STABLE ISOTOPE STUDY AND ORIGIN OF ALUNITE FROM ADVANCED ARGILLIC ALTERATION SYSTEMS IN BULGARIA

Catherine Lerouge[1], Christine Flehos[1], Angel Kunov[2], Atanas Hikov[2], Sylvina Georgieva[2], Jean-Luc Lescuyer[1], Rumen Petrunov[2], Nadezhda Velinova[2]

[1] BRGM, BP 6009, 45060 Orlйans cйdex 2, France, e-mail address: c.lerouge@brgm.fr
[2] Bulgarian Academy of Sciences, Geological Institute, Sofia, Bulgaria, e-mail address: angel@geology.bas.bg

Introduction

The zones of advanced argillic alteration (AAA) are major exploration targets for shallow high-sulphidation Cu-Au epithermal and deeper porphyry-type deposits. The formation of alunite results from the alteration of host volcanic and volcano-sedimentary rocks by acidic, sulphate-bearing hydrothermal fluids (Hemley et al., 1969). These fluids may be generated in different ways: magmatic-hydrothermal, steam-heated, magmatic steam and supergene environments, each one characterised by specific mineral assemblages and stable isotope signature of alunite (Rye et al., 1992). AAA alunites from major high-sulphidation Cu-Au ore deposits are dominantly magmatic-hydrothermal or magmatic-steam.

Bulgaria presents an interest, because of the discovery of at least thirty occurrences of alunite in various environments (Velinov et al., 2003). Alunite occurrences are hosted by volcanic and volcano-sedimentary rocks emplaced in a volcanic arc context at two stages of evolution of the Carpathian-Balkan belt (Dabovski et al., 1991), corresponding to the two metallogenic provinces of Bulgaria: the Late Cretaceous Srednogorie and the Palaeogene Rhodopes.

This study is based on mineralogy of alteration and on isotope systematic of alunite from nine occurrences of various type chosen among each district of both metallogenic provinces, for their different types: high-sulphidation epithermal deposit of Chelopech, porphyry copper/epithermal deposits of Assarel and Petelovo, subeconomic deposits spatially associated with low-sulphidation mineralization (Breznik, Madjarovo) and uneconomic occurrences of Ropotamo, Stomanovo, Boukovo and Sarnitsa. The aim was to test the potential use of combined mineralogy and stable isotopes of alunite to discriminate "fertile" from "barren" alunite.

Mineralogical and chemical data

Twelve samples of advanced argillic quartz + alunite alteration coming from nine locations were selected among one hundred collected rocks. In all the samples, the volcanic texture of the altered rock was preserved, although the mineralogy of the whole rock was entirely transformed into quartz + alunite with minor other mineral phases - kaolinite, dickite, alumino-phospho-sulphates (APS), diaspore, zunyite, pyrophyllite, pyrite. A late sericitization can be present. In each studied samples alunite and APS were characterised by their morphology, textural relationships and chemical composition (Table 1).

Table 1. Selected mineralogical and chemical data for alunite of the studied occurrences.

Occurrence	Morphology	Contents (wt. %) and peculiarity
Breznik	Tabular crystals and pseudocubic grains	Na_2O - 2.33; APS (Ca/Sr > 1)
Chelopech	Tabular crystals	Na_2O up to 3.05; APS (Ca/Sr > 1)
Assarel	Tabular crystals	Na_2O up to 3.05; APS (Ca/Sr > 1)
Petelovo	Tabular crystals	Na_2O up to 3.05; APS (Ca/Sr > 1)
Ropotamo	Tabular crystals	Na_2O up to 5.32; low Ba, Ca, Sr, and P
Stomanovo	Tabular crystals	Na_2O < 1.9; small P
Madjarovo	Tabular crystals	Na_2O < 0.5; small P
Boukovo	Tabular and pseudocubic grains	Na_2O < 0.5; low P; very fine alunite-APS zoning; rare P_2O_5 up to 17; Ca/Sr < 1
Sarnitsa	Tabular and pseudocubic grains	Na_2O < 0.5; low P; very fine alunite-APS zoning; rare P_2O_5 up to 12; Ca/Sr > 1

Three types of waters were collected during fieldtrip: marine water from Black Sea, meteoric water at Sozopol, 32 m above sea level during a storm, and exhaure water from the Assarel mine.

Isotopic results

Alunite was separated from quartz and other phases by intermediate heavy liquids and punctually purified by HF acid attack (Wasserman et al., 1992). O, H and S isotopes from alunites, sulphides and quartz were measured by gas-source spectrometry at the Laboratory of Stable isotopes and Low Radioactivity of the BRGM, Orlйans, France. Results are reported in unit per mil relative to international standards - V-SMOW for oxygen and hydrogen (Fig. 1) and CDT for sulphur.

Alunites from the Srednogorie belt and from the Rhodopes show quite similar ranges of $\delta^{34}S$ values, respectively from +17.4 to +24.4 ‰ and from +17.0 to +26.3 ‰. These values are consistent with scarce previous data on alunite obtained at Assarel and Pessovets, respectively +18.3 ‰ and +16.1 ‰

(Velinov et al., 1978). The high $\delta^{34}S$ values are classically described for magmatic-hydrothermal alunite (Rye et al., 1992). Pyrites coexisting with alunite in the sample SHD3c from Chelopech and in sample ASS785-63 m from Assarel have $\delta^{34}S$ values respectively of -3.7 and -2.6 ‰. The two coexisting alunite-pyrite pairs from the Assarel and Chelopech ore deposits have alunite-pyrite sulphur isotope fractionations of 21.1 and 26.5 ‰ respectively.

$\delta^{18}O$ of sulphate site of alunites from the Srednogorie belt (from +10.1 to +13.6 ‰) and from the Rhodopes (from +9.7 to +14.9 ‰) also show a quite similar range of values. At Assarel, $\delta^{18}O$ of quartz coexisting with alunite shows a quite similar value than $\delta^{18}O_{SO4}$ of alunite, indicating that this mineral pair may have approached oxygen equilibrium in the Assarel system.

Alunites from the Srednogorie belt show a large range of δD values, ranging between -41 and -11 ‰. Alunites from the Rhodopes are quite similar with a wider range of δD values (-45 to -24 ‰).

$\delta^{18}O$ and δD values of the exhaure water from the Assarel mine are clearly depleted in ^{18}O and D relative to the seawater, and are consistent with values of the meteoric water in the Panagyurishte district. The $\delta^{34}S$ of dissolved sulphates, around -6 ‰, is quite close to $\delta^{34}S$ of sulphides at equilibrium with alunite. That suggests a remobilization of sulphur by weathering processes without isotopic fractionation.

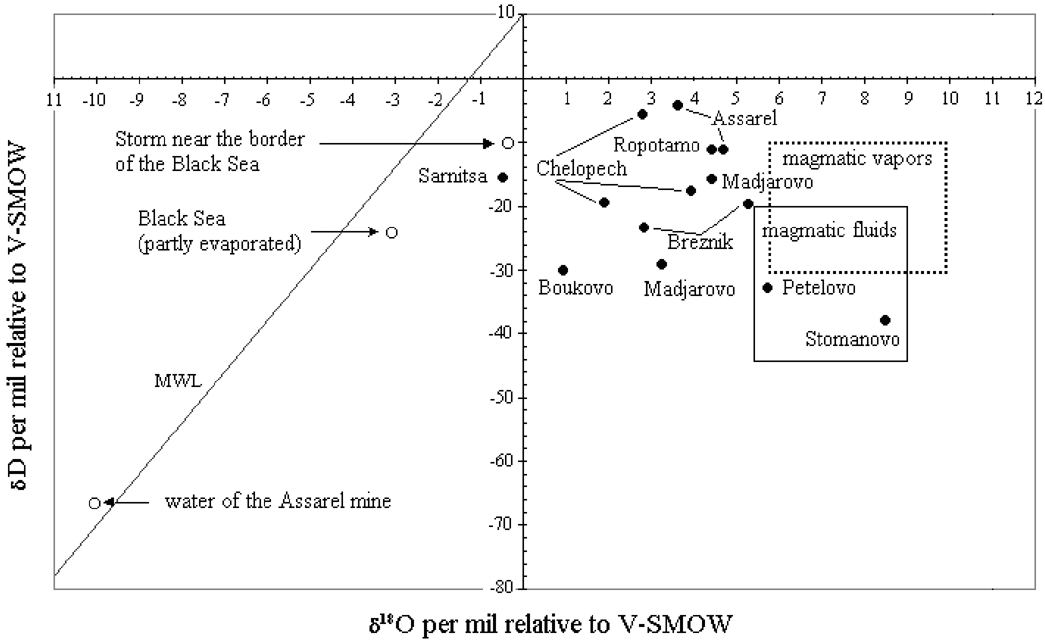

Fig. 1. $\delta^{18}O$ - δD diagram of alunites from Bulgarian occurrences relative to volcanic vapors (after Giggenbach, 1992), primary magmatic waters (after Taylor, 1992) and present-day waters

Formation temperatures of advanced argillic alteration

Formation temperatures of alunite were estimated using combined data from AAA mineralogy, isotopic thermometry and previous microthermometric data.

At Breznik and Chelopech, the alunite is stable with kaolinite/dickite and APS. The predominance of dickite and presence of APS with alunite suggest temperatures around 200-250°C. The isotope temperatures from the pyrite-alunite pair in the sample of Chelopech, of 210-215°C, are in good agreement with the temperature range predicted from the mineral assemblage above and previous works (mineralogical data in Georgieva et al., 2002; sulfur isotopic pyrite-barite thermometry in Velinov et al., 1978).

At Assarel, Petelovo and Madjarovo, alunite is stable with diaspore, pyrophyllite, zunyite. Coexisting pyrophyllite and diaspore suggest temperatures in excess of 285°C and very low pH of 1 to 1.5 (Hemley et al., 1980). Dickite-pyrophyllite-zunyite might be stable at temperatures up to 375°C, according to Berman et al. (1988). The isotope temperatures from the pyrite-alunite pair in the sample of Assarel, at 290-295°C, confirm higher temperatures than for alunite-dickite assemblage. Those data are consistent with previous temperatures obtained in other high-sulphidation ore deposits (e.g. Lepanto: Hedenquist et al., 1998; Rodalquilar: Arribas et al., 1995 and others).At Ropotamo and Stomanovo, the diaspore is the only phase present with alunite and quartz. Mineral assemblage suggests temperatures around 200-300°C. At Boukovo and Sarnitsa, formation temperatures are estimated to be slightly lower around 200°C.

The consistence of temperature data obtained by sulphur isotopic thermometry and by alteration mineralogy show that isotopic equilibrium between sulphates and sulphides is attained and preserved at temperatures as low as 200-250°C. That suggests a magmatic-hydrothermal origin of alunite at

Assarel and Chelopech, given the slow rates of sulphur isotope exchange between aqueous sulphate and sulphide (Ohmoto and Lasaga, 1982) and the common preservation of isotopic equilibrium among sulphate-sulphide in magmatic-hydrothermal acid sulphate systems at the opposite of supergene and steamheated acid sulphate systems (Rye et al., 1992).

Constraints on the source of AAA fluids

(H, O, S) isotopic signatures of alunite combined with mineralogical features from all the studied occurrences, whatever their type, show characteristics of magmatic-hydrothermal systems, according to Rye et al. (1992). Oxygen and hydrogen data indicate that magmatic fluids are dominant with a minor external component in most of the cases. In the Srednogorie belt, magmatic fluids are always dominant and external component is identified as seawater-derived fluids or meteoric water in the vicinity of a sea. Its participation can become important in the ore deposits of Chelopech and Assarel which are two deposits quite near in the Panagyurishte district. In the Rhodopes, external component is also represented by seawater-derived/basin fluid or meteoric water in the vicinity of sea. However the slight D- and ^{18}O- depletion indicates either an evaporation process (shallow water) or a larger distance from the sea. External fluids become dominant at Boukovo and Sarnitsa, superficial systems in which alunite is the most abundant mineral in rocks (more than 50 %) but sulphur has not only a magmatic origin. Sulphur isotopes indicate H_2S/SO_4 ratios > 1 for all the systems in which magmatic fluids are dominant and $H_2S/SO_4 < 1$ at Boukovo and Sarnitsa.

Discussion-Conclusion

All occurrences are formed at temperatures between 200 and 300°C. The lowest temperatures are estimated at Bukovo and Sarnitsa, whereas the highest ones are recorded in zunyite-bearing samples at Assarel, Madjarovo and Petelovo. Isotopic signatures of alunite combined with mineralogical features from all the studied occurrences, whatever their type, show characteristics of magmatic-hydrothermal systems, according to Rye et al. (1992). No mineralogical and isotopic criteria clearly allow to distinguish between economic and uneconomic systems. However they provide information on the fluid composition, formation conditions of the volcanic hydrothermal systems and consequently on the Upper Cretaceous and Oligocene paleogeography in Bulgaria. In most of AAA associated with economic ore (Cu-Au sulphidation deposit of Chelopech, Cu-porphyry deposits of Assarel and Petelovo, low-sulphidation deposit of Madjarovo) the presence of zunyite in the deep parts of the system indicate acid-fluorine-sulphate hydrothermal systems, whereas it is absent in uneconomic and barren advanced argillic alteration. Oxygen and hydrogen data indicate that magmatic fluids are dominant with a minor external component in most of the cases.

In the Srednogorie belt, magmatic fluids are always dominant and external component is identified as seawater-derived fluids or meteoric water close to sea. Its participation is relatively important in the Chelopech and Assarel deposits. In the Rhodopes, the external component is also represented by seawater-derived/basin fluid or near sea meteoric water. However the slight D- and ^{18}O- depletion indicates either an evaporation process (shallow seawater) or a larger distance from the sea. External fluids become dominant at Boukovo and Sarnitsa, which are superficial systems in which alunite is the most abundant mineral in rocks (more than 50 %) but sulphur has not only a magmatic origin. Sulphur isotopes indicate H_2S/SO_4 ratios > 1 for all the systems in which magmatic fluids are dominant and $H_2S/SO_4 < 1$ at Boukovo and Sarnitsa.

At this stage of the work, the presence of F-rich minerals such as zunyite in the hydrothermal system, the predominance of magmatic fluids and the H_2S/SO_4 ratio > 1 seem to be at least three conditions which are necessary but not sufficient to get mineralised systems. These conditions were also valuable for other economic high-sulphidation ore deposits in the world, such as Pueblo Viejo, Nansatsu, Rodalquilar, Lepanto and others.

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