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A NEW GOLD-BISMUTH OCCURRENCE AT PUNTA DEL FENAIO (GIGLIO ISLAND, TUSCANY)

Abstract - A new gold-bismuth occurrence has been found at Punta del Fenaio (Giglio Island, Tuscany) hosted by the monzogranite and contact aureole rocks. The geo-mineralogical features of the small gold-bearing mineralization are presented and briefly discussed with respect to the Tuscan magmatic-hydrothermal scenario. It is a high grade (Au concentrations up to thousands of ppm), yet small, ore concentration constituted by dominant native bismuth associated with gold and very minor amounts of bismuthinite and Bi-Te-S phases. Due to the very low melting point of bismuth (271°C) and the gold scavenging capacity of bismuth melt (up to 19 mol% Au), a mechanism of melt-collecting from the hydrothermal solutions is hypothesize for the Punta del Fenaio ore, where the Au-Bi-S-(Te) assemblage crystallized late, as part of the main adularia-quartz hydrothermal mineralization.

Key words - Gold, bismuth, ore deposits, granite, Tuscany.

Riassunto - *Nuovo ritrovamento di oro e bismuto a Punta del Fenaio (Isola del Giglio, Toscana).* In questo articolo viene descritta una nuova mineralizzazione a Bi-Au incassata nelle rocce granitiche e dell'aureola di contatto di Punta del Fenaio (Isola del Giglio, Toscana). Le caratteristiche geologiche e mineralogiche della piccola mineralizzazione aurifera vengono presentate e discusse rispetto al contesto magmatico-idrotermale toscano. La piccola mineralizzazione mostra dei tenori in oro elevatissimi (fino ad alcune migliaia di ppm) ed è costituita da bismuto nativo, oro, bismutinite, e alcune fasi di Bi-Te-S. Il basso punto di fusione del bismuto (271°C) e la sua capacità di sciogliere oro (fino a 19 moli% Au) suggerisce un meccanismo di scambio tra bismuto fuso e fluido idrotermale che può avere prodotto le elevate concentrazioni di oro osservate. Il fuso a bismuto è rimasto intrappolato nelle cavità della roccia idrotermale che si andava formando, per poi cristallizzare tardivamente la paragenesi a Au-Bi-S-(Te) solo quando la temperatura è scesa sotto i 271°C.

Parole chiave - Oro, bismuto, giacimenti minerari, granito, Toscana.

Introduction

Tuscany has been for at least 2500 years one of the major mining regions of Italy, with significant production of iron, copper, lead, zinc, silver, antimony, mercury and pyrite. Production of precious metals was limited to silver, which was extracted from silver-rich galena and Ag sulfosalts occurring in some ore deposits. The mines of the Bottino-Valdicastello area (Apuan Alps), and Massa Marittima-Campiglia area (southern Tuscany) provided a significant silver production only during short periods (Middle Age, Renaissance, XIX-XX century), sometimes giving rise to excessive expectations for their real consistency and wealth. At present, mining activities in Tuscany are closed and most of the mining localities have been incorporated into archeo-mining parks.

During the past centuries the presence of gold in Tuscany has been reported several times by naturalists, mining prospectors, scientists or inhabitants, but gold has been practically absent from Tuscan mining industry if not as a very minor by-product from a few mines (Bottino, Angina and Capanne Vecchie). The exploration activities undertaken during the past 30 years on deposits of the so-called «invisible» gold in southern Tuscany (Tanelli, 1988; Pipino, 1989; Tanelli & Scarsella, 1990) showed only a few anomalous areas unsuitable for economic exploitation.

A less known but no less effective exploratory activity, is carried out by the numerous Italian and foreign mineral collectors that consider Tuscany as one of the richest region in the world for minerals. Thanks to the field observation of one of these collectors (Walter Marinai) and the geo-mineralogical investigation conducted by the authors a new gold-bismuth occurrence has been found at Punta del Fenaio (Giglio Island) hosted by the monzogranite and contact aureole rocks. The geo-mineralogical features of the small gold-bearing mineralization are presented and briefly discussed with respect to the Tuscan magmatic-hydrothermal scenario. It is worth to note that although gold has never been mined during the extensive pyrite exploitation at Giglio Island (Campese-Cala dell'Allume mine), an old document (XVI century) describes the extraction of gold on the island. Giorgio di Giglio (1558), by writing to the Grand Duke of Florence Cosimo I, says that Cardinal Alessandro Farnese (Pope Paul III from 1534 to 1549) sent his uncle on the Island of Giglio where he did «una prova di oro et riusci de peso vinti dui carate et fecine sette verge di una libbra elluna così sene feci ogni suo bisogno…». Taking into account the weight of the old Tuscan pound (348 g), a total of about 2.4 kg of gold was produced. A significant amount, that could not be extracted from a low grade ore (at Giglio Island volumetrically important mineral excavations are not documented before 1800), while it is reliable from a high grade, yet small, mineral concentration as that described for Punta del Fenaio.

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Gold anomalies and mineralizations in Tuscany

The complex geological history of Tuscany produced a wide variety of mineral deposits that, in many cases, have been intensively exploited until a few years ago (Tanelli & Lattanzi, 1986; Dini, 2003). Four major metallogenic epochs can be defined (Lattanzi *et al.*, 1994: i) a Paleozoic epoch (Ordovician) which produced metal concentrations (Pb, Zn, Ag, Hg) hosted by the metavolcanic-metasedimentary sequences of Apuan Alps (Bottino, Levigliani, etc.); ii) a Triassic epoch, linked to an early stage of Tethys rifting (at the beginning of carbonate sedimentation), with the formation of Fe-Ba deposits in the Apuan Alps (Buca della Vena, Monte Arsiccio, etc.) and Fe oxides-pyrite deposits in southern Tuscany (Niccioleta, Rio Marina, etc.); iii) a Jurassic epoch linked to the spreading of Tethys Ocean during which the ophiolitic copper sulfide deposits formed (Montecatini Val di Cecina, Montecastelli, etc.); iv) an Apenninic epoch (Oligocene to Quaternary), characterized by hydrothermal circulation both in regional metamorphic settings (e.g., Apuan Metamorphic Complex, 27-8 Ma) and in magmatic settings (e.g., Tuscan Magmatic Province, from 8.5 to 0.2 Ma), responsible for a large variety of ore deposits (Hg, Sb, Cu-Pb-Zn, Sn) as well as for the local remobilisation of deposits formed during the previous metallogenic epochs.

Since 1983, mineral exploration projects have been conducted in Tuscany with the aim to define the gold potential of the region (Tanelli *et al.*, 1991). These studies allowed a better definition of the anomalous gold content of some ore deposits already exploited in the past for other metals, and the identification of a new type of gold mineralization in Tuscany, the epithermal disseminated gold deposits, hosted by carbonate rocks (Tanelli & Scarsella, 1990; Lattanzi, 1999). In the latter case, the gold-bearing mineralization occurs as fine-grained gold disseminations (few microns), dispersed in microcrystalline quartz (chalcedony, «jasperoids») replacing the carbonate rocks of the Tuscan Nappe and Ligurian Units. These non-economic gold mineralizations are often closely associated with the well-known antimony deposits, actively exploited in the past (Tafone, Cetine, Pereta, etc.).

As mentioned above, other types of ore deposits were already known in Tuscany for their gold content as shown by chemical and petrographic analyses. Most of the Pb-Zn-Ag-Cu deposits in the Apuan Metamorphic Complex (Bottino, Angina, Tambura, etc.) show significant gold concentrations (0.3 to 48 g/t; Jervis, 1862; Pelloux, 1922; Benvenuti *et al.*, 1992) and provided small-scale production of gold as by-product of lead, copper and silver (Jervis, 1868; Repetti, 1845). Some of the copper deposits hosted by ophiolitic rocks (the area between Libbiano and Serrazzano) had locally anomalous gold content (0.6 to 10 g/t; Jervis, 1862). Gold anomalies and modest production of gold are also documented from base metal sulfide deposits (Pb-Zn-Cu-Fe) in southern Tuscany: i) small grains of gold have been identified in polished section of Pb-Zn-Cu-Fe ores from Castellaccia-Poggio al Montone (Massa Marittima; Burtet Fabris & Omenetto, 1974a) and Argentario (Burtet Fabris & Omenetto, 1974b), ii) small gold production was provided, during the XIX century, by the Fenice Capanne mine (Massa Marittima; Savi, 1847), iii) gold anomalies were identified in the metasomatic rocks at the contact with the granite pluton of Botro ai Marmi (Campiglia Marittima; Tanelli *et al.*, 1991). Finally, alluvial gold was found in sediments of Serchio river (Pontecosi, Lucca; Biagioni, 2009), Albegna and Fiora rivers (Pipino, 1989), and in beach sands along the border between Tuscany and Lazio (Tanelli *et al.*, 1991).

The Tuscan epithermal disseminated gold deposits do not show a clear and direct link with intrusive/effusive magmatic systems and the source of the precious metal still needs to be defined. The small gold-bismuth mineralization at Punta del Fenaio is placed at direct contact with the Pliocene intrusive rocks and it may represents a key area for understanding magmatic-hydrothermal processes leading to gold mineralization, and shedding new lights on the epithermal gold deposits of southern Tuscany.

The Au-Bi occurrence at Punta del Fenaio: geology and mineralogy

The Island of Giglio, located 20 km off the Tuscan coast, rises to elevation near 500 m, a portion greater than 90% of its 23.8 km^2 of exposed surface area is underlain by monzogranite rocks. The acidic intrusives of the Island of Giglio are part of the Tuscan Magmatic Province (TMP) that developed during Miocene-Pliocene time (Innocenti *et al.*, 1992). On the basis of field, petrographic and geochemical studies, two main distinct intrusions have been defined (Westerman *et al.*, 1993): the Giglio monzogranite intrusion (GMI) and the Scole monzogranite intrusion (SMI). The older and much larger of the two (GMI), is consistently characterised by the presence of significant amounts of foliated metamorphic xenoliths and mafic microgranular enclaves, and it can be divided in two main facies showing a concentric shell pattern (Fig. 1a and 1d). The younger Scole monzogranite intrusion, apparently devoid of xenoliths and mafic enclaves, emplaced at the core/base of the previous intrusion mimicking the same pattern. Rb-Sr isotope dating of both the intrusions gave an age of 5 Ma (Westerman *et al.*, 1993).

Intrusive contact relationships between the GMI and the original surrounding country rock are preserved and exposed only at Punta del Fenaio at the north end of the island (Fig. 1b). There, roof pendants of strongly foliated and hornfelsed argillaceous metasediments dip gently to the north with consistent orientation in two areas covering a total of approximately 1,200 m^2. Hornfels rocks are made by biotite-andalusite schists and biotite quartzites that locally are replaced by irregular metasomatic masses of skarn (diopside, tremolite, allanite, etc.) crosscutting and/or following the early contact metamorphic foliation. Exposed intrusive contacts show sharp truncation of the gently dipping country rock foliation, and these contacts dip somewhat more steeply, also toward the north. Foundered blocks

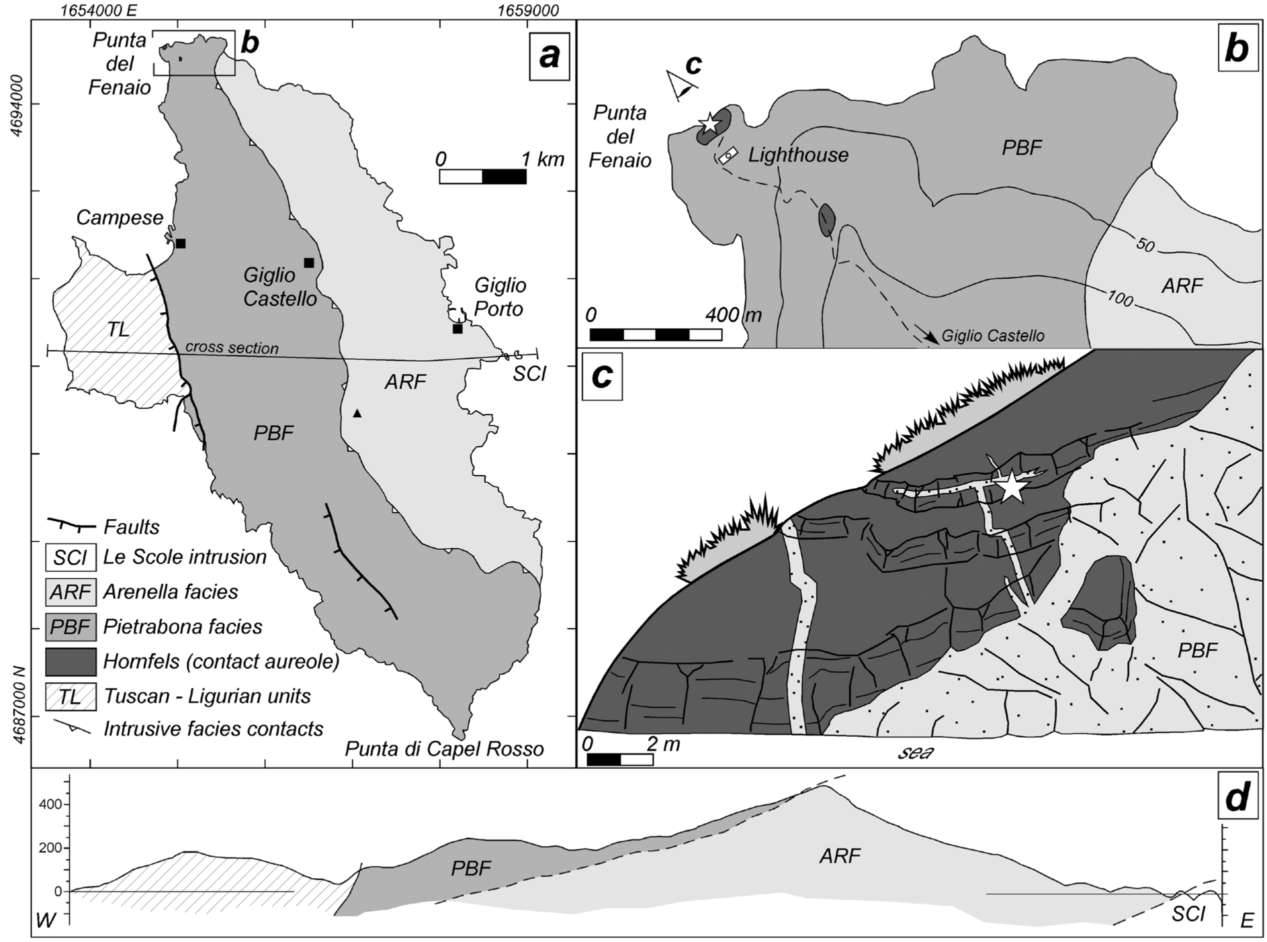

Fig. 1 - a) Schematic geological map of Giglio Island showing the internal structure of Giglio monzogranite intrusion (modified after Westerman *et al.*, 1993). The Giglio monzogranite intrusion (GMI) is divided in Arenella facies (ARF) and Pietrabona facies (PBF); b) Detailed geological map of Punta del Fenaio area with the two small outcrops of hornfels. The white star indicates the location of the Bi-Au ore occurrence; c) Sketch-drawing of the Punta del Fenaio outcrop where Bi-Au minerals have been found (white star). The dyke-sill microgranite apophyses controlling the Bi-Au mineralization are indicated (redrawn after a photo from the sea); d) simplified E-W geological cross section of the Giglio Island.

of the country rock occur near these contacts as rafts with random orientation.

Monzogranite rocks and relics of contact aureole are crosscut by dykes of leucogranites and aplite-pegmatites. These rocks are usually rich in black tourmaline, forming prismatic crystals up to 15 cm in length.

Along the western side of the island, an assemblage of Mesozoic regionally metamorphosed and sedimentary units is in fault contact with the intrusive rocks. Along the fault, these rocks show no evidence of contact metamorphism, suggesting that their juxtaposition with the igneous rocks involved movement from a sufficient distance over the vertical of the plutonic mass to have escaped significant heating/recrystallization. These relationships are coherent with the post-5 Ma tectonic history indicating extensional vertical movements that, together with erosion, produced the exhumation of the intrusive body.

Field observation

The Au-Bi occurrence is located under the lighthouse, down the stairs leading to the sea, amid a few dozen square meters of skarn and hornfels in direct contact with the granite. Some apophyses of monzogranite crosscut the contact metamorphic rocks forming dykes and sills orthogonal and parallel to the schistosity of the hornfels respectively. This locality is known since several years for providing beautiful specimens of allanite in black prismatic crystals associated with tremolite and diopside from the skarn masses.

In particular, a vertical dyke of biotite and tourmaline microgranite (Fig. 1c) breaks away from the main mass of granite and enters hornfels for a few meters following a NW-SE strike and then intrudes the metamorphic rock parallel to the schistosity forming a 20 cm thick sill. The SW branch of the sill and the hornfels at the dyke-sill inside-corner experienced a strong hydrothermal alteration with the formation of veins and irregular masses of quartz and K-feldspar (adularia). The resulting hydrothermal rock is made of a fine intergrowth of elongated prismatic quartz crystals and clusters of white «pseudorhombic» crystals of adularia. Numerous sub-millimetric cavities are present with walls lined by euhedral crystals of adularia.

The hydrothermal rocks display disseminations and larger masses (up to several kilograms) of native bismuth and rarer bismuthinite associated with small grains of native gold (up to 1 mm; Fig. 2). The largest grains of native gold (0.3 - 1 mm) are easily identifiable to the naked eye or with the aid of a magnifying lens (Fig. 2a). The gold grains have an irregular shape but in some cases triangular geometries resembling the faces of octahedron have been detected. External portions of bismuth grains/masses display a strong alteration in silky white, greyish, light green soft minerals, while the fresh fractures at the core show the typical step-like cleavage and pinkish silver color.

Mineralogy: reflected light petrography, X-ray and SEM-EDS data

Polished sections of the Au-Bi ore were studied in reflected light and analysed by SEM-EDS; small grains of minerals were separated and identified by means of X-ray powder diffraction study (Gandolfi camera).

As already observed in the field, bismuth is the most common phase representing almost 99% of the ore. Bismuth disseminations are interstitial when they occur into the leucogranite as anhedral grains associated with adularia and quartz wrapping out the still preserved subhedral magmatic crystals (plagioclase, K-feldspar, quartz and tourmaline). The largest masses of bismuth from the metasomatic adularia-quartz assemblage, hosted at the leucogranite-hornfels contact, display both anhedral and wedge-shaped texture. In reflected light bismuth show a creamy white-pinkish cream colour, a weak bireflectance and a distinct anisotropy that reveal internal polysynthetic twinnings with feather-like appearance (Fig. 2).

Bismuthinite (Bi_2S_3) usually occurs as single crystals and clusters of subhedral prismatic crystals closely associated with bismuth, especially at the outer rims of the bismuth masses/grains (Fig. 2e). Some euhedral crystals are partially embedded in bismuth. Replacive textures such as those occurring in systems characterised by late sulfidation of an early S-poor system were not observed (e.g. bismuthinite replacing the outer rims of bismuth masses; Ciobanu *et al.*, 2010). In reflected light bismuthinite is white-grey in colour with weak bireflectance and distinct grey to bluish-grey anisotropy; lamellar twinning locally occurs.

In polished sections gold grains (up to 1 mm in size) display the typical bright yellow colour and variable shapes (Fig. 2). Many grains have irregular shapes (as infill of small cracks and interstices of gangue minerals, and irregular grains in bismuth and bismuthinite), but in some cases a quite euhedral outline has been occasionally observed in crystals embedded in bismuth and bismuthinite. All the observed gold grains occur near the rims of bismuth masses/grains strictly associated with bismuthinite.

Both bismuth and bismuthinite underwent a deep alteration that produced bismoclite - (BiO)Cl and bismutite - $(BiO)_2CO_3$, along the outer rims of grains and crosscutting cracks (Fig. 2). Depending on orientation of cracks with respect of the bismuth crystal structure, bismoclite developed a dendritic, feather-like replacive texture including several small relics of bismuth. Bismutite outlines the outer rims of bismoclite aggregates at direct contact with native bismuth. Bismuthinite is less affected by alteration with respect to bismuth.

SEM-EDS study of polished sections and X-Ray diffraction analyses on separated mineral grains confirmed the data obtained in reflected light. In particular, qualitative and semi-quantitative analyses indicate that bismuth and bismuthinite do not contain detectable amounts of other elements. Bismoclite is easily distinguishable from bismutite due to its chlorine content. Gold grains display a quite constant Ag content around 10-15 wt %. A bismuth-tellurium-sulphur phase, as prismatic crystals associated with bismuth, gold and bismuthinite, has been singled out through SEM-EDS analyses and still needs to be investigated by X-Ray methods (Fig. 2f). X-ray diffraction analyses led to the identification of bismuth and bismuthinite; the study of oxy-chloride-carbonate phases provided identifiable diffraction lines that are coherent with the bismoclite and bismutite diffraction patterns.

Finally, some samples were selected for a first geochemical investigation (Tab. 1). In order to determine the Au, Ag, Te and S content of the metallic aggregates, two small masses of the bismuth-gold-bismuthinite assemblage (about 1 cm^3 each; samples PF1 and PF2) were isolated from the matrix and carefully cleaned by removing all the silicate grains. An additional representative bulk sample of the disseminated ore was also analysed (sample PF3). Gold concentration in bismuth masses is extremely high (4177 and 7654 ppm) as well as silver (569 and 1246 ppm); the disseminated ore gave 65.25 ppm of gold and 9.75 ppm of silver. Tellurium and sulfur concentrations in bismuth masses are respectively 314-540 ppm and 422-620 ppm; the disseminated ore contain 4.80 ppm of tellurium and 10.2 ppm of sulfur. Bismuth content in the latter sample is 9750 ppm, while it was not determined for the other two samples (closed to 99 wt %). The limited number of samples preclude any definitive interpretation but it is interesting to note the quite consistent Bi/Au, Bi/S, Au/Ag, S/Te ratios (Tab. 1).

Discussion

Although the widespread association between gold mineralisation and bismuth minerals has long attracted attention and has been interpreted in genetic terms (e.g. Spooner, 1993; Meinert, 2000), it is only recently that such associations have been considered pivotal for understanding processes of gold deposition and remobilisation (e.g. Tomkins & Mavrogenes, 2002; Tooth *et al.*, 2008; Ciobanu *et al.*, 2010). The new finding of native gold and bismuth at Punta del Fenaio represents the first well documented auriferous ore in Tuscany

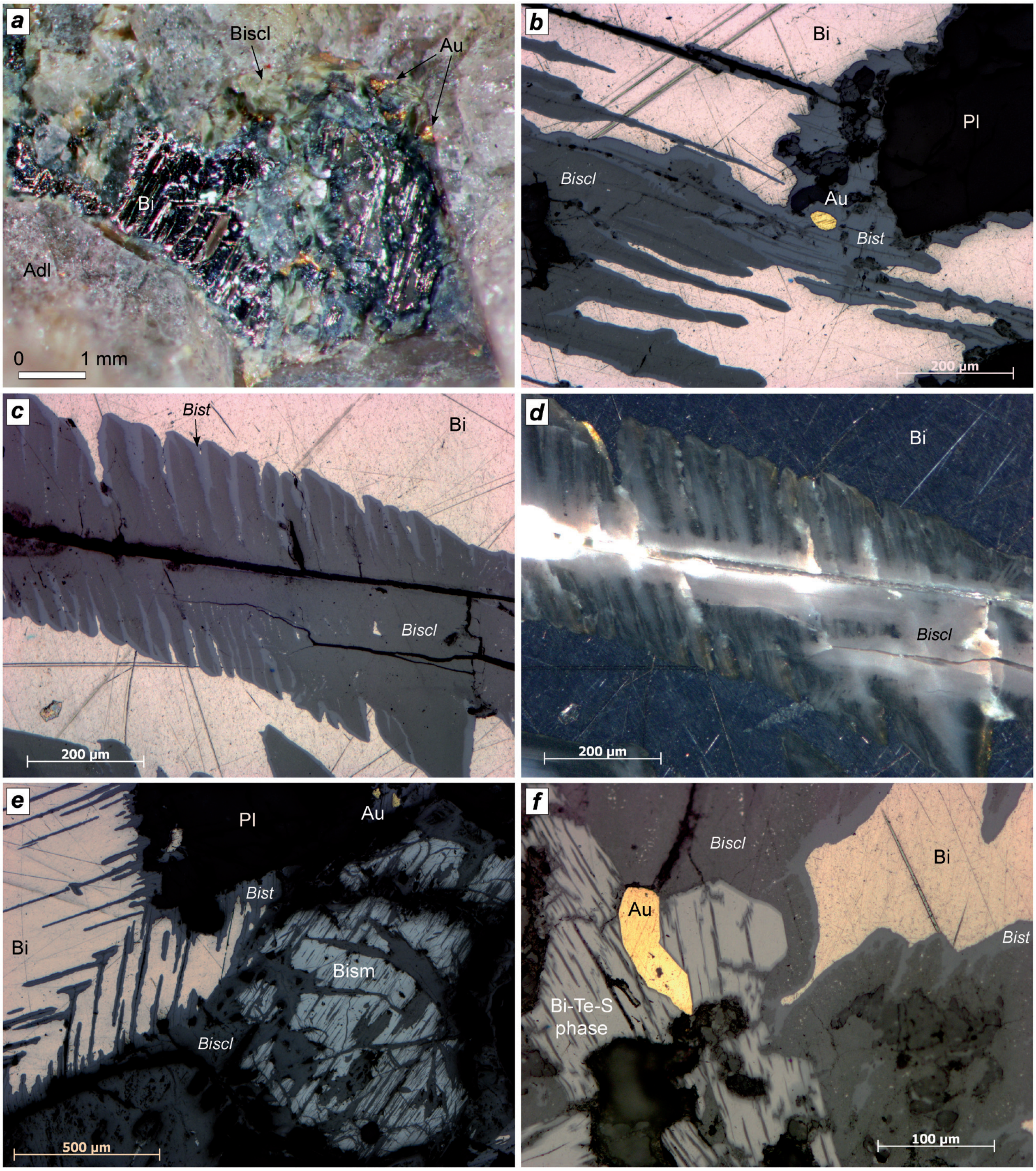

Fig. 2 - Photographs of Punta del Fenaio Bi-Au ore (Au = gold, Bi = native bismuth, Bism = bismuthinite, Biscl = bismoclite, Bist = Bimutite, Adl = adularia, Pl = plagioclase). a) representative grain of bismuth associated with gold filling a cavity of the adularia-quartz hydrothermal rock. The whitish-greenish mineral is bismoclite with minor bismutite (direct light, close-up view). b) Bismuth mass wrapping a subhedral crystal of plagioclase from the monzogranite host. Note the gold grain embedded by the alteration products (reflected light, parallel polars); c) feather-like aggregates of bismoclite and bismutite replacing native bismuth along a fracture (reflected light, parallel polars); d) Same as in figure c (reflected light, crossed polars); e) Bismuthinite subhedral crystal and gold grains along the outer rim of a bismuth mass (reflected light, parallel polars); f) Euhedral crystals of a Bi-Te-S phase associated with bismuth and gold.

Tab. 1 - Concentrations of Au, Ag, Te, S and Bi (ppm) for three ore samples. PF1 and PF2 are single masses of metallic ore without silicate matrix. PF3 is a representative sample of disseminated ore. Data are in ppm (µg/g); Bi content was determined for sample PF 3, while for PF 1 and PF 2 it was calculated by difference (in addition to the elements reported in table there are few ppm of other elements). Analyses were performed at ACME Ltd. (Canada) by using aqua regia extraction and ICP-MS. Elemental ratios are calculated on a molar base.

Sample	Au	Ag	Te	S	Bi	Bi/Au	Bi/S	Au/Ag	S/Te
PF 1	4177	569	314	422	*995000*	224.5	361.8	4.0	5.3
PF 2	7654	1246	540	620	*990000*	121.9	245.0	3.4	4.6
PF 3	65.25	9.75	4.8	10.2	9750	140.8	146.7	3.7	8.5

with a clear genetic link to the granite rocks of the Tuscan Magmatic Province. Miocene-Quaternary Tuscan granites have been already proposed as one of the primary sources for the epithermal gold mineralizations of southern Tuscany (Bencini *et al.*, 1990).

Gold metallogeny and granite intrusions in Tuscany

From Miocene to Quaternary, many episodes of magmatic activity produced intrusive, sub-volcanic and volcanic rocks in Tuscany showing a highly variable composition and geochemical affinity (see Innocenti *et al.*, 1992). Their emplacement generated hydrothermal circulation that in places resulted in important minerogenetic events (e.g. the Hg and Sb ore deposits of southern Tuscany). Moreover, various types of hydrothermal alteration (silicification, argillification and alunitization), locally associated with significant gold anomalies have been recently identified in severeal areas of the Sb and Hg Tuscan districts (Tanelli & Scarsella, 1990; Tanelli *et al.*, 1991). In spite of their limited economic potential, interesting questions arise about identification of the source-(s) of gold (magmatic, leached out from metamorphic units and/or ophiolites, etc.) transported and precipitated by the epithermal solutions.
The extensive geochemical study of Bencini *et al.* (1990; 244 samples) indicates that all the igneous rocks of Tuscan Magmatic Province are enriched in gold (up to 90 ppb) with respect to both the average value (0.5-2 ppb) given by Rock *et al.* (1988) for the «unmineralized ultramafic, komatiitic, mafic and felsic rocks», and the general average (4-6 ppb) given by Govett (1983) for igneous rocks. As stated by the authors the highest concentrations detected in Tuscan magmatic rocks cannot be strictly related to the original magmas, because of the widespread hydrothermal alteration affecting some of the studied magmatic centres (Campiglia Marittima, Gavorrano, Castel di Pietra). However, it is important to stress the significant gold concentrations found in the Monte Capanne monzogranite intrusion (Elba Island; average 6.5 ppb, max. 15 ppb) and in the aplite-pegmatite veins differentiated from the main intrusion (average 12.6 ppb, max. 20 ppb). In fact, the western Elba Island magmatic complex experienced negligible hydrothermal alteration with respect to the other Tuscan magmatic complexes (Dini *et al.*, 2002 and 2004), and the slight gold enrichment can be considered as a primary character of these rocks. It appears remarkable the gold enrichment produced during the magmatic differentiation from the early monzogranite magma to the late aplite-pegmatite melts.
Such a behaviour needs to be confirmed by a more detailed geochemical work, but it is interesting to note that also bismuth is enriched into the Monte Capanne aplite-pegmatite veins. Geochemical analyses of Monte Capanne monzogranite (12 samples) and associated aplite-pegmatite veins (9 samples) gave bismuth contents of respectively 0.1-0.4 ppm and 1.6-2.6 ppm (Dini, unpublished data). Moreover, native bismuth (Pezzotta & Lorenzoni, 2008) and bismuth sulfosalts (cannizzarite and lillianite; Orlandi & Pezzotta, 1996) have been found as late crystallization mineral phases in the aplite-pegmatite veins cropping out along the eastern edge of the Monte Capanne intrusion.
The geochemical association between gold and bismuth in the Tuscan granite intrusions, in the aplite-pegmatite differentiates, and in the associated metasomatic-hydrothermal products deserves a thorough study to clarify the possible relationships between Miocene-Quaternary magmatism and the epithermal gold deposits of southern Tuscany.

Bismuth melts as Au scavengers and ore-grade enhancer

Interpretation of textures and phase relationships observed in ores where sulfosalts and tellurides are minor components has led to the relatively new concept of partial melting as a viable mechanism to concentrate metals since these minor minerals are composed of one or more low melting point chalcophile elements (Bi, Te, Pb, etc.; Frost *et al.*, 2002).
More important in the topic here discussed is the possible role played by melts in scavenging gold, with excellent application to the Au-Bi-Te-(S, Se) mineral systems (Ciobanu *et al.*, 2005). Native bismuth (melting point 271°C) and Bi-rich polymetallic assemblages (e.g., Au-Bi with a eutectic of 241°C; Fig. 3) are molten at temperatures that overlap with the formation conditions of a large range of gold deposits. The implications of this aspect were illustrated by Douglas *et al.* (2000), who presented preliminary experiments in which Au was scavenged from hydrothermal solutions at temperature of ~300°C by Bi melt, a process they termed the «liquid bismuth collector model». A model involving Au-Bi-Te-(S) melts precipitated from hydrothermal fluids has been considered, based on textural and phase relationships, for interpretation of various deposit types. These include intrusion-related gold (Pogo and Fort Knox, Tintina Belt, Alaska; McCoy, 2000), epithermal-porphyry systems (Larga, Golden Quadrilateral, Romania; Cook & Ciobanu, 2004),

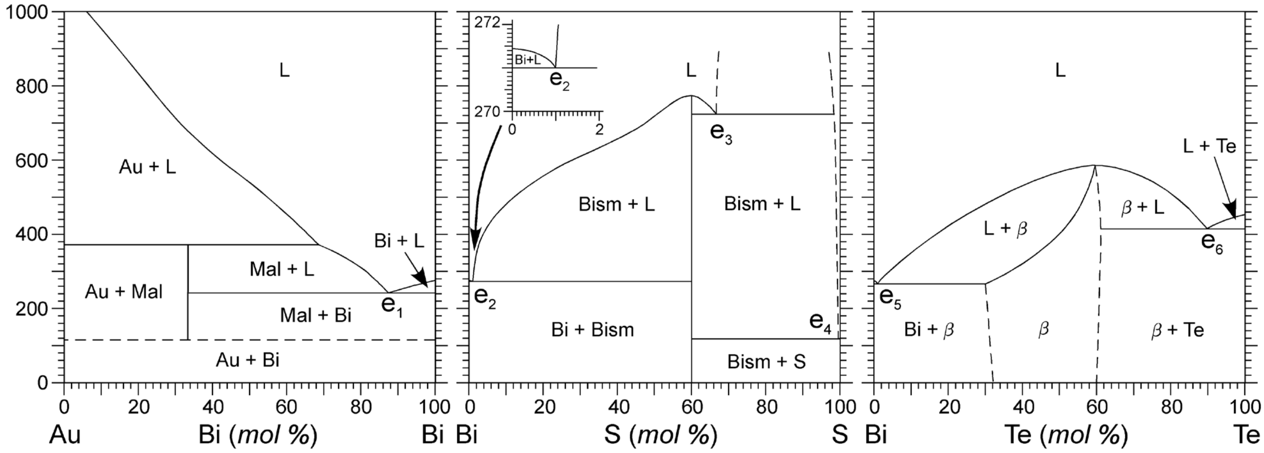

Fig. 3 - Phase diagrams of Au-Bi, Bi-S and Bi-Te systems (modified after Tooth *et al.*, 2008; Gather & Blachnik, 1980). (Au = gold, Bi = native bismuth, Bism = bismuthinite, Mal = maldonite, S = sulfur, Te = tellurium, β = tellurobismuthite, L = liquid).

recent volcanic massive sulphide systems (Escanaba Trough, S Gorda Ridge; Törmänen & Koski, 2005), skarn deposits such as Fe skarns (Ocna de Fier and Baisoara, Romania; Ciobanu *et al.*, 2003; Ciobanu & Cook, 2004) and Au skarns (Ortosa and El Valle, Rio Narcea Gold Belt, Spain; Cepedal *et al.*, 2006), as well as for orogenic gold systems (Viceroy Mine, Harare-Bindura-Shamva greenstone belt, Zimbabwe; Oberthür & Weiser, 2008). Moreover, melts can scavenge Au from a pre-existing ore if partial melting of crustal rocks occurs during deformation associated with high-grade metamorphism (e.g. Tomkins *et al.*, 2007). In the case of Bi-dominant melts, this can be initiated as low as the upper greenschist facies (400°C), e.g. the estimated conditions for Alpine Au-Bi-S remobilizates from the Highis Massif, Romania (Ciobanu *et al.*, 2006). The net result of such processes is a distinct geochemical correlation between Au and Bi in several gold deposits. For example, an Au-Bi correlation is distinctive in intrusion-related gold (IRG) systems with correlation coefficients of 0.7-0.9 commonly reported (e.g., Baker *et al.*, 2005). Au skarns also display strong Au-Bi correlations (e.g., Meinert, 2000), as do some orogenic systems (e.g., Hattu Schist Belt, Finland; Nurmi & Sorjonen-Ward, 1993).

The phase relationships of the Au-Bi binary system have been well described in metallurgical literature. The Au-Bi binary phase diagram illustrates the potential of Bi melt as a gold scavenger (Fig. 3). An Au-Bi melt has a eutectic with ~19 wt% Au at 241°C (at atmospheric pressure; at higher pressure, the eutectic temperature is likely to be even lower due to bismuth's negative dP/dT solid-liquid univariant; Ponyatovskii, 1960), and thus is able to incorporate much higher Au concentrations than aqueous fluids at this and higher temperatures. This solubility difference means that Au is expected to partition into Bi melts even from undersaturated aqueous solutions. This model has been recently assessed by Tooth *et al.* (2008) and Wagner (2007) who investigated the effect of gold scavenging by bismuth melts using equilibrium thermodynamic modeling of an aqueous solution-mineral-melt system. The calculations for the Au-Bi-Na-Cl-S-H-O system, performed at temperatures between 300 and 450°C, demonstrate that Au concentrations in the melt are several orders of magnitude higher than in the coexisting fluid, indicating the possible formation of economic gold deposits and/or high-grade Au local concentrations from undersaturated aqueous fluids, in which mineralization would not be expected in the absence of a bismuth melt. Other systems that are relevant for the discussion are: Bi-S and Bi-Te (Fig. 3). These systems display similar behaviour; in fact both diagrams have two eutectic points that lie very close to the melting points of the pure elements (Bi, S and Te), with intermediate compounds (bismuthinite - Bi_2S_3 and tellurobismuthite - Bi_2Te_3) that congruently melt at higher temperatures. Thus, the presence of S and Te into the system Bi-Au produces similar effects on eutectic points and liquidus curves of the ternary system Bi-Au-(S, Te).

For the sake of simplicity we discuss the Au-Bi-S system only. There are no experimental data for the system Au-Bi-S, although a hypothetical diagram projecting the liquidus surface has nonetheless been proposed (Prince *et al.*, 1990; Fig. 4). The portion of the diagram relevant to the discussion of Punta del Fenaio mineral assemblage is the Bi-Au_2Bi-Bi_2S_3 triangle. The eutectic points e_1 and e_2 in each of the binary systems Bi-Au and Bi-S, project into the ternary systems as boundary curves converging in the ternary eutectic e_{t1} (the point with the lowest liquidus temperature of the system). A melt with an initial composition close to the Bi corner should start crystallization around 270°C forming native bismuth in the early stage and a more complex assemblage (bismuth + bismuthinite + maldonite) as the composition of the melt intercepts the e_1-e_{t1} boundary curve and finally end into the ternary eutectic e_{t1}.

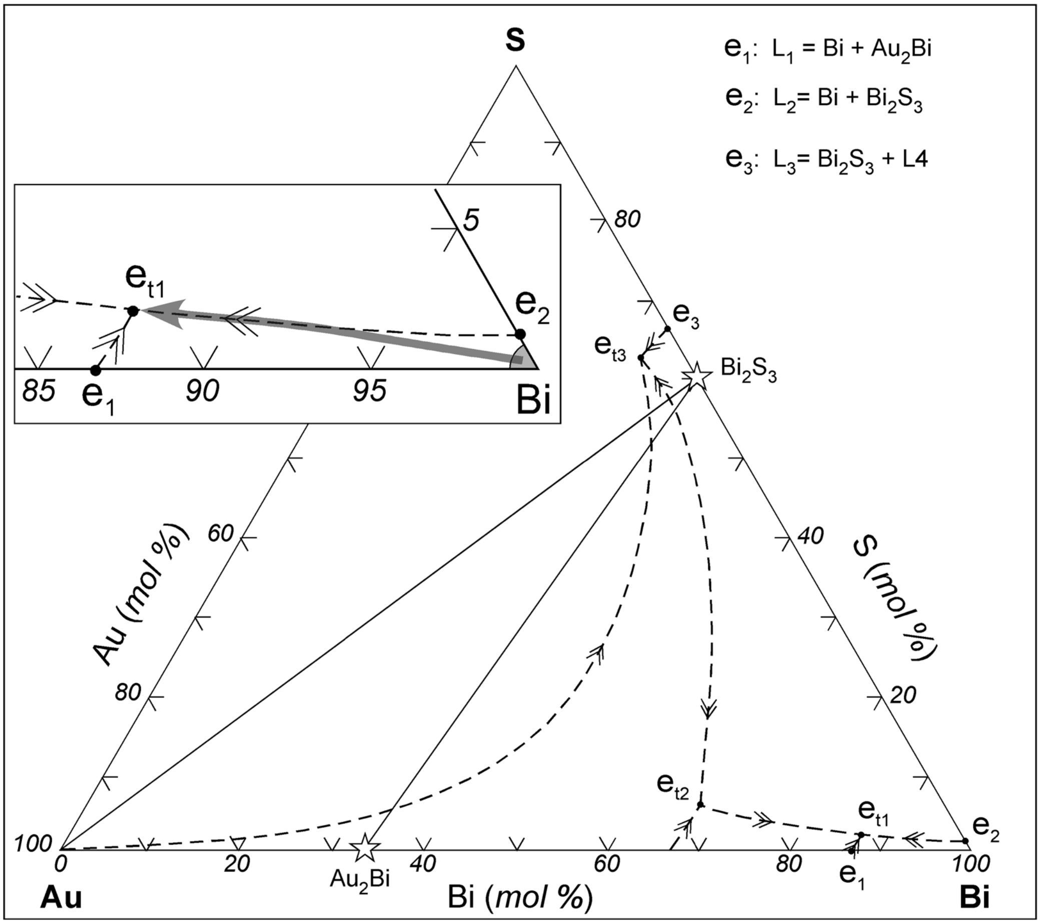

Fig. 4 - Ternary diagram of Au-Bi-S system showing the main eutectic points and boundary curves as determined by Prince *et al.*, 1990. The inset display the possible path of Bi-Au-S melt at Punta del Fenaio (grey arrow). For the details see the text.

Bismuth melts and hydrothermal fluids at Punta del Fenaio

The bismuth-bismuthinite-gold masses and disseminations at Punta del Fenaio can be at least partially explained by crystallisation of melts from the system Bi-Au-(S-Te) coexisting with hydrothermal fluids exsolved during crystallization of the microgranite dyke. The ore mineral association includes phases representing eutectic assemblages formed at the end of partial crystallisation along the liquidus curves of the Au-Bi-S (-Te) system as represented in Figure 4. Predominance of native bismuth and the very minor occurrence of bismuthinite and other Bi-Te-S phases indicate that the overall fS_2 of the system was low and even lower the activity of tellurium. Moreover, sulfur- and tellurium-bearing phases as well as gold grains have been observed only at the rims and/or in the outer portion of the bismuth masses and grains, suggesting a late formation of these phases. This behaviour is indicative of a crystallization process that started close to the Bi corner of diagram in Figure 4.

Hydrothermal fluids involved in the contact aureoles of Tuscan granite intrusions (e.g. Rossetti *et al.*, 2007; Ricci, 2000; Rossato, 1999) are characterised by temperatures (280-450°C) well above the melting point of bismuth and liquidus surfaces of the system Bi-Au-S-(Te). For this reason the Bi-Au-S-(Te) melt we hypothesize for Punta del Fenaio should have intersected the liquidus when temperature decreased around 270°C (Fig. 4). During the high temperature stage (450-270°C), hydrothermal fluids interacted with the microgranite dyke/sill and the hornfels triggering the widespread formation of adularia, quartz, allanite, tremolite, etc. As the Bi-Au-S-(Te) eutectics occurs at lower temperature relative to that of the hydrothermal assemblage, inclusions of polymetallic melt would have remained at least partially molten after entrapment into the numerous cavities of the hydrothermal rock. Thus, at lower temperature, the Bi-Au-S-(Te) melt started to crystallize filling the cavities.

The first phase to crystallize was native bismuth, while the melt composition started to shift toward the ternary eutectic e_{t1} following the possible path reported in Figure 4. In accordance with petrographic and geochemical data, bismuth formation characterized most of the crystallization history until the melt composition intercepted the boundary curve e_2-e_{t1} producing the late crystallization of bismuth + bismuthinite. Finally, the system reached the ternary eutectic e_{t1} where bismuth, bismuthinite and a gold-rich phase crystallised. It is worth to note that the expected formation of maldonite (Au_2Bi) did not occur while native gold represent the stable phase at Punta del Fenaio. The absence of both maldonite and symplectitic aggregates of bismuth and gold (indicative of subsolidus exsolution from original maldonite grains) can be explained by a late increase of sulfur fugacity in the system with the consequent destabilization of maldonite that allowed the direct precipitation of gold (Nekrasov, 1996).

Conclusion

The close association of native gold, native bismuth, bismuthinite and other Bi-Te-S phases at Punta del Fenaio suggests that gold was scavenged from the hydrothermal fluids by Bi-S-(Te) melts. We hypothesize that a liquid/melt-collecting mechanism was probably active at Punta del Fenaio, where the distinct Au-Bi-S-(Te) assemblage formed late as part of the main adularia-quartz dominant mineralization. The potential role of granite magmatism as a source of gold for the Tuscan epithermal ores should be carefully evaluated. In particular, a detailed geochemical study of the main granite intrusions and their microgranite-aplite-pegmatite differentiates should be performed to test the proposed hypothesis.

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