EPITHERMAL AU-AG- BI -TE MINERALIZATION IN THE SE AFAR RIFT, REPUBLIC OF DJIBOUTI

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Epithermal gold mineralization were recently discovered in the SE part of the Afar volcanic Triangle, Republic of Djibouti. Mineralization generally occur as veins and are mainly associated with acidic volcanic intrusions along the faults at the edges of graben structures established during the last 4 Ma. Sixty samples were analyzed from 4 different sites representative of 4 major volcanic events. Mineralogical analyses based on optical reflected light microscopy, X-Ray diffractometry, X-Ray fluorescence, inductively coupled plasma mass spectroscopy, electron microprobe and scanning electron microprobe, led us to identify different types of gold mineralization (i) native gold, electrum, hessite ($Ag_{1,98}Te_{1,02}$), tetradymite ($Bi_{1,99}Te_{2,13}S_{0,88}$) and sulfides (chalcopyrite, pyrite, sphalerite, galena, bornite, digenite, marcasite) in massive quartz breccias and banded chalcedony, (ii) gold, electrum, pyrite, hematite, magnetite, traces minerals (argentite) and adularia in banded chalcedony. Gold-telluride associations are generally regarded as characteristics of low sulfidation epithermal gold deposits. Te is found in three different forms (i) Te occurs as invisible or submicrometer-size inclusions of hessite in pyrite where a high content (up to 41 wt %) of Te were measured; (ii) as visible independent telluride grains (hessite ($Ag_{1,98}Te_{1,02}$) and tetradymite ($Bi_{1,99}Te_{2,13}S_{0,88}$)) disseminated in quartz and (iii) as grains of hessite up to 50 µm with pyrite inclusions (10 µm). Tellurium is preferentially transported in a gas phase and may result from condensation of magmatically derived $H_2Te_{(g)}$ and $Te_{(g)}$ into deep-level of chloride waters [1]. At Hes Daba site, sulfur isotopic ratios of pyrite indicate values of $\delta^{34}S$ between

–9.20‰ to 1.45 ‰. The $\delta^{34}S$ values of pyrite close to 0‰ are typically reported to volcanic rocks and the negative $\delta^{34}S$ values classically indicate a source of sulfur from magmatic fluids. Thus in our samples telluride mineralization and sulfur isotopic studies of sulfides suggest that gold can be related to a magmatic fluid contribution and is precipitated in the deep high temperature part of the epithermal system.

[1] Cooke & McPhail., 2001, Econ Geol, v 96 pp 109-131

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INTRODUCTION

Telluride minerals have long been regarded as rare mineral. The modern microanalytical methods have changed considerably this view (Oberthur and Weiser, 2008). Gold-telluride associations are typically regarded as characteristic of epithermal gold deposits as defined by Hedenquist et al. 2000 and Sillitoe and Hedenquist 2003. The most common occurrence of Te is the low sulfidation type that is spatially associated with alkaline igneous rocks (Voudouris, 2006). A Well known example is (i) the Emperor Mine, Fiji, (Ahmad et al 1987, Pals and Spry, 2003); and (ii) the Cripple Creek, Colorado (Thompson et al 1985). Telluride minerals can also be related to calc-alkaline rocks and intermediate sulfidation deposits such as the Baguio District, Philippines (Cooke and McPhail 2001), the Golden Quadrilateral, Romania (Cook and Ciobanu 2004); high sulfidation deposits at El Indio, Chile (Jannas et al 1990) and the mixed high-intermediate sulfidation deposit at Kochbulak, Uzbekistan (Kovalenker et al 1997). Te-bearing minerals offer potential for the understanding of the physicochemical conditions of ore formation because they are valuable indicators of changes in temperature and sulfidation state (Cook and Ciobanu, 2002). In fact, hydrothermal mineral ore deposits is the results of changes of physical and chemical variables such as temperature, pressure, acidity, redox, salinity and concentrations of sulfur, carbon and ligands (Cooke and McPhail, 2001).

In term of paragenetic assemblages; Te deposition is classically restricted to one or two stages that always follow initial deposition of sulfides (e.g. pyrite, chalcopyrite, sphalerite and galena; Afifi et al. 1998b).

The occurrence of Au together with Bi-telluride has long been observed in many ore deposits. Marcoux et al. (1996) considered this association as pathfinders for gold in the stringer zones of massive sulfide deposits (Iberian Pyrite Belt).

In this study, we report the first Au-Ag-Bi-Te-bearing ores, detailed mineralogical and chemical studies of gold-telluride minerals from 2 different sites representative of two major volcanic events consisting, in ascending stratigraphic order, of (1) the 15-11 Ma Mabla acidic series (Ali Adde), and (2) the 3.3-1.0 Ma Stratoid basaltics series (Hes Daba). In order to understand the conditions of formation of ore deposits, we used sulfur isotope.

GEOLOGICAL SETTINGS

The Afar Depression resulted from the intersection of the Red Sea, Gulf of Aden and Ethiopian rift axes during the Miocene (Fig. 1). The main expression of the crustal rifting process in Afar is, in addition to extensional faulting, the bimodal magmatism. The volcanic activity started as early as 30 Ma with the emplacement of trap volcanism in Yemen and Ethiopia (Barberi and Varet 1977). The first evidence of synrift magmatism in SE Afar of the Republic of Djibouti, is the 28-19 Ma Ali Sabieh mafic complex, and the more widespread Mabla rhyolites which erupted at 15-11 Ma (Barberi et al. 1975; Varet and Gasse 1978; Gadalia 1980). The subsequent volcanic events were essentially basaltic, with locally minor acidic differentiates. They include 1) the Dalha (9-4 Ma), 2) the Stratoid (4-1 Ma), and 3) the Gulf (3-1 Ma) series (Gaulier and Huchon 1991). Dominantly felsic activity in a restricted area involving the Arta transverse zone (Fig. 2) is recorded by the Ribta volcanic products (4-3 Ma). The Stratoid trap-like lavas cover two thirds of the Afar depression and are commonly regarded as incipient oceanic crust (Barberi et al. 1975; Robineau 1979). There are numerous felsic silica centers near Lake Abhe (2 and 5 Ma): Babba Alou massif (1 and 8 Ma), and Egeraleyta massif (<1 Ma), immediately south of the Asal rift (Gaulier and Huchon 1991).

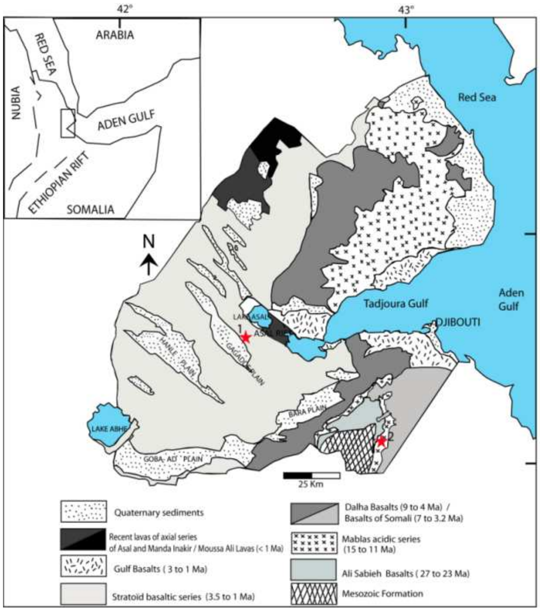

Figure 1 : Schematical geological map of the Republic of Djibouti (SE Afar Triangle) after Piguet & Velutini (1995). Red stars (and corresponding numbers) are the two hydrothermal sites studied in this work. 1 Hes Daba 2, Ali Addé.

METHODS

Polished-thin sections of ore samples were examined with a reflected-transmitted light microscope at magnification up to 1000 in dry air and oil. Additional studies were performed, using: (1) X-Ray Diffraction analyses to determine major minerals in gangue and alteration zones and (2) X-ray elemental mapping using CAMECA SX100 electron-microprobe with PAP correction program (Pouchou and Pichoir, 1984). To search telluride minerals, operating conditions consisted in accelerating voltage at 25 KV, beam current at 20 nA and beam size at 1 μm^3. The present work has been conducted at “Laboratoire de Géochimie et Métallogénie, IFREMER, Brest".

Sulfur isotopes were analyzed in mineralized samples at “Laboratory of Stable Isotopes, Royal Holloway University of London”. They were performed with the procedures using EA-IRMS which were developed by Grassineau et al. (2006).

RESULTS

From geological and mineralogical view, the two sites with Au-Ag-Bi-Te mineralization have been broadly detailed in Moussa et al. 2010 (submitted). Short descriptions of the hydrothermal alteration and mineralization of the areas studied are presented below and the results are summarized in Table 1.

Hes Daba

The mineralization is hosted by trachytic lavas and quartz constitutes the principal gangue in the veins. Early mineralization consists of sulfides (chalcopyrite, pyrite sphalerite, galena, bornite, digenite, covellite and marcasite) as disseminations and fracture fillings in quartz veins. The late-stage of mineralization is mainly composed of iron oxides (goethite and hematite). Late banded and massive quartz ± carbonate veins postdate and overprint a quartz stockwork. Telluride minerals have not yet been observed in this area. Fault controlled silicic alteration has 130 NW direction. Telluride minerals are expressed as (i) visible independent telluride grains (hessite ($Ag_{1,98}Te_{1,02}$)) disseminated in quartz (Fig. 2).

In term of sulfur isotope, pyrite is characterized by values ranging from -9.20 to 1.45 ‰.

Ali Addé

Pollymetallic sulfides such as chalcopyrite, pyrite sphalerite, galena, bornite, digenite, marcasite in massive quartz breccias; banded chalcedony and native elements; constitute the main expressions of the mineralization. Two stages of mineralization have been distinguished: initial deposition of sulfides followed by telluride minerals. Te is found in different forms (i) Te occurs as invisible or submicrometer-size inclusions of hessite in pyrite, (ii) as visible independent telluride grains (hessite ($Ag_{1,98}Te_{1,02}$), tetradymite ($Bi_{1,99}Te_{2,13}S_{0,88}$) disseminated in quartz and (iii) as grains of hessite up to 50 µm (Fig.2) with pyrite inclusions (10 µm). Native Te grains has been observed in this site. $\delta^{34}S$ values of pyrite correspond to -2.58 and 5.87 ‰ respectively.

Table 1: Microprobe analysis results of selected sulfide and telluride minerals (w %).

	Cu	Fe	Bi	Ag	S	As	Te
Pyrite FeS_2		45.97			53.32		
Hessite ($Ag_{1,98}Te_{1,02}$)				62.55			38.30
Tetradymite ($Bi_{1,99}Te_{2,13}S_{0,88}$)			56.96		3.86		37.12
Native Te							100

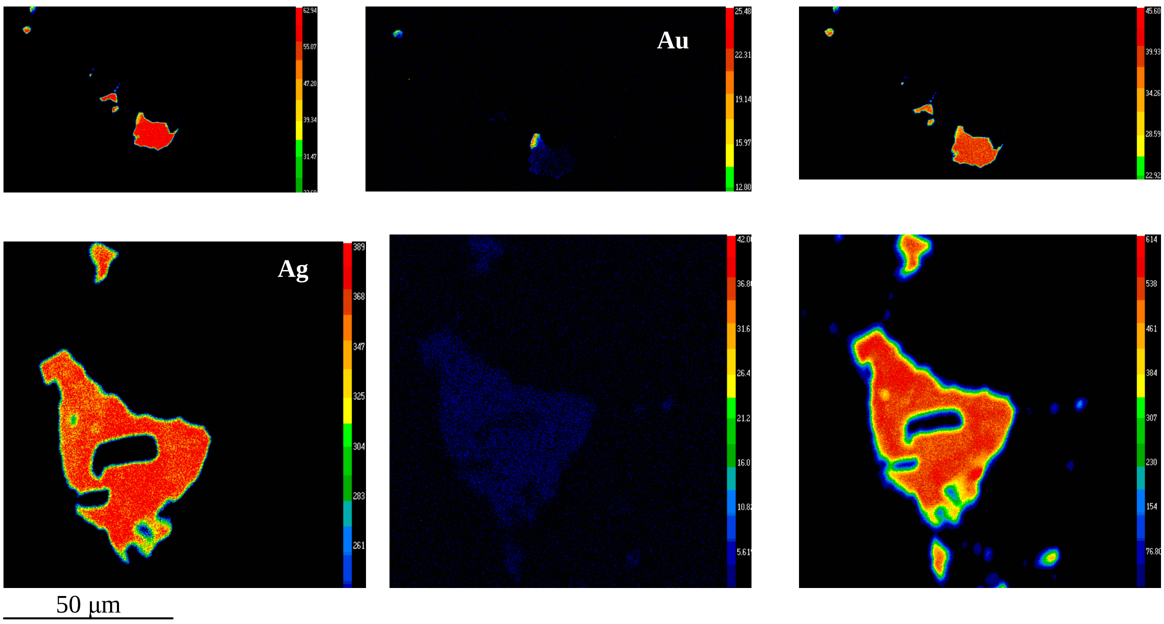

Figure 2: Electron Microprobe images illustrating Au-telluride assemblage in hydrothermal quartz veins from acidic volcanic lavas. A : Au-Ag-Te assemblages from Hes Daba hydrothermal site (Stratoid Fm). B : Ag-Te assemblage from Ali Addé hydrothermal site (Mabla Fm). Au lack in this assemblage.

DISCUSSION AND CONCLUSIONS

Mineralogical studies of the two hydrothermal sites show two major paragenetic sequences:

- High temperature paragenesis mainly composed by native gold, electrum, hessite, tetradymite, native tellurium and sulfides (chalcopyrite, pyrite, sphalerite, galena, bornite, digenite, marcasite) in massive quartz breccias and banded chalcedony.
- Lower temperature assemblage characterized by iron oxides (goethite, hematite, magnetite) in massive and breccias quartz.

Telluride minerals have long been considered, as a key of the understanding of the physicochemical conditions of ore formation. In fact, Zhang and Spry 1994 calculated the stability of (i) aqueous tellurium species and (ii) calverite and hessite. They conclude that

Te_2^{2-} is the most common important aqueous tellurium species in equilibrium with native tellurium in epithermal deposits and the stability of hessite covers most conditions of ore formation (e.g. oxidizing to reducing, and acid to alkaline) and is a less useful indicator of ore-forming conditions. Cooke and McPhail 2001 indicate that in Acupan, Philippines; the 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)-telluride minerals.

By contrast, the occurrences of bismuth telluride have widely investigated by many workers. For Ciobanu et al 2005; bismuth telluride provides a “melt-precipitates window” for the formation of the main types of Au deposits. They suggest that Bi-rich melt-precipitates are constrained to reducing fluids and temperature >300°C whereas Te-rich form from oxidized fluids with temperatures of at least 400°C. Ciobanu et al. 2005; Tooth et al. 2008 defined that Bi-Te has the role of Au-scavenging in many gold deposits.

However in the most interpretation; Te is considered to be transported as aqueous species in epithermal fluids (Ciobanu et al. 2006).

The mineralogical assemblages of Hes Daba and Ali Addé sites, possess the highest sulfide content (chalcopyrite, pyrite, sphalerite, galena, bornite, digenite, marcasite). Bi and Te are also present. $\delta^{34}S$ values of sulfides spread between –9.2 to 5.87 ‰. The δ 34S values of pyrite close to 0‰ are typically reported to volcanic rocks whereas the negative $\delta^{34}S$ values of sulfides can be explained by the disproportionation of magmatic SO_2 that causes the enrichment of ^{32}S in the sulfides.

The occurrences of Bi-Te-bearing minerals and the negative values of sulfur isotopes suggest that gold can be related to a magmatic fluid contribution and is precipitated in the deep high temperature part of the epithermal system.

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