Genesis of the Pb–Zn deposit at Sant'Antonio di Val D'Aspra, Southern Tuscany (Italy): disparity between geo-petrographic data and fluid inclusion microthermometry

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Abstract

The Pb–Zn deposit at Sant'Antonio di Val d'Aspra in the Farma Valley (Southern Tuscany) is hosted by Lower Moscovian carbonate rocks and shows many characters commonly found in Mississippi Valley type (MVT) deposits. Ore minerals (essentially sphalerite and galena) are closely confined to dolomitized portions of an only partly preserved black limestone. Mineralized carbonate rocks appear to have been eroded before the deposition of the overlying Upper Moscovian (Late Podolskian) shales. The diffuse presence of structures frequently found in internal sediments of karstic cavities indicates that supergene mechanisms have played an important role in the history of the deposit. A fluid inclusion study carried out on ore and gangue minerals revealed the presence of two different types of inclusions. The homogenization temperatures ranged from 120 °C to 225 °C but the most frequently found values were around 170 °C. Salinity ranged from moderately low values up to 20 eq. wt.% NaCl. Lead isotopic composition rules out any relationship between the Sant'Antonio mineralization and Tertiary hydrothermal base metal occurrences in the same area. When all the data are taken together, a contrast is evident between geo-petrographic and isotopic data on the one hand, and fluid-inclusion microthermometry on the other.

KEYWORDS: Pb–Zn deposit, fluid-inclusion microthermometry.

Introduction

MICROTHERMOMETRIC data on fluid inclusions in ore and gangue minerals has played a crucial role in the interpretation of the genesis of MVT deposits. The inferred trapping temperatures generally range from 50 to 150 °C ruling out any theory implying near surface temperature fluids (i.e. a strictly supergene process). In order to identify the origin of the 'hydrothermal' fluids responsible for MVT deposits, various deposition models have been proposed, none of which are completely satisfactory.

The study of the fluid inclusions in ore and gangue minerals of the Sant'Antonio deposit revealed the classical picture of a relatively high-temperature pattern in contrast to other evidence, such as ore texture and distribution, which seems to be more compatible with a supergene environment.

Geological setting

The geology of the Sant'Antonio Mine area (Fig. 1*a*) is dominated by extensive outcrops of silico–clastic deposits spanning the Upper Palaeozoic and Lower Triassic. The Monticiano–Roccastrada Ridge is deeply cut from west to east by the Farma River, revealing a sequence of arenaceous, shaley and carbonate rocks beneath the basal terrains of the Tuscan series (Verrucano group). These rocks date back to the Carboniferous and Permian and are the oldest palaeontologically-dated outcrop in the Northern Appennines (Cocozza, 1965; Azzaro *et al.*, 1976; Pasini, 1979; Puxeddu *et al.*, 1979; Troja, 1981; Di Vincenzo, 1985).

Some of the Carboniferous rocks have flyschoid characteristics and contain calcarenite lenses, calcareous conglomerates and limestone pebbles with Carboniferous fossil associations, interpreted as olistolites and olistostromes from a

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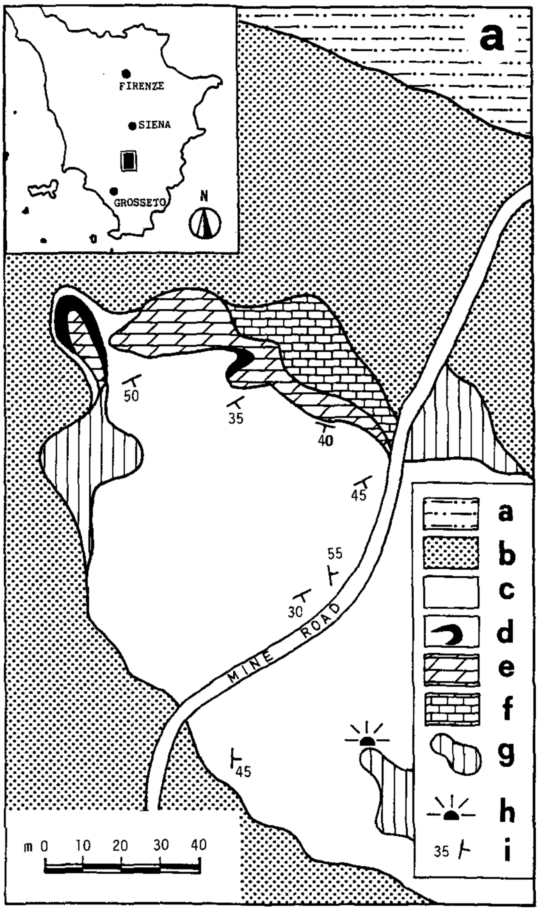

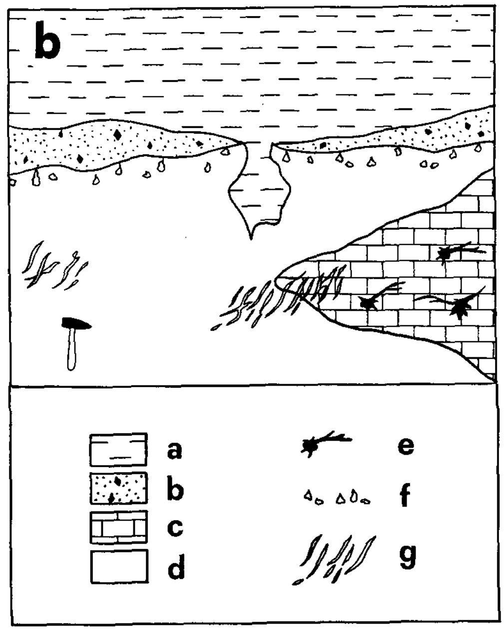

FIG. 1. (*a*) Geological map of Sant'Antonio mine area. *a*, Verrucano group (Lower Triassic). *b*, Poggio al Carpino formation (Upper Permian). *c*, Spirifer-bearing shales (Upper Moscovian–Late Podolskian). *d*, Yellowish-red paleosoil or paleogossan. *e*, Dolomitized limestone. *f*, Sant'Antonio black limestone (Lower Moscovian). *g*, Dump. *h*, Entry of tunnel. *i*, Dip and strike of bedding. (*b*) Sketch map of ore geology at Sant'Antonio mine. *a*, Spirifer-bearing shales. *b*, Yellowish-red paleosoil or paleogossan with oxidized galena 'rognons'. *c*, Sant'Antonio black limestone. *d*, Dolomitized limestone. *e*, Diagenetic sparry black calcite (calcite I). *f*, Dissolution caves filled with post-ore calcite (calcite II). *g*, Sigmoidal late calcite veins (calcite III).

nearby carbonate platform. The largest exposed portion of this platform is in the Sant'Antonio Mine area and hosts the deposit.

Ore geology

The Pb–Zn deposit at Sant'Antonio, although of minor economic value, is quite peculiar in the complex picture of the Tuscan metallogenic province. It is the only example in the region of MVT mineralization, and it is one of the few deposits for which a Palaeozoic age has been established.

Referring for details to the work of Troja (1981) we summarize hereafter the relevant features of the Sant'Antonio deposit.

(1) The Sant'Antonio orebody is closely confined to the dolomitized part of a small outcrop of Lower Moscovian black limestone. Only small areas of undolomitized black limestone remain.

(2) The ore mineral assemblage is simple, mainly consisting of galena and sphalerite with very minor amounts of marcasite and pyrite, and traces of chalcopyrite and fluorite. The gangue is iron-rich dolomite, locally accompanied by small quantities of quartz.

(3) Ore minerals occur both as spotted crystals and microveins in the dolomitized limestone, as ore-rich beds in intrakarstic sediments, and breccia cement (see Fig. 2*a, b, c*).

(4) The preserved unmineralized black limestone very frequently shows small pockets of sparry black calcite with bladed or equant grains produced by vadose diagenesis (calcite I). Sigmoidal milky calcite veins, most probably connected with

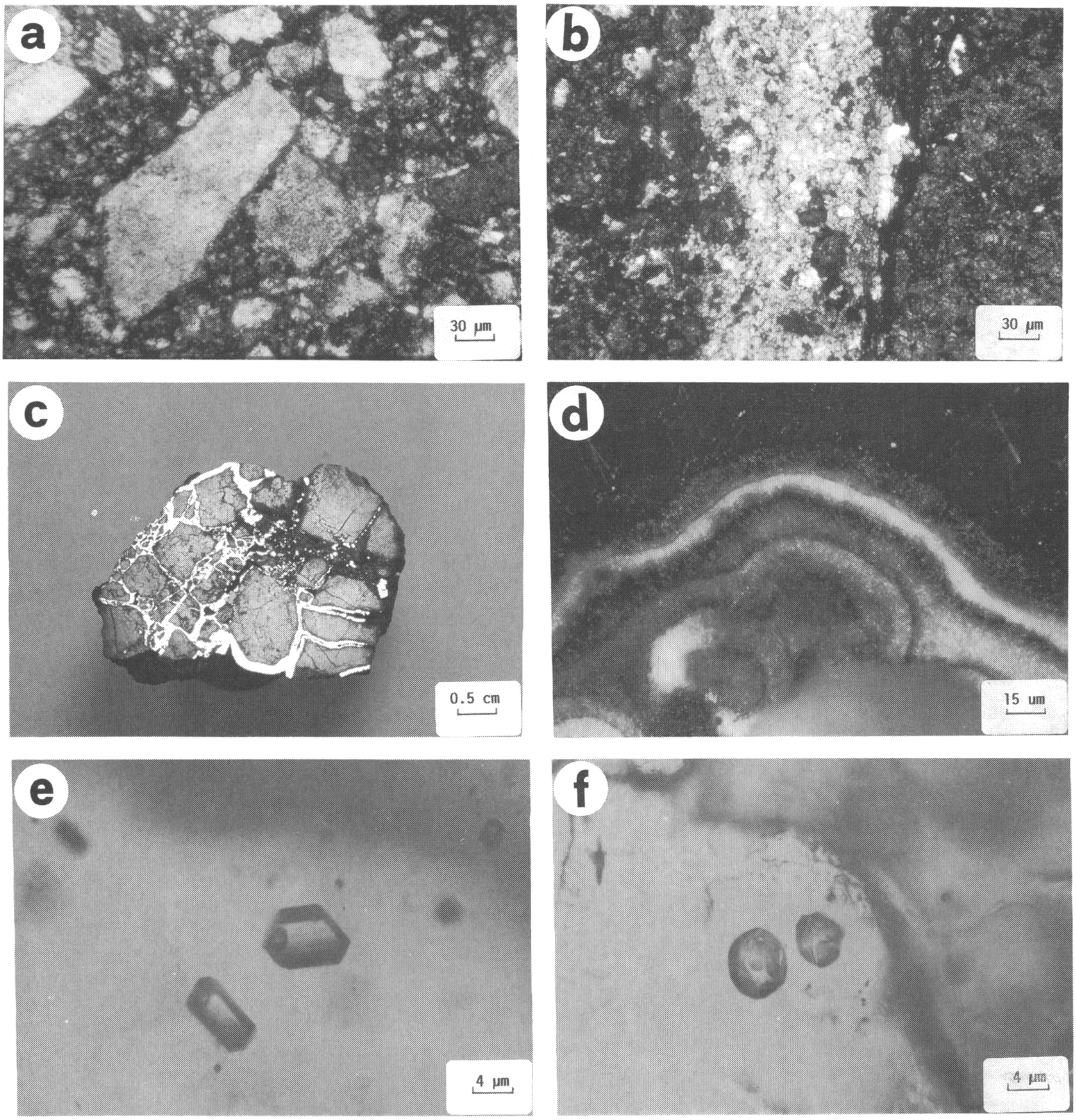

FIG. 2. (*a*) Sphalerite and white Fe-dolomite clasts in sandy intrakarstic sediments. (*b*) Sphalerite-rich (black) and Fe-dolomite-rich (white) beds in sand-sized intrakarstic sediments. *c*, Breccia of oxidized Fe-dolomite fragments cemented by marcasite. *d*, Reflected light crossed nicols view of polished section of galena 'rognon'. Black ribbons are galena and white are lead oxides. *e*, Negative crystal-shaped inclusions in sphalerite. *f*, Solid globules of bitumen (?) in sphalerite.

late (Alpine?) extensional stresses, are also present (calcite III) both in limestone and dolomite.

(5) At the eroded top of the dolomitized and mineralized limestone (see Fig. 1*b*) there is a several decimetre-thick yellowish-red-stained 'paleosoil' or rather 'paleogossan' (which contains kidney-shaped masses of oxidized galena, see Fig. 2*d*).

(6) Beneath the yellowish-red-stained horizon, dolomitic host rock shows a pinkish-yellow hue and there are small dissolution caves filled with sparry calcite (calcite II). Microscope observation demonstrates advanced dedolomitization phenomena and 'rusting' of iron-rich dolomite crystals.

(7) The carbonate unit capped with the gossan is unconformably covered by Spirifer-bearing

shales of Upper Moscovian (Late Podolskian) age. (8) Preliminary data on isotopic lead composition at Sant'Antonio* fall very close to a single-stage growth curve with $\mu = 10$. The $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios of Sant'Antonio galena are 15.6565 ± 0.0035 and 18.2921 ± 0.0020 respectively, which are congruent with a Palaeozoic age. These values are remarkably different from those obtained from galenas of other deposits of the district which range from 15.6788 ± 0.0050 to 15.7034 ± 0.0150 for the $^{207}Pb/^{204}Pb$ ratio and 18.7363 ± 0.0030 to 18.8497 ± 0.0045 for $^{206}Pb/^{204}Pb$, making them much younger.

In summary, geo-petrographic evidence suggests that the Sant'Antonio mineralization was formed in a supergene environment. The ore is spatially linked to the dolomitization event and appears to be at least partly synchronous with it. Although the exact link between dolomitization and mineralization can hardly be specified we observe that the dolomitization environment was compatible with sulphide deposition, as identical clusters of framboidal pyrite are present both in black limestone and in its dolomitized counterpart. The dolomitized and mineralized limestone was eroded before the deposition of Spirifer-bearing shales enabling the dolomitization-mineralization phenomena to be accurately attributed to the pre-Podolskian. The data available on lead isotope composition also supports the geologically inferred Palaeozoic age of the sulphides.

Fluid inclusions study

To investigate the nature of the fluids involved in the mineralizing phenomena, fluid inclusions in the following minerals were analysed: dolomite, sphalerite, quartz, calcite I, calcite II and calcite III. Multiple doubly-polished 100–500 μm thick wafers and chips were made from all samples.

The instrumentation used was a gas-flow heating–freezing stage designed by USGS, appropriately calibrated. The precision of the temperature measurements during the freezing runs was ±0.1 °C and ±2 °C in the heating runs. All the inclusions considered were primary according to the criteria of Roedder (1984).

Inclusion typology

Two types of fluid inclusion were found: the majority were aqueous inclusions with liquid and vapour phase at room temperature, degree of filling 0.90–0.95 (type 1); the others were solid dark globules, probably of bitumen (type 2). Most were in the size range 5–15 μm, with a few exceptions at 25 μm.

In sphalerite (Figs. 2*e,f*), dolomite and calcite I there were both type 1 and type 2 inclusions, whereas quartz, calcite II and calcite III only showed type 1 inclusions.

Heating–freezing runs

About 200 heating and freezing runs were carried out on the fluid inclusions in the ore and gangue minerals. Because of poor observation conditions (small inclusions, opacity of the host mineral) it was not possible to determine the first melting temperature (Tfm) of any of the inclusions. For the same reasons it was difficult to measure the final ice melting temperature (Tm) in calcite and dolomite.

Homogenization temperatures

The homogenization temperatures (Th), all in the liquid phase, ranged from a minimum of 120 °C in calcite III, to a maximum of 225 °C in dolomite (Fig. 3). The inclusions in quartz showed two frequency peaks for Th: one at 190 °C for the maximum number of inclusions and the other at 170 °C. For sphalerite and sparry black calcite the maximum frequency occurred at 160 °C. Calcite II and calcite III gave values of 120–185 °C. The values in dolomite ranged from 150 to 225 °C.

Salinity

The values of eq. wt.% NaCl calculated from Tm_{ice} (Potter *et al.*, 1978) were in the range 3–7.5 in quartz, sphalerite, dolomite and calcite III (Fig. 3). Calcite I and calcite II showed the highest values (13.20 eq. wt.% NaCl).

A few inclusions however showed anomalous behaviour during freezing runs. Sudden movements of the bubble at 10–15 °C were observed, as usually happen during clathrate dissociation. Nevertheless carbon dioxide was not found nor were hydrocarbons detected under UV illumination. These inclusions were excluded when plotting the histograms.

Discussion and conclusions

The microthermometric data gave comparable values of temperature and salinity for ore and gangue minerals. These values were fully in agreement with those from the literature on mineralizations of this type.

On the other hand, similar temperature values were also obtained for the three types of calcite.

* The isotopic measurements were performed by Dr E. Curti under Prof. V. Köppel at the E.T.H. in Zurich.

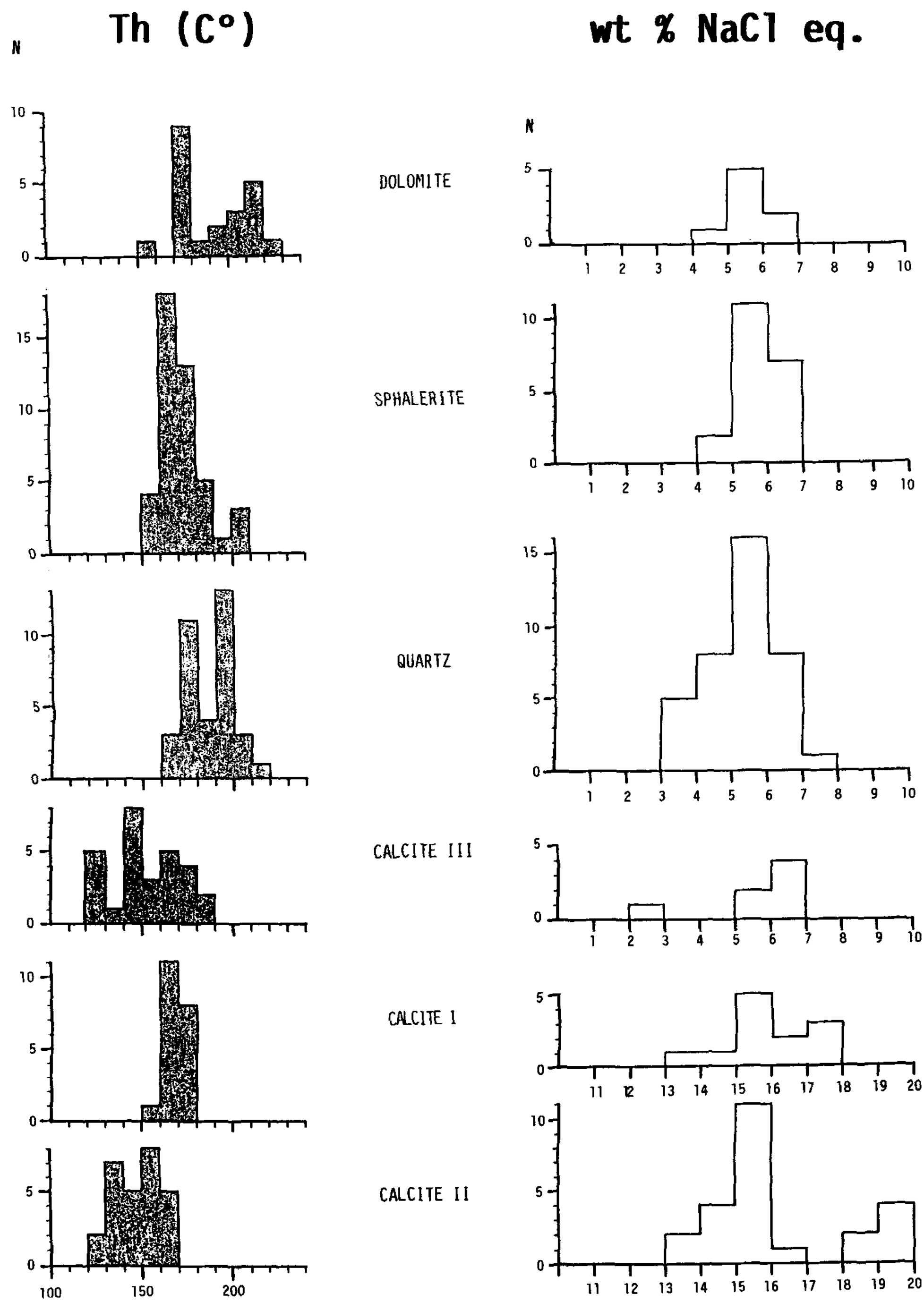

FIG. 3. Frequency distribution of homogenization temperatures and salinity. Calcite I means diagenetic black calcite in preserved limestone. Calcite II is post-ore vug-filling calcite in host dolomite. Calcite III is from late (Alpine?) calcite veins which transect both limestone and dolomite.

It is worth recalling that sparry black calcite (calcite I) is linked with early vadose diagenesis, vug-filling calcite (calcite II) with a phenomenon of dedolomitization consequent to post-ore emersion, and sparry white calcite (calcite III) with tension phenomena, undergone by the entire formation, probably during Alpine orogenesis.

Hence these calcites were formed at very different times, and at a different time from the mineralization. At least two of them seem certain to have crystallized at low temperature and pressure.

The overall data could be interpreted as a phenomenon of general reset of temperatures due to a thermal event (Alpine?) but indeed the formation does not appear at all metamorphosed and, for instance, in the black limestone even structures as delicate as the calcareous alga *Archaeolythophyllum missouriensis* (Johnson) are perfectly visible and preserved.

Recent work (Goldstein, 1986; Prezbindowski and Larese, 1987; Barker and Halley, 1988) on fluid inclusions in calcite formed at near surface (25 °C) temperature and pressure showed abnormally high values of T, presumably attributable to the low trapping pressure. These authors advise care in the interpretation of data of this type, even if well grouped.

If this is true, nothing prevents us from speculating that even ore minerals from a mineralizing process taking place at low temperature and pressure, as the geo-petrographic data would indicate is the case at Sant'Antonio, should not give similar unrealistically high-temperature values, simulating the effect of higher-temperature fluids.

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