Unravelling hypogean mineralizing fluids from the geochemistry of epigean travertines: insights from central-southern Tuscan (Italy)

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Southern Tuscany was one of the most important mining regions of Italy: pyrite, iron oxides, base metals, mercury, antimony and silver were mined since the Etruscan age up until the early '90s of the XX century. The region is interested by post-apenninic extensional tectonics progressively migrating eastwards. This extension caused Neogene-Quaternary magmatism that acted as heat source for a widespread hydrothermal activity, often leading to the formation of mineral deposits. Starting from the mid '80s of the XX century, some carbonate-hosted Sb-Hg (and minor Au) mineralizations belonging to the so-called Carlin type were identified in southern Tuscany, mainly at the edges of Larderello and Mt. Amiata geothermal fields. This type of deposit is genetically linked to sustained hydrothermal circulation and jasperoid alteration at depth.

Travertine can be considered a notable paleo-surface expression of these fossil hydrothermal systems. It is a continental limestone that forms where hydrothermal waters emerge. Another kind of continental chemically-precipitated limestone is cold-water travertine, also known as tufa.

The goal of this study is to verify if travertine and tufa composition can act as geochemical pathfinder for the occurrence of mineralization at depth. This will be done looking for relationships between secondary chemical features (such as trace elements abundances, REE partitioning and C, O and Sr isotope composition) of these rocks, their thermal affinity and the presence of associated epithermal mineralization.

This research has been carried out on many samples collected in central and southern Tuscany. The collected samples come both from mineralized (Sb-Hg ± Au) and unmineralized areas for comparison. Tufa and travertine samples were investigated by optical microscopy and back-scattered imaging with SEM-EDS, and analyzed for trace elements (Li, Be, V, Cr, Co, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Ag, Sn, Cd, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Tl, Pb, Bi, Th, U with ICP-MS, Hg with DMA-80). Stable ($\delta^{18}O$ and $\delta^{13}C$) and radiogenic ($^{87}Sr/^{86}Sr$) isotopes were also determined.

The results allow discriminating between the epigenic and hypogenic origin of parent fluids. The metal contents vary, with the majority of samples showing both positive and negative anomalies, which could be related with the fluids origin, their temperature and the lithologies they passed through.

If the results show consistent correlation, this study will not only strengthen the role of travertine analyses as geochemical indirect methodology for mineral exploration in certain contexts but could also imply other uses, such as getting insights on potentially toxic elements natural occurrences or helping to model the underlying hydrologic reservoir lithologies where the fluids passed through.