Bismuth tellurides as gold scavengers

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Abstract. Bi-Te melts have potential as Au scavengers in different types of gold deposits. Using phase equilibria, we define 'melt-(precipitation) windows' within which the Bi-Te scavenging mechanism can operate. Predicted assemblages correlate well with those in natural samples and can be applied in other cases to explain the distribution of telluride minerals in Au deposits.

Keywords. Bismuth tellurides, gold scavenger, melt precipitates, epithermal, skarn, orogenic gold

1   Introduction

Telluride minerals are commonly abundant in Au deposits of various types and ages. When highly concentrated throughout, or in limited parts of a deposit, Au-(Ag)-tellurides may themselves constitute an economic ore (Cook and Ciobanu, this volume). Bismuth-tellurides, on the other hand, are not themselves, exploitable minerals, but may be an important part of the Au association. Maldonite (Au_2Bi) and unnamed Au_5BiS_4 are the only known Au-Bi compounds and may attain exploitable concentrations within certain deposits; there are no Bi-Te-Au compounds as such.

In many cases the occurrence of Au together with Bi-tellurides is as droplets or droplet-derived patches hosted within common ore minerals (Ciobanu and Cook 2002). Such morphologies are highly indicative of precipitation in a molten state. Indeed, droplets of sulphide-Au-Bi-maldonite in annealed samples from Challenger (S. Australia) showed quenched textures that support their origin as polymetallic melts formed during metamorphism of a pre-existing ore (Tomkins and Mavrogenes 2002).

The hypothesis that metals precipitated above their melting points (as melts) from fluids can extract Au from those fluids was proven experimentally for native Bi (Douglas et al. 2000). Using hydrothermal fluids undersaturated in Au for the experiments, this mechanism was shown to be a more efficient alternative in extracting Au from a fluid than precipitation upon saturation, i.e. a proper 'scavenger' for Au. Once precipitated, Bi melt remains mobile and will continue to attract Au until crystallisation is complete.

We discuss the potential that Bi-Te melts have as Au scavengers in relevant templates of Au-mineralisation. This in turn allows us to define a 'melt-(precipitation) window' that can be used to explain and understand distribution of tellurides in Au deposits. Such an approach emphasizes the importance of Bi-tellurides as Au pathfinders, as much as their implied involvement in the formation of Au-telluride deposits, other than those in which only tellurides of Au and Au-Ag are present. Maldonite is not a telluride but should be consid-ered alongside Bi-tellurides when Au-concentrating mechanisms via Bi-Te melts are discussed.

2   Bismuth tellurides

Bi-tellurides represent a group of chalcogenides with modular structures. They form a polytypoid series with general formula $mBi_2 \cdot nBi_2Te_3$, in which individual members are characterised by distinct stacking sequences of two types of layer, the 2-atom 'BiBi' layer and the 5-atom 'TeBiTeBiTe' layer (Imamov and Semiletov 1971). Bi-sulphotellurides and selenides are structurally related compounds that have similar configuration, but Te is partially or totally replaced by S and/or Se in the 5-atom layer. Currently recognised mineral species can be grouped in several isoseries (Cook et al. in press).
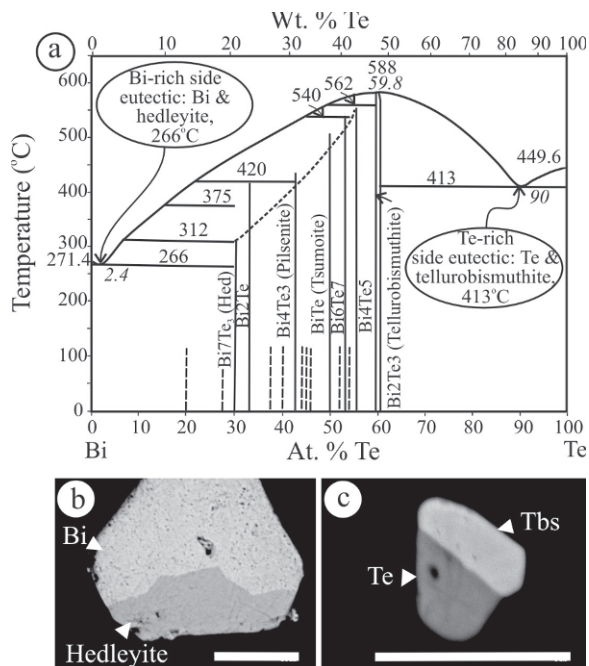
Figure 1: a) Bi-Te phase diagram after Okamoto and Tanner (1990); b) and c) BSE images of associations representing the two eutectics formed at 266°C (a, Baisoara, Romania) and at 413°C (b, Kochbulak, Uzbekistan). Tbs: tellurobis-muthite. Scales: 10μm.
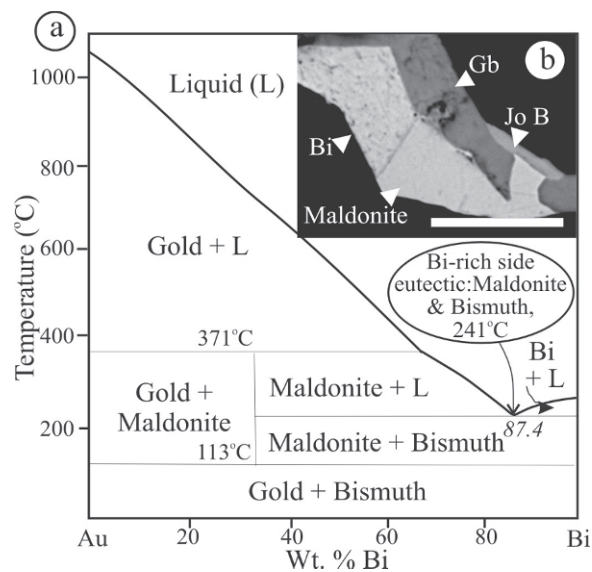
Figure 2: a) Au–Bi phase diagram after Okamoto & Massalski (1983); b) BSE image of association representing the eutectic at 241°C (Baisoara, Romania). Gb: galenobismuthite, Jo B: joseite-B. Scale: 10 μm.

Table 1: Eutectics in the Bi-Au and Bi-Te-Au systems

Eutectic	Melt (at. %)	T°C	References
maldonite+Bi	$Bi_{82.8}Au_{17.2}$	241	Okamoto & Massalski 1983
Bi_5Te_3+maldonite+Bi	$Bi_{84.5}Au_{14}Te_{1.5}$	235	Gather & Blachnik 1974
tellurobismuthite +calaverite + Te	$Bi_{7.5}Au_{10.5}Te_{82}$	383	Gather & Blachnik 1974
tellurobismuthite +calaverite + Au	$Bi_{10}Au_{37}Te_{53}$	402	Gather & Blachnik 1974

2.1 Bi-Te phase diagram

In the simple Bi-Te diagram (Fig. 1a), telluro-bismuthite has the highest thermal stability (588°C; Okamoto and Tanner 1990). The eutectic on the Bi-side (266°C) is close to the m.p. of native Bi (271°C), and the eutectic on the Te-side (413°C) is close to the m.p. of native Te (450°C). Although structural formulae were derived for a larger number of synthetic compounds in the Bi-Te series (Fig. 1a), there are only a limited number of tellurides defined (Cook et al. in press).

2.2 Gold incorporation in Bi- and Bi-Te-melts

The only eutectic on the binary Au-Bi phase diagram indicates that liquid Bi can incorporate as much as 17 at.% Au and will crystallise as Bi+maldonite at 241°C (Fig. 2a, Table 1); beyond the solubility capacity of any fluid at any temperature. The potential of melts to dissolve Au is even higher for Bi-Te melts (10-37 at.% Au) - see eutectics in the Au-Bi-Te system (Table 1).
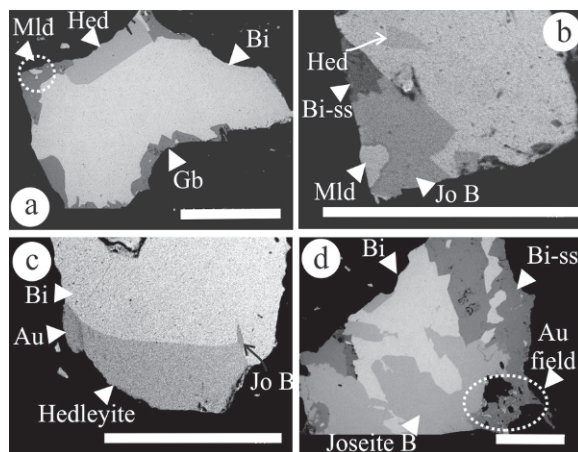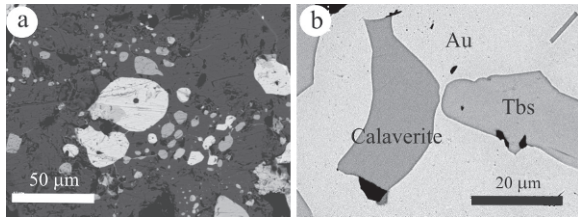

Figure 3: BSE images of droplets representing the Bi-Te-Au association formed during sulphidation of Mt (to Po) (Baisoara, Romania). Bi-ss: Bi-sulphosalt; Gb: galeno-bismuthite; Hed: hedleyite; Jo-B: Joseite-B, Bi_4Te_2S; Mld: maldonite. Scale: 50μm.

2.3 Application to natural samples

When present in natural samples, eutectic associations (Figs. 1, 2, 4b) provide minimum formation temperatures for the respective Bi-Te±Au assemblages. It is rare, however, that the droplets consist only of tellurides; in most cases, they also include sulphotellurides and/or Bi-sulphosalts (Fig. 3). Maldonite (Figs. 3a, b) or Au (Figs. 3c, d) is included within one or the other mineral components, proving that Bi- and Bi-Te-(S) melts can scavenge Au in each of the respective Au-bearing systems, not only at eutectic composition. Collectively, droplet chemistry (Fig. 3) represents a compositional range close to the eutectic on the Bi-rich side of the Bi-Te system. Similar associations are reported from many Au skarns (Meinert 2000).

Even though virtually all intermediate compositions between Bi and Te can be stabilised by structural modulation in Bi-tellurides (sulpho-tellurides, -selenides), the chemistry of telluride droplets that are paragenetically related covers a certain range of intermediate compositions on either Bi- or Te-rich sides of the Bi-Te(Se,S) and/or Bi-Te(Se,S)-Au systems. Based on theoretical considerations (Afifi et al. 1988) and observation of speciation in Bi-telluride associations found in deposits spanning the metamorphic and magmatic to hydrothermal spectrum, the ratio Bi/Te+Se+S ($R_{Bi/Te}$) is found to be relevant for oxidizing/ reducing conditions in fS_2-fO_2 space (Ciobanu and Cook 2002). Tsumoite (BiTe) spans both reduced environments (Po,Mt) characterised by Bi-tellurides with $R_{Bi/Te}>1$, native Bi and maldonite, and oxidized environments (Py,Hm) including Bi-tellurides with $R_{Bi/Te}<1$, Au-Ag-tellurides and native Te.

Figure 4: BSE images illustrating Au-telluride assemblages in bonanza ores from pipes at Kochbulak. a) Telluride droplets (Au-Ag-Pb-Bi-Sb-Te association) in tetrahedrite; b) Association of Au, tellurobismuthite (Tbs) and calaverite, representing the eutectic at 402°C in Au-Bi-Te system.

3 Application of melt hypotheses

3.1 Au-concentration by partial melting

Frost et al. (2002) pointed to the fact that a number of chalcophile elements form low-melting point sulphides (LMCE) and thus will assist partial melting of a sulphide ore if this undergoes metamorphism at temperatures above the m.p. of available LMCE in the system. Of relevance here is the fact that both Bi and Te are included within the LMCE group. The importance of partial melting of a pre-existing ore *via* LMCE is that such melts will act as scavengers for Au, a metal that otherwise has a high melting point (Fig. 2a), e.g. Challenger deposit (Tomkins and Mavrogenes 2002).

Emphasising the importance of LMCE melts in concentrating Au is the formation of telluride-rich high-grade ore (including bonanza ore Au, ~200 g/t) in tectonically controlled pipes at Kochbulak, Uzbekistan (Stenina et al. 2003). Native Au is associated with Au-(Ag)-tellurides (calaverite, $AuTe_2$; sylvanite, $(Au,Ag)_2Te_4$, petzite, Ag_3AuTe_2; hessite Ag_2Te), Bi-tellurides (tellurobismuthite, tetradymite), altaite, $PbTe$). Evidence for incorporation of Au and Ag in melts during partial melting of sulphosalts (fahlore, bismuthinite) and sulphides from preexisting epithermal ore is seen in a series of emulsion-like textures displayed between Au and various combinations of tellurides and sulphosalts/ sulphides. Especially relevant to melt involvement are the telluride droplets within tetrahedrite, $Tet_{88}Ten_{11}$ (Fig. 4a), highly reminiscent of liquid magmatic ores formed by immiscibility between sulphide and silicate melts. An estimated melt temperature of >400°C is based on the two eutectics recorded within telluride associations (Figs. 1c, 4b).

3.2 The melt-precipitation window: Au extraction from hydrothermal fluids

Fractionation of melts from a fluid (precipitation of metals above the solvus curve) is controlled by two factors: (1) temperature above m.p. (T_{melt}) along the liquid/solid curve,

and (2) insolubility of metal complexes in the fluid at the respective temperature. The latter is, in turn, controlled by chemistry of the fluid, e.g. sulphidation/oxidation (fS_2/fO_2) and redox (Ph/Eh) characteristics of the fluid.

3.3 Epithermal deposits

The stability of native Te broadly covers the pyrite field in fS_2/fO_2 space with a solubility minimum close to the Mt/Hm buffer at 300°C (McPhail 1995). This explains the presence of native Te in many epithermal deposits since there is a significant overlap between the above conditions and those considered for fluids that form this type of ore (Cooke and Simmons 2000). However, most epithermal Au ores in the Pacific Rim lack Bi-tellurides; Te+Au-(Ag)-telluride signature is instead prominent. This is because the minimum temp-erature of the melt window is at least 413°C (Fig. 1a), even though the chemistry of epithermal fluids is otherwise suited for formation of melts in the tellurobismuthite-Te range. Consequently, Au-scavenging from fluids by formation of Bi-Te melts (with Te>Bi) is likely to happen in epithermal systems only if T> 400°C is reached (some HS systems; Cooke and Simmons 2000). In LS epithermal systems formed at lower T (<300°C), other precipitation mechanisms, e.g. condensation of Te vapor(s), followed by reaction with Au-Ag-bearing fluids, is invoked to explain the presence of Au-(Ag)-tellurides+Te (Acupan, Phillipines; Cooke and McPhail 2001). Temperatures >400°C can nonetheless be attained in LS epithermal systems at the porphyry to epithermal transition if this is triggered early in the porphyry evolution by active strike-slip tectonics (some deposits in Apuseni Mts., Romania). The association of Bi-tellurides ($R_{Bi/Te}$ <1), typical for deeper parts of kin-veins, opened onto an immature porphyry root at Larga (Cook and Ciobanu 2004), is evidence for Au-scavenging. Porphyry and epithermal Cu deposits (both HS & LS) in the Banatitic Belt (SE Europe, Late Cretaceous) include Au-enriched ores with Bi-telluride signature ($R_{Bi/Te}$<1; tetradymite, telluro-bismuthite) ± Te ± Au-(Ag)-tellurides) that are formed by similar mechanisms, at T=400°C and at the Mt/Py± Hm buffer (Ciobanu et al. 2003).

3.4 Skarn and orogenic Au

In contrast to native Te, the stability of native Bi covers Po-Mt fields in fS_2/fO_2 space (Skirrow and Walshe 2002). Partitioning of liquid Bi (melt) was obtained experimentally from fluid at fS_2 below the Po/Py buffer and temperatures above the m.p. of Bi (271°C) (Douglas et al. 2000). Importantly, Au was also partitioned from fluid into liquid Bi, proving the point that destabilisation of soluble metal complexes at T above the solvus curve can induce precipitation irrespective of their saturation at the time.

Minimum T for the Bi-Te melt window is 266°C on the Bi side (Fig. 1a) and 241°C for Bi-Au melts (Fig. 2a). Although such temperatures are in the epithermal range, associations of native Bi, maldonite and tellurides ($R_{Bi/Te}$>1) require more reducing conditions than those considered for epithermal systems. Such reducing conditions are met in skarns during sulphidation at the Mt/Po buffer (e.g. droplets in Figs. 2b, 3 are found only in Mt replaced by Po in Baisoara Fe skarn) or reducing reactions at the Hm/Mt buffer (Fe skarn at Ocna de Fier, Romania; Ciobanu et al. 2003). The templates of many Au skarns (Meinert 2000) and orogenic Au (e.g. Maiskoe, Ukraine; Cook et al. 2002) replicate the experiments of Douglas et al. (2000) below the Po/Py buffer.

Two distinct Bi-telluride associations, (1) Au+ Bi-tellurides ($R_{Bi/Te}$>1)+Bi±maldonite; (2) Au+Bi-tellurides ($R_{Bi/Te}$<1)±Te±Au-(Ag)-tellurides, are often seen in skarns and orogenic Au, either separately or together (Ciobanu et al. 2003, 2004; Mudrovska et al. 2004). The type association will reflect the reducing (1) or oxidizing (2) character of sulphidation reactions, e.g. at redox fronts, often the case of interaction between orogenic Au fluids and BIF, or during retrograde stages in skarns. Bi-tellurides are hence excellent pathfinders for Au in such deposits, where they are abundant.

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