

## Decoupled Geochemical Behaviour of Tl, Au, As in Sea-floor Massive Sulphides, Kolumbo Arc-volcano: Evidence from LA-ICP-MS Elemental Mapping of Arsenian Pyrite

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Thallium (Tl) is considered as toxic for human and animal organisms, microorganisms and plants (Peter and Viraraghavan, 2005; Karbowska, 2016). Thallium is redox active and has two oxidation states (Tl<sup>1+</sup> and Tl<sup>3+</sup>), while Tl<sup>1+</sup> is believed to be the most common in Tl minerals (Xiong, 2007; George et al., 2019); monovalent Tl (Tl<sup>1+</sup>), believed to be the most common in Tl minerals (Xiong, 2007; George et al., 2019), is very mobile, and potentially released into the environment under a range of physicochemical conditions, being easily transported in aqueous form due to its high solubility (Peter and Viraraghavan, 2005).

Recent studies of terrestrial ore deposits have demonstrated the ability of pyrite to host concentrations from a few ppm up to weight per cent (e.g.,  $\leq 3.5$  wt%) levels of Tl (Zhou et al., 2005; D' Orazio et al., 2017; George et al., 2018; 2019; Muntean et al., 2011). Regardless its potential to release Tl into the environment under a range of physicochemical conditions, the speciation of Tl in pyrite is not very well understood. Metal incorporation in pyrite is complex (e.g., Deditius et al., 2014; Deditius and Reich, 2016), and it has not been evidently shown whether Tl enters the crystal structure of pyrite or tends to occur as micro- to nano-particles of Tl-bearing phases. It has been suggested that the occurrence of Tl<sup>1+</sup> in pyrite is coupled with the presence of Sb<sup>3+</sup> and As<sup>3+</sup>. More specifically, the occurrence of Tl in As-pyrite (Tl<sup>1+</sup>-bearing nanoparticles or structurally bound Tl) is strongly reliant on As contents (Deditius and Reich, 2016). Moreover, Tl<sup>1+</sup> can be lattice-bound in pyrite by a simple coupled heterovalent substitution, i.e.,  $2\text{Fe}^{2+} \leftrightarrow \text{Tl}^{1+} + \text{Sb}^{3+}$  (D' Orazio et al. 2017; George et al., 2018). However, more recent studies (George et al., 2019) have questioned the model of a coupled Tl<sup>1+</sup> and Sb<sup>3+</sup> substitution, suggesting that Tl<sup>1+</sup> could occur in structural defects in pyrite.

Understanding the pathways and processes of the mineralogical sequestration of Tl and other minor elements (e.g., As, Sb, Hg, etc.) is key to economic factors in SMS environmental impact, as well as prospecting and extraction. Consequently, investigation is required of how the minor elements (e.g., Tl, As, Sb) are distributed among key ore minerals and accessory SMS phases, and how this distribution is changed during precipitation, later recrystallisation (dissolution–reprecipitation), and sea water weathering (halmyrolysis). The Kolumbo shallow submarine arc-volcano, located in the 5 Ma-to-present Hellenic Volcanic Arc (HVA) in Greece, hosts an active hydrothermal system currently forming polymetallic SMS mineralisation, the only known SMS deposit associated with continental margin volcanism (Kiliass et al., 2013). Polymetallic sulphide-sulphate (baryte) chimneys are uniquely enriched in Tl (mean: 510 ppm; max.: >1,000 ppm) and Sb (mean: 8330 ppm; max.: 2.2 wt.%) ( $\pm$ Hg, As, Au, Ag, Zn). The maximum concentrations of Kolumbo Tl (>1,000 ppm), are the highest reported from modern SMS deposits located on arc volcanoes, which rarely exceed 100 ppm (Monecke et al., 2016). Consequently, Kolumbo is an ideal natural laboratory to investigate the department of potentially toxic Tl (and other metal contaminants, As, Sb) in the Aegean Sea.

The studied sulphide-sulphate chimneys exhibit concentric mineral zones, formed at successive stages of chimney growth (Kiliass et al., 2013): a lithified inner sulphide-sulphate core (ISSC) mantled by an outer As-sulphide layer (OAsL), which in turn is covered by a Fe-rich crust (SFeC) (Kiliass et al., 2013). Pyrite is the dominant sulphide mineral in the ISSC, followed by marcasite, sphalerite, galena, Sb-Pb-sulphosalts, and minor, chalcopyrite, anglesite, Al-silicates, and Sb-Zn-sulphosalts. The OAsL consists chiefly of amorphous orpiment (As<sub>2</sub>S<sub>3</sub>)-like, and realgar (AsS)-like As-sulphides, stibnite, and Pb-Sb (-As) sulphosalts, in a baryte matrix, and rare opal; the OAsL is overgrown by amorphous ferrihydrite-like Fe-oxyhydroxides (SFeC).

Here we report LA-ICP-MS trace element analyses and maps showing the concentration, distribution and zonation of Tl, Au, As, Sb, and Mo in: (1) primary colloform-crustiform and moss textured pyrite (Py 1 – up to: 131 ppm Au; 5870 ppm As; 64,600 ppm Sb; 22 ppm Mo, and 10,140 ppm Tl); (2) later recrystallised (dissolution–reprecipitation) fine-grained pseudobladed pyrite (Py 2) – (up to: 65 ppm Au; 13,290 ppm As; 36,100 ppm Sb; 7.8 ppm Mo, and 2390 ppm Tl); (3) euhedral zonal pyrite (Py 3) – (up to: 54 ppm Au; 17,870 ppm As; 11,580 ppm Sb; 2.2 ppm Mo, and 1163 ppm Tl); and (4) sphalerite (Sph) – (up to: 40 ppm Au; 3920 ppm As; 29,700 ppm Sb; 12.1 ppm Mo, and 7470 ppm Tl) from the 'inner' ISSC zone; (5) colloform pyrite (Py1A) – (up to: 58.3 ppm Au; 7930 ppm As; 10.6 ppm Mo; 46,800 ppm Sb, and 1661 ppm Tl); (6) orpiment (As<sub>2</sub>S<sub>3</sub>)-type As-rich sulphides ('As<sub>2</sub>S<sub>3</sub>') – (up to: 861 ppm Au; 90 ppm Mo; 12,300 ppm Sb, and 82,200 ppm Tl); (7) stibnite (Stb) – (up to: 64 ppm Au; 21,800 ppm As; 94 ppm Mo, and 21,800 ppm Tl), and Sb-Pb sulphosalts – (up to: 89.5 ppm Au; 6550 ppm As; 14 ppm Mo, and 1381 ppm Tl) from the 'outer' OAsL zone. Ablation profiles for As, Sb, Tl and Au can be either irregular or smooth, indicating both lattice substitutions and nanoparticle inclusions (e.g., George et al., 2019). ISSC pyrite and sphalerite, are particularly rich in Tl ( $\leq 10,140$  ppm, Py1;  $\leq 2390$  ppm, Py2;  $\leq 1163$  ppm, Py3; 7470 ppm, Sph), Sb ( $\leq 64,600$  ppm, Py 1;  $\leq 29,700$  ppm), and As ( $\leq 17870$  ppm, Py 3; 3920 ppm), and Stb in Tl ( $\leq 21,800$  ppm) and As ( $\leq 21,800$  ppm); Au may be present above 100 ppm in Py 1 ( $\leq 131$  ppm), and

above 800 in 'As<sub>2</sub>S<sub>3</sub>' ( $\leq 861$  ppm), and Mo may be present above 20 ppm in Py1 ( $\leq 22$  ppm), As<sub>2</sub>S<sub>3</sub> ( $\leq 90$  ppm) and Stb ( $\leq 94$  ppm). LA-ICP-MS analyses show good correlation of Tl and Sb ( $R^2 = 0.52$ ) in Py1; Tl and Mo in Py1 ( $R^2 = 0.86$ ); Py2 ( $R^2 = 0.82$ ) and Py1A ( $R^2 = 0.57$ ); Sb and Au in sphalerite ( $R^2 = 0.76$ ), and, Tl and As in stibnite ( $R^2 = 0.52$ ). Concentrations of Au, Sb, Mo and Tl drop significantly from Py1 to Py3, and further to Sph, in the ISSC, while, in the OAsL the opposite trend is observed, i.e., Au is increased in Py1A and 'As<sub>2</sub>S<sub>3</sub>', and, Mo and Tl are enriched in 'As<sub>2</sub>S<sub>3</sub>' and stibnite, compared to the respective ISSC sulphide phases; Sb is generally comparatively decreased in the OAsL.

Trace element mapping using LA-ICP-MS of colloform Py1 reveals a marked compositional zoning with respect to Tl, As, Sb, Au and Mo (also Pb and Ag). Based on the LA-ICP-MS mapping, Tl shows no clear correlative relationship with Au or As, but only with Sb and Mo. This is supported by interelement Tl vs Au, and Tl vs As trends, which show no correlation ( $R^2 = 0.20$   $R^2 = 0.13$ , respectively).

Our findings suggest that:

1. During the growth of each zone sequence, i.e., ISSC, OAsL, sulphide assemblages and their trace elements are modified by redox processes, overprinting fluids, recrystallisation, exsolution of metastable phases, or boiling, during initial precipitation and later recrystallisation (a dissolution–reprecipitation process); as a result a large proportion of these elements (Au, Sb, Mo and Tl) are expelled possibly as composite nano-particles (George *et al.*, 2019), causing a zone refinement of the elements present in the various formed chimney minerals, strongly supporting zone refinement to be indispensable for polymetallic chimney growth at Kolumbo.
2. Observed decoupled behaviour between Tl and Au, Tl and As, and coupled behaviour between Tl and Sb (at least in colloform Py1), contradicts the paradigm of strong dependence of Tl uptake on As and Au contents of pyrite (Deditius and Reich, 2016), as it has also been before documented for Au and Cu for the Kolumbo SMS mineralisation (Zygouri *et al.*, 2018). In addition, statistically significant coupled behaviour exists between Tl and Mo in Py1 and Py2.
3. The incorporation of Tl into colloform pyrite seems to be facilitated by the presence of Sb, and not As that generally facilitates Au incorporation (Zygouri *et al.*, 2018) in the Kolumbo hydrothermal vent system. Our results corroborate that Tl is possibly incorporated in Py1 mainly in micro- to nano-particles (NPs) of other Tl-bearing phases, possibly Tl-stibnite, with important implications from an economic and environmental point of view.

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