Sulfur and strontium isotopic study of epithermal mineralization: A case study from the SE Afar Rift, Djibouti

Moussa Nima [1, 3, 4, *], Rouxel Olivier [2, 3], Grassineau N.V. [5], Ponzevera Emmanuel [3], Nonnotte P. [4], Fouquet Yves [3], Le Gall B. [5]

[1] IST, Centre d'Etude et de Recherche de Djibouti, BP 486, Djibouti
[2] University of Hawaii, Honolulu, HI 96822, USA
[3] IFREMER, Centre de Brest, BP 70-29280, Plouzané, France
[4] UMR 6538 Domaines Océaniques, UBO-IUEM, Place Copernic, 29280 Plouzané, France
[5] Department of Earth Sciences, Royal Holloway University of London, Egham, Surrey TW20 0EX, UK

* Corresponding author : Nima Moussa, email address : nmoussae@gmail.com

Abstract :

Epithermal mineralization was recently described in synrift volcanic rocks from the SE Afar Rift in Djibouti. To infer fluid sources in this system, coupled sulfur and strontium isotopic analyses were performed on mineralized samples from hydrothermal veins and stockwork zones. Mineralization includes gypsum and chalcedony, and/or quartz ± carbonate containing gold and sulfides. Sulfur isotopic compositions of sulfides and sulfates were determined using Multicollector-Inductively Coupled Plasma Mass Spectrometer (MC ICPMS); Laser Ablation MC ICPMS; and Continuous Flow Elemental Analyzer-Isotope Ratio Mass Spectrometry while strontium isotopes were determined by Thermal Ionisation Mass Spectrometry (TIMS) methods. Sulfur isotopic composition of sulfides (mainly pyrite) varies from − 9.2 to + 6.6‰. These values are classically reported for hydrothermal sulfides resulting from the mixing of variable S sources such as seawater sulfate and magmatic source. In addition, individual pyrite grains within the same sample show both positive and negative $\delta^{34}S$ values suggesting multi-phase mineralization processes. Coupled sulfur and strontium isotopic compositions of seven sulfate samples hosted in (i) gypsum mound, (ii) evaporites, (iii) stockwork veins in sediments or in volcanic rocks were also investigated to characterize the sources of Sr and S. The $\delta^{34}S$ values of the sulfate ranged from − 0.8 to + 14.3‰ while the $^{87}Sr/^{86}Sr$ ranged from 0.70389 to 0.70639 consistent with variable mixing ratios of Sr and S derived from volcanic sources and seawater-derived sulfate. This study shows that, although precious-metal deposition is related to low-sulfidation epithermal environment, both acidic fluid of magmatic and saline origins contributed to the hydrothermal system in the SE Afar Rift.

Graphical abstract

Schematic representation of the model proposed. The numbers correspond to (1) Da'asbiyo2, Ali Addé, Hes Daba, Arta, Asa Leyta and Babba Alou; (2) Arta Plage, Babba Alou and Asa Leyta and (3) Lake Asal.
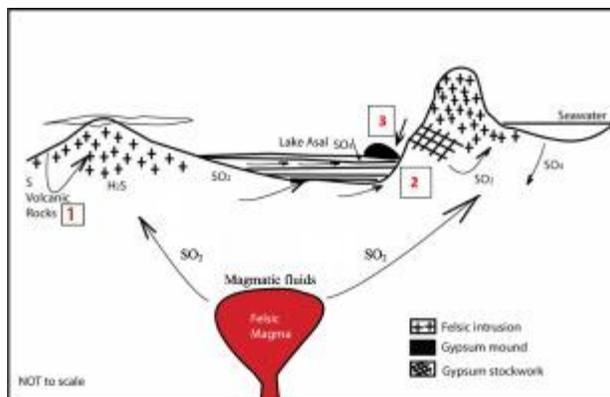
Highlights

► Sulfur and strontium isotopic compositions of sulfides and sulfates of hydrothermal veins from the SE Afar Rift (Djibouti). ► Sulfur isotopic compositions of sulfides (mainly pyrite) vary from − 9.2 to + 6.6‰. ► Strontium compositions of mineralized veins fall between 0.7039 and 0.7079. ► The δ^{34}S values of the sulfate (gypsum) range from − 0.8 to + 14.3‰. ► The ^{87}Sr/^{86}Sr values of the sulfate fall in the range of 0.70389 to 0.70639. ► Magmatic and saline fluids contributed to the hydrothermal system in the SE Afar Rift.

Keywords : Hydrothermal system, Sulfur isotopes, Strontium isotopes, SE afar rift, Epithermal

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1. Introduction

Epithermal deposits are important economic sources of Au and Ag in the world (White and Hedenquist1990; Hedenquist et al. 2000; Simmons et al. 2005). Epithermal deposits form in the shallow parts of high-temperature magmatic-hydrothermal systems (Simmons et al., 2000, 2005) and are generally grouped into high, intermediate and low sulfidation types based on mineral assemblages and their sulfidation states (e.g., Hedenquist et al. 2000; Sillitoe and Hedenquist 2003; Einaudi et al. 2003). There has been considerable debate on the origin of hydrothermal fluids leading to the formation of both high and low sulfidation epithermal deposits. Previous studies identified the importance of magmatic fluids while others argued that epithermal deposits form through the circulation of meteoric (sub-surface) fluids, without a direct relationship to a magmatic source (Henley and Ellis, 1983; Hayba et al., 1985; Simmons et al., 2005). High-sulfidation deposits are considered to form by magmatic fluids (Arribas, 1995) while low sulfidation deposits principally involve meteoric fluids with still significant contribution of magmatic fluids (Simmons, 1995).

Recent field investigations in the SE Afar rift (Djibouti) aimed at addressing the importance of hydrothermal fluids in rift-related volcanic complexes and their relation to the formation of epithermal deposits (Fig. 1) (Moussa et al., 2012). This region has been widely investigated since 1970 as it represents an active geological laboratory to investigate tectono-magmatic rift systems (Stieljes et al., 1973; Barberi et al., 1975; Le Gall et al., 2010; Pinzutti et al., 2013). The most active area is the Asal Rift which has been recognized as a subaerial analogue of slow-spreading ridges where active tectonics and volcanism can be directly observed. Based on geochemical and field studies, several types of hydrothermal ore deposits were identified in the Djibouti rift system (Moussa et al. 2012). The high abundance of gold in the base metal deposits from Hes Daba and Asa Leyta located nearby the Asal Rift (Fig. 1) provide an ideal analogue, of larger epithermal systems. In this paper, we aim to assess the origin and mixing relationships of the ore fluids in eight different sites from the Asal Rift. We applied coupled sulfur and strontium isotope studies of mineralized

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veins in the deposits to quantify the sources and interactions of the ore fluids with the source rocks and marine sulfate deposits.

Sulfur isotopic compositions have been widely used to investigate sulfide and sulfate deposition processes, and as tracers of sulfur sources (e.g. volcanic rocks, magmatic volatiles and seawater). Sulfur isotopic compositions of sulfides of epithermal deposits generally yield $\delta^{34}S$ values ranging from -15 to 5 ‰ depending on their geological settings: (i) -6 and + 5 ‰ for low-sulfidation with most values close to 0‰ (Ohmoto and Rye, 1979; Field and Fifarek, 1985); (ii) -15 to +8‰ for alkalic epithermal deposits (Richards, 1995) and (iii) -10 to +8‰ for high-sulfidation deposits (Arribas, 1995). Heaviest $\delta^{34}S$ values are considered to represent a major contribution of seawater-derived sulfate, while negative $\delta^{34}S$ values are best explained by magmatic fluid contribution. In modern seawater, sulfur is found in an oxidized form as sulfate with an homogeneous $\delta^{34}S$ composition of 21 ±0.2 ‰ (Rees et al., 1978), although this value is known to have varied from 10 to 30 ‰ during the Phanerozoic (e.g. Claypool et al., 1980; Paytan et al., 1998). Magmatic rocks derived from the upper mantle have sulfur isotopic composition similar to that of meteorites ($\delta^{34}S \approx$ 0±2 ‰) (Thode et al., 1961; Sakai et al., 1984), although recent data have pointed to significant heterogeneity of $\delta^{34}S$ values in the mantle (Labidi et al., 2013). Sedimentary sulfides have a wide range of $\delta^{34}S$ values (-70 to + 70 ‰) (Claypool et al., 1980; Shen et al., 2000; Canfield, 2001) reflecting large S isotope fractionation during microbial sulfate reduction and diagenetic processes. Although sedimentary (i.e. biogenic) contribution may in theory explain the occurrence of isotopically light S isotope signatures in epithermal deposits, the abiotic disproportionation of magmatic SO_2 is considered to be the main mechanism producing sulfide (i.e. H_2S) with negative $\delta^{34}S$ values.

Sulfur isotopic compositions have been also intensely investigated in seafloor hydrothermal systems located along fast and slow spreading ridges and in back-arc settings (e.g. Arnold et al., 1981; Alt et al., 1989; Shanks et al., 1995; Rouxel et al., 2004, Ono et al., 2007). These studies demonstrated that along mid-oceanic ridges, seafloor hydrothermal sulfides (active and inactive deposits) commonly

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yield $\delta^{34}S$ values from -1 to +11‰. These values are explained by a major contribution of sulfur derived from the basalt and a smaller contribution from inorganically reduced seawater sulfate (Arnold et al., 1981; Shanks et al., 1995). Using multiple S-isotope ratios (^{32}S, ^{33}S and ^{34}S), Ono et al. (2007) have also addressed the importance of partial $H_2S\text{-}SO_4^{2-}$ isotope exchange in hydrothermal chimney environments. The $\delta^{34}S$ values for hydrothermal sulfides from sedimented mid-ocean ridges spread between -4 to +17‰ (Escanaba Trough, Guaymas and Middle Valley). In these environments, it has been suggested that sulfur has multiple sources including basalts, inorganically reduced seawater sulfate and isotopically light biogenic sulfur remobilized from marine sediments (e.g. Goldhaber and Kaplan, 1974; Zierenberg 1994; Herzig et al., 1998b). In back-arc environments, hydrothermal deposits have $\delta^{34}S$ values ranging from -8 to +16 ‰ (Herzig et al., 1998a; Gemmell et al., 2004; Kim et al., 2004, 2006). The light $\delta^{34}S$ values in sulfides have been commonly explained by the isotope fractionation effects which accompany the disproportionation of magmatic SO_2 into H_2S and H_2SO_4 (Herzig et al., 1998a; Gemmell et al., 1999; Reeves et al., 2010).

Strontium isotopes have been also used to infer the source of ore fluids in different types of hydrothermal systems including epithermal systems and active or fossil seafloor hydrothermal systems (Elderfield and Greaves, 1981; Richard, 1995; Arribas et al., 1995; Arribas, 1995; Polliand and Moritz, 1999; Rainbow et al., 2005). Unlike S isotopes, Sr isotopes reflect predominantly the signatures of the source rocks from which Sr has been leached. Combining Sr and S isotope analyses of sulfate may therefore provide complementary constraints on the source of mineralization fluids and potential contributions of marine waters or evaporites (Shikazono et al., 1983; Mills et al., 1998; Teagle et al., 1998; Mills and Tivey, 1999; Paytan et al., 2002; Alt and Teagle, 2003; Kim et al., 2004; Craddock et al., 2008;). Here we aim at using a similar approach by applying coupled S and Sr isotope composition of sulfate mineral assemblages from the Afar Rift as indicators of fluid-wall rock interaction and mineralization fluid sources.

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2. Geological setting

The Afar rift system is located at the triple junction between the onshore prolongation of the Red Sea and Gulf of Aden ridges, and the Main Ethiopian continental rift (Fig. 1). The Afar lithosphere recorded long-lived tectonic and magmatic accretionary processes in relation to the initial emplacement of the Afar mantle plume 30 Ma ago, and subsequent far-field extension (Barberi et al., 1975; Audin et al., 2004). This resulted in incipient continental rupturing along discrete tectono-volcanic ranges, one of them occurring in SE Afar, Djibouti, along the Tadjoura-Ghoubbet-Asal axis (Manighetti et al., 1997; Pinzutti et al., 2013).

The most complete section of the Afar synrift volcanic succession is exposed in Djibouti, including the 21-28 Ma-old Ali Sabieh mafic series, the extensively distributed basalts of the 1-3 Ma-old Stratoid-Gulf series and the more localized and younger Asal volcanics (Gasse et al., 1986; Le Gall et al., 2010). Hydrothermal processes are known to have occurred over the 28 Ma-long Afar rift history in Djibouti (Moussa et al., 2012). The area considered for this study has been previously described in terms of geological setting and hydrothermal mineralization in Moussa et al. (2012). It consists of several sites: *Ali Addé*, *Da'asbiyo2, Arta Plage, Arta, Babba Alou, Hes Daba, Asa Leyta* and *Lake Asal* (Fig. 1)

The *Ali Addé* and *Da'asbiyo2* sites are hosted by the 11-15 Ma-old felsic series that forms the outer rim of the Ali Sabieh antiform, South Djibouti (Barberi et al., 1975; Gadalia, 1980; Le Gall et al., 2010). The latter consists of rhyolites, ignimbrites and minor basaltic lava flows and the associated felsic feeder dykes (Gadalia 1980).

The *Arta Plage* site occurs on the southern coast of the Tadjoura Gulf where 4-9 Ma-old Dahla basalts, and younger felsic lavas and intrusions of the Ribta formation (4-3 Ma) build up a large N-S-elongated antiform, unconformably overlain by Stratoid (1-4 Ma) and Gulf (1-3 Ma) basalts (Robineau, 1979; Deniel et al., 1994; Daoud et al., 2011).

The *Babba Alou, Hes Daba* and *Asa Leyta* sites are hosted by the 1-3 Ma Stratoid trap-like volcanic series that covers about two-thirds of the Afar depression. Hydrothermal activity is related to felsic

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centers emplaced within the Stratoid mafic pile, such as the <2 Ma-old *Babba Alou* massif, near the Lake Abhé (Gasse and Street 1978), and within intermediate Stratoid basalts, such as the *Hes Daba* and *Asa Leyta* sites, between the Gaggadé and the Asal faulted depressions.

The *Lake Asal* site occurs in exceptional geological, topographical and hydrogeological settings. It is located 155 m below sea level and ~12 km away from the Red Sea, along the tectonically active floor of the Asal rift (Gasse and Fontes 1989). The Asal rift is the locus of still active hot springs forming carbonate chimneys and fumaroles associated with young (< 1 Ma) volcanism (Stieljes, 1973; de Chabalier and Avouac, 1994) (Fig. 2- A). The thermal spring and geothermal waters recovered from wells drilled at depths ranging from 1150 to ~2000 m in the southern flank of the rift have been already studied in terms of geochemical and isotopic (Sr, C, O) compositions (Bosch et al., 1977; Fontes et al., 1979; Fouillac et al., 1983; Sanjuan et al., 1990). These previous studies concluded that the hydrothermal fluids result from (i) basalt-seawater interaction, associated with high rates of evaporation in response to intense aridity and (ii) mixing between deep geothermal water and seawater or *Lake Asal* water. The *Lake Asal* is one of the few modern examples of marine-fed rift basin that is actively accumulating evaporites (Warren, 1997). Gypsum precipitation dominates in the southeastern part of the lake depression whereas the older layered and mounded gypsum beds crop out around the lake edge, as high as 55 m above the present lake level (Stieljes, 1973).

3. Methodology

3.1 Sample preparation

Prior to sample preparation for S and Sr isotope analyses, detailed mineralogical studies of hand specimen from the eight different sites were performed using reflected light microscopy at magnification up to 1000 in dry air and oil. Additional studies were performed involving X-Ray diffraction analysis to determine major minerals in gangue and alteration zones.

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Sulfur isotope analyses (δ^{34}S) were performed by EA-IRMS (Elemental Analyzer Ion Ratio Mass Spectrometer) and MC-ICPMS (Multicollector Inductively Coupled Plasma Mass Spectrometer) as described below. Sulfur isotope compositions of sulfide and sulfate minerals were analyzed at the Stable Isotopes Laboratory, Royal Holloway University of London by EA-IRMS VG/Fisons/Micromass "Isochrom-EA" system. This instrument consists of an elemental analyzer (EA1500 series 2) on line to an Optima mass spectrometer. The analytical procedure followed the method described in Grassineau (2006). Sulfide mineral separates were prepared by hand picking under a binocular microscope. Samples were weighed using a microbalance and crimped in tin capsules. The analyses were done by combustion of the samples and oxidation of the sulfur released to SO_2 (Grassineau et al., 2000, 2001a). Sulfur isotope compositions of sulfides of mineralized veins were also analyzed by MC-ICPMS Thermo Scientific Neptune at the PSO (Pôle Spectrométrie Océan, Brest, France) following the analytical method described in Craddock and Bach (2010) and Craddock et al. (2008). For sulfur isotope analysis of pyrite, nineteen samples were crushed in a small agate mortar and 1 g of sample was weighed into a 15 ml PTFE (polytetrafluoroethylene) digestion vessel. Samples were first reacted for 1 hour with 10 ml of 0.2 M HCl acid in ultrasonic bath in order to dissolve carbonate and anhydrite. After centrifugation for 10 min at 3000 rpm and discarding the surnageant, 2 ml of distilled water were added to the residue and further centrifugated. The residue was dissolved in 5 ml of 13.8M HNO_3 by heating at 100°C for at least 5 days and then evaporated to dryness. This step allows a complete digestion of pyrite and oxidation of sulfur to sulfate while leaving quartz (and other silicates) as a residue. The residues were then dissolved in 5 ml of 0.28M HNO_3 and the solution was purified through cationic exchange chromatographic column. The column was filled with 2.5 ml of AG50 X8 resin (Biorad) and washed with 20 ml of H_2O. After loading 5 ml of sample solution, the column was then washed with 15 ml of 0.28M HNO_3 to obtain the final solution. Analyses of sulfur isotopes were reported as standard δ^{34}S notation relative to Vienna Canyon Diablo Troilite (V-CDT) using a set of calibrated internal standards and IAEA standards, as reported in Craddock et al. (2008). The reproducibility for

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measurements of sulfide and sulfate samples was 0.16 ‰ (2σ) based on multiple analyses of both in-house and international standards (IAEA-S1, IAEA-S-2, IAEA-S-3, AMR8-ZnS, FL-DR-03-Cpy, Laminita-FeS$_2$, WARD'S-FES and NBS 123). We also applied a spatially-resolved method to measure S isotope ratios in pyrite (9 samples) using laser-ablation coupled to MC-ICPMS. Appropriate laser parameters for the determination of S isotopes were previously described by Craddock et al. (2008). The reproducibility of δ^{34}S measurements of sulfide samples was 0.25 ‰ (2σ) based on multiple analyses of our internal pyrite standards (GAV-18) which has been calibrated with respect to international standards as described in Craddock et al. (2008).

Strontium isotope analyses of 25 samples from mineralized veins were performed by Thermal Ionisation Mass Spectrometer (TIMS) (Thermo Scientific Triton) at PSO. Chemical purification of Sr was performed using a two-stage chromatography procedure: (1) on cationic Dowex AG50 X8 columns, and (2) a purification of the Sr part on Sr Spec resin (Chu et al., 2006). Accuracy of the analyses of ^{87}Sr/^{86}Sr was checked against the international standard NBS-987 and we obtained an average value of 0.710258 with a reproducibility of 0.000010 (2σ, n=11).

A total of eight gypsum-rich samples were also analyzed by MC-ICPMS for coupled sulfur and strontium isotopes. We used a leaching procedure to recover S and Sr from gypsum. About 100 mg of sample was first reacted with 10 ml of diluted HNO$_3$ (0.5 M) for several hours. The surnageant was then recovered after centrifugation, and purified for S and Sr isotope analyses following the methods described above.

4. Results

4.1 Mineralogy

In all sites, sulfide mineralization occurs in chalcedony ± massive quartz and carbonate veins with adularia (Fig. 3). The *Da'asbiyo2* site is characterized by goethite and pyrite in breccia veinlets. In the *Ali Addé* area, quartz constitutes the principal gangue mineral and early

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mineralization consists of chalcopyrite, pyrite, hessite, tetradymite, sphalerite, galena and hematite (Fig. 2-C). Adularia is disseminated in quartz veins. Secondary minerals consist of bornite, digenite, covellite, marcasite and goethite. Alteration minerals such as illite and chlorite are also present. In contrast to other sites, the veins from *Arta* site contain gold, electrum, pyrite, argentite, hematite, goethite associated with chalcedony (Fig. 2-D-F). Opaque minerals of the *Hes Daba* site are composed of both hypogene minerals (e.g. pyrite, chalcopyrite, sphalerite, galena, hessite, petzite, tetradymite, pyrrhotite, hematite and magnetite) and supergene minerals (bornite, digenite, covellite, chalcocite, native Cu, native Ag and goethite). They occur in banded chalcedony ± adularia veins or breccias (Fig. 2-G). Late carbonate veins of barren sulfides and gold are common. Pyrite predominantly occurs as fine grains (5 to 100 micrometers in size) scattered throughout the rocks. Pyrite can also fill cracks or occurs in breccias at *Babba Alou* site, nearby the margins of the felsic intrusion. Sulfate minerals (i.e. gypsum) are encountered in (i) a gypsum mound; (ii) evaporites, (iii) stockwork veins in sediments or in volcanic rocks.

At *Arta Plage* site, a mineral assemblage of aragonite, calcite, dolomite, ankerite, and quartz is observed in veins in the altered volcanic rocks together with a stockwork of gypsum (Fig. 2-H). In the *Asa Leyta* area, two stockworks of gypsum containing small amounts of anhydrite probably related to an ancient saline lake, were identified along the main extensional fault zone through both the felsic lavas and the lacustrine sediments (Fig. 2-B). XRD analyses show that most of the samples of this study consist of rather pure gypsum. The most common accessory mineral associated with gypsum is anhydrite occurring as traces.

4.2 Sulfur and strontium isotope ratios of sulfides and hydrothermal veins

Sulfur isotopic composition of pyrite as well as sulfur and strontium isotopic compositions of hydrothermal veins are reported for more than 40 samples. The results are reported in Tables 1 and 2 and Figure 3. The $\delta^{34}S$ values of pyrite from the Mablas rhyolitic series (i.e. *Da'asbiyo2* and *Ali Addé* sites) are relatively heavy (1.5 to 5.9‰) and the $^{87}Sr/^{86}Sr$ ratios of mineralized veins from *Ali*

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Addé range from 0.7072 to 0.7079. At *Arta*, sulfur isotopic compositions of sulfides (pyrite) show two types of distributions: (i) light δ^{34}S values down to -2.1‰ and (ii) heavy δ^{34}S values (up to 6.6‰) while ^{87}Sr/^{86}Sr values of mineralized veins range from 0.7044 to 0.7065. Sulfur isotopic composition of pyrite from *Babba Alou* show light δ^{34}S values from -2.8 to -0.2‰. Unfortunately, strontium isotope ratios were not analyzed in the *Babba Alou* area. Sulfur isotope compositions from the *Hes Daba* site lie between –9.2 and 5.2 ‰ and ^{87}Sr/^{86}Sr of mineralized veins range from 0.7039 to 0.7057. At *Asa Leyta*, δ^{34}S values of pyrite spread between -6.4 and 5.9 ‰ while ^{87}Sr/^{86}Sr values of veins range from 0.7039 to 0.7074.

4.3 Strontium and sulfur isotope ratios of gypsum

Coupled S and Sr isotope ratios of gypsum from *Asa Leyta* and *Arta Plage* sites are reported in Table 1. As a whole, ^{87}Sr/^{86}Sr ratios of gypsum vary between 0.7039 and 0.7064. At *Asa Leyta* ^{87}Sr/^{86}Sr and δ^{34}S range from 0.7046 to 0.7058 and – 0.8 to 3.5‰, respectively. At *Babba Alou* site, the δ^{34}S values of gypsum cluster between -1.5 and -0.2‰. At *Arta Plage*, ^{87}Sr/^{86}Sr range from 0.7039 to 0.7064 while δ^{34}S values of gypsum range from -0.8 to 16.3 ‰ (Fig.4). The δ^{34}S value of gypsum from *Lake Asal* yields the heaviest values at 21.3‰.

5. Discussion

5.1. *Magmatic origin of sulfur and the potential importance of fluid boiling*

Sulfur isotopic compositions of sulfides (i.e. pyrite) from *Hes Daba, Arta, Asa Leyta* and *Babba Alou* sites are systematically light, with the lowest δ^{34}S value of -9.2 ‰ measured at *Hes Daba*. Such values are consistent with the range of δ^{34}S values reported for epithermal gold deposits (Field and Fifarek, 1985; Arribas 1995; Cooke et al., 2011) and suggest a magmatic contribution (Fig. 5). Cooke et al. (2011) reported similar δ^{34}S values (-6.9 to 0.8 ‰) for the high sulfidation Baguio

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deposits (Philippines), and interpreted the results as reflecting a significant magmatic source. Similar interpretation was also proposed for modern seafloor hydrothermal deposits in back-arc basins where $\delta^{34}S$ values as low as -7.7‰ were reported for pyrite at Hine Hina site in the Lau Basin (Herzig et al., 1998a; Gemmel et al., 1999). Sulfur isotope composition of gypsum from *Asa Leyta* ($\delta^{34}S$ from -0.8 to 3.5‰) and *Babba Alou* ($\delta^{34}S$ from -1.5 to -0.2‰) are also much lighter than typical seawater sulfate signature of 21‰. Such light $\delta^{34}S$ values for sulfate are comparable to $\delta^{34}S$ of acid-sulfate minerals (e.g. alunite) measured in back-arc seafloor hydrothermal systems (Herzig et al., 1998a). Alunite is considered to reflect a magmatic component as suggested for its occurrence in some subaerial epithermal systems (Aoki 1991; Herzig et al., 1997) and requires the presence of additional acids such as H_2SO_4 derived from volcanic SO_2 in order to precipitate (Henley et al., 1980; Rye 2005). In general, the H_2S/SO_2 ratio of evolved magmatic fluids is a function of the oxidation state of the magma, temperature and pressure (e.g., Symonds et al., 1994) and isotopically light $\delta^{34}S$ values of both sulfides and sulfates result from the input of magmatic SO_2 according to the following reaction (e.g., Holland, 1965; Drummond, 1981; Herzig et al., 1998a) :

$$4SO_2 + 4H_2O = H_2S + 3H_2SO_4$$

The disproportionation of SO_2 into reduced and oxidized species is accompanied by an isotope effect which causes the sulfide to become enriched in ^{32}S and the sulfate enriched in ^{34}S relative to magmatic SO_2 (Ohmoto and Rye, 1979). In the near surface, H_2SO_4 leads to the formation of characteristic acid-sulfate alteration assemblages with $\delta^{34}S > 0$ ‰, although typically lower than seawater sulfate. Such disproportionation reaction, however, is generally difficult to identify since the produced sulfide and sulfate mineral assemblages are rarely coexisting in single sample specimen considering the contrasted mobility and stability of H_2S and H_2SO_4. Likewise, this type of acid-sulfate alteration assemblage has not yet been observed in the Djibouti rift system, preventing us to firmly conclude about the presence of magmatic acidic fluids in the system.

Further constraints on S isotope fractionation processes are provided by in situ $\delta^{34}S$ analyses (LA-MC-ICPMS) that show small-scale variations between individual pyrite crystals from *Hes*

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Daba, Arta, Asa Leyta and *Babba Alou* (Table 1). These variations suggest dynamic changes of H_2S/SO_2 ratios in the fluid source and/or variable mixing ratios between magmatic H_2S and H_2S derived from fluid-rock interactions and reduction of seawater sulfate. Previous studies proposed that boiling process in hydrothermal system involves a preferential loss of H_2 and H_2S into the vapor phase, thereby causing an increase in the oxidation state of the residual liquid. This mechanism may result in rapid shifts of S isotope composition of sulfides, from positive to negative $\delta^{34}S$ values with great heterogeneity in individual samples (e.g. Mckibben and Eldrige,1990) as those observed in our study. The evidences for boiling conditions in the epithermal deposits at Djibouti have been also supported by the presence of adularia, platy calcite and arsenic indicative of phase separation (Moussa et al., 2012). Phase separation may also play an important control on the precipitation of precious metals in Djibouti, as found elsewhere (Saunders and Schoenly, 1995; Simmons et al., 2005).

5.2. *Strontium isotope systematics: importance of evaporites in ore-forming processes of epithermal deposits*

Altogether, hydrothermal veins and gypsum $\pm$ anhydrite from the different sites yield a range of $^{87}Sr/^{86}Sr$ between 0.7038 and 0.7079. By comparison, $^{87}Sr/^{86}Sr$ ratios ranging from 0.7030 and 0.707 have been reported for the rhyolites and basalts of Djibouti (Barrat et al., 1993). Such values reflect heterogeneities in the lavas erupted before the opening of the Gulf of Tadjoura due to significant contamination by continental crust whereas more recent lavas were contaminated by hydrothermally altered mafic crust (Barrat et al., 1993). Hence, according to the $^{87}Sr/^{86}Sr$ isotope systematics, three different groups could be identified: 1) $^{87}Sr/^{86}Sr$ between 0.7035 and ~ 0.704 which characterize the *Hes Daba, Asa Leyta, Arta* and *Arta Plage* sites, within the range of igneous rocks values from Djibouti (Barrat et al., 1993); 2) more radiogenic $^{87}Sr/^{86}Sr$ values from 0.704 to 0.706 observed in the *Hes Daba, Arta* and *Asa Leyta* sites, indicative of significant alteration of the

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underlying volcanic rocks; 3) $^{87}Sr/^{86}Sr$ ratios (0.7072 to 0.7079) of the mineralized veins from *Ali Addé* site suggesting an important contribution of seawater-derived sulfate (0.7090).

Hydrothermal activity is ubiquitous in the Djibouti rift system (Moussa et al., 2012) and the intense extensional fault activity greatly favored the circulation of hydrothermal fluids (Fouillac et al., 1989). The Sr isotopic composition in veins and gypsum can be modified by interactions with variably altered rocks and by mixing with different fluids having different isotopic ratios (e.g. Kusakabe et al., 1990; Bach and Humphris, 1999; Paytan et al., 2002; Roberts et al., 2003; Alt and Teagle, 2003). The highest $^{87}Sr/^{86}Sr$ values at 0.707 may reflect the contribution of Sr derived from hydrothermally-altered substrate rocks. Gasse et al. (1986) proposed that the Mablas rhyolites were affected by intense alteration with the deposits of gypsum. If we consider the paleogeographical evolution of the SE Afar rift, most of its southeastern part has been affected by marine infiltration from the Red Sea. In this context, more radiogenic $^{87}Sr/^{86}Sr$ values are consistent with precipitation from hydrothermal fluids, although the relative contribution of Sr derived from altered crust and evaporitic sequences cannot be easily discriminated using Sr isotope systematics alone. Distinguishing between these two sources is important considering that evaporites play a role in the genesis of a large base metal ore bodies by the provision of anions for complexing metals in solution and by providing the sulfur necessary to precipitate the metals (Kyle, 1991; Warren, 1997; Palmer et al., 2004). In the section below, we applied combined S and Sr isotopes to provide further constraints.

5.3. *Combined Sr-S isotope data of sulfate and establishment of genetic model for epithermal deposits*

A comparison of $\delta^{34}S$ *versus* $^{87}Sr/^{86}Sr$ signatures of gypsum from *Asa Leyta* and *Arta Plage* is reported in Figure 4. In each site, elevated (i.e. more radiogenic) $^{87}Sr/^{86}Sr$ ratios in gypsum correspond to heavier $\delta^{34}S$ values, consistent with the contribution of seawater-derived sulfate. The presences of sulfate minerals with relatively lower $^{87}Sr/^{86}Sr$ ratios (~0.704) and $\delta^{34}S$ (~2‰) are

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consistent with a predominantly volcanic rock-derived source, either resulting from SO_2 magmatic contribution or oxidation of hydrothermally-derived H_2S. In either cases, $\delta^{34}S$ and $^{87}Sr/^{86}Sr$ values indicate mixing between magmatic/hydrothermal fluid and seawater sulfate.

For *Babba Alou, Hes Daba, Arta* and *Asa Leyta* sites, light isotopic composition of sulfur (<0‰) indicate SO_2 magma degassing in the deep parts of the hydrothermal system. The $^{87}Sr/^{86}Sr$ ratios for *Hes Daba, Arta* and *Asa Leyta* sites range between 0.7038 and 0.7064 which is consistent with hydrothermal fluid signatures and suggesting that the magmatic volatiles interacted with igneous rocks. The *Ali Addé, Da'asbiyo2, Hes Daba, Babba Alou, Arta* and *Asa Leyta* sites, sulfur and strontium isotopic compositions show Sr and S isotope signatures similar to volcanic rocks (Fig. 6). The *Arta Plage, Babba Alou* and *Asa Leyta* show both light and variable $\delta^{34}S$ values (-1.5 to 16.3‰) with more radiogenic strontium isotope ratios (0.7064 for Arta Plage).

Figure 4 shows a compilation of $\delta^{34}S$ values of sulfides and sulfates from worldwide epithermal systems, modern seafloor hydrothermal systems and the Djibouti rift. Although sulfide $\delta^{34}S$ data from Djibouti overlap with different types of epithermal deposits, they are most similar to epithermal portion of alkalic and low sulfidation deposits.

Based on field and mineralogical observations, Moussa et al. (2012) identified different types of mineralization corresponding to different depths in the Djibouti hydrothermal rift system. Apart from the deepest zone in the hydrothermal system which recorded epidote alteration in the south of Djibouti and the Asal Rift, hydrothermal mineralization were encountered at two different depths 1) deep, with massive quartz veins containing sulfides (*Hes Daba, Ali Addé* and *Arta* sites) and brecciated veins (*Da'asbiyo, Babba Alou* and *Asa Leyta*); 2) shallow, with evidence of boiling conditions, where chalcedony with adularia and platy calcite are common (*Ali Addé, Hes Daba, Arta* and *Asa Leyta* sites). The highest Au concentration occurs in the latter type. Gold is mostly concentrated in banded chalcedony, whereas massive quartz or breccias are less enriched or barren. A third type is represented by sublacustrine hydrothermal precipitates consisting of gypsum mounds (*Lake Asal*) or stockworks (*Babba Alou, Arta Plage* and *Asa Leyta* sites). The $\delta^{34}S$ value of gypsum

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corresponds to the *Lake Asal* site with value of 21.3‰. The *Lake Asal* remains hypersaline with about 300 g/L NaCl which is 8 to 9 times the salinity of seawater (Gasse and Fontes, 1989). In addition, paleoenvironment and paleohydrology studies of the Lake Asal have shown that the latter was periodically affected by the infiltration of marine water (Gasse and Fontes, 1989). Therefore, a $\delta^{34}S$ value of 21.3‰ for gypsum from the lake obtained in our study is fully consistent with a marine origin (Rees et al., 1978; Paris et al., 2013). Combining sulfur and strontium isotope systematics further allows to identify the source of mineralization in the area. If we consider the different levels of the hydrothermal system in the Djibouti rift (see above), we can suggest that two major types of fluids contributed to the formation of the deposits: 1) hydrothermal fluids enriched in magmatic volatiles leading to significant leaching of the underlying volcanic rocks (e.g. *Da'asbiyo2, Ali Addé, Hes Daba, Arta and Babba Alou*; 2) hydrothermal fluids, probably initially enriched in magmatic SO_2, but that underwent significant dilution with seawater and/or contamination with evaporite layers that dissolved during the circulation of hydrothermal fluid passes (e.g. *Babba Alou, Arta Plage* and *Asa Leyta* sites).

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Conclusions

Sulfur and strontium isotopic analyses of sulfide and sulfate of mineralized veins from the SE Afar rift have been measured to characterize the sources of the mineralizing fluids. Light δ^{34}S values of pyrite provide evidence for magmatic SO_2 contribution while ^{87}Sr/^{86}Sr of mineralized veins suggests the contribution of variably altered volcanic rock sources. Coupled δ^{34}S and^{87}Sr/^{86}Sr values of gypsum suggest variable extent of mixing between seawater-derived sulfate and hydrothermal fluids. The variable δ^{34}S values of pyrite and the presence of platy calcite, adularia, arsenic, suggest possible boiling conditions in some sites (*i.e. Ali Addé, Hes Daba, Arta* and *Asa Leyta*).

These results allow us to identify that gold deposits in the region are mainly related to magmatic contribution, allowing to classify the deposits as epithermal gold systems, probably close to low sulfidation end-member. By analogy with modern seafloor epithermal-hydrothermal deposits, the observed alteration (illite, chlorite, adularia and platy calcite) suggests that interaction with seawater or underlying evaporites may have buffered the acidity of the magmatic fluid causing a near neutral pH alteration assemblages to form. In previous studies, the relationship between low-sulfidation epithermal ore deposits and magmatic volatile contribution was difficult to establish due to the predominance of meteoric waters within hydrothermal fluids. To further constrain the origin of the mineralized fluid in Djibouti, additional analysis of C, O, Pb isotope compositions of mineralization; and quartz microthermometry in veins may be required.

In addition, efficient exploration and interpretation of the origin of hydrothermal fluid in the SE Afar rift require integration of all geochemical (textures, mineralogy), geophysical (three-dimensional interpretation) and geological data.

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Figure Captions

Fig.1: Schematical geological map of the Republic of Djibouti (SE Afar Triangle) after Piguet and Vellutini (1994). Yellow stars (and corresponding numbers) are the hydrothermal sites studied in this work. 1 = Da'asbiyo 2; 2= Ali Addé; 3= Arta Plage; 4= Arta; 5 = Babba Alou; 6 = Hes Daba; 7= Asa Leyta; 8 = Asal. In the inset: schematic map of the Afar Depression with the location of Djibouti (black rectangle) and the dashed red lines = Red Sea and Gulf of Aden spreading centers.

Fig.2: A- Photograph of the Lake Asal located in the Asal active rift system. The red arrow indicates location of the studied gypsum from Lake Asal. B- Layers of gypsum (Gy) from the Asa Leyta hydrothermally altered site. C- Example of analyzed veins containing pyrite (black layer) from Ali Addé site. D - E- Reflected light microphotograph of pyrite (Py) from the Arta (D) and Ali Addé (E) sites. The gangue mineral is quartz (Q). F- Banded chalcedony veins (Arta). G- Breccia like veins enriched in sulfides (Hes Daba). H- Stockwork of gypsum veins hosted by felsic volcanic material.

Fig 3: Paragenetic sequence of the studied sites.

Fig. 4: $\delta^{34}S$ *v.* $^{87}Sr/^{86}Sr$ diagram for sulfate minerals from this study (Arta and Asa Leyta = black squares). The blue squares correspond to anhydrites from hydrothermal chimneys from the Pacmanus hydrothermal site (Kim et al., 2004) and the red square - basalts from Djibouti (data from Barra et al., 1993). The green triangle corresponds to seawater sulfur and strontium isotopic composition (Barra et al., 1993).

Fig. 5: Values of $\delta^{34}S$ (‰, CDT) for sulfides and sulfates of epithermal (i) high-sulfidation (Arribas, 1995), (ii) low-sulfidation (Field and Fifarek, 1985), and (iii) modern systems (Gemmell et al. 2004), compared to $\delta^{34}S$ values of sulfide and sulfate minerals from Djibouti.

Fig. 6: Schematic representation of the model proposed. The numbers correspond to (1) Da'asbiyo2, Ali Addé, Hes Daba, Arta, Asa Leyta and Babba Alou; (2) Arta Plage, Babba Alou and Asa Leyta and (3) Lake Asal.

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Fig.1:
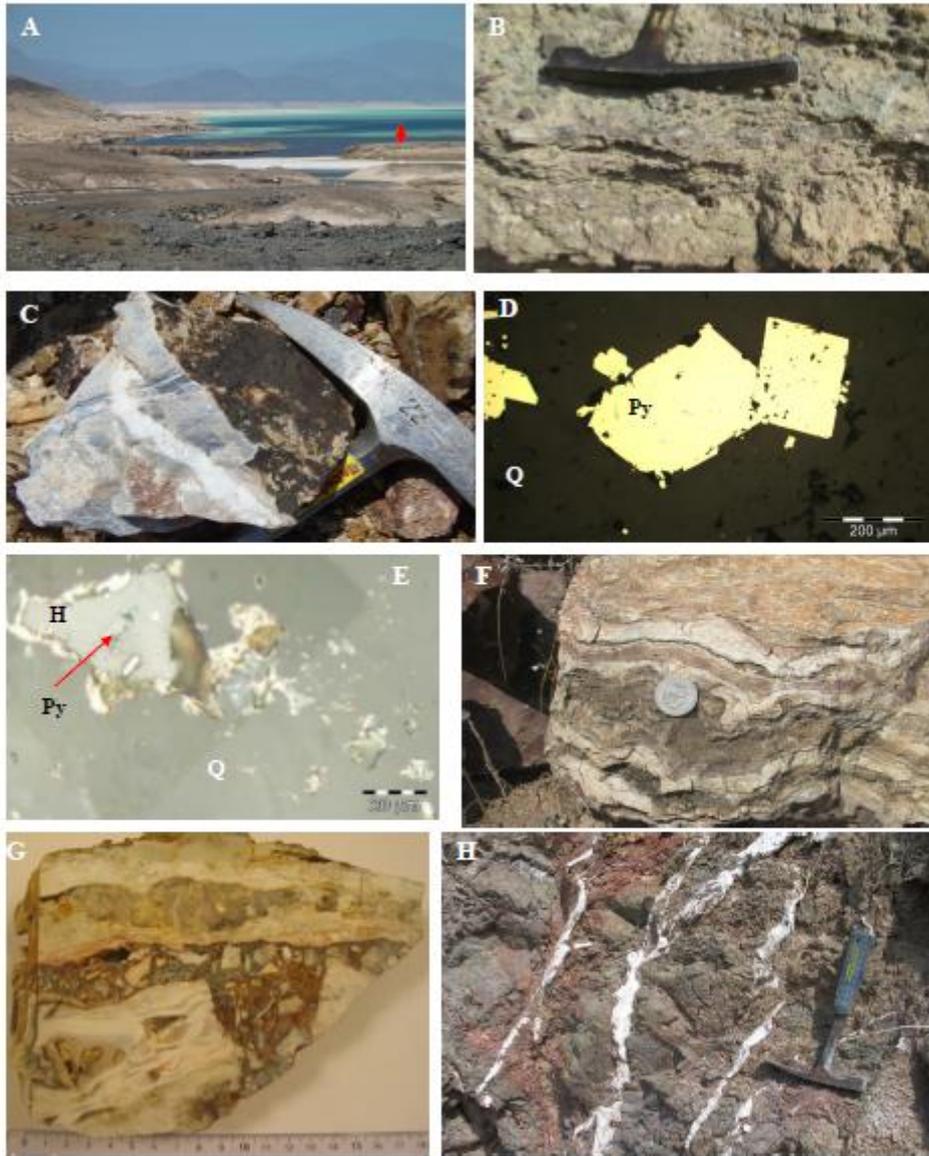
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Fig.2:

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Minerals / Sites	Asal (<1 Ma)	Asa Leyta (<3 Ma)	Hes Daba (<3.3 Ma)	Babba Alou (<3.3 Ma)	Arta Plage (<4 Ma)	Arta (<4 Ma)	Ali Addé (15 to 11Ma)	Da'asbiyo2 (15 to 11Ma)
Hypogene minerals								
Chalcopyrite CuFeS2			+				+	
Pyrrhotite FeS		+	+				+	
Pyrite FeS2		+	+	+		+	+	+
Sphalerite (Zn,Fe)S			+				+	
Galena PbS			+				+	
Gold Au			+			+		
Electrum AuAg			+			+		
Argentite AgS			+			+		
Petzite Ag3AuTe			+					
Hessite Ag2Te			+			+		
Tetradymite Bi2Te2S							+	
Magnetite Fe3O4						+		
Hematite Fe2O3			+			+	+	
Supergene minerals								
Chalcocite Cu2S							+	
Covellite CuS			+				+	
Digenite Cu9S5			+				+	
Native Silver Ag			+					
Native Copper Cu			+					
Goethite FeO(OH)		+	+	+		+	+	+
Bornite CuS Fe S4			+					
Marcasite FeS2			+				+	
Gangue								
Adularia KAlSi3O8		+	+			+	+	
Massive Quartz SiO2		+	+	+	+	+	+	+
Chalcedony SiO2		+	+			+	+	
Carbonates CaCO3		+	+		+	+	+	
Gypsum CaSO4 2(H2O)	+	+		+	+			

Fig 3:

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Fig. 4:

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Fig. 5:

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Fig. 6:

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Graphical Abstract

Schematic representation of the model proposed. The numbers correspond to (1) Da'asbiyo2, Ali Addé, Hes Daba, Arta, Asa Leyta and Babba Alou; (2) Arta Plage, Babba Alou and Asa Leyta and (3) Lake Asal.

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Sites	Samples	δ^{34}S v-cdt [a]	δ^{34}S v-cdt[b]	δ^{34}S v-cdt[c]	^{87}Sr/ ^{86}Sr	δ^{34}S v-cdt[d]
Da'asbiyo	DJ0207					1.5
		5.3	4.6	-		5.9
Ali Addé	DJ3807	-	4.8	-		
		-	4.6	-		
	DJ1309	3.6	-	-		
		-	-1.3	-		
Babba Alou	DJ 24-07C	-0.1	-2.9	-		-1.2
		-	-2.3	-		
	DJ2407B (Gy)					-0.2
	DJ2407A (Gy)					-1.5
						1.0
	AA-02					
		0.3	-	-		
Arta	DJ0507	-	0.3	-		
		1.7	-1.6	-		
		-	-1.3	-		
	DJ1207b	-	2.1	-		-0.3
		-	-1.5	-		
		-	-2.1	-		
	A-05	6.6	-	-		-0.4
Hes Daba		-	1.4	-		
	DJ-69 08	-	1.6	-		
		-	1.3	-		
		-	2.9	-		
		-0.7	0.3	-		-9.2
	HD 02 07		0.4	-		
			0.2	-		
			0.6	-		
		-0.1	-1.8	-		1.4
	DJ3407a	-	4.2	-		
		-	2.8	-		
	DJ1009B	5.2	-	-		
	Reef1	1.2	-	-		
	Reef3BF3H	2.1	-	-		
	Reef3H	1.3	-	-		
	Reef3M	0.5		-		
	DJ1R1B					1.2
Asa Leyta		-	0.7	-		
	DJ 70-08	-	0.6	-		
		-	1.2	-		
		-	-1.5	-		
	DJ 76 08	-	-0.4	-		
			-0.4	-		
		4.2	-6.4	-		
	DJ0207	-	1.8	-		
			-4.4	-		
	DJ8108	-0.1	-	-		
	AL	-0.1	-	-		
	DJ 05 07 B	3.7	-	-		-1.2
	AL 02	-0.6	-	-		-0.6
	S Lacq*	16.7	-	-		
	DJ0707 (Gy)					1.9
Arta Plage						
	DJ-09-09 (Gy)	-	-	-0.8	0,70451	
	DJ-74-08 (Gy)	-	-	0.7	0,70492	
	AGD (Gy)	-	-	0.1	0,70460	
	DJ4709-A1 (Gy)	-	-	1.6	0,70391	

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DJ73-08-A (Gy)	-	-	3.5	0,70547	
DJ-01-09-A (Gy)	-	-	14.3	0,70638	
DJ75-08-A (Gy)	-	-	1.8	0,70577	
DJ4709-A (Gy)	-	-	0.6	0,70389	
NBS 123	-	-	17.47		
DJ2807 (Gy)					16.3
DJ2707 (Gy)					1.1
DJ2607 (Gy)					3.7
Lac Asal DJ0107 (Gy)					21.3

Tab. 1: Sulfur isotopic compositions of pyrite (Py) and gypsum (Gy) and Sr isotopic composition of gypsum. * Sulfur from the Lacq (internal standard). Analyses by MC ICPMS (a-bulk powder with 2s=0.29; c with 2s=0.16), Laser methods (b- pyrite in polished section with 2s=0.25) and EA-IRMS (d- pyrite) methods.

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Sites	Samples	Sulfide Mineralogy	Gangue Minerals	Types of Hydrothermal deposits	$^{87}Sr/\ ^{86}Sr$
Arta	DJ1207-A-2	Py, Go, IO	Q	Breccia	0,704364
	DJ8508F40H	Py, Au, Go, IO	Q	Banded Chl	0,706446
		Py, Au, Ad, Go,	Q	Banded Chl	
	F2BN140ARTA	IO		Banded Chl	0,704205
	DJ8708A	Py, Ad, Go	Q	Banded Chl	0,704477
	DJ12BRUB*	-	-	-	0,704316
	DJ1210A1	Py, Go	Q	Breccia	0,704442
	DJ1410B	Py, Go	Q	Breccia	0,704951
	DJ1610-RM*	-	-	-	0,704524
	DJ1810*	-	-	-	0,704877
	DJ1210B1	Py, Go	Q	Breccia	0,704709
	DJ4809*	-	-	-	0,703543
Arta Plage	DJ2607E	Gy	Gy	Gypsum	0,704067
	DJ2907B	Hm	Q	Breccia	0,704682
Hes Daba	DJ3407	Cpy, Py, Cu, Bn, ZnS, Ga, Dgn, CuS, Cv	Q	Breccia	0,704600
	F1N02C	Au, Py, Ag,	Q	Banded Chl	0,703918
	DJ1009A	Py, Go	Q	Breccia	0,704736
	DJ1009D	Py, Go	Q, Ca	Breccia	0,704125
	DJ4808A*	-	-	-	0,703937
Asa Leyta	DJ7708	Py	Q	Breccia	0,705120
	DJ2308	Py, Go	Q	Banded Chl	0,706124
	DJ0809	Gy	Gy	Breccia	0,703884
	DJ7608A	Py	Q	Breccia	0,704458
	DJ2110	Py,Go	Q	Banded Chl	0,704359
Ali Addé	DJ3807	Cpy, Py, Au, Bn, ZnS, Ga, Cc, Dgn, CuS	Q	Breccia	0,707204
	DJ1309	Cpy, Py, Po, Au, Sp, Bn, Cv, Cc, Dgn, Hs, Ttd, Mg, Cu	Q	Breccia Breccia	0,707988

Tab.2: Strontium isotope ratios of mineralized vein samples and rocks (*). Cpy chalcopyrite, Py pyrite, Hs hessite, Po pyrrhotite Ca calcite, Cc chalcocite, Elt electrum, Ep epidote, Ga galena, Au gold, Bn bornite, Dg digenite, Go goethite, Gy gypsum, Hm hematite, Sp sphalerite, Mg magnetite, IO iron oxides , Ttd tetradymite, Q quartz, Mc marcasite. Native Cu and native Ag. Chl Chalcedony