

NEW COMPOSITIONAL DATA CONCERNING AU-AG ALLOYS FROM THE NORTHERN PART OF ROȘIA MONTANĂ DEPOSIT, METALIFERI MOUNTAINS, ROMANIA

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Abstract: This paper presents the results of the new investigations by optical microscopy, scanning electron microscopy (SEM) and electron-probe micro-analysis (EPMA) performed on samples collected from Orlea adit from Roșia Montană Au-Ag deposit, Romania. Based on composition, three types of Au-Ag alloy were described. At Roșia Montană, galena, pyrite, chalcopyrite and sphalerite are intimately associated with gold, electrum and tellurium-bearing minerals. At Roșia Montană, the precipitation of Au-Ag alloy with variable composition can be assigned to compositional changes of the parent hydrothermal solutions during deposition due to boiling, fluid dilution and cooling.

Keywords: electrum, gold, Roșia Montană, Orlea, Metaliferi Mountains.

Introduction

The great variety of mineral deposits of the Metaliferi Mountains reflects the complex geotectonic environments and the intimate relationship between igneous and hydrothermal activities that have taken place during Miocene. These events are responsible for the formation of a very rich mining district so-called the "Golden Quadrilateral" (Fig. 1). This is one of the most productive mining districts of Europe for over 2000 years, concentrating over 60 gold deposits in about 900 km². Due to the Golden Quadrilateral, for many years, Romania was one of the main gold producers of Europe. Roșia Montană Au-Ag deposit is located in the northeastern part of the Metaliferi Mountains (Romania), in the Roșia-Bucium metallogenetic district. It is one of the largest Au-Ag deposits of Europe, being discovered during Roman times, known under the name of Alburnus Maior.

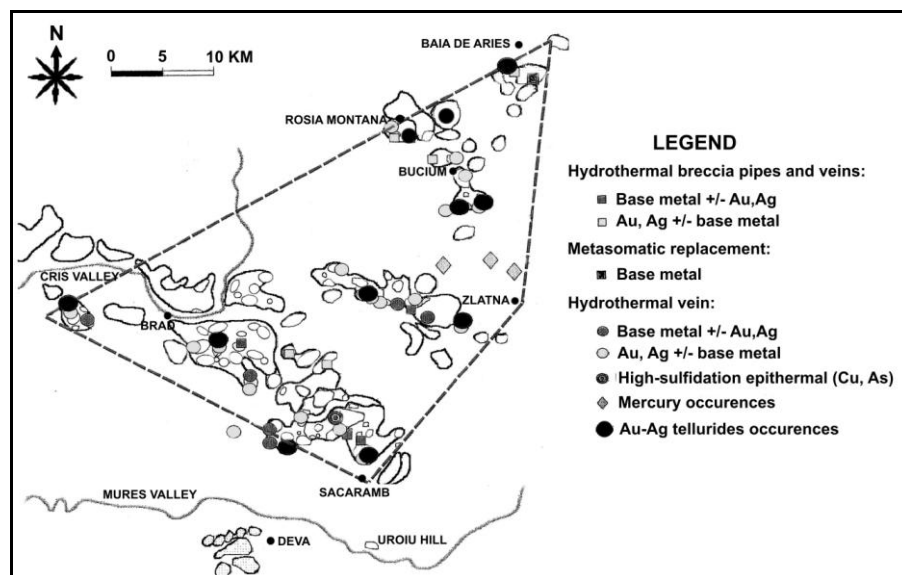


Fig. 1. Sketch map of the Golden Quadrilateral (after Udubașa et al., 2001)

"electrum" has been used to refer to Au-Ag alloys of a compositional range between 20 and 80 wt % gold, based on the classification of Boyle (1979). This distinction is ignored in the present paper, and the term of Au-Ag alloy is used as a synonym for all Au-Ag alloys present in our samples, including electrum, so-called "native" gold and "native" silver.

The remained reserves are estimated at 214.9 million tons of ore, with average contents of 1.46 g/t Au and 6.9 g/t Ag, representing 10.1 million ounces (314 t) Au and 47.6 million ounces (1480 t) Ag (as from Roșia Montană Gold Corporation).

This paper describes the occurrence and chemistry of Au-Ag alloy and its distribution inside the analyzed ore veins in order to understand the factors that led to deposition from the hydrothermal fluids.

Traditionally, the term

Geological setting

The Metaliferi Mountains in Romania cover an area of about 11000 km² situated in the South Apuseni Mountains.

The calc-alkaline Miocene magmatism in the South Apuseni Mountains was related to transtensional and rotational tectonics being focused within NW-SE oriented extensional basins (Roşu et al, 2004) that became hosts of major metallogenetic units strongly related to the extensional stress fields.

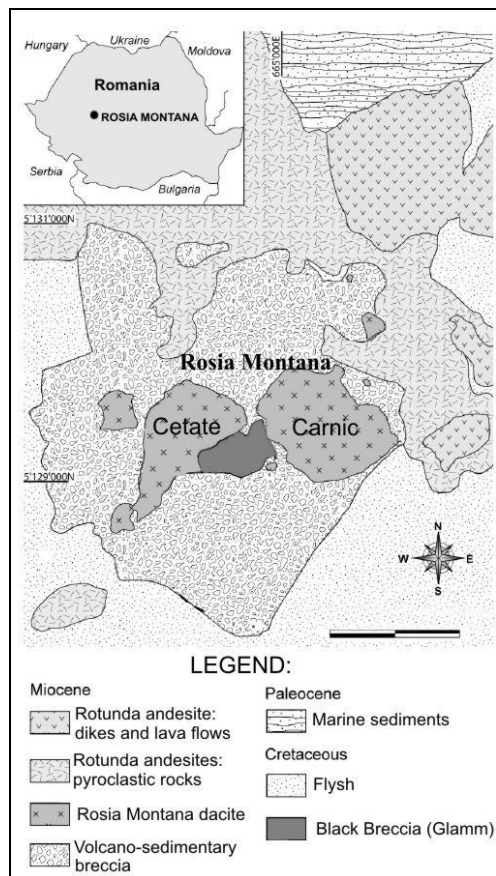


Fig. 2. Roşia Montană sketch map (after Kouzmanov et al., 2005)

The Neogene calc-alkaline magmatic rocks are widespread in the Metaliferi Mountains and host the major deposits of this region. The volcanic and intrusive activity took place, in three episodes, between 14.7 and 7.4 Ma and they were accompanied by metallogenetic processes (Borcoş et al. 1986, Roşu et al. 2004) resulting in the following metallogenetic districts: Roşia Montană-Bucium-Baia de Arieş, Brad-Săcărâmb-Deva and Zlatna-Stănişia.

Roşia Montană deposit (Fig. 2) is a breccia hosted epithermal system, spatially related to the Roşia Montană dacite bodies intruded during the Neogene, being followed by hydrothermal activity. The ore deposition at the Roşia Montană deposit evolved from an early Au-(Ag) low-sulfidation character to a late Ag-Te-(Ge-Au) intermediate-sulfidation character, and may be correlated with late magmatic pulses (Tămaş, 2010).

Alterations are widespread, four major types being distinguished by macroscopic observations and optical microscopy on transmitted light: phyllic, silicification, propylitic and argillic.

Materials and methods:

For the purpose of the present study, we have used 50 samples collected from the Orlea gallery, situated in the northern part of Roşia Montană Au-Ag deposit, during several field campaigns.

The optical microscopy observations in reflected light were made using a Nikon Eclipse LV100POL microscope with an attached Leica DFC 420c digital camera for the photomicrographs.

Following reflected light microscopy to identify the ore-mineral assemblages, the polished sections were studied with a JEOL JSM 6400 Scanning Electron Microscope (SEM) equipped with EDX detector at Ecole Nationale Supérieure des Mines, Saint Etienne, France. Reconnaissance quantitative compositional data were determined using a Cameca SX 50 electron microprobe with an acceleration voltage of 19.98 kV at G2R Laboratory (University of Nancy, France). Later analyses were done using Cameca SX 100 electron microprobe with an acceleration voltage of 15kV at the Magmas and Volcans Laboratory in Clermont-Ferrand, France.

Measurements were performed on polished sections coated with 2nm of carbon using EMS150R ES Rotary-Pumped Modular Coating Systems at Ecole Nationale Supérieure des Mines, Saint Etienne, France.

Results and discussions:

During optical microscopy observations on polished sections in reflected light and with the Scanning Electron Microscope, we could identify the following ore minerals (Fig. 3): gold, electrum, pyrite, chalcopyrite, galena, sphalerite, marcasite, tetrahedrite, arsenopyrite, magnetite, tellurium-bearing minerals (hessite, altaite, sylvanite, petzite, cervelleite, alburnite, argyrodite) and uytenbogaardtite.

Quartz, carbonates (calcite, rhodocrosite) and adularia occur as gangue minerals.

In reflected light, it was observed that gold grains present various shades of yellow due to the variable composition and gave information about the presence of electrum (Au-Ag alloy) with different Au:Ag ratio. Later studies showed that almost pure gold is dark yellow. Electrum shows light to very light yellow nuances due to the presence of different amounts of Ag.

The Au-Ag alloys associated with pyrite, chalcopyrite and sphalerite present three different variable compositions as follows: 1. Gold-rich alloy, where Au concentration ranges between 65 and 88 wt%; 2. Alloy with Au-Ag concentrations in almost equal proportions, with Au ranging between 45 and 55 wt% and 3. Silver-rich alloy where Au concentration is between 22 and 35 wt% (Figs. 4 and 5). The SEM elemental mapping showed that the concentration of the two precious metals is variable inside a grain but with no clear pattern (Figs. 4-6).

We noticed that Au-rich grains (native gold) are usually associated with sphalerite and have Au content higher than 85 wt% (Fig. 6).

We could separate the following mineral assemblages in which gold occurs: Au-Ag alloy with pyrite and sphalerite, gold in sphalerite, Au-Ag alloy with chalcopyrite and pyrite, Au-Ag alloy in carbonates, gold in pyrite and gold and gold-silver tellurides in pyrite.

The most important depositional mechanism for gold in electrum is the boiling of ore fluids. This causes an increase of pH. Silver deposition in electrum is caused by this pH change as well as decreasing temperature, H₂ degassing and dilution (decrease of Cl concentration) (Shikazono, 2003).

Galena, sphalerite and chalcopyrite also precipitate due to the increase of pH induced by the breakdown of base metal complexes with Cl, accompanied by boiling (Shikazono, 2003).

Fluid inclusion studies indicate the dilution of the magmatic fluids (Wallier et al., 2006), the mixing of boiled fluid with meteoric water causing the deposition of gold and electrum in the Roşia Montană hydrothermal system. The abrupt cooling of the hydrothermal fluids caused the oversaturation in dissolved components and the precipitation of ore minerals.

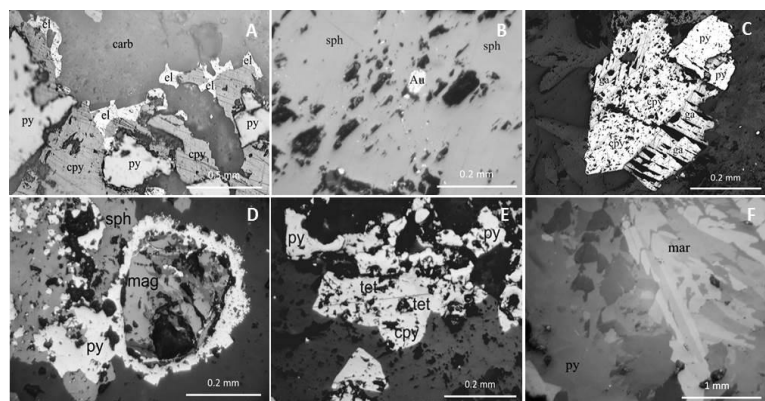


Fig. 3. Photomicrographs of the polished sections at the optical microscope. A. electrum-pyrite-chalcopyrite-carbonates assemblage, // nicols; B. gold in sphalerite, // nicols; C. pyrite-chalcopyrite-galena assemblage, // nicols; D. magnetite-sphalerite-pyrite assemblage, // nicols; E. pyrite-chalcopyrite-tetrahedrite assemblage, // nicols; F. pyrite-marcasite, X nicols. Abbreviations: Au-gold, carb-carbonates, cpy-chalcopyrite, el-electrum, ga-galena, mag-magnetite, mar-marcasite, py-pyrite, sph-sphalerite, tet-tetrahedrite.

Fig. 4. SEM photomicrograph of electrum-sulfides-carbonates assemblage (left) and elemental mapping for Au, Ag, Cu and Fe of the sample (right) showing the different content in Au and Ag of electrum grains.

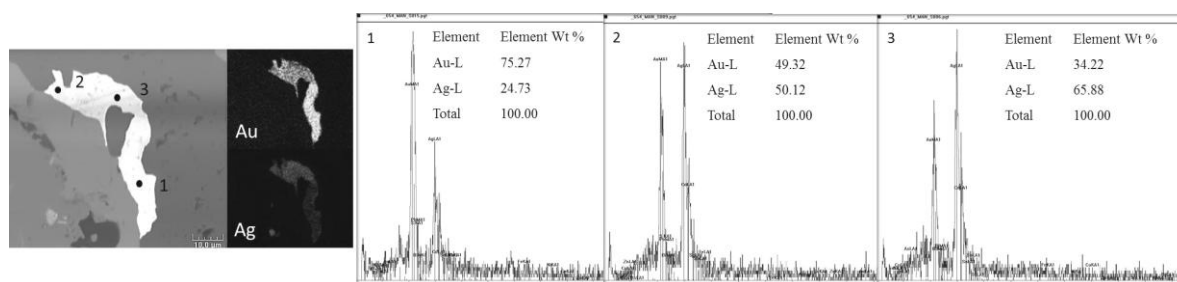
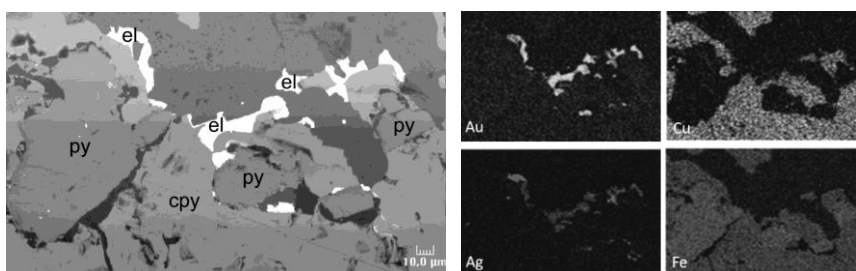


Fig. 5. SEM photomicrograph and elemental mapping for Au and Ag (left) of the electrum grain. SEM-EDX and EPMA analysis showing three different compositions within the electrum grain.

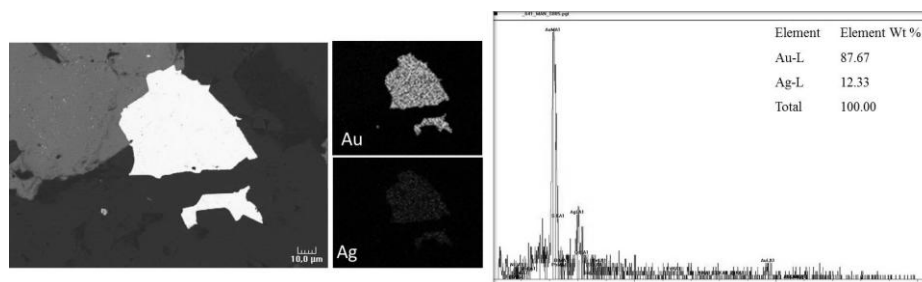


Fig. 6. Photomicrograph and elemental mapping for Au and Ag of a native gold grain associated with sphalerite (left). SEM-EDX and EPMA analysis of the grain (right).

Conclusions:

The precipitation of Au-Ag alloys with different Au:Ag ratios at Roșia Montană, can be assigned to compositional changes of the parent hydrothermal solutions during deposition due to boiling, fluid dilution and cooling. The resulting alloys may be Au rich or Au poor, depending on the temperature, chemical environment and mechanisms of ore deposition.

At Roșia Montană, the metallic load of the hydrothermal fluids is reflected by the wide range of ore minerals precipitated in veins, disseminated or forming stockworks: gold, electrum, pyrite, chalcopyrite, galena, sphalerite, marcasite, tetrahedrite, arsenopyrite, magnetite, tellurium-bearing minerals (hessite, altaite, sylvanite, petzite, cervelleite, alburnite, argyrodite) and uytenbogaardtite.

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