БЪЛГАРСКА АКАДЕМИЯ НА НАУКИТЕ • BULGARIAN ACADEMY OF SCIENCES
GEOCHEMISTRY, MINERALOGY AND PETROLOGY • 43 • SOFIA • 2005

Au-Ag-Te-Se deposits
IGCP Project 486, 2005 Field Workshop, Kiten, Bulgaria, 14-19 September 2005

Chemical variations in tetrahedrite - tennantite minerals from the Furtei epithermal Au deposit, Sardinia, Italy: Mineral zoning and ore fluids evolution

Sandro Fadda[1], Maddalena Fiori[1], Silvana Maria Grillo[2]

[1]Istituto di Geologia Ambientale e Geoingegneria del CNR, Cagliari, Italy; [2]Dipartimento di Geoingegneria e Tecnologie Ambientali, Università di Cagliari, Italy

Abstract. Tetrahedrite–tennantite series minerals occur extensively in hydrothermal deposits although in minor quantities compared with other sulfides. Quantitative electron microprobe analysis show that, in the Furtei epithermal gold deposit, these minerals exhibit compositional variations in which base metals substitute for copper, Sb for As, and there is substitution of Te^{4+} for $(Sb, As)^{3+}$; goldfieldite, tellurian tetrahedrite, tennantite and Te-free tetrahedrite coexist in a polymetallic assemblage highly enriched in telluride minerals. The association of hessite, stützite, sylvanite, petzite, coloradoite, altaite, with native tellurium indicates direct magmatic inputs to the mineralizing solutions: a transition of this zoned magmatic hydrothermal system from porphyry to high sulfidation epithermal mineralization environments is envisaged. Sulfidation states of telluride-bearing ore fluids fluctuated between IS and HS conditions within the same mineralization, with telluride minerals and sulfosalts related to both HS and IS assemblages. On the basis of available chemical data for tennantite-tetrahedrite series minerals and the telluride-rich parts of drillcore samples, the relationship between mineral assemblages and sulfidation states is assessed, and the evolution of ore solutions outlined.

Keywords: Sardinia, tetrahedrite, porphyry, epithermal, tellurides, hydrothermal zoning, sulfidation state

Introduction

Minerals of the tetrahedrite series are minor but almost ubiquitous components of many hydrothermal deposits. They carry significance for genetic interpretation where they display chemical variations which are a response to evolving fluid chemistry from which they crystallized. (Wu and Petersen, 1977). Tetrahedrite series minerals are themselves ore minerals of Cu and Sb and may be sensitive indicators of physicochemical conditions during ore deposition and therefore can be used as a tool for outlining the center of hydrothermal emanation, and the flow pattern and fluid evolution with respect to time and space. However, only generalizations are possible because tetrahedrite has a highly complex crystal chemistry, exhibits extensive substitution and its geochemistry in hydrothermal systems is poorly understood. It commonly occurs as small anhedral grains often intimately mixed with or in other phases of galena, sphalerite, chalcopyrite, pyrite, arsenopyrite, enargite-luzonite and other sulfosalts.

Te-bearing minerals and sulfosalts, as well as their mutual relationships in epithermal precious metal systems, offer potential for deciphering changes in temperature and sulfidation state (Cook and Ciobanu, 2002). Their deposition is traditionally restricted to one or two stages that always follows initial sulfide deposition. Epithermal Au-(Ag) deposits may be broadly grouped into high-sulfidation (HS) and low-sulfidation (LS) types, based on the sulfidation state of their primary sulfide assemblage. In all reported occurrences, gold or electrum is deposited either with, or following tellurides, but not before the telluride-bearing stage.

In Sardinia (Italy), tertiary porphyry- and epithermal style ore deposits host telluride ore minerals as major gold carriers. Highly acidic fluids form advanced argillic alteration halos and/or silicic lithocaps over porphyry systems which may host subsequent HS mineralization introduced by higher-pH, moderate- to low-salinity fluids. The aim of this work is to investigate the connection between the acid sulfate type gold deposit at Furtei and a porphyry-style shallow intrusion located beneath the zone of most intense hydrothermal alteration (Meloni, 1994). The Te-rich paragenetic assemblages is examined to investigate the spatial variation in tetrahedrite chemistry and sulfidation states in the evolving hydrothermal column, at the present level of erosion, from plutonic to epithermal zones.

Ore mineralogy and the occurrence of tellurides and sulfosalts

The Furtei Au deposit is the only example of HS mineralization in Sardinia. It is typically acid-sulfate in style with the mineralized bodies of S. Miali-Is Concas, Sa Perrima and a small, economically unimportant but mineralogically interesting, gold showing located near Bruncu Sa Casa. Under the surficial oxidized zone of supergene nature, the primary sulfide zone is largely hosted by diatreme breccia and characterized by a vertical zoning of the mineral assemblage, dominated by pyrite-enargite-luzonite-gold at higher levels, whereas in the deep zone tetrahedrite$_{ss}$, minor base metal sulfides and Te-rich minerals are present, especially in the deeper parts of the orebodies. Gold mostly occurs as high-fineness native metal and within some tellurides. A quantitative approach to the study of hydrothermal zoning was pursued by systematic, detailed microanalytical and high-magnification investigations of the telluride-rich samples and sulfosalts from different parts of the ore-bodies of the mine. Several samples were selected from drill cores from economic and non-economic parts of the mine to establish the continuity of the zones and the spatial association among the deposits. The lateral distribution of minerals allows for the exposure of a cross-section of the mineralized column, at the present level of erosion, from porphyry (Bruncu Sa Casa sector) to peripheral veins having epithermal characteristics (S. Miali - Is Concas sector). Samples for analysis were selected from open pits and drill cores chosen to represent the stages of ore formation over the vertical and lateral extent of the mine.

Electron-microprobe analyses carried out using an Applied Research Laboratories ARL-SEMQ microprobe. Wavelength-dispersion analyses were done at 15 kV operating voltage, 4 nA probe current and 100 s count times. Data were processed with full-matrix (ZAF) corrections. Concentrations of ten elements (Cu, Ag, Fe, Zn, As, Sb, Pb, Bi, Te, and S) were determined at each point. Table 1 shows the three main ore mineral assemblages in the Furtei deposit. Pyrite is ubiquitous and may, in places, be abundant - up to 20 vol.%. In the near-surface environment, the oxidation of sulfide minerals is controlled by the present surface topography and might extend in fractures down to 60 m from the surface. At surface, the ore mineral assemblage only includes free gold plus associated oxides. Supergene alteration grades downward into primary sulfide zones. The As-sulfosalt assemblage grades into the telluride assemblage with increasing depth. In the deeper parts of the system the paragenesis evolves into a Te- and Sb- rich assemblage with the presence of increasing tetrahedrite and Te-rich tetrahedrite up to goldfieldite, calaverite and krennerite, sometimes associated with native Te. Native Au in drill core samples always appears as blebs within enargite. It is ubiquitous and fairly pure, with a maximum Ag content around 6%.

Table 1. Mineral assemblages in the Furtei deposit

	Mineral assemblages
Oxidized surface (shallow)	Jarosite (with native Au max 1-2% Ag), gypsum, Fe-Mn-hydroxides, digenite, covellite, scorodite.
Sulfide (shallow)	enargite-luzonite, pyrite, chalcopyrite, sphalerite, covellite, digenite, galena, arsenopyrite, native Au (max 1-2% Ag), bornite in enargite.
Sulfide (deep)	Tennantite-tetrahedrite, Te-bearing tetrahedrite up to goldfieldite, pyrite, calaverite, krennerite, coloradoite, native Te, enargite, aikinite, native Au (max. content 6% Ag), chalcopyrite, stannite and native tin in enargite-luzonite

Minerals of the tetrahedrite series, ranging from tetrahedrite, $Cu_{12}Sb_4S_{13}$, to tennantite, $Cu_{12}As_4S_{13}$, occur in minor amounts in all ore types often including gold and tellurium phases such as native tellurium and tellurides. Other varieties are due to substitutions of Te for (Sb, As). However the most abundant and ubiquitous ore minerals are enargite and luzonite, pyrite sphalerite and arsenopyrite are also of importance. Chalcopyrite can be fairly common in places, but is always present in the upper levels with covellite and sulfosalts. Tetrahedrite commonly appears as veinlets and swarms disseminated in chalcopyrite, or occurs as interstitial grains with the other sulfides or fills the interstices of pyrite and chalcopyrite; some tetrahedrite grains grew in the holes of porous vuggy silica.

Chemical variation in tetrahedrite

The atomic proportions of representative microanalyses of tennantite, tellurian tetrahedrite, i.e., Sb>(Te+As) and goldfieldite, i.e., Te>(As+Sb) from the Furtei mine are shown in Tables 2 and 3. The number of Cu atoms in Te-free tennantites from Bruncu Sa Casa sector ranges from 10.36 to 10.71, based on a unit formula of 29 atoms. The empirical formulae are all close to $Cu_{10.5}Fe_{1.5}(As, Sb)_4S_{13,}$ The number of Cu atoms in tellurian tetrahedrites (Te content up to 8.43%) is also greater then ten, ranging from 10.03 to 11.31, and in goldfieldite from 11.25 to 11.99. The Te content of the latter is up to 21.27%.

Table 2. Atomic proportions of selected microanalyses of tennantite-tetrahedrite-goldfieldite from Bruncu Sa Casa sector

	Cu	Fe	Zn	As	Sb	Te	S
1	10.53	1.52	nd	3.94	nd	nd	13.00
2	10.36	1.53	nd	3.97	nd	nd	13.00
3	10.71	1.41	nd	3.98	nd	nd	13.00
4	10.14	0.94	0.98	3.87	0.13	0.02	12.92
5	10.03	0.26	1.48	0.93	2.92	0.15	13.00
6	10.21	0.28	1.28	0.98	2.69	0.26	13.00
7	10.53	0.31	1.23	1.16	2.42	0.38	13.00
8	11.31	0.69	0.25	1.24	2.20	0.51	13.00
9	10.85	0.22	0.98	1.17	2.09	0.71	13.00
10	10.69	0.06	0.89	1.03	2.07	0.87	13.00
11	10.86	0.18	0.82	0.79	2.33	1.08	13.00
12	11.99	0.10	nd	1.93	0.02	1.95	12.96
13	11.87	0.06	nd	1.69	0.03	2.25	12.93
14	11.25	0.71	nd	1.10	0.03	2.63	12.96

nd = not detected

The general formulae of tellurian tetrahedrite is close to $Cu_{10+x}(Fe,Zn)_{2-x}(Sb, As)_{4-x}Te_xS_{13}$, where x ranges from 0 to 1.0; and those of (arsenian) goldfieldite are close to $Cu_{12}(Te,As,Sb)_4S_{13}$, with Te <2 and $Cu_{12-X}(Te,Sb,As)_4S_{13}$ with Te = 2 to 2.63, $x \leq 0.75$. Note that $\sum(Cu+Fe+Zn)$ is less than twelve in the case of varieties where Te>2. The sum of Sb and As is nearly constant, and the As content rises monotonically as Sb decreases. Iron and zinc show variations in the tetrahedrite series minerals of the Furtei deposit with a general tendency for the two elements to vary in reciprocal manner from an approximate composition of $Cu_{10}Fe_2(Sb,Te,As)_4S_{13}$, with compositions with practically no Zn to $Cu_{10+x}Fe_{0.5}Zn_{1.5}(Sb,Te,As)_4S_{13}$, where $0<x\leq1$. However most of the tetrahedrites at Bruncu Sa Casa contain three times more Zn than Fe, while at Is Concas tetrahedrite was found to contain much more Fe and with dramatic fluctuations in the Fe/Zn ratio. The number of Cu atoms in tetrahedrite from Is Concas is also greater than ten. Tellurium and silver contents range from zero or nearly so to respectively 1.06% and 0.36%. Bismuth, which might substitute for arsenic and antimony has been detected only in one sample at about 0.16 at.%.

Table 3. Atomic proportions of selected microanalyses of tennantite-tetrahedrite from Is Concas sector

	Cu	Fe	Zn	Ag	Pb	Te	Sb	As
1	10.71	1.01	.09	.03	.01	.01	2.10	1.85
2	10.29	1.88	.07	nd	.01	.01	0.85	3.20
3	10.77	0.80	.39	.02	.02	nd	2.92	1.69
4	10.76	0.85	.48	nd	.01	nd	2.40	1.55
5	10.37	1.61	.03	nd	.01	.03	0.93	3.14
6	11.03	0.91	.19	.03	.03	nd	2.34	1.63
7	10.49	1.67	.07	.01	.01	.03	0.94	3.04
8	10.98	0.94	.11	nd	.01	nd	2.43	1.62
9	11.01	0.98	.10	nd	.01	nd	2.23	1.84
10	10.64	1.50	.05	nd	.02	.03	0.67	3.30
11	11.11	0.99	.07	.03	.01	nd	2.14	1.84
12	11.12	1.04	.04	nd	.01	nd	2.10	1.99
13	10.87	1.03	.12	nd	.01	.01	1.47	2.44
14	10.71	1.15	.07	.05	.01	.10	0.21	3.69
15	10.78	1.29	.05	.01	.01	.03	0.69	3.23
16	11.12	0.77	.05	nd	nd	.12	0.37	3.51
17	11.03	0.94	.05	nd	nd	nd	0.18	3.78

Number of sulfur atoms =13; nd = not detected

The empirical formulae on the basis of total atoms = 29 are all close to $(Cu,Ag)_{10}(Cu,Fe,Zn,Ag,Pb)_2(Sb,As,Te,Bi)_4S_{13}$.

Discussion and conclusions

Geophysical evidence for the presence of a relatively shallow intrusion at 1 to 1.5 km present depth is reported by Meloni (1994). Volumes of high temperature fluids were rapidly flushed upwards from the already emplaced porphyry into a ready network of fractures, breccias and channelways. Fluid inclusion data (Ruggieri et al., 1997) are similar to those found in many porphyry Cu deposits, including Calabona in NW Sardinia suggesting that epithermal mineralization at Furtei may be associated with a porphyry system with a fluid of magmatic derivation circulating at deeper level followed by the mixing of the high-temperature magmatic hypersaline brine with cooler low-salinity meteoric water at shallow depth. The epithermal mineralization of Furtei can be divided into two stages postdating the silicic, and much of the advanced argillic alteration and was characterized by a distinct zoning with depth: the HS-state sulfosalts, enargite and luzonite are the principal Cu minerals in the orebody and occur at a shallow level, with abundant euhedral pyrite and gold. At depth tennantite-tetrahedrite, chalcopyrite, stannite, Au, Ag-tellurides including coloradoite, petzite, hessite are present. Deposition of sulfide-gold mineralization at shallow depth occurred under comparatively high fS_2, whereas deep assemblages where characterized by lower fS_2 (Ruggeri et al., 1997). Gold mineralization is associated with tennantite and chalcopyrite which partially replaces enargite; luzonite appearing paragenetically later. Because Te solubilities are predicted to be low in auriferous chloride waters (Cooke et al., 2001), deposition of tellurides and native tellurium in IS/LS environments may result from condensation of magmatically-derived $H_2Te_{(g)}$ and $Te_{2(g)}$ into deep-level chloride waters. Such magmatic input into the hydrothermal system is later than the input of sulfur, since telluride deposition is always preceded by that of sulfides. The fugacity of Te_2 is very important and is controlled by the supply of this element from the source, and also locally controlled by reactions between the fluid and rock minerals or changes in fluid chemistry. Whether gold occurs in the native form, in petzite or in sylvanite is influenced by variations of this parameter. The relative stabilities of hessite and calaverite depend on the initial tellurium concentration and Ag:Au ratio in the water. However, minor amounts of Te can dissolve into chloride waters and could precipitate into lower temperature surficial acid sulfate waters by cooling or fluid mixing producing geochemical anomalies only or Te-rich mineralizations.

Study of the mineral assemblages in the Furtei ore bodies demonstrates that introduction of gold in HS ores is related to IS assemblages, indicating an evolution from an IS towards HS environment. This implies that HS-style epithermal mineral assemblages may be precipitated from Au-bearing LS/IS waters with a distinct vertical zonation of electrum and Te-bearing species. In fact, the deeper part of the ore is characterized by tetrahedrites$_{ss}$, Te-rich minerals, including precious metal tellurides, Te-tetrahedrite and native tellurium evolving in shallow level to enargite-luzonite, Cu-Fe-sulfides and native gold. The ore minerals also indicate that a part of gold introduction (in native form and in sulfosalts) has taken place contemporaneously with deposition of the HS assemblage, thus suggesting a genetic link between the two sulfidation states in the same ore deposition environment.

There is a strong suggestion that the magmatic-hydrothermal system at Furtei underwent an evolution from an earlier IS porphyry-style mineralization, to IS-HS mineralizations in porphyry related, base metal- and epithermal precious metal veins. Tellurium was introduced by both HS and IS solutions in a succession of phases of progressively lower Te content until the establishment of the observed paragenesis. The initial increase in $f\text{Te}_2$ from the magmatic source led to saturation, with the appearance of native Te and di-tellurides (sylvanite, calaverite, krennerite), followed in turn by altaite, coloradoite, hessite, petzite and finally gold with gradual decreasing $f\text{Te}_2$ values. Condensation of Te-bearing magmatic volatiles may be essential for the formation of Te-rich mineral assemblages at depth, thus consuming the major part of the initial available tellurium. For aqueous tellurium species, cooling and mixing of fluids are predicted to be an effective, temperature dependent depositional mechanism. During multistage boiling, sufficient tellurium may be transported in the gas phase through the epithermal environment up to the shallow zones where it could condense back into groundwater leading to the observed vertical zonation from goldfieldite at depth to Te-free tetrahedrites in the outer zones. This chemical zonation suggests a component of vertical migration for the mineralizing fluids progressing away from the pluton which seems to have acted not only as a heat source but provided material input. The relationship between the proportion of Te and (Sb+As) in tetrahedrite-goldfieldite from deep to shallow level ore bodies of the Furtei mine verifies the substitution of (Sb+As) by tellurium until the end-member goldfieldite is reached (Fig. 1).

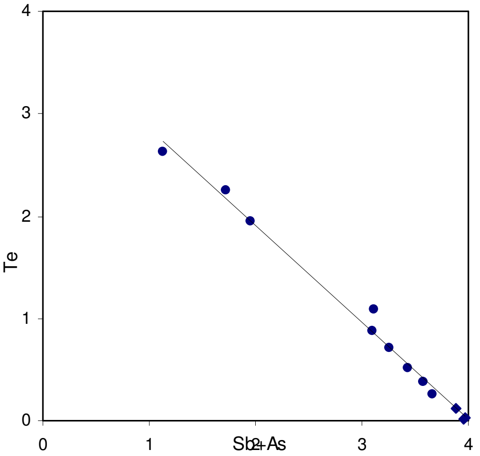

Fig 1. Relationship between Te and (Sb+As) in goldfieldite-tetrahedrite from Furtei mine

The limited number of Sb/(Sb+As) values, used elsewhere for zoning studies, makes any conclusion premature. However, the Sb/(Sb+As) values grouped together and averaged for the two locations under study, show a distinct variation from high values in the deeper levels (~0.7) to lower values (~0.55) in the shallow levels, where the greater As content reflects the activity of this element which can easily enter the (Sb, As)$^{3+}$ position.

Arsenic content rises as antimony content decreases, demonstrating the diadochy of these two elements. It seems that ore fluids are preferentially depleted in antimony and enriched in arsenic as deposition proceeds away from the presumed igneous source.

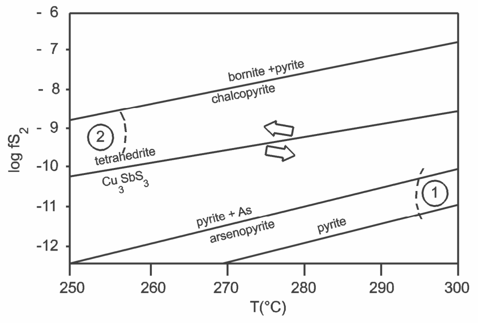

Fig. 2. Transition between paragenesis of arsenopyrite evolving to tetrahedrite-bearing assemblage. Thermodynamic data are taken from Craig and Barton (1973)

Chemical zonation involving metals shows Ag and Pb values for tetrahedrite increasing upward to the peripheral levels of the deposit in the S. Miali- Is Concas sector. Fe/Zn values in tetrahedrite are highest at the outer extremity of the system. Iron increases from 0.4 to 1.5 atoms as Zn decreases from 1.4 to 0.1 atoms per 13 sulfur atoms. However, mixing of different fluids at shallow levels seems to have been important in controlling the chemistry of tetrahedrite series, and late stage fluids may have been oxidized as indicated by the presence of barite in the epithermal assemblage. In the ore assemblage, the presence of arsenopyrite indicates that the mineralizing fluids had a generally low sulfidation state. For tetrahedrite and chalcopyrite to have followed this mineral in the paragenetic sequence, a slight increase in fS_2 and/or decrease in temperature would have been necessary (Fig. 2).

In conclusion, the chemical composition of tetrahedrite can record some of the chemical variables of the hydrothermal fluids at the time of mineralisation. The correlation of compositional variations of this mineral series through the Furtei deposit can delineate a zoning pattern in which Ag and Pb in tetrahedrite increase, whereas Te decreases away from a presumable, porphyry-style center of the hydrothermal system.

Acknowledgments. The research has been supported by the CNR, Istituto di Geologia Ambientale e Geoingegneria, IGAG, Cagliari, Italy.

References

Cook, N.J., Ciobanu, C.L. 2002. Tellurides: More than mineralogical curiosities, but also markers of fS_2-fO_2 evolution in zoned hydrothermal systems. *IMA, 18th General Meeting, Edinburgh,* Programme with Abstracst, p. 283.

Cooke, D.R., McPhail, D.C. 2001. Epithermal Au-Ag-Te mineralization, Acupan, Baguio District, Philippines: Numerical simulations of mineral deposition. *Economic Geology*, **96**, 109-131.

Craig, J.R., Barton, P.B. 1973. Thermochemical approximations for sulfosalts. *Economic Geology*, **68**, 493-506.

Fiori, M., Grillo, S.M. 2001. The Furtei high-sulfidation epithermal gold deposit (Sardinia, Italy): Mineral assemblage and its evolution. In: A. Piestrzynski et al. (Eds.), *Mineral Deposits at the Beginning of the 21st Century*. Swets and Zeitlinger, 739-742.

Meloni, P. 1994. Metodologie di prospezione geomineraria e geofisica di mineralizzazioni sepolte tipo porphyry copper. Studio del settore di Serrenti-Furtei (Sardegna Meridionale): Unpublished PhD thesis, University of Cagliari (English abstract in *Plinius*, **13**, 145-148).

Ruggieri, G., Lattanzi, P., Luxoro, S., Dessì, R., Benvenuti, M., Tanelli, G. 1997. Geology, mineralogy, and fluid inclusion data of the Furtei high-sulfidation gold deposit, Sardinia, Italy. *Economic Geology*, **92**, 1-19.

Wu, I., Peterson, U. 1977. Geochemistry of tetrahedrite and mineral zoning at Casapalca, Perù. *Economic Geology*, **72**, 993-1016.