Gold-oxysulphides in copper deposits of the Greywacke Zone, Austria: A mineral chemical and infrared fluid inclusion study

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A B S T R A C T

Native gold and unusual gold-oxysulphides, both associated with tetrahedrite, occur in several abandoned copper deposits in the low grade Palaeozoic Greywacke Zone in the Eastern Alps. The ore mineralogy, the mineral chemistry and fluid inclusions in tetrahedrite and quartz were studied from historic Cu mines at Larzenbach/Hüttau, St. Veit im Pongau, and Mitterberg (all Salzburg Province, Austria). Fluid inclusions in tetrahedrite, which is non-transparent in visible light, were studied by infrared (IR) microthermometry; tetrahedrite containing up to 2.5 wt.% As is transparent for infrared light.

Fluid inclusions within tetrahedrite occur as isolated inclusions, in clusters and along trails. At room temperature these are aqueous two-phase liquid (L)+vapour (V) inclusions of low to moderate total salinity (Tm = 3 to 14 °C). Homogenisation temperatures (Tm, V→L) range between 85 and 200 °C. The composition of these tetrahedrite-hosted fluid inclusions corresponds to that one type of fluid inclusion in quartz showing a similar range in salinity (Tm = 3 to 12 °C) and total homogenisation temperatures (Tm, V→L, 715 to 250 °C). Another type of higher saline aqueous two-phase (L+V) inclusions in quartz is apparently unrelated to gold mineralisation.

Fluid inclusions within tetrahedrite coexist with solid inclusions of chloropirite, gold-oxysulphides, minor arsenopyrite and gold that is rich in gold-oxysulphide microinclusions and occur along re-healed microfractures within tetrahedrite. These microfractures also control the replacement of As-poor tetrahedrite by arseniferous (up to 3.16 wt.% As) tetrahedrite. It is suggested that in addition to cooling the exchange of As for Sb on tetrahedrite surfaces was one of the factors controlling precipitation of gold. Oxysulphides are associated with (a) native gold in unweathered primary ores and (b) remobilised Cu-rich gold in weathered ores. Gold thiosulphate and possibly thioarsenite complexes are the preferred species for the transport of gold in the low-temperature (< 250 °C) hydrothermal fluids and gold thiosulphate complexes were involved in the supergene remobilisation of gold.

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1. Introduction

Oxoacids of sulphur such as thiosulphate, thionate or sulphite form as transitional species during the oxidation of reduced sulphur to sulphate, or vice versa, during reduction of sulphate to sulphide sulphur (e.g., Goldhaber, 1983; Greenwood and Earnshaw, 1984). Oxysulphides can be defined as solid chemical compounds incorporating sulphur as well as oxygen in their structure in addition to metallic cations (M). They are distinguished from sulphates by their inlet sulphur as well as oxygen in their structure in addition to 

valence compounds such as gold–copper oxysulphides dealt with in this paper.

Only a few compounds with mixed or intermediate sulphur valences have so far been accepted by the International Mineralogical Association (IMA-CNMMN) as minerals. These include: scotlandite PbS2O3 (Paar et al., 1984), hannebachite CaSO3·0.5H2O (Hentschel et al., 1985), gravegliaite MnSO3·3H2O (Basso et al., 1991), bazhenovite Ca2Cr15O22·6Ca(OH)2·20H2O (Chesnokov et al., 1987), and vaneite (Fe,Pb)2S6O (Kucha et al., 1996). From a mineralogical perspective, oxysulphides are therefore interesting as a rare group of possibly new minerals.

Mineralogically less well-characterised oxysulphides have been reported from several gold deposits before by the first author. None of these phases has so far been accepted as a new mineral, mostly because of lacking structural data; the phases are normally too small for structural analysis. The phases reported so far include iron thiosulphates associated with pyrite and gold from mesothermal vein-type gold deposits in eastern Australia and South Africa (Kucha...
et al., 1994), the Amelia Mine, Southwest Wisconsin (Kucha and Barnes, 1995) as well as copper thiosulphates and gold oxysulphides associated with gold in Cu-ores in the Greywacke Zone of the Eastern Alps (Fig. 1; Kucha et al., 1995, 1997b, 2003). In this paper we provide further evidence that these easily overlooked phases are distributed on a regional to orogenic scale within the Eastern Alps and could be possibly neglected as carriers of gold.

From experimental studies it is known that thiosulphates are stable below ~240 °C (Giggenbach, 1974) in the near neutral to slightly alkaline pH range and under intermediate redox conditions (Webster, 1986). Hence, thiosulphate complexes of gold can be expected to occur in lower temperature hydrothermal to supergene ore deposits. They were for example confirmed in hydrothermal fluids in geothermal systems (e.g., hot springs in Waipatui, New Zealand and Yellowstone, U.S.A.; Xu et al., 1998; Pope et al., 2005) and seem to be of special importance for the mobilisation of gold in the supergene environment (Webster, 1986; Benedetti and Boulegue, 1991; Bowell et al., 1993).

Finally, the presence of oxysulphides in gold ores has practical implications for the recovery of gold in hydrometallurgical processes. The capacity of thiosulphate complexes for low-temperature leaching of gold has been intensely studied by hydrometallurgists because thiosulphate leaching may be an environment-friendly alternative to cyanide leaching of gold ores (see review by Aylmore and Muir, 2001). The aims of this paper are: (1) to document the occurrence and mineral chemical composition of native gold and associated tetra-hedrite and gold oxysulphides in the Greywacke Zone, Eastern Alps; (2) to constrain the T–X conditions of fluids involved in formation of gold-bearing ore assemblages by using infrared (IR) microthermometry; (3) to discuss the relevance of our findings for understanding the transport and mobilisation of gold in low-temperature hydrothermal and supergene environments.

2. Geological setting

Geologically, the gold occurrences studied are located in the Greywacke Zone, which is part of the Upper Austroalpine very low- to low-grade basement units of the Eastern Alps (Ebner, 1997). It is subdivided into the Eastern (EGZ) and Western Greywacke Zone (WGZ, Fig. 1). The Eastern Greywacke Zone consists of metavolcano-sedimentary rocks of Palaeozoic age and is further subdivided into four Alpine-age tectonic nappes (Neubauer et al., 1994). The two most important of these are the tectonically deeper Veitsch nappe and the tectonically higher Noric nappe. The Veitsch nappe includes Early Carboniferous to Permian clastic and carbonate metasediments, the Noric nappe contains metamorphosed Ordovician to Namurian clastic to carbonate shelf and slope sediments, as well as felsic metavolcanics of Ordovician and metabasites of Silurian age.

Two major tectonic units are also distinguished in the Western Greywacke Zone. The northern Wildseealoder unit with Late Ordovician meta-ignimbrites and Silurian to Devonian carbonate platform sediments and the southern Glemmtal unit with a several thousand metres thick sequence of siliciclastic rocks deposited in a marine basin at a passive continental margin (Heinisch, 1988). The intra-plate geochemical characteristics of Late Devonian mafic volcanism is also consistent with this interpretation (Heinisch, 1988).

Regional metamorphism in the Eastern Greywacke Zone is of very low- to low-grade and is predominantly of Eoalpine (i.e., Cretaceous) age (Hönkes et al., 1999). Metamorphic conditions transitional between sub-greenschist and greenschist facies are recorded from higher structural levels in the Western Greywacke Zone (e.g., around Mitterberg; Kralik et al., 1987) and generally increase to lower greenschist facies conditions towards the lower structural units. Metamorphic conditions of about 450 °C and 0.3 to
0.4 GPa have been suggested for the Veitsch nappe (Ratschbacher and Klima, 1985). The study of carbonaceous material much better quantified metamorphic temperatures during Eoalpine thrusting (Rantitsch et al., 2004); they were 360–60 °C and confirm metamorphic temperatures recorded from the Veitsch nappe (360 to 410 °C).

3. Gold-bearing tetrahedrite occurrences in the Greewacke Zone

Gold associated with tetrahedrite has been confirmed from the following locations (Fig. 1): Veitsch magnesite quarry, Erzberg siderite mine at Eisenerz, Rottemann, and the abandoned historic copper deposits at Larenzach, Gleisch, Igelsbach, St. Veit in Pongau, Mühlbichl am Hochkönig, and Mitterberg.

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Note: z – below indicated detection limit.

3. Gold-bearing tetrahedrite occurrences in the Greewacke Zone

Gold associated with tetrahedrite has been confirmed from the following locations (Fig. 1): Veitsch magnesite quarry, Erzberg siderite mine at Eisenerz, Rottemann, and the abandoned historic copper deposits at Larenzach, Gleisch, Igelsbach, St. Veit in Pongau, Mühlbichl am Hochkönig, and Mitterberg.
This study focuses on gold-bearing Cu mineralisation at Larzenbach/Hüttau and St. Veit im Pongau where small-scale historical mining took place between the 13th and 18th Centuries (Günther, 1978). These occurrences are part of the copper district Mitterberg–Mühlbach–Larzenbach where the largest Cu mine of the Eastern Alps located at Mitterberg (total Cu content ca. 250,000 t; Weber, 1997) was mined until the 1970s. Details about gold mineralisation and oxysulphides from Mitterberg and Veitsch have been published previously (Kucha et al., 1995, 1997a,b).

The ores at Larzenbach are hosted by low-grade metasedimentary rocks (phyllites, black schists, quartzites), metabasites and metatuffs and, at St. Veit, in metacarbonates (marbles, calcareous phyllites). Stratabound as well as clearly discordant vein-type ores are known. At Larzenbach the main orebody is lens-shaped and was mined ca. 170 m along strike and ca. 60 m along depth. The NW-striking orebody has a maximum thickness of 8 m and dips at ca. 40°–50° to the NE. Whereas thin cm to dm-thick ore stringers are mostly concordant to the main foliation, the major vein locally exhibits clear discordant contacts between ore and the main foliation. At Larzenbach the ores were affected by several ductile and brittle deformation events causing an irregular distribution and discontinuity of the orebodies (Feitzinger, 2000). The average gold content in tetrahedrite-rich ore is 4 g/t (Günther, 1978).

Vein-type copper mineralisation at Mitterberg (“Hauptgang”) is clearly discordant and connected to an 11 km long and 0.2 to 4 m thick carbonate-quartz vein of Cretaceous age (for references see Weber, 1997). In contrast, orebodies south of Mitterberg (“Mühlbach Südrevier”) lie concordant within the host rocks (Weber et al., 1972). The main ore minerals in these Cu-dominated ores are chalcocite, tetrahedrite and minor Ni-Co minerals. Common gangue minerals are quartz and Fe-carbonates.

Gold contents of ~11 g/t in tetrahedrite were reported from Mitterberg by Böhme (1931). He described a paragenesis of native gold, tetrahedrite, gersdorffite and chalcocite from the younger sulphide-quartz veins that postdate the main Cu vein. Spectacular specimens of native gold associated with U–Ni–Te mineralisation were found in the uppermost part of the Mitterberg Cu vein where the vein crosscuts Carboniferous–Permain metaclastic host rocks (Paar and Köppel, 1978). Uraninite from this paragenesis was dated at 90±5 Ma (Köppel in Paar and Köppel, 1978). This age confirms that the main Cu vein at Mitterberg formed during the Eoalpine orogeny.

4. Methods

Samples were polished on a Rehwalt polishing machine using light oil as a lubricant. Final polishing was done with 1 µm diamond spray. Water has been avoided as a lubricant because it causes dissolution of oxysulphides present in these samples.

Microanalysis and fluid inclusion study were carried out at the fluid inclusion laboratory of the Department of Applied Geosciences and Geophysics, University of Leoben. The chemical compositions of mineral phases and valence-related SKα and SKβ peak shifts were determined with an ARL SEMQ automated electron microprobe (EMP). For principles and details regarding valence determination of sulphur by EMP the reader is referred to Kucha et al. (1989, 1995). Gold valences in oxysulphides were measured by EMP at 23 kV using the normalised Au Mα/Mβ emission efficiency ratios compared to standards of metallic gold (valence 0, Mα/Mβ = 0.8003 ± 0.0029), AuT2 (valence +1, Mα/Mβ = 0.8079 ± 0.0034), and AuBr3 (valence +3, Mα/Mβ = 0.7655 ± 0.0230) (Kucha et al., 1998; Kucha and Przylowicz, 1999).

Infrared (IR) microthermometric measurements on tetrahedrite were accomplished in transmitted light using an Infrared CCD camera (λ ≤ 2.5 µm) attached to a Olympus BX60 microscope. Cooling–heating experiments were performed with a Linkam MDS 600 stage. Synthetic fluid inclusions were used for calibration. The accuracy of the measurements were ±1 °C during heating and ±0.5 °C during freezing runs. Total salinities of salt-bearing aqueous fluid inclusions and bulk densities were calculated from the final ice melting temperatures (Tm) and the total homogenisation temperatures (Tb) using the software package FLUIDS 1 by Bakker (2003). Total salinities are given as mass % NaCl equivalent or mass % CaCl2 equivalent (when Tm was below the eutectic temperature of the pure H2O–NaCl system).

5. Ore mineralogy, mineral chemistry and valence determinations

5.1. Tetrahedrite–tennantite series

Members of the tetrahedrite–tennantite series are mostly Sb-dominated (Table 1) and classified as tetrahedrite. The ratio Sb/As in...
samples from Larzenbach is lower \((\text{Sb}/(\text{Sb} + \text{As})=0.83 \text{ to } 0.88)\) compared to those from St. Veit (0.93 to 0.95). In contrast the St. Veit samples are richer in Zn (Table 1). Tetrahedrite is converted into tennantite only around microfractures carrying gold inclusions (Table 1; analysis LA2 A11, \(\text{Sb}/(\text{Sb} + \text{As})=0.02\)). Previously published microprobe traverses across microfractures containing gold show that the tetrahedrite close to the microfractures is in addition to As also enriched in Zn and Ag but depleted in Fe and Hg (Kucha et al., 1997b).

Tetrahedrite contains inclusions of cubanite, chalcopyrite, talnakhite, pyrite, arsenopyrite, gersdorffite, uillianite, safflorite–lollingite–rammelsbergite, galena, gold, graphite and the gangue minerals quartz, muscovite, and calcite. Cuprite, covellite and limonite formed during supergene alteration of the sulphide ores. Tetrahedrite is crosscut by multiple fractures and microfractures. Minerals identified in microfractures within tetrahedrite include native gold and gold-oxysulphides (see Section 5.3), chalcopyrite, talnakhite, haycockite, arsenopyrite, pyrite, cuprite, malachite, gersdorffite, uillianite and rare tennantite (see above).

5.2. Gold

Trace element contents analysed on hand-picked sulphide-rich bulk samples from Veitsch and Mitterberg were previously published (Kucha et al., 1995, 1997b). In massive tetrahedrite, Au ranges from (in ppm) 5 to 52.5, Ag from 350 to 1320, and Pb from 67 to 350; Pt and Pd contents are at the few ppb level. The gold content of massive chalcopyrite is much lower; it ranges from 0.3 to 1.5 ppm Au. Native gold occurring in tetrahedrite varies in size from a few to 250 µm. Most of the visible gold is found within and close to microfractures within tetrahedrite. The remaining visible gold is intergrown with or encapsulated by sulphoarsenides (mainly arsenopyrite) and often contains large amounts of low reflectance Au-oxysulphides.

**Fig. 3.** Reflected light microphotograph (A) and secondary electron images (B–F). A. Gold (Au) with minute inclusions of gold-oxysulphides (Au-OS) in tetrahedrite (Tet); sample SV4 St. Veit. B. Native gold (Au) with a myriad of inclusions of Type 1 gold oxysulphides (Au-OS) in tetrahedrite (Tet); sample SV2, St. Veit im Pongau. C. Complex intergrowths of spongy gold with dark inclusions of Type 1 gold oxysulphides; sample LA1, Larzenbach/Hüttau. D. Native gold and Type-2 gold oxysulphides (Au, Au-OS) with limonite (Lim) and cuprite (Cup); sample SV1003, St. Veit im Pongau. E. Native gold, Cu–Fe-oxysulphides (OS) and talnakhite (tal); sample SV1003, St. Veit im Pongau. F. Detail of E (field-emission SEM image) showing inclusion-free primary gold (Au (pr)) and spongy, Cu-rich secondary gold (Au (sec)); the latter is intergrown with dark Type 2 oxysulphides; arrow points out replacement of primary gold by secondary gold plus gold oxysulphides.
Analyses of gold from Larzenbach and St. Veit are listed in Table 2 and shown in Fig. 2. Gold composition as determined by electron microprobe depends on the mineral assemblage in which gold occurs (Kucha et al., 1995, 1997a,b, 2003). Six types of gold can be distinguished in the Greywacke Zone:

1. Primary (?) gold is present in massive, non-fractured tetrahedrite. This gold usually forms grains from a few to rarely 20 µm. At Larzenbach and St. Veit these primary gold inclusions were too small to obtain high-quality analyses. The average composition (n=10 measurements, wt.%) of this type of gold from Veitsch and Mitterberg is: Ag 25.18, Au 67.39, and Hg 7.05. The Cu content is below detection limit (Kucha et al., 1995, 1997a).

2. Native gold and electrum present within microfractures in tetrahedrite together with pyrite, gersdorffite, chalcopyrite, cubanite, arsenopyrite and quartz. This gold is free of oxysulphide inclusions. The finest gold occurs together with Cu–As-bearing pyrite replacing tetrahedrite. Ag-rich gold is associated with quartz inclusions. At Larzenbach microfracture-hosted gold in tetrahedrite is Ag- and Hg-rich (9.44 to 25.59 wt.% Ag, 4.58 to 21.25 wt.% Hg), and contains 10.5 to 3.88 wt.% Cu (Table 2). Composition of chalcopyrite-hosted gold from St. Veit is similar to that in tetrahedrite microfractures (SV1003 B2, B3, Table 2). At Mitterberg the Cu content in this gold is usually between ≤0.06 and 2.0 wt.% and the Hg concentration varies from ≤0.09 to 9.80 wt.% (Kucha et al., 1997a). Arsenopyrite-hosted gold from St. Veit im Pongau, Teufelrauchfang (SV2 B3–B5), contains 0.34–1.07 wt.% Cu and has some Ag (2.34 to 3.02 wt.%). At St. Veit the Ag content is enriched in (wt.% Cu 3.73 to 4.94, and Sb 3.17 to 4.44 but has very low contents of Ag (≤0.03 to 0.14) and Hg (≤0.03 to 0.21; Kucha et al., 1997a).

3. An unnamed Ag2Au3Hg phase occurs in fractures in tetrahedrite at Ag 0.037 to 0.067, Au 0.017 to 0.122, Cu 0.013 to 0.037, Hg 0.016 to 0.037, Sb 0.016 to 0.021, Fe 0.016 to 0.022, and O diff ≤0.06 to 0.21; Kucha et al., 1997a). This new Ag2Au3Hg phase has a different chemical formula than weishanite (Au,Ag)3Hg2 and it is optically isotropic while weishanite is weakly anisotropic. Weishanite has significantly higher reflectance of 76.3% at 534 nm, and 81.3% at 589 nm, while for the new Ag2Au3Hg phase 8% for these wavelengths is 59.2 and 69.7, respectively. Therefore chemical composition and optical properties clearly distinguish the Ag2Au3Hg phase from weishanite.

4. Gold intergrown with oxysulphides of Type 1 (see Section 5.3) from the hydrothermal paragenesis. This type of gold has a weak pink hue in reflected light and is spotted with µm-size dark inclusions of oxysulphides (Fig. 3A–D). At Larzenbach this type of gold (LA2 A1, A5, A6, A10; LA2 D7; Table 2) has (in wt.) 5.55 to 16.97 Ag, 1.26 to 6.57 Hg, 2.13 to 2.91 Cu and up to 1.78 Sb. In addition two analyses have higher As contents (LA1 D4, D5, Table 2).

5. Gold from the superegene weathering paragenesis is characterised by the highest Cu contents (4.6 to 22.07 wt.%, Fig. 2, Table 2). In reflected light this secondary gold has a strong pink hue and is intergrown with oxysulphides of Type 2 (Section 5.3, Fig. 3E, F), cuprite, limonite and less often malachite. It is variable in Ag (<0.06 to 14.87 wt.%), Hg (<0.06 to 4.68) and can contain considerable amounts of Sb (1.04 to 15.73) and minor amounts of S, Fe, and As. The source of this Cu-rich gold is earlier gold present as inclusions in chalcopyrite or talnakhite (Fig. 3F).

6. Refractory gold. Concentrations of invisible gold are up to 0.54 wt.% in tetrahedrite and up to 4.60 wt.% in tennantite (Table 1). Gold valence measured by microprobe in Au-richer microareas within tetrahedrite is 0 (normalised Au Mβ/Mα = 0.8009 ± 0.0022), suggesting that gold is present as sub-microscopic inclusions of native gold. The highest gold concentrations are associated with strong, local enrichment in As in the surrounding tetrahedrite matrix (Table 1, LA2 A11). Cu–As-pyrite present in fractures in tetrahedrite shows two groups of Au Mβ/Mα ratios – one close to 0.8010±0.0027 suggesting valence 0 connected with submicroscopic inclusions of metallic gold, and another close to 0.8079±0.0022 suggesting valence +1 and therefore chemically bound to the host lattice.

5.3. Oxysulphides

Textural relations of oxysulphides to gold and other minerals are illustrated in Fig. 3, representative analyses are listed in Table 3. Under crossed polars oxysulphides show a weak optical anisotropy discernible at grain boundaries with colours of variable brightness and greenish hue. In plain polarised light they are grey with a weak brownish hue. Oxysulphides with submicroscopic exsolutions of gold show yellow-brownish hue. No internal reflections have been observed so far.

Two types of oxysulphides are distinguished: Type 1 oxysulphides are associated with primary gold and preserved as inclusions in gold and in microfractures within tetrahedrite. These oxysulphides are intergrown with native gold of high fineness and rarely occur together with haycockite, chalcopyrite, ulmanite and arsenopyrite. They are also present as myriads of rounded inclusions within larger gold grains (up to 250 µm) enveloped by arsenopyrite and encapsulated in tetrahedrite.
Oxysulphides of Type 1 are not interconnected along microfractures in gold but are present as isolated solid inclusions (Fig. 3A,C). This observation indicates that Type 1 oxysulphides precipitated coevally with the hydrothermal gold (Type 4 gold, see Section 5.2). Type 1 oxysulphides from Larzenbach have (wt. %): Au 31.87 to 44.09, Cu 7.73 to 14.40, Ag 4.03 to 7.25, Fe 1.67 to 3.01, Sb 2.41 to 7.51 and S 6.07 to 13.11 (Table 3); they are quite variable in Hg (0.98 to 12.75). For comparison, oxysulphides from Mitterberg have (in wt. %): Au 40.11 to 44.20, Cu 14.07 to 24.06, Sb 3.11 to 3.59, and S 15.40 to 18.31 (Kucha et al., 1997b, 2003).

The sulphur valence determinations on oxysulphides by electron microprobe clearly indicate the presence of mixed sulphur valences in these compounds. Similar to the Na2S2O3 reference material they show splitting of the main SKβ peak between 2455 and 2470 eV indicating the presence of sulphur +6 and −2 (Fig. 4). Moreover, they show characteristic satellite peaks indicative of S6+. The S6+ satellite peak in these oxysulphides is either slightly higher (PR1BC13) or slightly lower (PR1B3C12) than in the Na2S2O3 reference material.

Type 2 oxysulphides formed during weathering of tetrahedrite-rich ores and are associated with cuprite, limonite and, less often, malachite. They are associated with secondary gold. It is important to note that in this supergene paragenesis, oxysulphide grains are interconnected (Fig. 3E,F) and the textures indicate local dissolution and re-precipitation of gold (Fig. 3F). During this process the size of the secondary gold grains has increased. Native gold associated with Type 2 oxysulphides has a high Cu content (Table 2, Fig. 2). Oxysulphides of Type 2 are lower in gold and contain (in wt. %) Au 6.95 to 10.22, Cu 22.02 to 24.77, Ag 1.83 to 2.74, Sb 12.40 to 12.79, and S 18.02 to 19.17. Actually they could be oxysulphide–oxyantimonide compounds (Table 3, LA2 A3a, LA2 A2c).

Spectral reflectance measurements for oxysulphides of Type 1 are presented in Fig. 5. Gold–copper oxysulphides (curve PR1B4 A4) are characterised by low reflectance throughout the spectral range (10 to 15%) and flat convex spectral curves. Reflectance increases dramatically in the 520 to 680 nm range when nanometre-sized inclusions of gold are present in the oxysulphides (curve PR1B4 A18).

6. Fluid inclusions

6.1. Transparency of tetrahedrite in infrared light

Infrared microthermometry is an established but not widely used method allowing study of fluid inclusions in some ore minerals, which are opaque in visible light (e.g., Lueders 1996). In the spectral range λ≤2.5 μm some oxides (e.g., wolframite, hematite) and some
sulphides (e.g., stibnite, sphalerite, to some extent pyrite etc.) become transparent (Campbell and Robinson-Cook, 1987; Lueders, 1996; Lueders et al., 1999; Bailly et al., 2000, 2002; Kouzmanov et al., 2002). IR microthermometry has not been widely applied for studying members of the tetrahedrite–tennantite series mostly because their IR-transparency is limited by chemical composition; only As-poor tetrahedrite is IR-transparent whereas tennantite remains opaque also in the IR spectral range (Lueders, personal communication).

Our combined IR and mineral chemical study confirmed that IR transparency is restricted to As-poor tetrahedrite. Tetrahedrite from St. Veit is more transparent than from Larzenbach reflecting the lower As content in the former (Table 1). The approximate As content where tetrahedrite becomes IR-opaque is ca. 2 to 2.5 wt.% As. Higher As contents cause rapid increase in opacity. In addition, it was observed that temperature has a significant reversible effect on tetrahedrite transparency, i.e., above ~120 °C the opacity of tetrahedrite containing about 2 wt.% As increases significantly making precise microthermometric measurements impossible. Transparency is immediately recovered when temperature drops below ~120 °C.

6.2. Tetrahedrite microtextures

Due to the opacity of arseniferous tetrahedrite the system of microfractures developed in tetrahedrite can be made visible in infrared light (Fig. 6A,E). Under smaller magnification a complex fracture network including larger cracks several tens of µm thick, as well as thin microfractures are to be seen (Fig. 6A,B,E). Small microfractures may coalesce to produce semi-massive dark areas of opaque arseniferous

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**Fig. 6.** Microphotographs illustrating microfracturing in tetrahedrite and fluid inclusions in tetrahedrite and quartz. A, B. Infrared (IR) photographs showing IR-transparent tetrahedrite. The microfractures are filled with arseniferous tetrahedrite, which is opaque in the near IR spectral range. The cloudy domains within tetrahedrite are rich in solid and fluid inclusions. B. IR-microphotograph showing details of A. Aqueous two-phase (L+V) fluid inclusions (arrows, Fl) within tetrahedrite are of low salinity and represent the Au transporting fluid. Sample SV3, St. Veit im Pongau. C. Transparent quartz intergrown with opaque tetrahedrite. Quartz is rich in opaque solid and aqueous fluid inclusions. D. Trail of aqueous two-phase (L+V) fluid inclusions in quartz. These inclusions represent the higher saline fluids unrelated to Au mineralisation. Sample SV3, St. Veit im Pongau; C and D normal polarised light. E. IR photograph showing in part crystallographically controlled IR-opaque microfractures in tetrahedrite. Sample LA4, Larzenbach. F. IR-microphotograph showing aqueous two-phase L+V fluid (arrow, Fl) and opaque solid inclusions in tetrahedrite. Sample LA1, Larzenbach.
tetrahedrite (Fig. 6E). Under higher (~600×) magnification fluid inclusions can be observed in vicinity of these opaque microfractures (Fig. 6B,F). In addition some (micro)fractures contain black, IR-opaque solid inclusions (Fig. 6B,F) that were identified in reflected light mainly as chalcopyrite, gold and Type 1 oxysulphides.

Tetrahedrite from Larzenbach has a similar system of fractures and microfractures controlling replacement of tetrahedrite by arseniferous tetrahedrite, but it also shows larger areas spotted with small inclusions of finely dispersed arseniferous tetrahedrite; these elongate inclusions are partly interconnected and seem to be crystallographically controlled, e.g., by cleavage planes (Fig. 6E).

6.3. Fluid inclusions in tetrahedrite

Fluid inclusions in tetrahedrite were observed close to microfractures (Fig. 6A,B,F). They are usually accompanied by myriads of small solid, opaque inclusions of chalcopyrite, minor arsenopyrite and rarely oxysulphides and gold (Fig. 6B,F). Presence of these minerals has been confirmed by reflected light microscopy and SEM studies on polished surfaces of tetrahedrite containing fluid inclusions.

Fluid inclusions from tetrahedrite sample SV3 St. Veit are of irregular shape and commonly smaller than 10 µm. They occur as individual inclusions but mostly along trails (Fig. 6B); at least the latter must be of secondary origin. The inclusions are two-phase aqueous inclusions containing a liquid (L) and a vapour (V) phase and homogenise into the liquid phase (V → L). Within a single trail they show consistent L:V ratios (estimated L:V=70:30). Fluid inclusions of sample SV3 yielded temperatures of homogenisation (T_h) between 140 and 185 °C (Table 4; Fig. 7). Temperatures of final ice melting (T_m) vary between −14 °C and indicate fluids of low to moderate salinity (Table 4, Fig. 7).

Fluid inclusions in tetrahedrite sample LA1 from Larzenbach are of irregular to rounded shape. They occur in clusters and as small (b 10 µm) isolated inclusions together with opaque solid inclusions (Fig. 6F). Because of the small inclusion size estimation of the L:V ratio is difficult but it seems to be less consistent than in sample SV3; T_h (V → L) ranges between 85 and 190 °C, T_m between −3 to −8.5 °C (Table 4, Fig. 7).

6.4. Fluid inclusions in quartz

Fluid inclusions in quartz are much more common than in tetrahedrite; these were studied in normal visible light in sample

<table>
<thead>
<tr>
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<tr>
<td>Summary of microthermometric measurements and calculations of fluid properties for fluid inclusions from Larzenbach (LA1) and St. Veit im Pongau (SV3), Salzburg Province, Austria</td>
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<table>
<thead>
<tr>
<th></th>
<th>T_h</th>
<th>T_m</th>
<th>Density</th>
<th>Mass %</th>
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<td></td>
<td>°C</td>
<td>°C</td>
<td>g/cc</td>
<td>NaCl eq</td>
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<td>Mean</td>
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<td>8.08</td>
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<td>Std. dev.</td>
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Microthermometric data for tetrahedrite were obtained using IR-microthermometry. T_h total homogenisation temperature, T_m final ice melting temperature.
SV3 from St. Veit in which two types of fluid inclusions in quartz are distinguished:

Quartz Type 1 (lower salinity). The occurrence of many small fluid inclusions in quartz, which is intimately intergrown with As-poor tetrahedrite, may give the latter a clouded appearance in transmitted light (Fig. 6C). These fluid inclusions occur in clusters rather than in trails, are of irregular to rounded shape, and small (<5 µm). They are aqueous-two-phase (L+V) to one-phase (? L) and have variable L-V ratios. T_m (V → L) of individual two-phase inclusions within this cluster varies considerably (72 to 195 °C; with one outlier at 250 °C); T_m for FI Type 1 inclusions ranges from ~3 to ~12 °C.

Quartz Type 2 (higher salinity). The majority of fluid inclusions in quartz, however, are of higher salinity (T_m down to ~44 °C) and homogenise at lower temperatures (60 to 150 °C; Table 4, Fig. 7). These inclusions are not directly related to tetrahedrite. These aqueous-two-phase inclusions are small (<5 to 10 µm) show consistent L-V (90:10) ratios and preferentially occur along secondary inclusion trails (Fig. 6D). Larger (c. 10 µm) solitary fluid inclusions of irregular shape are irregularly distributed in quartz. They are aqueous-two-phase (L+V) inclusions and always show large and well visible gas bubbles. These larger inclusions have high salinity and T_m between 120 and 150 °C. Low eutectic temperatures T_e (e.g., quite consistently below c. ~56 °C) and the observation of final ice melting between ~36.5 and ~32 °C suggest that in addition to NaCl, there are other salts (MgCl_2?) present in the fluid.

7. Discussion

7.1. Fluid composition and origin

The gold mineralising fluids entrapped in tetrahedrite are characterised as moderately saline aqueous solutions. The salinities (T_m) show considerable overlap with lower salinity (Type 1) fluid inclusions in quartz although the latter show slightly lower mean T_m and higher densities (Table 4). The fluid inclusions in tetrahedrite are preferentially found along microfractures healed by arseniferous tetrahedrite and are associated with gold encapsulating solid inclusions of gold-oxysulphides. From textural relationships it is, therefore, concluded that formation of native gold with inclusions of Au-oxysulphides is related to these low-salinity fluids. Obviously gold mineralisation is not related to the high-salinity fluids entrapped in Type 2 fluid inclusions in quartz, which have comparable range in T_m but much lower T_m values.

Previous studies of fluid inclusions from the main vein of the Mitterberg Cu deposit (part of the same ore district as Larzenbach and St. Veit) demonstrated the presence of several populations of aqueous fluids with high salinity in this deposit (Belocky, 1992; Pohl and Belocky, 1999). Highly saline halite-saturated (L+V+halite+calcite, T_m 127±38, 26 to 38 wt.% NaCl equiv.) brines evolve to saline halite-saturated (L+V; T_m 100 °C, 21 to 23 wt.% NaCl equiv.) fluids. Formation conditions deduced for L+V+halite inclusions were consistent with the interpretation of syn-orogenic Austroalpine fluid protoliths (Pohl and Belocky, 1999). The low to moderately saline fluids that we document from tetrahedrite and quartz have, however, not been reported before. It is important to note that gold mineralisation in the copper deposits of the Greywacke Zone is related to this latter fluid type and not to the synthetic highly saline brines, which were interpreted to have formed by de-volatilisation of crustal rocks likely involving evaporitic sequences during Eoalpine subduction and collision of Penninic underneath Austroalpine tectonic units (Pohl and Belocky, 1999).

The gold mineralising fluids in the polymetallic Cu deposits of the Greywacke Zone also differ significantly from those observed in Neoalpine mesothermal vein type gold deposits in the Alps (Belocky, 1992; Horner et al., 1997; Pettke et al., 2000) and world-wide (Ridley and Diamond, 2000); in these low-salinity mixed aqueous-carbonic fluids predominate. Hence, compositionally gold mineralising fluids in the Greywacke Zone do not resemble syn-metamorphic fluids formed during devolatilisation of deeper crustal rocks during Eoalpine regional metamorphism or late orogenic fluids involved in formation of Neoalpine gold–quartz veins in the Alps.

On the other hand there are field and textural arguments suggesting that formation of gold mineralisation in the copper deposits in the Greywacke Zone must be related to Eoalpine regional metamorphism and deformation. Field relations indicate that Cu (−Au) mineralisation at Mitterberg and at Larzenbach is hosted by discordant as well as concordant veins. Although syngenetic models were proposed for the discordant ore type by some authors (see discussion in Weber, 1997) there is at least agreement that formation of the main discordant copper vein at Mitterberg is of Cretaceous age (Petrachsek, 1978). Paragenetic studies at Mitterberg also document that tetrahedrite, now to be recognised as the main host mineral of Au, is a late stage mineral in the ore paragenesis (Bernhard, 1966).

Microtextural evidence presented in this paper supports the view that gold and oxysulphides postdate tetrahedrite formation. Gold was brought into the rocks when the deformation style changed from ductile to brittle as indicated by the control of gold by microfracturing of tetrahedrite. The minimum formation temperatures of this mineralisation event can be deduced from homogenisation temperatures (Larzenbach LAI: 122±36 °C, St. Veit SV3: 165±13 °C) of fluid inclusions in tetrahedrite. Using isochores calculated for tetrahedrite-hosted inclusion data and assuming maximum pressures of 200 MPa as deduced for the final stage of mineralisation at Mitterberg (Belocky, 1992) maximum formation temperatures of gold mineralisation are estimated to be ~180 to 300 °C for Larzenbach and ~250 to 300 °C for St. Veit (Fig. 8). Most likely pressures were below 200 MPa and temperatures during the gold mineralisation stage did not exceed ~250 °C as deduced from the upper stability limit of oxysulphides (Giggenbach, 1974).

In summary, we interpret gold mineralisation in the Greywacke Zone to be related to late to post-orogenic processes. Compared to typical mesothermal orogenic gold deposits (e.g., in the Tauern window) the deduced temperatures are lower and the H_2O–CO_2 dominated fluids are lacking. Gold mineralising fluids in the GWZ are characterised as lower saline aqueous fluids.

7.2. Transport and precipitation of gold

The aqueous speciation, the transport and the precipitation of gold in/ from hydrothermal solutions are controlled by many factors, such as solution composition, temperature, pressure, oxidation potential, and pH (Seward, 1984). Chloro- and hydroxochloro-complexes (e.g., AuCl_4^-) are important in high temperature hydrothermal fluids with high activity of chlorine and low activity of reduced sulphur species (Henley, 1973; Seward, 1984, 1991; Tossell, 1996; Stefansson and Seward, 2004). At temperatures between 150 to 350 °C with oxidation states buffered by sulphate–sulphide or H_2S at neutral or alkaline pH the dominant Au species will be Au(HS)_2^- (Shenberger and Barnes, 1989). At acidic pH Au(HS)_2^- may become an important species in reduced sulphur-containing hydrothermal solutions (Benning and Seward, 1996) whereas in dilute chloride and sulphide solutions gold hydroxo–complexes (e.g., Au(OH)) can become important (Stefansson and Seward, 2004).

Reduced hydrosulphido complexes of gold such as Au(HS)_2^- are the most accepted species for transporting gold in the Earth’s crust in weakly acidic solutions.
oversaturated with respect to reduced Au–activity of chlorine, as documented by the low total salinity of the hydrothermal fluids of low salinity that were below ~250 °C. The low fluid pressure limit deduced for fluid inclusion entrapment at Mitterberg (according to Belocky, 1992).

The presence of gold oxysulphides, as documented for the low-salinity fluids of the low-temperature hydrothermal regime (Kucha et al., 1994). The presence of thiosulphate among the species studied in fluid inclusions from the Omai gold deposit, Guyana, also supports the importance of thiosulphate complexing of gold in some vein-type gold deposits (Voicu and Hallbauer, 2005).

P–T–X conditions suitable for transport of gold as thiosulphate complexes are also to be expected in the upper levels of hydrothermal systems and these species were actually confirmed in hydrothermal fluids from hot springs in Waiotapu, New Zealand (Pope et al., 2005) and Yellowstone, USA (Xu et al., 1998). For the Champagne Pool, Waiotapu, New Zealand, dissolved gold contents up to 109 ng L⁻¹ were reported and high gold concentrations (40 to 90 ng L⁻¹) were also noted further downstream in acidified geothermal fluids. These runoff waters are oversaturated with respect to reduced Au–species and hence Pope et al. (2005) assumed that in these fluids gold is transported by ligands such as polysulphides, thiosulphates or colloidal particles.

From the present fluid inclusion study it can be concluded that gold in the Au-bearing Cu deposits of the GWZ was transported by hydrothermal fluids of low salinity that were below ~250 °C. The low activity of chlorine, as documented by the low total salinity of the fluid inclusions, and the temperature constraints of the transporting fluids therefore make the transport of gold by chloro- and hydroxycchloro complexes unlikely. Rather, gold sulphur complexes are the preferable species for gold transport.

The presence of gold oxysulphides, i.e., solid compounds of intermediate sulphur valence containing sulphur and oxygen, and their intimate nanoscale intergrowth with native gold in the studied occurrences in the GWZ is a strong argument for the transport of gold by oxoacids of sulphur such as gold thiosulphate complexes. Because gold oxysulphides are now documented along 350 km in E–W direction in the GWZ (Fig. 1) we argue that transport and mobilisation of gold by these complexes is not a local phenomenon but must have occurred on a regional scale in the Alpine orogen.

Possible processes for precipitating gold from hydrothermal solutions include cooling, fluid immiscibility (e.g., boiling), fluid mixing, changes in $f_2O$ of the fluid (e.g., by formation of sulphides co-precipitated with the gold), changes of pH and $fO_2$ (e.g., by interaction with the wall rock) or adsorption of gold on mineral surfaces or colloids; among these processes cooling and boiling are regarded as the most effective ones (e.g., Seward, 1991). Based on the study of fluid inclusions boiling or fluid mixing can, however, be excluded for the GWZ. There is no evidence for heterogeneous fluid entrapment as to be expected for fluids undergoing phase separation during boiling and there is no systematic trend to be seen in the $T_m$ vs. $T_h$ diagram, what would be expected when fluids of different temperature and salinity would have undergone mixing. The large variation in $T_h$, as documented for the low-salinity fluid inclusion population (e.g., Larzenbach $T_h$ of fluid inclusions in tetrahedrite ranges from ca. 80 to 180 °C, Fig. 7), rather indicates cooling of the hydrothermal fluids making this a viable process for precipitation of gold.

7.3. Association of arsenic and gold

Other aspects that need to be discussed are the close spatial association of gold with tetrahedrite, the higher gold grades of tetrahedrite-rich ores and especially the change of tetrahedrite composition close to the gold containing microfractures. As revealed by bulk rock analyses of sulphide concentrates tetrahedrite has much higher gold content compared to co-existing chalcopyrite (see section 5.2). Moreover, the composition of tetrahedrite changes from As-poor to arseniferous tetrahedrite or even tennantite close to Au-bearing microfractures. From these observations we conclude that there exists a genetic link between arsenic and gold.

The close association between the distribution of gold and arsenic in various types of gold deposits has long been recognised. In sediment-hosted (Carlin-type) gold deposits Au and As are chemically closely associated and gold is commonly hosted in arsenian sulphides (especially arsenian pyrite; Arehart et al., 1993; Fleet and Mumim, 1997; Simon et al., 1999b; Cline, 2001). A similar close association of these two elements is known from some Au-bearing volcanic massive sulphide deposits (e.g., McClenaghan et al., 2004) or active geothermal systems (e.g., Rotokawa, New Zealand; Krupp and Seward, 1987).

Furthermore, arsenic, mostly present as arsenopyrite, is a common element in gold deposits in metamorphic terranes, especially in mesothermal orogenic gold deposits hosted by metasediments (Goldfarb et al., 2005). Some of these deposits, such as the Salsigne deposit, France (Demange et al., 2006), have been major resources of arsenic in addition to gold. Arsenic dominated organic gold deposits were also mined in the Eastern Alps. There, structurally controlled mesothermal vein type to replacement As–Au–Ag–(Bi) mineralisation developed in the metamorphic dome complex of the Tauern Window during post-collisional uplift (e.g., Rotgünden area, Austria, Horner et al., 1997).

Although As is not a dominant element in the studied Au-bearing Cu deposits of the Greywacke Zone there is an undeniable association of arsenic and gold even in these deposits. As documented in this study gold and Type 1 gold oxysulphides are preferentially found in microfractures within tetrahedrite. Along and around these re-healed microfractures tetrahedrite is becoming increasingly arseniferous making tetrahedrite non-transparent in the IR spectral range (Fig. 6). To explain this close association of gold and arsenic we have to assume that As was either transported together with Au in the hydrothermal solutions or that As played a key role in scavenging Au by adsorption processes on As-containing sulphide surfaces. Because of the geochemical association of gold with arsenic and antimony, especially in epithermal gold deposits, already Seward (1973) suggested that...
“arseniothio and atimoniothio complexes [e.g., Au(AsS2)_3, Au(AsS3)_2, Au(SbS4)_2, etc.] may be of importance in the transport of gold in some hydrothermal ore solutions”. Adsorption has been identified as an important process for fixing gold on sulphide surfaces and triggering its precipitation from gold-undersaturated solutions (e.g., Arehart et al., 1993; Simon et al., 1999a; Reich et al., 2005).

For the studied Greywacke Zone ores we must assume joint transport of arsenic and gold in the hydrothermal solutions because tetrahedrite from the pre-gold chalcopyrite–tetrahedrite assemblage is quite poor in As (Table 1) whereas it was enriched during the gold forming stage.

Transport of arsenic in natural waters is mainly in the form of oxo-anion complexes where arsenic occurs in the nominal As^3+ or As^5+ valence state. Depending on pH and redox conditions the most important aqueous species are either arsenite (e.g., H_3AsO_3^-) or arsenate complexes (e.g., H_2AsO_4^- or HAsO_4^{2-}). Based on theoretical calculations Tossell (2000) concluded that a similar gold hypothesis for the Greywacke Zone. In these gold-bearing polymetallic systems of these oxoacids (preferably a Au-thiosulphate complex) as evidenced by the intimate intergrowth of gold with oxysulphide phases. The many inclusions of Type 2 oxysulphides within native gold indicate that oxysulphides could have been the metastable precursor phases of metallic gold, which precipitated during continuing oxidation.

Gold was not the only element mobilised during weathering. At least Cu must also have been mobile as indicated by the Cu-rich composition of the oxyx sulphides and the Cu enrichment in secondary gold. Leaching experiments have shown that Cu too is soluble in thiosulphate solutions and that Cu ions in thiosulphate solutions even have a catalytic effect in speeding up the dissolution of gold considerably (Aylmore and Muir, 2001). The close spatial association of secondary gold and gold oxysulphides with primary gold might indicate that remobilisation and re-precipitation of gold occurred on a very local (cm–dm?) scale. Bowell et al. (1993) also argued that thiosulphate complexes are mostly causing local redistribution of gold (up to the metre scale) in lateritic soils. In the uppermost metres of soil profiles Eh and pH values show considerable variation and the ground water table is an important redox boundary where Au can be enriched (Webster and Mann, 1984; Bowell et al., 1993). Kinetic barriers are to be overcome by catalytic effects of redox sensitive transition metal ions (Fe^3+, Cu^2+) or thiotbohydrate (Benedetti and Boulegue, 1991; Lengke and Southam, 2005).

Weathering of sulphides (tetrahedrite, chalcopyrite) would provide the necessary sulphur.

The observation that both primary gold of hydrothermal origin as well as remobilised gold formed during weathering are intimately intergrown with oxysulphides can be regarded as strong evidence that oxoacids of sulphur played a crucial role in transporting gold in the Au-bearing polymetallic ores of the Greywacke Zone. Remobilisation and re-precipitation of secondary Cu-rich gold must have occurred in the presence of these oxoacids (preferably a Au-thiosulphate complex) of the oxysulphides and the Cu enrichment in secondary gold. Leaching experiments have shown that Cu too is soluble in thiosulphate solutions and that Cu ions in thiosulphate solutions even have a catalytic effect in speeding up the dissolution of gold considerably (Aylmore and Muir, 2001). The close spatial association of secondary gold and gold oxysulphides with primary gold might indicate that remobilisation and re-precipitation of gold occurred on a very local (cm–dm?) scale. Bowell et al. (1993) also argued that thiosulphate complexes are mostly causing local redistribution of gold (up to the metre scale) in lateritic soils. In the uppermost metres of soil profiles Eh and pH values show considerable variation and the ground water table is an important redox boundary where Au can be enriched (Webster and Mann, 1984; Bowell et al., 1993). Kinetic barriers are to be overcome by catalytic effects of redox sensitive transition metal ions (Fe^3+, Cu^2+) or thiotochondrates (Benedetti and Boulegue, 1991; Lengke and Southam, 2005).

Weathering of gold–bearing sulphide ores is a very complex open system process and hence we can only speculate about the detailed mechanisms of remobilisation, transport and re-precipitation of gold. Because pH was likely buffered by dissolution of carbonates, which are
common in host rocks of the ore deposits studied, oxidation is regarded as a key process for destabilising the thiosulphate complex and causing precipitation of metallic gold in the studied examples.

8. Conclusions

Our results indicate that infrared microscopy is a valuable tool in studying textural relationships between As-poor tetrahedrite, which is transparent in infrared light and more arseniferous opaque members of the tetrahedrite–tennantite series. Tetrahedrite is transparent for infrared light when arsenic content is below ca. 2.5 wt.% As. Fluid inclusions in tetrahedrite are coeval with solid inclusions of chalcopyrite, gold oxysulphides and minor arsenopyrite and gold with oxysulphide inclusions. Fluid inclusions in tetrahedrite are of low to moderate salinity and homogenisation temperatures (minimum formation temperatures) range between 85 and 190 °C. In quartz a similar type of fluid inclusions was found in addition to more saline aqueous fluids, which are unrelated to gold mineralisation.

Gold-oxysulphides are part of the hydrothermal as well as of the weathering mineral assemblages; in the latter they are associated with Cu-rich secondary gold and minerals formed during supergene alteration. The intimate association of gold and gold-oxysulphides indicates that in the Greywacke Zone gold likely was transported and remobilised by thiosulphate complexes. This study demonstrates that gold-oxysulphides are occurring on a regional to even orogenic scale in the Eastern Alps. Because gold-oxysulphides are easily overlooked phases we believe that they should be much more common in other ore districts. Recognition of these phases is relevant because they could be alternative carriers of gold in various low-temperature ore deposits and are expected to influence the processing and recovery of gold in hydrometallurgical processes.

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