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Understanding gold-(silver)-telluride-(selenide) mineral deposits

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Gold-(silver)-telluride (selenide) ores occur as epithermal orogenic and intrusion related deposits. Although Te and Se are chalcophile elements and share geochemical affinity with Au, formation of selenides and other elements Ag-Au require acidic or reducing environments. The thermodynamic stability conditions for Au and Ag-tellurides and native tellurium indicate an epithermal environment. Analysis of mineral paragenesis, textures and compositional variation in tellurides/selenides suggest petrogenetic processes involving interaction with fluids leading to Au scavenging and entrapment in tellurides, changes in chemistry/rates of fluid infiltration and attaining equilibrium in a given assemblage.

Introduction

Gold-(silver)-telluride-(selenide) deposits are not described as a discrete class of ore deposit. Many fall, instead, into the more familiar classes of epithermal, orogenic and intrusion-related deposits, with their distinctive character linked to telluride-, and more rarely, selenide-rich mineralogy, rather than any shared genesis. The interplay between mineralogy and ore genesis provided motivation for International Geoscience Programme (IGCP) project 486 (2003-2008). IGCP-486 allowed researchers from more than 30 countries the opportunity to share scientific results at scales ranging from micro-scale study of mineral assemblages to that of gold deposit distribution within an orogenic collage.

The synthetic analogues of Bi-tellurides have structures that are appreciated for their strong semiconducting p-type properties related to van der Waals gaps and are at the forefront of new semi-conductor technology.

Interest in research on tellurides extends beyond the Earth, with the possible presence of a metallic ‘mist’ in the atmosphere on Venus which contains tellurium and volatile elements, including Pb, As, Sb and Bi, forming halides or chalcogenides with high vapour pressures (Schaefer and Fegley, 2004).

What is a gold-telluride deposit? – the starting point for IGCP-486

Lindgren (1933) introduced the subclass of “gold-telluride veins”

as part of the epithermal deposit spectrum in his textbook “Mineral deposits”. Telluride-enrichment is, however, observed in a far wider range of deposit types, e.g., Au-rich VMS deposits, porphyry Au(Cu) and Au skarns. In at least some of these, a proportion of the gold occurs as Au-(Ag)-tellurides, or as native gold/Au-minerals paragenetically tied with tellurides of other elements, notably bismuth. Despite their enrichment in Te, gold deposits formed under reducing conditions are generally not acknowledged as Au-telluride deposits, because the telluride-rich character is largely expressed through an abundance of Bi-telluride species, commonly stable together with native bismuth. Gold-Bi compounds, such as maldonite and/or jonassonite, contribute to the mineralogical balance of gold ore, instead of Au(Ag)-tellurides (Ciobanu et al., 2005). A modified definition of the term ‘gold-telluride deposits’ was thus proposed (Cook and Ciobanu, 2005) to encompass the genetic connotation given by the presence of tellurides other than those of Au-Ag.

In a preface to a special issue of *Mineralogy and Petrology*, Ciobanu et al. (2006a) posed a series of questions concerning the ‘how?’ and ‘why?’ of gold-telluride deposit formation. They questioned some of the established thinking about how these deposits were understood, not because the ideas are wrong (on the contrary!), but to encourage debate, and look beyond the confines of what was known and which fitted well to certain epithermal deposits. Likewise, Cook and Ciobanu (2005) attempted to build a framework for the role of other types of hydrothermal systems in the generation of telluride-bearing deposits, raising certain taboos about classification, alternative settings and deposition mechanisms, the role of tellurides in orogenic gold systems and skarns, and what studies of trace mineralogy could contribute to the broader ore genesis perspective? They stressed the need to expand thermodynamic databases and modelling of ore-forming systems (Afifi et al., 1988; Zhang and Spry, 1994a; Simon et al., 1997) to cover a broader range of formation conditions, e.g., pH/eH variation vs. activity/fugacity of various aqueous/gas species in a hydrothermal system.

Within a given deposit, telluride-rich ores can be precipitated either at the same site or separately from native gold ore, depending upon precipitation mechanisms and local setting. Contemporary perspectives (e.g., Cooke and McPhail, 2001) include a Te-rich source, generally magmatically-derived, transport of Te as aqueous/vapour species within hydrothermal fluid, and precipitation of Au-Ag-tellurides due to multi-stage boiling. In an epithermal-porphyry environment (<5 km), these vapours are transported at the upper part of the veins forming a low-grade Au-Te cap on top of the main Au mineralisation underneath. Whereas this model fits some telluride-bearing Au deposits (e.g.,

Jensen and Barton, 2000) there are other examples of epithermal deposits for which this model is not suitable. Where can the model of Cooke and McPhail (2001) be applied? – does it always work? – can zonation always be expected?

Good examples also exist of telluride-bearing Au deposits formed in deeper (>5 km) settings, e.g., intrusion-related and orogenic gold deposits. For example, the giant Golden Mile deposit, Kalgoorlie (W.A.; Shackleton et al., 2003), which at 1,500 tonnes contained Au is the largest single lode gold system in the world. Whereas phase separation is commonly attributed to boiling in epithermal systems, this is associated with a catastrophic drop in fluid pressure in orogenic Au systems (Mikucki, 1998).

An association between alkaline magmatism and telluride-bearing epithermal mineralisation has often been assumed (e.g., Richards, 1995); many classic epithermal Au-Te systems (Cripple Creek, Emperor, Porgera, Ladolam and the Montana Au-Ag telluride belt) are associated with alkaline magmatism. Some such systems grade downwards into porphyry-type Cu-(Au) or Mo-(Au) deposits. Commenting on the association of tellurides with alkaline magmatism, Jensen and Barton (2000) emphasised that melting of Te-rich ocean floor sediments may be a key source of mantle-sourced alkaline magmas in subduction settings. Cook and Ciobanu (2005) and Ciobanu et al. (2006a) questioned whether the link to alkaline magmatism may have been overstated. Examples of telluride-enriched epithermal mineralisation in calc-alkaline volcanic rocks include the Baguio District, Philippines (Cooke and McPhail, 2001) and numerous Cretaceous-Quaternary deposits in Japan. The Golden Quadrilateral (Romania) and the Kurama Belt (Tien Shan, Uzbekistan), which both received attention during IGCP-486, are also associated with calc-alkaline volcanic rocks.

The present contribution summarises the main results of IGCP-486.

Distribution of tellurides in gold provinces

During the lifetime of the project, more than 100 occurrences worldwide were described and several key deposits and districts were visited (e.g., Golden Quadrilateral, Romania; Kurama belt, Uzbekistan; Cripple Creek, Colorado). More detailed work was carried out in the collage of terranes making up the European segment of the Tethyan belt, in Central Asia and in China (Fig. 1), even though other provinces including shield areas (e.g., Ukrainian and Fennoscandian Shields) also received coverage. The programme also included areas where less previous work was done on the telluride-selenide-bearing assemblages (e.g., epithermal deposits in the Bulgarian Rhodopes or porphyry/epithermal systems in Turkey).

Cripple Creek, Colorado, USA

Cripple Creek is a world-class, telluride-rich epithermal gold deposit (~28 Moz Au production) hosted by an Oligocene alkaline diatreme complex resulting from phonolitic lamprophyric magmatism (Kelley et al., 1998; Jensen, 2007; Jensen and Barton, 2007). The deposit features an outstanding mineralogy (Carnein and Bartos, 2005), with spectacular finds of telluride minerals during earlier mining. Gold mineralisation is mainly hosted by thin (typically <5 cm) seams of quartz. Intense potassium metasomatism was broadly developed throughout the diatreme which makes up the upper, explored part of the igneous complex. Ore-formation

appears restricted to the latest stages of magmatism and many veins are characterised by a single stage of mineral deposition. Ore-forming fluids were dominated by low temperature (<225°C), dilute, CO₂-rich magmatically-derived fluids; phase separation by boiling and effervescence played key roles in gold precipitation. The abundance of tellurides at Cripple Creek is attributed to volatile-rich fluids associated with alkaline magmatism (Jensen and Barton, 2007).

Emperor and Tuvatu deposits, Fiji

The low-sulphidation epithermal gold-telluride deposit of Emperor, Fiji (11.5 Moz) is hosted by Late Miocene-Early Pliocene shoshonitic rocks and is one of the best studied examples (e.g., Pals and Spry, 2003; Pals et al., 2003). Although much of the gold occurs as invisible gold in pyrite, 10-50% of the gold occurs as gold telluride minerals.

The nearby Tuvatu deposit (Scherbarth and Spry, 2006) also contains a suite of unusual V-bearing minerals, including roscoelite and karelianite (Spry and Scherbarth, 2006). Thermodynamic calculations show that the stability fields of these minerals coincide with those of calaverite, the main gold telluride, and that V is likely derived from the same alkalic intrusive rocks, which are also considered as the source of Au and Te. These two gold telluride deposits, the largest in Fiji, are noted for their relatively high grades (~9 g/t Au), spatial association with the regional Viti Levu lineament, the Tuvau and Navilawa volcanic calderas, and low-grade porphyry copper mineralisation within the calderas (Begg, 2007; Spry, 2007). A direct relationship to volcanic calderas is also observed at Ladolam, Lihir Island (Carman, 2003).

Peri-Tethyan domains in Europe (Alpine-Balkans-Carpathians-Dinarides)

Magmatic belts in Peri-Tethyan domains in Europe (Alpine-Balkans-Carpathians-Dinarides) have provided much of the impetus for IGCP-486.

Carpathians of Slovakia and Ukraine

Neogene metallogenic provinces of central and eastern Slovakia has been an important source of precious and base metal ores for many centuries. The number of known occurrences of tellurides and selenides (Kremnica – where they are abundant, the Banská Štiavnica-Banská Hodruša ore district, Javorie Mts. and Zlatá Bana - Byšta deposits), confirm a widespread Te-signature. Despite this, the assemblages were only recently studied (Jelen et al., 2004; Mat' o et al., 2006), enabling identification of new telluride species (e.g., within advanced-argillic type of alteration in the Vihorlatské vrchy Mts.; Rídkošil et al., 2001; Skála et al., 2007). Occurrences in the Ukrainian Transcarpathians (e.g., Melnikov and Bondarenko, 2004; Melnikov et al., 2005) are of similar type.

Golden Quadrilateral (Romania)

The 900 km² Golden Quadrilateral, Romania (GQ), has a special place among telluride-bearing gold provinces (Cook and Ciobanu, 2004a and references therein). Mineralisation formed in a volcanic environment during Neogene calc-alkaline magmatism. The district

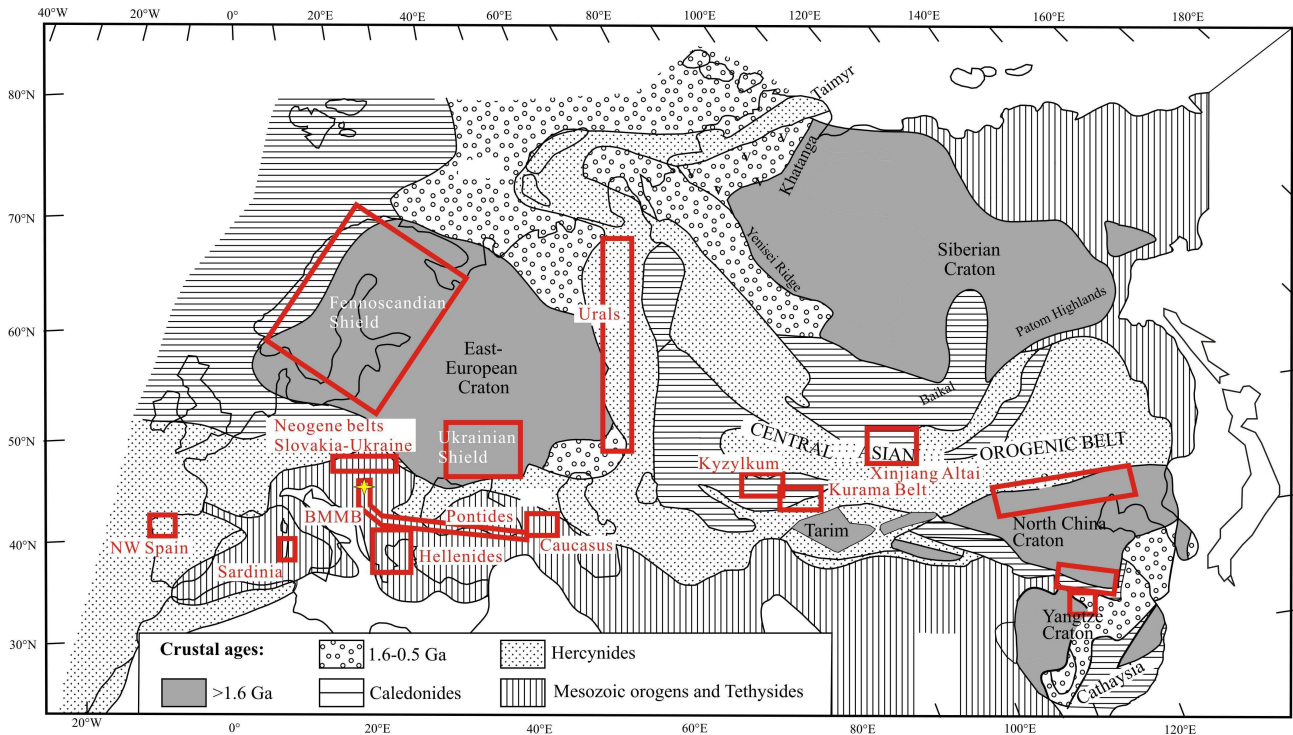


Figure 1. Map showing telluride-bearing belts and deposits in Eurasia considered during IGCP-486. Base map modified from Pirajno et al. (2009).

only contains a single deposit (Săcărîmb) in which Au-(Ag)-tellurides are the dominant ore minerals, but tellurides are common accessories in more than half the deposits and across the deposit spectrum - illustrated by the occurrence of tellurides in the giant Rosia Montana diatreme-hosted deposit (Cook and Ciobanu, 2004a; Tamas et al., 2006).

Tellurides can be used to decipher orefield zonation across porphyry-epithermal systems, e.g., in the Fata Baii-Larga orefield (Cook and Ciobanu, 2004b). Here, native gold and tellurides are present throughout the 1 km vertical extent of the hydrothermal system. Gold and Au-Ag tellurides are dominant at upper levels and Bi-tellurides at depth, with free gold in both associations. The deposit does not, therefore, follow the zonation model of Cooke and McPhail (2001) for epithermal gold-telluride deposits. The sulphidation reaction (löllingite + pyrrhotite → arsenopyrite + pyrite) recorded in the deeper part of the veins opened above an (immature) porphyry root, is considered the main process destabilising metal complexes in the fluid.

The model of Cooke and McPhail (2001) is also contradicted by the inverse zonation trends at Săcărîmb, a low-sulphidation (LS) epithermal deposit with no substantial evidence for boiling during vein formation (Alderton and Fallick, 2000). Here, telluride-rich ore forming the high-grade median part of the veins is situated underneath lower-grade native gold ore at the top. Observations of textures among telluride assemblages (Cook and Ciobanu, 2004a; Ciobanu et al., 2008) indicate deformation and overprinting during vein (re)opening. The position of the deposit, at the intersection of different fault systems, was optimal for development of sustained fluid throttling producing effervescence, probably the main mechanism of Au deposition at Săcărîmb.

Banatitic Magmatic and Metallogenic Belt

More than 50 porphyry, epithermal and skarn deposits occur

within the Late Cretaceous Banatitic Magmatic and Metallogenic Belt (BMMB; Ciobanu et al., 2002a), southeastern Europe, the westernmost portion of the Tethyan Eurasian Metallogenic belt (TEMB; Jankovic, 1997). The belt is one product of the subduction and obduction of ocean basins in the Tethyan region since the Mesozoic, as a result of the collision of Africa with Europe and other smaller microplates. The L-shaped belt extends from the North Apuseni Mountains (Romania) through the Timok region (Serbia), and across Bulgaria to the Black Sea. The eastern extension of the TEMB can be found in the Pontides of Turkey, and extends at least as far as Pakistan.

Although essentially a Cu-Au belt, the BMMB has a pronounced Bi-Te signature, recognisable in styles of mineralisation ranging from skarns to porphyry and epithermal types. An association of Bi-tellurides with gold is evident even in cases where gold was neither exploited nor suspected (e.g., Ciobanu and Cook, 2004). The speciation of Bi-tellurides is dependent on the redox conditions. Assemblages differ markedly between skarns not associated with porphyries, many of which show reduced conditions with pyrrhotite and magnetite stable (e.g., Baisoara, Baita Bihor, Ocna de Fier), and porphyry Cu(Au) deposits (e.g., Moldova Noua) and Cu- or Zn-skarns associated with them (e.g., at Majdanpek), where oxidised assemblages with pyrite and hematite stable prevail (Ciobanu et al., 2003).

Gold-(Ag)- and Bi-tellurides are both reported from all deposit types in the Panagyurishte district (Bulgaria), demonstrating common fluid sources for the different mineralisation styles. The district contains porphyry (Elatsite and Assarel) and epithermal deposits that range from high (Chelopech) to intermediate (Radka) and LS types (Elshitsa), (e.g., Bogdanov et al., 2004; 2005; Kouzmanov et al., 2005). Te-bearing species that are specific to the high sulphidation (HS) environment, such as goldfieldite, are present at Chelopech. The district includes PGE-bearing porphyry systems (e.g., Elatsite), where a telluride, merenskyite (PdTe₂), is documented as the main PGE-carrier (Tarkian et al., 2003).

A telluride signature in the major epithermal, porphyry and skarn-type gold deposits of the eastwards extension of the belt is poorly documented (Bogdanov and Filipov, 2006), even if tellurides were occasionally reported (e.g., from the Murgul and Çayeli volcanogenic Cu deposits, Turkey; Zaykov et al., 2006).

The Hellenide tectonic collage

Work carried out in the Hellenides, part of the Alpine-Himalayan orogen, and formed when Apulia collided with Europe in the Late Cretaceous to Tertiary, is illustrative of the IGCP-486 approach to identify new areas characterised by telluride-bearing signatures (Fig. 2). In Greece, the tectono-structural collage comprises from NE to SW: the Rhodope (RM) and Serbomacedonian Massifs (SM), the Vardar Zone, the Pelagonian Zone and the Attico-Cycladic Massif (ACM, Internal Hellenides) and the External Hellenides built up by Mesozoic and Cenozoic rocks. Telluride enrichment occurs in three

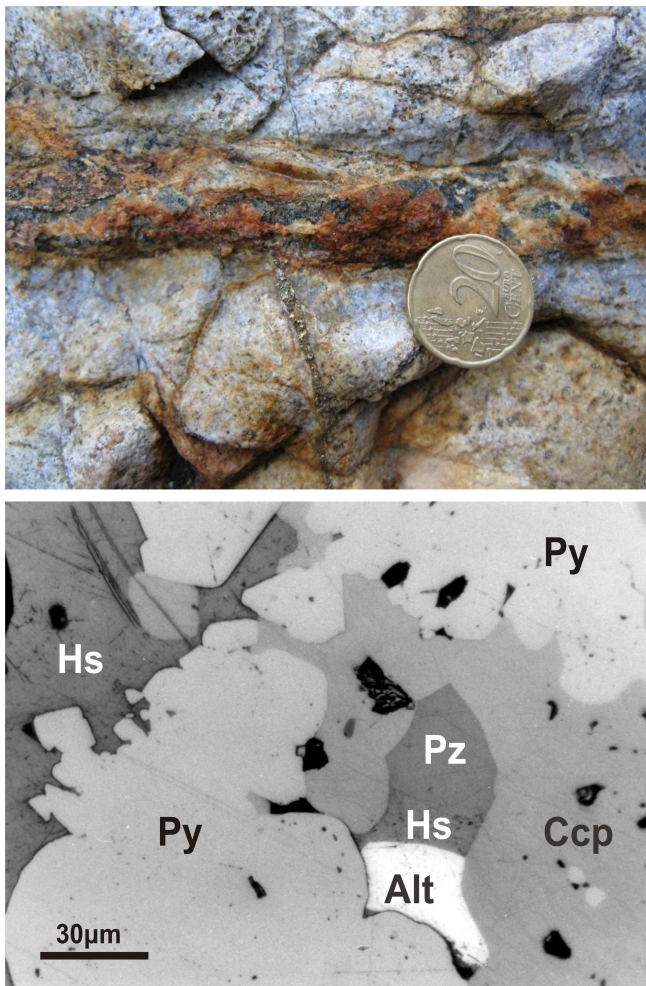


Figure 2. (top) Quartz+pyrite+molybdenite veins (Qtz) related to transitional sodic/potassic-sericitic alteration crosscut by late carbonate-quartz vein (Cal) with precious metal tellurides. Pagoni Rachi/Kirki, telescoped porphyry-epithermal Mo-Cu-Au-Te deposit, Greece. (bottom) Reflected light photomicrograph (black and white) showing altaite (Alt), hessite (Hs), petzite (Pz) and chalcopyrite (Ccp) surrounding pyrite (Py), Kassiteres/Sappes carbonate-quartz epithermal veins underlying and postdating high-sulphidation ores, Greece.

of these units: RM, SM and ACM and is found in both epigenetic deposits hosted in the metamorphic basement as well as in those affiliated with Tertiary-Quaternary magmatism.

In the SM, shear zone-hosted gold ores include both Ag-Au- and Bi-tellurides, e.g., at the Stanos/Chalkidiki and Laodikino-Koronouda/Kilkis occurrences (Voudouris and Sakellaris, 2008). Gold mineralisation relates to late Cretaceous to Eocene crustal stretching and unroofing that produced shearing and flattening of the gneissic host rock at upper greenschist to amphibolite facies.

Tertiary epithermal and porphyry gold deposits in the RM include Au-Ag-tellurides. They relate to calc-alkaline to alkaline magmatism generated in a post-collisional setting. In addition, Bi-tellurides and -sulphosalts are noted in veins of HS-IS type (e.g., Viper, St. Demetrios, Kassiteres, Perama Hill, Pefka/Western Thrace; Voudouris, 2006; Voudouris et al., 2009). The RM also includes an example of a reduced intrusion-related gold (RIRG) system, e.g., Kavala (Melfos et al., 2008). Au-Bi-Te-Pb-Sb mineralisation occurs in sheeted quartz veins that crosscut the 21 Ma Kavala granodiorite and adjacent gneisses and marbles.

In the ACM, quartz veins hosted in Mesozoic marbles at Panormos Bay (Tinos island) and in metamorphic rocks of the Cycladic Blueschist Unit at Kallianou area (southern Evia island) contain electrum and a suite of Au-Ag (sulpho)tellurides (Tombros et al., 2004; 2007a,b; Voudouris and Spry 2008). At Panormos Bay, mineralisation relates to a 14 Ma, peraluminous leucogranite (Tombros et al., 2007b). At Kallianou, veins formed under ductile to brittle deformation in the footwall block of an exhumed metamorphic core complex and are discordant to syn-metamorphic structures. Both occurrences could be interpreted as RIRG systems. Gold-Ag tellurides are also present in volcanic-hosted epithermal veinlets crosscutting the Upper Pliocene Profitis Ilias rhyodacitic cryptodome, Milos island, part of the active south Aegean volcanic arc (Alfieri and Voudouris, 2006a, b).

The telluride enrichment observed in deposits ranging from HS and LS epithermal to metamorphogenic gold systems in the Hellenides (Voudouris et al., 2007) may suggest that fluid sources are enriched in Te during mantle underplating and/or metasomatism. Further investigation is aimed at identifying whether this enrichment is due to several stages of remobilisation during successive accretion-extension episodes from Carboniferous to Pleistocene.

Tien Shan and Altaids, Central Asia

Tellurides and selenides are conspicuous components of several Paleozoic gold orefields of central Asia. In deposits of western Uzbekistan, such as Muruntau, Muytenbay, Charmitan and Gujumsay, they are restricted to Bi-bearing species (Koneev et al., 2005, 2008; Khalmatov, 2008; Mun, 2008).

Au(-Ag) tellurides are prominent in the Kurama belt, Middle Tien Shan, which hosts giant Au-Cu porphyry (e.g., Kalmakyr) and epithermal deposits associated with Paleozoic calc-alkaline volcanism. Many of the epithermal deposits (e.g., Kochbulak, Kayragach, Kyzylalmasay) are proper gold-telluride deposits and may contain a dozen or more different tellurides and selenides (Fig. 3). The speciation and relative proportion between tellurides and selenides provide clues to vertical zonation, e.g., Kyzylalmasay (Khalmatov, 2008). Selenides, especially those of Bi or Ag, are dominant at upper levels, whereas Ag-, Au-, Hg-, Sb-, Pb- and Bi-tellurides prevail at depth (Koneev et al., 2005; 2008). The evolution of telluride paragenesis with time in the Kochbulak and Kairagach deposits

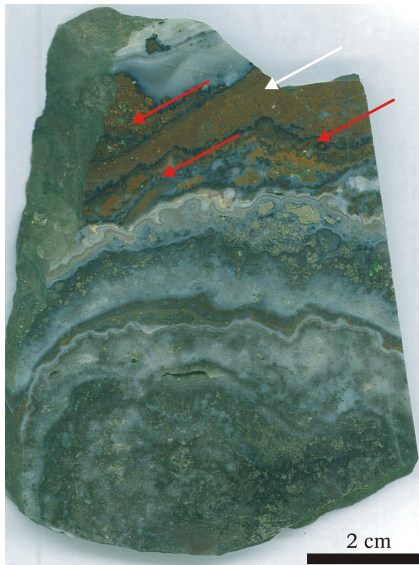


Figure 3. Hand specimen of high-grade gold ores from bonanza pipes, Kochbulak epithermal deposit, Uzbekistan. Note bands enriched in gold (white arrow) and Au-(Ag)-tellurides (red arrows). The matrix mostly consists of quartz. Sample kindly provided by R. Koneev.

(Kovalenker et al., 1997, 2003, 2004; Plotinskaya et al., 2006a) correlates with a decrease in temperature, $f\text{Te}_2$ and $f\text{O}_2$ and an increase in pH.

A special feature of the Kochbulak deposit is the incidence of bonanza ore pipes with spectacular enrichment of tellurides relative to the rest of the orefield. Textures among Au-(Ag)- and Bi-tellurides indicate the role of active tectonics in ore formation, as well as possible partial melting of a pre-existing ore (Ciobanu et al., 2006c), even if other workers (e.g., Kovalenker et al., 1997; Plotinskaya et

al., 2006a) explain the same features via an explosive hydrothermal breccia model.

Elsewhere in the central Asian Tian Shan-Altai super-collision, other major deposits are equally well endowed with tellurides. Notable examples in Kyrgyzstan include Kumtor, possibly one of the largest tellurium-bearing deposits in the world, Jerooy, Taldy-bulak Levoberezhny and Nau-M (Djenchu-raeva, 2006). Jerooy is a low-sulphide gold deposit, particularly rich in tellurides. Au-Ag tellurides are present only at upper levels, whereas Bi-tellurides are common components of the ore. An outstanding example is the Chalkuyruk skarn deposit where 80% of gold is present as tellurides.

The Altai of Xinjiang, China, represent an emerging telluride-bearing gold province, e.g., Duolanasayi (Xiao et al., 2008) and several other recently-discovered deposits.

Volcanic-hosted massive sulphide deposits in the Urals

Volcanic-hosted massive sulphide (VHMS) deposits are sometimes Te-bearing. For example, telluride-rich stringer zones are known and can offer clues about deposit morphology and genesis (e.g., Marcoux et al., 1996). The Urals province contains many examples of Au-enriched VHMS systems that carry tellurides, e.g., Silurian-Devonian deposits at Safjanovsk, Uzelginsk, Gayskoye, Severo-Uvaryažskoe, Tash-Tau, Babaryk, Yaman-Kasy, Spahyanovka, Valentorka and Alexandrinskoye, which are representative of the different sub-types in the Uralian province (Vikentyev, 2006; Novoselov et al., 2006; Vikentyev et al., 2006; Maslennikova et al., 2008). More than a dozen Au-Ag and Bi-bearing telluride species have been reported, some of which may be significant gold-carriers.

Vikentyev (2006) considered that the appearance of visible tellurides within common sulphides may have, in part, resulted from recrystallisation and coarsening of gold during late (low-temperature) hydrothermal processes and/or overprinting during prehnite-

pumpellyite-greenschist facies metamorphism. Maslennikova et al. (2008) explained the abundance of tellurides and sulphosalts in the various chimney types in the Uralian VMS province, relative to Kuroko and Cyprus-type VHMS deposits, by sulphidation and/or oxidation during interaction of reduced hydrothermal fluids and oxidised seawater.

Belogub et al. (2008) report selenides from the supergene zones of the Gayskoye, Zapadno-Ozernoye, Dzhusinskoye and Alexandrinskoye deposits. These result from liberation of Se from the common sulphides during oxidation and associated bacterial activity. Although mineralisation in the Urals is dominantly of VHMS type, tellurides are also prevalent in other types of deposit, e.g., orogenic or epithermal type. Precious metal tellurides occur, for example, in the Bereznyakovskoe HS gold-telluride deposit, southern Urals (Plotinskaya et al., 2006b). This deposit was first described by Lehmann et al. (1999), with special emphasis on the gold-telluride connection.

Alpine-Yanshanian magmatism in China

An increasing number of telluride-bearing gold deposits are known from China. These include deposits of intrusion-related, orogenic and epithermal type. Understanding the significance of the telluride-rich signature for both ore genesis and exploitation became clearer as a result of IGCP-486 (e.g., Mao et al., 2004; Zhao et al., 2005).

Debate on telluride-bearing deposits from the northern margin of the North China Craton (NCC), e.g., Dongping, Huantualiang, Zhongshangou and Xiaoyinpan has centred on their origin as intrusion-related or orogenic deposits formed during multiple late Paleozoic–Mesozoic mineralizing events, and whether their association with alkaline magmatism carries genetic significance (e.g., Mao et al., 2003). Analogues on the southern margin of the North China Craton include Jingchangyu (Yanshan district) and Wulashan.

The Pingyi area of western Shandong, on the southeastern margin of the North China Craton, is a second telluride-enriched gold province in China. Gold mineralisation relates to epithermal systems associated with the Early Jurassic Tongshi magmatic complex, e.g., Guilaizhuang, Lifanggou and Mofanggou (Hu et al., 2006). Fluid inclusion and isotope data for these deposits show that pressure release and fluid boiling, as well as fluid-rock interaction (Lifanggou and Mofanggou) and mixing of magmatically-derived fluids with meteoritic waters (Guilaizhuang) played an important role in ore formation.

The large Dashuigou Te-(Au) deposit, at the western margin of the Yangtze craton, Sichuan Province, is a spectacularly telluride-rich deposit interpreted as the product of a Permian large igneous province-related mantle plume (Chen et al., 1996; Mao et al., 1995; 2004; Zhao et al., 2005). Ores containing as much as 10 wt.% Te occur as veins within the metabasalts.

Fennoscandian and Ukrainian Shields

Tellurides and selenides can be conspicuous accessory minerals in gold deposits in Archaean or Proterozoic Shields. Bismuth and Te are useful pathfinder elements in exploration and tellurides have potential for understanding ore evolution. Deposits in such environments may be of orogenic type, but others are interpreted as metamorphosed VHMS, epithermal or porphyry deposits.

From the 100 or so more important gold deposits in the Fennoscandian Shield (Sundblad, 2002), at least 38 contain Bi-

tellurides (selenides) (Ciobanu et al., 2004a). There exists a strong spatial and paragenetic link between gold and the presence of Bi-tellurides/selenides. Assemblages can be used to draw parallels between orefields situated in different units, such as between metamorphosed VHMS deposits at Falun (Bergslagen, Sweden) and Orijärvi-Ilijärvi (Uusima Belt, SW Finland; Ciobanu et al., 2002b). Kojonen (2006) reviewed the main gold provinces in Finland, drawing attention to the Au-Ag selenide-telluride deposits: Orivesi (Kutemajärvi, Tampere schist belt), Jokisivu (Huittinen), the Ilomantsi gold showings and Pampalo test mine, Kylmäkangas (Orijärvi) and the Juomasuo gold deposit (Kuusamo). Kojonen (2006) considered all as metamorphosed epigenetic deposits occurring in shear zones with extensive alteration. Bi-tellurides are abundant in some ore pipes of the Orivesi deposit and in other deposits from the shield (e.g., Glava, Sweden), and may be significant Au-carriers (Cook et al., 2007d; Ciobanu et al., 2009b). Bismuth tellurides/selenides are also abundant in Au-Ag occurrences from Russian Karelia, e.g., in the Raikonkoski orogenic gold occurrence (Ivaschenko et al., 2007).

Syntheses of telluride occurrences in the Ukrainian Shield indicate the presence of Bi-tellurides within orogenic gold deposits, e.g., at Mayskoe (Mudrovskaya et al., 2004; Bondarenko et al., 2005).

Other areas

Another example of telluride-bearing hydrothermal systems associated with calc-alkaline magmatism resulting from IGCP-486 is the Tertiary Furtei Au deposit, Sardinia, Italy (Fadda et al., 2005a; b). Here, the system underwent evolution from an earlier intermediate sulphidation (IS) porphyry to an HS-epithermal system. Gold-Ag-tellurides are more abundant in deeper, sulphide-rich IS mineralisation; Te-bearing tetrahedrite and native tellurium appear stable in shallower, HS parts of the system dominated by enargite and luzonite. The Te content of tetrahedrite decreases away from the porphyry-style centre of the hydrothermal system.

Mineralogy was used to model Au-(Cu) skarn formation in the Rio Narcea Belt, northern Spain (Cepedal et al., 2006). Bi-tellurides and accompanying Au-minerals were shown to be efficient monitors of the oxidation state of the skarn systems at both Ortosa and El Valle, with assemblages varying with the dominant Fe-sulphide or oxide.

Gold-(Ag) tellurides are widespread in magmatic provinces from Argentina (Paar et al., 2005) and are especially abundant in epithermal HS and LS deposits and they contribute to the precious metal grades (e.g., La Mejicana, Famatina; Farallón Negro). Many of these deposits are genetically related to Miocene-Pliocene volcanism.

Among the many Au occurrences in southeastern B.C., Canada, that show RIRG affiliation is the CLY Group of prospects (Nelson district; Howard et al., 2007). Bi-tellurides and gold occur together in some of the sulphide-poor veins and the variation in Au contents in the Bi-tellurides, was interpreted to indicate zonation and/or overprinting during a later (orogenic?) episode (Cook et al., 2007c; Ciobanu et al., 2009b).

Telluride and selenide mineralogy – new results

Telluride and selenide minerals – new data

New minerals described in the past six years include telluronevskite (Rídkošil et al., 2001), schlemaitite, $(\text{Cu}, \square)_6(\text{Pb}, \text{Bi})\text{Se}_4$

(Förster et al., 2003), mazzettiite, $\text{Ag}_3\text{HgPbSbTe}_5$ (Bindi and Cipriani, 2004a), museumite, $\text{Pb}_5\text{AuSbTe}_2\text{S}_{12}$ (Bindi and Cipriani, 2004b), selenojapaite, Ag_3CuSe_2 (Bindi and Pratesi, 2005), vihorlatite (Skála et al., 2007) and vavrinite, Ni_2SbTe_2 (Laufek et al., 2007). Although not a Te- or Se-bearing mineral, jonassonite, Bi_4AuS_3 (Paar et al., 2006) is always associated with Bi-chalcogenides.

Studies have generated new data on several Au-(Ag)-telluride minerals, including nagyágite (Ciobanu et al., 2008), empressite (Bindi et al., 2004), sylvanite (Cook and Ciobanu, 2004a), montbrayite (Shackleton and Spry, 2003), kostovite (Bonev et al., 2005) and cervelleite (see below). Reported unnamed phases include As-bearing Au-Ag-tellurides with empirical formulae $(\text{Ag}_{1.83}, \text{Au}_{0.22})_{2.05}\text{As}_{0.95}\text{Te}_2$ (Ciobanu et al., 2008) and $(\text{Au}_{1.62}, \text{Ag}_{0.33})_{1.95}\text{As}_{1.08}\text{Pb}_{0.24}\text{Bi}_{0.03}\text{Te}_{1.70}$ (Sung et al., 2007).

Nagyágite

Among the gold-tellurides, nagyágite, $\text{Pb}_3(\text{Pb}, \text{Sb}, \text{As})_3\text{S}_6(\text{Au}, \text{Te})_3$, stands out in terms of its complex chemical-structural modularity combining (Au,Te) telluride layers stacked between $2x[\text{Pb}_2(\text{Sb}, \text{As}, \text{Bi})_2\text{S}_2]$ sulphosalt modules (Effenberger et al., 1999). Mineral modularity allows for chemical substitutions to be mapped onto structural sites, providing a petrogenetic tool. An example is the reinvestigation of material from the type locality (Săcărîmb, Romania), the only deposit where several compositional varieties of nagyágite are described (Ciobanu et al., 2008 and references therein). Their formation was interpreted in relation to pseudomorphic replacement during coupled dissolution reprecipitation reaction (CDRR) and linked to high fluid acidity. Replacement of nagyágite by galena-altaite symplectites is also attributed to CDRR, but instead reflects changes in $f\text{Te}_2/f\text{S}_2$ of a slightly alkaline fluid. A geological context for variation in fluid characteristics is provided by the reopening of veins during rotation of the duplex fault-system responsible for vein formation.

CDRR-assisted replacement of nagyágite by galena-altaite symplectites is also reported from the Sunrise Dam orogenic Au deposit, Yilgarn Craton, Western Australia (Sung et al., 2007). No compositional variation is seen, inferring unchanged fluid composition during syn-deformational overprinting. Precipitation of native gold, retained within the symplectites, accompanies destabilisation of nagyágite.

Cervelleite

Cook and Ciobanu (2003a) summarised published data for cervelleite, and added new data from skarn (Ocna de Fier and Baita Bihor) and epithermal (Larga) occurrences in Romania. Cervelleite, ideally Ag_4TeS , may incorporate significant Cu, within the range Ag_4TeS to approximately $(\text{Ag}_{3.2}\text{Cu}_{0.8})\text{TeS}$. An additional phase, $\text{Ag}_2\text{Cu}_2\text{TeS}$, possibly the first quaternary phase in the system Ag-Cu-Te-S, was identified in two occurrences. Cervelleite from VHMS deposits in the southern Urals shows comparable levels of Cu-for-Ag substitution; several unnamed mineral species are also present (Novoselov et al., 2006). The latter are distinguished, not only by variable Cu contents, but also by Te/S ratios that depart from the 1:1 ratio in cervelleite, or by apparent cation deficiencies. Other unnamed Ag-Cu sulphotellurides were described from Greece: $[(\text{Ag}, \text{Cu})_{12}\text{Te}_3\text{S}_2]$ and Ag-Au-Cu $[(\text{Ag}, \text{Au}, \text{Cu})_9\text{Te}_2\text{S}_3]$ or $[(\text{Ag}, \text{Cu})_{25}\text{Au}_2\text{Te}_6\text{S}_9]$ from Tinos Island (Tombros et al., 2004) and Ag_2CuTeS and $(\text{Ag}, \text{Cu})_2\text{TeS}$

from Kallianou (Voudouris and Spry, 2008). Compositional variation among phases of the cervelleite group may be yet another case to explore further as a source of petrogenetic information. For example, in skarns, these minerals are part of broader 'exotic', volatile-rich mineral parageneses tracing retrograde stages (Cook and Ciobanu, 2001, 2003b; Ciobanu and Cook, 2000, 2004; Ciobanu et al., 2004b).

Bismuth and bismuth-lead tellurides

The tetradymite group

Bismuth tellurides (as well as selenides, tellurosulphides and telluroselenides) are prominent components of many gold deposits (Fig. 4). They are grouped in a homologous series of mixed-layer compounds with rhombohedral or trigonal symmetry derived from a 5-layer X-Bi-X-Bi-X module (X=Te, Se, S), known as the 'tetradymite archetype', by incremental addition of Bi-Bi leading to the structural formula $n\text{Bi}_2\text{X}_3\text{mBi}_2\text{X}_3$ (n = number of Bi_2X_3 units; m =number of Bi_2X_3 units; Cook et al., 2007a). This type of modular structure enables any discrete composition in the interval Bi_2X_3 -Bi to be represented by a specific stacking sequence. Each stoichiometry (Bi:X ratio) within the group (e.g., Bi_2X_3 , Bi_4X_3) represents an isoseries – e.g., tellurobismuthite Bi_2Te_3 , tetradymite $\text{Bi}_2\text{Te}_2\text{S}$, kawazulite $\text{Bi}_2\text{Te}_2\text{Se}$). Ciobanu et al. (2009a) used high-resolution transmission electron microscopy (HR-TEM) to study compounds in the compositional range Bi_2Te_3 - Bi_8Te_3 . Although the Bi_2 and Bi_2X_3 units can be imaged, they do not underpin homology in the group. Instead, the layer-modules and homology are defined by the structural formula

$S'(\text{Bi}_{2k}\text{X}_3)\cdot L(\text{Bi}_{2(k+1)}\text{X}_3)$ (X=chalcogen; S', L=number of short and long modules, respectively); all phases are N-fold (N=total number of layers in the stacking sequence) superstructures of a rhombohedral subcell.

Such a formula provides an easy method for calculation of the stacking sequences from electron diffractions and their simulation using computer software (MSCG; appendix to Ciobanu et al., 2009a). This further allows for definition of single phases from random polysomes and thus assists with establishing equilibrium vs. disequilibrium during crystallisation. This is an important step in analysing naturally-occurring 'minerals' from the series that often may contain variable lengths of polysomes embedded in the stacking sequences (Ciobanu et al., 2010). An illustration of this approach is shown for tsumoite (BiTe) from the type locality in Fig. 5.

The 'aleksite' series

A second homologous series of Bi-Pb-compounds that can be derived from the same 'tetradymite' archetype by adding Pb(Bi)-X instead of Bi-Bi layers (X=chalcogen), is informally known as the 'aleksite' series (Cook et al., 2007b; Ciobanu et al., 2009a). They are found almost exclusively within Au-bearing deposits. Structures of compounds from the two series that have the same number of individual layers (N) are isoconfigurational one with another. Moëlo et al. (2008) classify these phases within the broader family of sulphosalts despite the fact that their structures feature X-X bonds, one of the forbidden characteristics in this group.

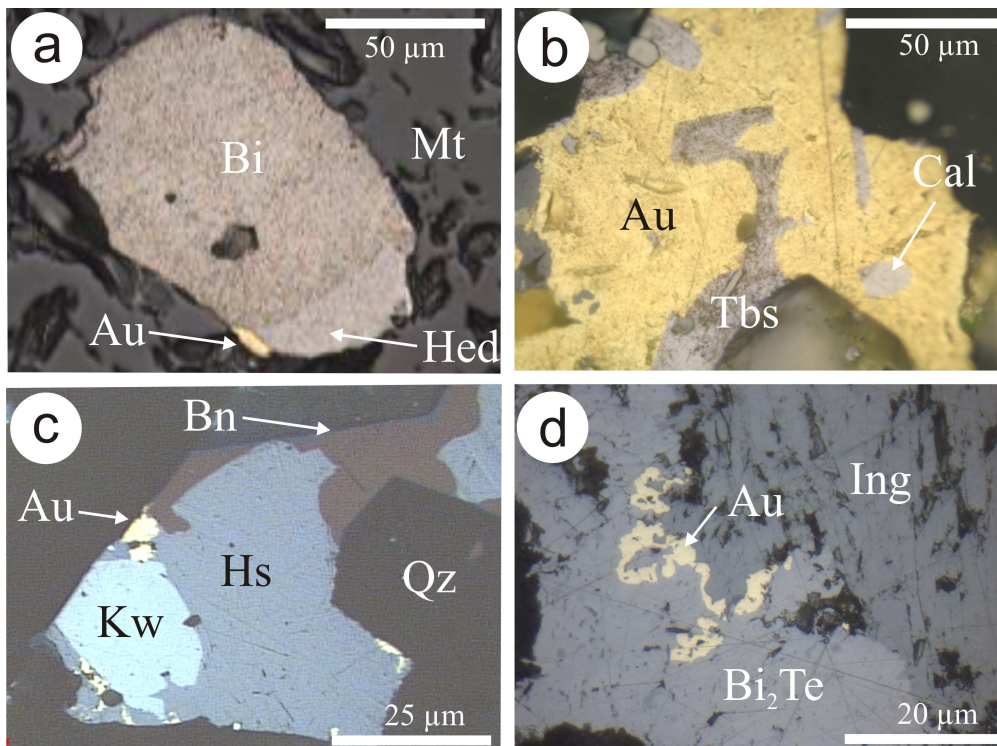


Figure 4. Reflected light microscope images showing associations of Bi-tellurides with gold in different deposit types. (a) Fe-skarn, Baisoara, Romania. Native bismuth (Bi) and gold (Au) coexisting with hedleyite (Hed) in a matrix of magnetite (Mt). (b) Epithermal bonanza-pipe, Kochbulak, Uzbekistan. Assemblage of tellurobismuthite (Tbs), native gold (Au) and calaverite (Cal). (c) orogenic Au-(Ag), Glava, Sweden. Assemblage of hessite (Hs), kawazulite (Kw) and gold (Au), together with bornite (Bn) in a matrix of quartz (Qz). (d) Intrusion-related gold, CLY prospect, B.C., Canada. Assemblage of unnamed Bi_2Te and ingodite (Ing) with native gold (Au) at the margin between the two.

Phase systems and constraints on mineral stabilities

Despite the wealth of data compiled by Afifi et al. (1988), construction of phase diagrams to represent observed assemblages in many tellurium-bearing systems remains difficult due to the lack of reliable thermodynamic data for some minerals. New data for the system Ag-Au-X (X=S, Se, Te) (Echmaeva and Osadchii, 2008) is thus welcome, as are improved thermodynamic data for the systems Au-Te (Wang et al., 2006), Au-Bi-Sb (Wang et al., 2007) or the systems Au-Bi and Ag-Au-Bi (Servant et al., 2006; Zoro et al., 2007), the last four allowing greater accuracy in modelling the critical system Au-Bi-Te (Wagner, 2007; Tooth et al., 2008; see below). Fundamental thermodynamic information for Se-bearing systems has also become available (e.g., Xiong, 2003; Akinfiyev and Tagirov, 2006a; b; Osadchii and Echmaeva, 2007), allowing detailed modelling of, for example,

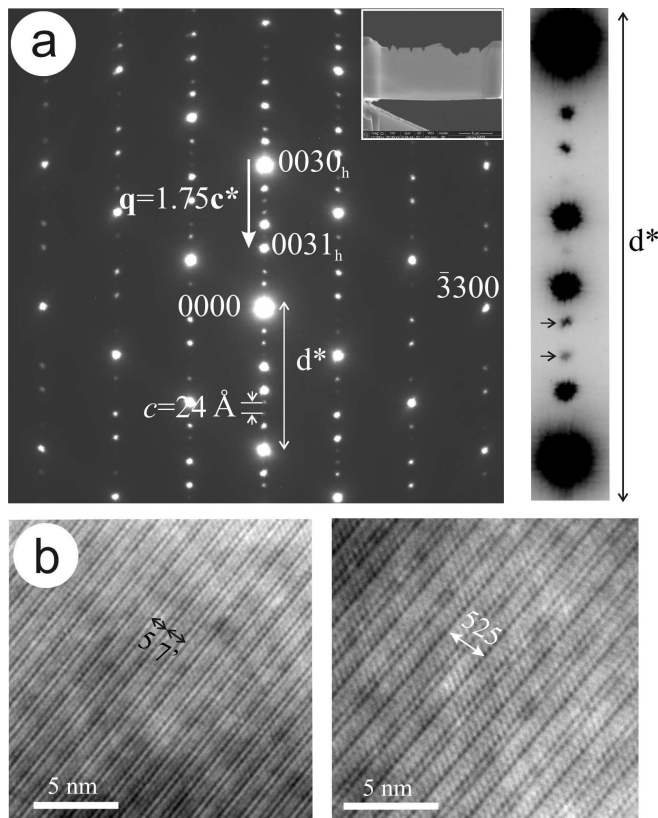


Figure 5. Characterisation of tsumoite from Tsumo (Japan) using electron diffraction and high-resolution transmission electron imaging (HR-TEM). This work was done on a TEM foil (inset on a) prepared by Focused Ion Beam (FIB) methods using a FEI Helios nanoLab DualBeam FIB/SEM system, AMMRF, Adelaide. (a) Electron diffraction pattern (EDP) on $[110]_h$ zone axis. Four-integer ($hkl.m$) indexing is with respect to hexagonal cell setting (subscript h ; 4D group $P:R3:m11$; Lind and Lidin, 2003). The modulation vector (q ; arrow) is used to index the superstructure reflections (see Ciobanu et al., 2009a). The strip underneath shows the d^* (corresponding to $d \sim 0.2$ nm) interval between two main reflections along $(000l)$ rows. The smallest distance (arrows) between two superstructure reflections corresponds to $(1/12)d^*$ indicating a 12-fold superstructure (total number of layers in the unit cell $N = 12$). (b) HR-TEM images at different defocus illustrating the stacking sequence interpreted either as 7:5 (thinner and wider lamellae; left side) or 5:25 (right side). 7': non-symmetric 7-layer module (Te-Bi-Te-Bi-Te-Bi-Te); 5: 5-layer module (Te-Bi-Te-Bi-Te); 2: 2-layer module (Bi-Bi). Sample kindly provided to NJC/CLC by M. Shimizu.

selenide-bearing vein and VHMS deposits (Layton-Matthews et al., 2008) and unconformity-related and sandstone-hosted uranium deposits.

Better constraints on the Te behaviour under hydrothermal conditions are required, including complexation and transport (e.g., McPhail, 1995; Grundler et al., 2009a, b). Application of stable Se isotopes can track fluid sources and transportation in geological environments (e.g., Layton-Matthews et al., 2003). Radiogenic Te isotopes can be used for dating ores (Thomas et al., 2005).

Gold-telluride deposits are often considered to result only from low-temperature ($<300^\circ\text{C}$) processes; telluride-bearing parageneses being attributed to a late depositional events. Primary depositional

features are, however, often obliterated by exsolution and recrystallisation of tellurides (e.g., Zhang and Spry, 1994b; Spry et al., 1997; Shackleton et al., 2003; Scherbarth and Spry, 2006). Put simply, observed assemblages are the final result of a protracted history of crystallisation during cooling and are often complicated by overprinting events.

Confirming the predictions of Cabri (1965) for the system Au-Ag-Te, observation of calaverite-sylvanite-hessite (Golden Mile deposit, Kalgoorlie, Western Australia) has shown that calaverite-hessite is a non-equilibrium assemblage, whereas hessite-sylvanite is the stable one, and results, via stützite, from the breakdown of the higher-temperature ($>300^\circ\text{C}$) metastable $\bar{\alpha}$ - or $\bar{\beta}$ -phases below 120°C (Bindi et al., 2005). The debated sylvanite-hessite-petzite triple-point (Prince et al., 1990) has been observed in Săcărîmb (Ciobanu et al., 2008) and obtained in experiments using solid-state galvanic cell electrochemical methods (Echmaeva and Osadchii, 2008).

Petrogenetic implications and new ideas

Melt scavengers for gold

A recent breakthrough idea is the recognition of the role of low-melting-point chalcophile elements (LMCE; Frost et al., 2002) in assisting Au-enrichment in ores. Partial melting of a sulphide ore is achieved, for example, if it undergoes metamorphism at temperatures above the melting-point of some of the contained ore minerals. The LMCE group includes elements which commonly occur in remobilised assemblages (Bi, Sb, As, Te etc.), and which form chalcogenides (sulphosalts and tellurides/selenides). The importance of LMCE melts lies in the fact that they can act as scavengers for Au, a metal that otherwise has a high melting-point. Generation of Bi-rich melts can be initiated at conditions as low as upper greenschist facies (Highiş Massif, Romania; Ciobanu et al., 2006b). Tomkins et al., (2007) provided a comprehensive study of phase diagrams showing the conditions at which anatexis is initiated for various LMCE polymetallic melts.

The idea that melts can be precipitated directly from hydrothermal fluids and thus provide a more efficient mechanism of Au scavenging from those fluids than the commonly invoked 'precipitation upon saturation' process, has been tested experimentally for melts from the Au-Bi system (the 'Bi-melt collector model'; Douglas et al., 2000). In this case, the crystallisation products should include phases formed along a solvus ending with eutectic assemblages in a given LMCE system, at the lower temperature limit. As discussed by Ciobanu et al. (2005) formation conditions of many deposit types, in particular skarn, intrusion-related and orogenic Au, overlap with the temperature range ($234\text{--}475^\circ\text{C}$) of the 10 eutectics in the Au-Bi-Te system; 8 of the eutectics include gold minerals. Annealing-quenching experiments, using telluride assemblages from the systems Au-Pb-Te and Au-Bi-Te in representative epithermal and intrusion-related ores from Musariu (Romania) and Oya (Japan), respectively, were undertaken to test models involving eutectic crystallisation from these LMCE systems (Ciobanu et al., 2007a, b). Wagner (2007) and Tooth et al. (2008) provided thermodynamic modelling of Au-Bi-Te and Au-Bi melts, respectively, co-existing with hydrothermal fluids. Both models show the efficiency of such melts for extracting Au even from fluids undersaturated in this element.

Applications of the melt model include: intrusion-related gold

(Pogo and Fort Knox, Tintina Belt, Alaska; McCoy, 2000; epithermal-porphry systems (Larga, Romania; Cook and Ciobanu, 2004b), skarns (Ocna de Fier, Romania; Ciobanu and Cook, 2004; Baisoara, Romania; Ciobanu et al., 2003; Ortosa and El Valle, Rio Narcea Gold Belt, Spain; Cepedal et al., 2006), orogenic gold systems (Viceroy Mine, Harare-Bindura-Shamva greenstone belt, Zimbabwe; Oberthür and Weiser, 2008) and present-day seafloor chimneys (Törmänen and Koski, 2005).

Can tellurium assist incorporation of gold into pyrite?

Invisible gold includes both lattice-bound gold and sub-microscopic inclusions of gold minerals in common sulphides, e.g., pyrite and arsenopyrite. Gold-bearing pyrite is commonly As-bearing, leading to a paradigm for gold trapped in pyrite in which As is considered essential for Au to enter the pyrite structure (e.g., Reich et al., 2005). The highest gold concentration (~1 wt.%) measured in arsenian pyrite is from Emperor, Fiji (Pals et al., 2003) but in this case, there is also a stronger correlation between gold and tellurium. Can Te-bearing, As-free pyrite carry gold?

A LA-ICP-MS study of invisible gold in pyrite from the Dongping and Huantuanling deposits, Hebei Province, China (Cook et al., 2009) confirms this to be the case. Superimposed microshearing and fracturing/brecciation and pyrite recrystallisation control the distribution of invisible gold in As-free pyrite in a telluride-bearing mineralised system, with highest gold values in pyrite (up to 1 wt.%) correlating with clustering of telluride inclusions. Textural and LA-ICP-MS data suggest that the distribution of telluride inclusions extends from micron- to nanoscale, including that lattice-bound gold is present, correlating strongly with Te. It was concluded that tellurium and other "LMCE" that form tellurides (e.g., Ag, Pb, Cu, Bi) play a role in governing gold distribution patterns during the protracted geologic history. Transient porosity developed during CDRR affecting pyrite could provide sites of precipitation for the clustered (nano)particles; Au and LMCE were either remobilised from the initial pyrite or introduced from the fluid.

In a recent study of arsenian pyrite textures correlated with zonation trends in sediment-hosted gold deposits affected by metamorphism, has shown that weakly-bonded elements include Te and Bi and are released during pyrite recrystallisation (Large et al., 2009).

Bi-chalcogenides as gold-carriers

The paragenetic association of gold minerals with Bi-tellurides and -sulphosalts led Ciobanu et al. (2009b) to assess whether Bi-chalcogenides might carry gold. *In-situ* laser-ablation inductively-coupled mass spectroscopy (LA-ICPMS) analysis of a range of Bi-chalcogenides from 28 worldwide occurrences (including epithermal, skarns, intrusion-related and orogenic gold) has shown that they can indeed carry gold at concentrations of up to thousands of ppm (in the same range as arsenian pyrite). Hitherto-neglected gold locked within these minerals can contribute to low gold recoveries in deposits in which these minerals are abundant. Trace element trends suggest that Au incorporation is underpinned by statistical substitution of Ag and Pb into the Bi octahedron in the Bi-telluride structures. Gold entrapment may also be linked to the presence of Van der Waals bonds at chalcogen-chalcogen contacts (Ciobanu et

al., 2009a), which act as structural traps for gold nanoparticles. Altaite (PbTe) is also identified as a Au carrier (Vikentyev, 2006; Ciobanu et al., 2009b).

Ciobanu et al. (2009b) have also shown that trends of Au content in Bi-chalcogenides, if well understood in the context of phase relationships, are useful to define field zonation, overlapping events and allow discrimination between processes involving equilibrium or disequilibrium, i.e., crystallisation from melts or scavenging from fluids, respectively.

Concluding remarks

1. Whereas telluride/selenide-trace mineralogy is widespread in deposits of many types (MVT deposits are a notable exception), deposits in which Au(Ag)-tellurides form a part of the exploitable ore, are appreciably rarer (only some dozens are known at present).
2. Although Te and Se are both chalcophile elements and share a geochemical affinity with Au, they occur together mainly when Ag and/or Bi are present (e.g., phases from the tetradymite and/or aleksite groups). Formation of selenides of other elements such as Cu or Ag requires acidic (e.g., high-sulphidation systems) or reducing environment (e.g., black shales, uranium deposits).
3. Telluride-rich gold deposits, in which Au(Ag)-tellurides are typical species, stand out as 'mineralogical anomalies' (>10 different Te- and/or Se-bearing species present). Such deposits can be related to specific metallogenic environments. Known deposits fall broadly into two categories with respect to tellurium source:
 - a. Deposition from Te-rich fluids generated in specific local and/or regional settings, e.g., Te-enrichment in the mantle where alkaline magmas are generated, due to subduction of Te-rich ocean-floor sediments, as seen around the Pacific Rim.
 - b. Deposition from Te-bearing fluids, where the concentration of Te would normally result in, at best, generation of a Te-enriched trace telluride signature, but where destabilisation and co-precipitation of Te with Au(Ag)-species from the fluids is enhanced by the action of sustained phase-separation processes in a depositional trap, e.g., fault-valve mechanism, one of the tectonic models for orogenic gold systems (at Golden Mile, Kalgoorlie, W.A. or Ilomantsi and Pampalo, Finland, etc). The same mechanism may operate during duplex-fault rotation which controls formation of the epithermal vein-mesh in the buried volcano at Săcărîmb (Romania). In the absence of a depositional trap, formation of low-grade Te-Au(Ag)-rich caps at the top of gold systems is, instead, predictable.
4. Considering the vapour-phase affinity of Te, pressure-variation or multistage boiling processes rather than fluid-rock interaction, cooling or mixing, are more likely to fulfil the conditions required under point 3b. Vapour-phase release during magmatic brecciation is another viable scenario. This has been invoked by some authors for bonanza pipes at Kochbulak (Uzbekistan) and also for telluride-rich breccia pipes at Cripple-Creek (USA).
5. The convergence between the thermodynamic stability conditions for Au- and Ag-tellurides and native tellurium with those offered by an epithermal environment (hematite, pyrite stability; high

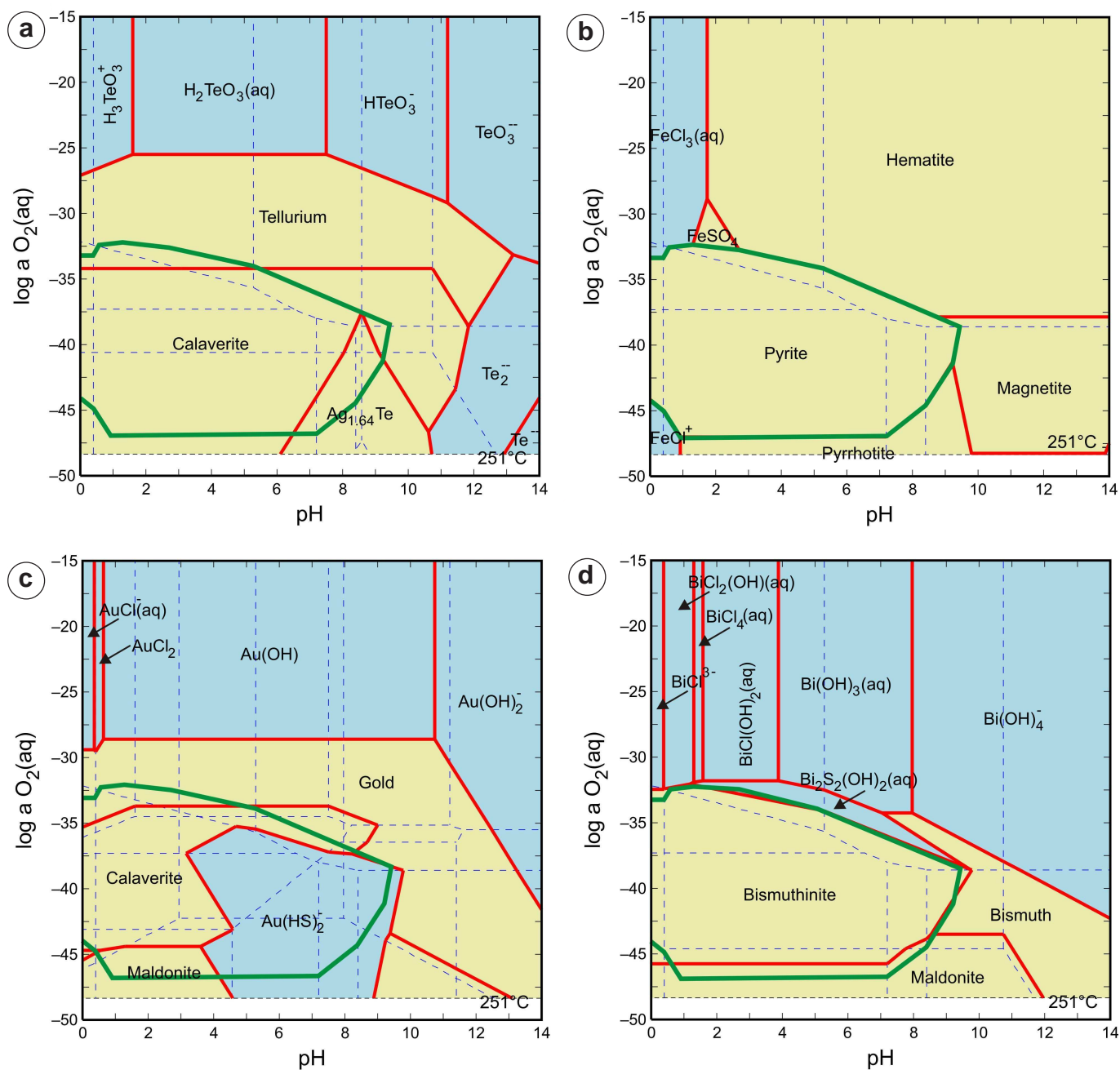


Figure 6. Diagrams in $\log a O_2$ vs. pH space showing the coincidence between the stability fields of Te-Au-Ag-Bi-minerals and iron sulphides/oxides, and related aqueous species, at 251°C. (a) Te-bearing minerals (native tellurium, calaverite (Au_2Te) and the phase $Ag_{11.64}Te$ (~stützite); (b) Fe-bearing minerals (pyrite, hematite, magnetite and pyrrhotite); (c) Au-bearing minerals (native gold, maldonite (Au_2Bi) and calaverite); and (d) Bi-bearing minerals (native bismuth, bismuthinite and maldonite). Conditions: $\log a Au^+ = -9$ (on a), -6 (on c) and -10 (on d); $\log a Bi(OH)_{3(aq)} = -12$ (on c) and -6 (on d); $\log a H_2TeO_{3(aq)} = -3$ (on a) and -12 (on c); $Ag^+ = -15$ (on a); $\log a Cl^- = -1$; $\log a H_2O = 0$; $\log a SO_4^{2-} = 0$ and $\log a Fe^{2+} = 0$. These conditions were chosen to illustrate the appearance of Te-, Au-, Ag- and Bi-minerals as discussed in the text. Note that at sulphur concentrations high enough to show an extended pyrite field in (b), the species $Au(HS)_2$ and bismuthinite also have large stability fields (on c and d, respectively). An arbitrary pressure of 500 bar is taken. The pyrite field (in green) from (b) is superimposed on the other diagrams. Note the broad overlap between pyrite and calaverite in (a) and (c), and between pyrite and bismuthinite in (d). In (a), tellurium is stable at more oxidizing conditions than calaverite, plotting at the upper limit of pyrite and extending into the hematite field. In the presence of Bi (c and d), maldonite and bismuth are stable at more reducing conditions (pyrrhotite and magnetite fields). At $\log a SO_4^{2-} = 0$ used for the diagrams, bismuthinite is stable. Thermodynamic data used for Au-, Bi- and Te-minerals and -species, except for native Au, derive from the updated thermodynamic database of the Minerals, Metals and Solutions Group, South Australian Museum; see also data depository in Tooth et al. (2008) for maldonite and bismuthinite. Data for native Au and iron minerals are from the GWB default database (thermo.com.V8.R6), oct94. Since Bi-tellurides are not included in the database, they are not shown on diagrams (a) and (d); work is in progress to address this.

oxidation state; Fig. 6a-c) explains the greater abundance of Au-telluride deposits in such geological settings. Similar neutral to weakly-alkaline pH, low-salinity fluids are also typical for orogenic gold systems, especially at epi- to mesozonal crustal levels, e.g., Sunrise Dam, Golden Mile, Kalgoorlie (Western Australia).

6. Telluride-rich gold deposits in which phases from the tetradymite group (those with $\text{Bi} > (\text{Te}, \text{Se}, \text{S})$) are the dominant tellurides, and these co-exist with Au-Bi compounds (maldonite and jonassonite) instead of Au(Ag)-tellurides, are constrained to reduced depositional environments (pyrrhotite, magnetite stability; low oxidation state). Native bismuth and maldonite are stable at reduced conditions (Fig. 6b-d). This is often concordant with conditions attained during fluid-rock interaction, mixing or discharge at redox fronts, processes that are most typical during stages of gold deposition in skarns and intrusion-related gold deposits, as well as in some orogenic gold and VHMS systems.
7. Tellurides represent ideal melt scavengers for gold, if LMCE melts are either exsolved directly from hydrothermal fluids or are formed during metamorphic deformation. Coupled dissolution-precipitation reactions, if assisted by LMCEs, will lead to crystal-scale remobilisation of gold within Au carriers such as pyrite, even in the absence of As, e.g., in the aforementioned Chinese deposits. Gold remobilises with LMCE-rich signatures are present, for example, in metamorphosed deposits of different genetic types including VHMS, throughout the Fennoscandian Shield.
8. Comparative analysis of paragenesis, textures and compositional variation in tellurides/ selenides, especially those with crystal-structural modularity, has an hitherto unexploited petrogenetic potential to reveal: (i) interaction with fluids, e.g., Au scavenging and entrapment in Bi(Pb)-tellurides; (ii) changes in the chemistry/ rates of fluid infiltration, e.g., nagyágite; (iii) equilibrium state in a given assemblage, e.g., homology in the tetradymite group.

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