LA-ICP-MS evidence for decoupled geochemical behavior of Tl, As and Au in modern SMS, Kolumbo arc-volcano (Santorini), Greece

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Understanding the pathways and processes of the sequestration of Tl in modern SMS is key to VMS genetic and geometallurgical factors[1]. LA-ICP-MS trace element analyses of primary colloform pyrite (Py1) and recrystallized fine-grained pyrite (Py2) and euhedral zonal pyrite (Py3), and sphalerite (Sph) (inner sulfide-barite core), and, orpiment-type As-sulfides ("As_2S_3"), stibnite (Sb_2S_3) and Pb-Sb sulfosalts (PbSb) (outer As-sulfide rind), from currently forming polymetallic SMS chimney structures, Kolumbo shallow-submarine arc-volcano show: (i) Pyrite and Sph are particularly rich in, Tl (≤10,140 ppm, Py1; ≤7,470, Sph), Sb (≤64,600 ppm, Py1; ≤29700 ppm, Sph), **As** (5,870 ppm, Py1; 13,290 ppm, Py2; ≤17,870 ppm, Py3), and Au (≤131 ppm, Py1; ≤40 ppm, Sph); (ii) "As_2S_3", in Tl (≤82,200), Sb (≤12,300 ppm), and Au (≤861 ppm); (iii) Sb_2S_3, in Tl (≤21,800 ppm), As (≤21,800 ppm) and Au (≤64 ppm Au); and, (iv) PbSb, in Tl (≤1,381 ppm) and Au (≤89.5 ppm Au). Mo is present: Py1 (≤22 ppm), As_2S_3 (≤90 ppm) and Stb (≤94 ppm). Ablation profiles for As, Sb, Tl, Mo, and Au can be either irregular or smooth. LA-ICP-MS trace element mapping of Py1 reveals that Tl shows no clear correlative relationship with As or Au, but only with Sb and Mo. This is supported by good correlation of Tl and Sb (R^2=0.52), and Tl and Mo (R^2=0.86); Tl vs Au, and Tl vs As pairs, show no correlation in any analyzed sulfide phase (R^2<0.20). Observed decoupled behavior between Tl and As, and, Au, challenges the paradigm of Tl-uptake dependence on As contents of pyrite[2], previously documented for Au and Cu[2,3]. Coupled Tl-Sb, and Tl-Mo, behavior and enrichment, may suggest that Sb, and Mo, facilitate incorporation of micro-particle inclusions of Tl(-Sb-Mo)-bearing phases in pyrite.

[1] Monecke *et al.* (2016) *Rev. Econ. Geol.* **18**, *245–306* [2] Deditius and Reich, (2016) *Am. Mineral,* ***101****, 1451–1459* [3] Santoro *et al.* (2018) *Applied Earth Science,* **127***, 46-79.*