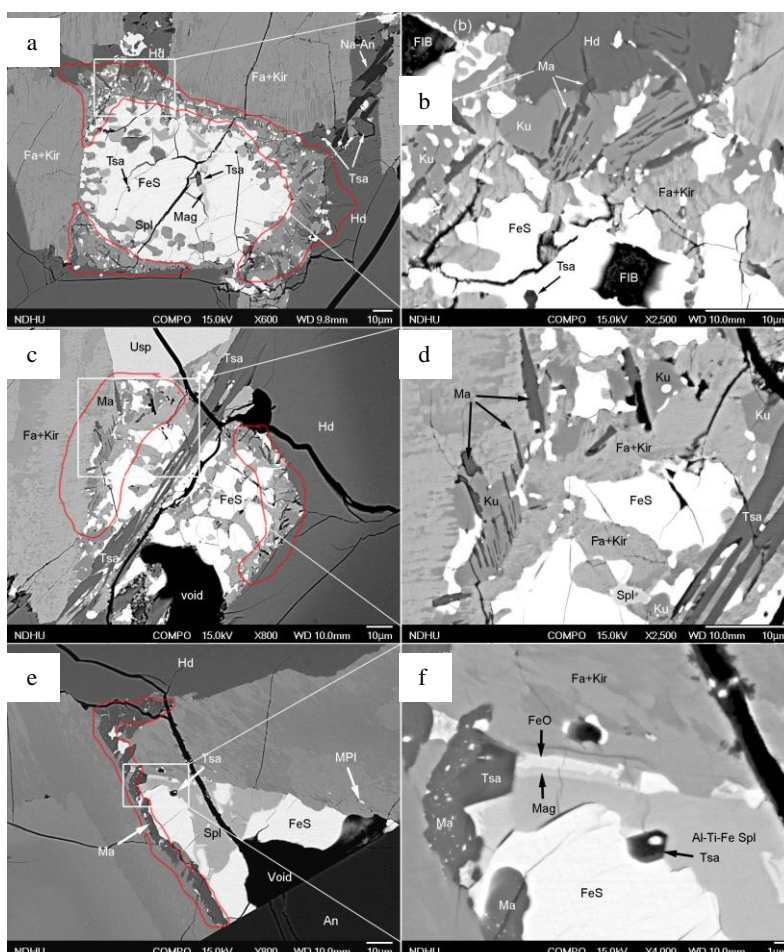


Figure 2: SEM-BE-TOPO micrographs showing the concurrent presence of (a-d) tsangpoite at the core and matyhte at the rim of resorbed Fe-sulfide (in red envelop), and (e, f) tsangpoite at the core and matyhte at the areas of contact with Fa-Kir overgrowth of a partially altered Fe-sulfide.

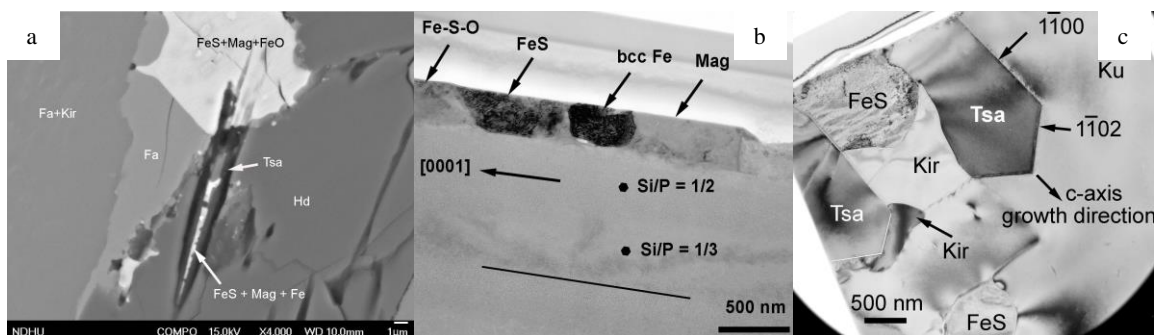


Figure 3: a) SEM-BE-TOPO micrographs of an oblique tsangpoite crystal nucleated from the FeS crystal with central tube filled by FeS + magnetite + Fe. b) The corresponding TEM image showing Fe-assemblage at central tube and the variable Si/P ratios from core to rim of the tsangpoite. c) Association of tsangpoite + kuratite. The two branches of tsangpoite grew around FeS is faceted by  $\{1\bar{1}00\}$  and  $\{1\bar{1}02\}$  planes.