Fluid evolution within Eastern Rhodopian sedimentary rock-hosted low-sulfidation epithermal gold deposits, Bulgaria

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The low-sulfidation epithermal gold prospects from the Eastern Rhodopes, Bulgaria are dominantly hosted by syn-detachment sedimentary rocks of Maastrichtian-Paleocene age. On the basis of the alteration mineralogy and textural relationships, it is concluded that gold may have been deposited as a consequence of different physical-chemical processes in the various prospects: cooling or boiling of the ore fluid, oxidation or other changes caused by mixing of two fluids, or wall rock reactions such as reduction of fluids by organic matter or sulfidation. The gold transport as a bisulfide complex and the importance of sulfidation as depositional process is suggested by: 1) sulphidation of host rock iron; 2) mass transfer studies; 3) low salinity of the fluids; and 4) high Au/Ag ratios in electrum. Given that gold was transported as a bisulfide complex, knowledge of the sites of H_2S generation is crucial to gather information about the source and the pathways of the ore-forming fluids. The combined oxygen and wide range sulfur isotopic compositions suggests a variety of sources: including magmatic/metamorphic fluids, or surficial waters equilibrated with magmatic and metamorphic rocks, as well as dissolution of pyrite, and thermochemical sulfate reduction in sedimentary rocks in various prospects.

Key Words: Eastern Rhodopes, Bulgaria, gold transport and deposition, sulfur isotopes, sulfidation.

Introduction

The recently discovered Tertiary epithermal gold deposits with a low-sulfidation character at Ada Tepe, Bulgaria and surrounding prospects are dominantly hosted by syn-detachment sedimentary rocks of Maastrichtian-Paleocene age. A low angle normal fault between the metamorphic basement and the sedimentary rocks constitutes the major ore-controlling associated structure (Marchev *et al.*, 2004).

The above mentioned deposits and occurrences belong to the Tethyan Metallogenic Belt, which itself is part of the Alpine-Himalayan orogenic system. Other gold and iron deposits of the Tethyan Metallogenic Belt, with comparable structural and metallogenetic styles as the ones of the Eastern Rhodopes include the Menderes Massif in Western Turkey (*Yigit, 2006*), iron-oxide deposits in Western Crete, Greece (*Seidel et al., 2005*) and gold prospects at Rosino, Stremtsi and Sedefche in the Kardzali Area, Bulgaria (*Marchev et al., 2004*). These are typically interpreted within a "classic" detachment fault-related metallogenic model, analogous to the deposits from the Basin and Range Province in the Western United States (*Long, 1992*).

The discovery of Ada Tepe opens up new exploration possibilities in this part of the Tethyan Metallogenic Belt. There is presently the potential open pit mining at the Ada Tepe deposit with high grade ore (5.2 Mt @ 5.0 g/t Au), with a total of 835000 ounces of gold indicated by *Balkan Mineral and Mining (Report on Feasibility Study,* *2005*). Another prospect at Rosino, Bulgaria has been developed up to the feasibility level with a 6.07 Mt of ore but at a lower grade (2.3 g/t Au) estimated by *Cambridge Mineral Resources Plc.* (*Press Release, 2005*).

This study presents new geological, stable isotope and fluid inclusion constraints on the Eastern Rhodopian sedimentary-rock hosted gold deposits. Emphasis is placed on comparison of alteration, ore textures, mineralogy and geochemical data from different occurrences. The likely source of fluids and the evolution during the gold deposition is discussed based on stable isotope data.

Geological Setting

The studied gold deposits are located along the northern part of the N-NE-oriented Kessebir-Kardamos and Biala Reka metamorphic dome complexes, which is a prominent geological feature in the Eastern Rhodopes (Fig. 1). The main lithotectonic units and structural elements include (Bonev et al, 2006): (1) Maastrichtian – Oligocene sedimentary rocks, including conglomerate and sandstone, which are in tectonic contact with or transgressively deposited on metamorphic basement rocks; (2) a Variegated metamorphic Complex, consisting mainly of pre-Alpine and Alpine amphibolite facies meta-sedimentary and meta-igneous rocks, remnants of meta-ophiolitic sequence and marbles; (3) a Gneiss- Migmatite Complex within the core of the dome; and (4) a major low-angle or thrust zone. The hanging wall of the detachment fault consists of sedimentary rocks, with a breccia-conglomerate component, defined as the Shavar Formation. The footwall of the detachment fault consists of shear zones with a mylonitic fabric, which have deformed the upper part of the Gneiss-Migmatite and Variegated Complexes. Geologic structures around the Ada Tepe deposit and adjacent prospects can generally be modeled by domino-style rotational normal faulting in the upper plate above the detachment fault (Márton *et al.*, 2006).

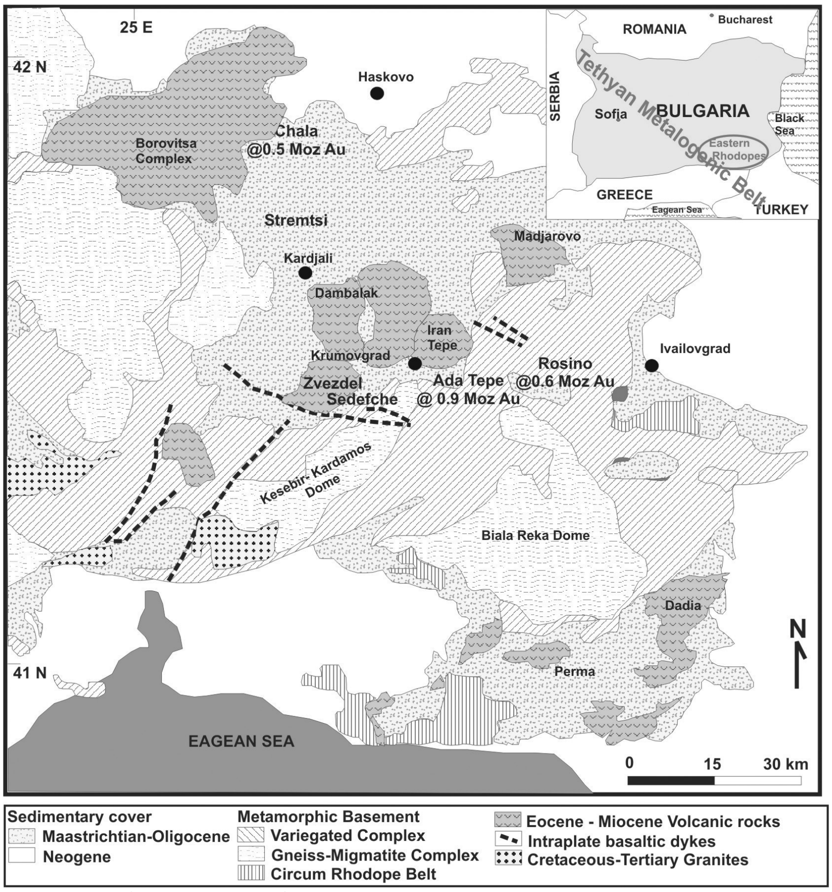

Figure 1. Simplified geology of the Eastern Rhodopes, showing the main gold deposits. Modified after Marchev *et al* (2004) and Bonev *et al.* (2005).

$^{40}Ar/^{39}Ar$ adularia dating from the Ada Tepe deposit indicates that the ore was deposited at 35.0 ± 0.2 Ma. This age is ~3 Ma younger than the $^{40}Ar/^{39}Ar$ cooling age of metamorphic muscovite and biotite at ~350 °C in the underlying basement, and 3 Ma older than sanidine in the nearest rhyolite (Fig. 2.). The available age data preclude local magmatism as a source of fluids or heat *(Marchev et al., 2004)*.

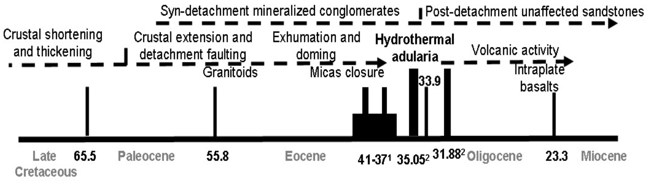

Figure 2. Sketch showing the Tertiary evolution of the Eastern Rhodopes. Absolute ages are only shown just for the Eocene-Oligocene period and are based on: 1) biotite-muscovite Ar/Ar ages from gneisses in Lips (2000), Mukasa (2003), & Bonev *et al.*, (2004) and 2) adularia and sanidine Ar/Ar ages from Marchev *et al.* (2004).

Morphology, Alteration and Mineralogy of the Deposits

The geometry of the ore bodies reveals the structural and lithological controls on the mineralization. They include: (a) strongly faulted rocks of the highly permeable sedimentary unit that offered a favorable channel-way for fluid circulation generating open space filling bonanza type mineralization in veins with a general E-W direction; (b) the deformed metamorphic rocks with a ductile fabric and the cataclasticly deformed detachment zone were the loci of focused fluid flow, toward lower pressure areas, where a massive, tabular ore body was formed immediately above the detachment fault. These zones consist of strongly altered rocks, replaced by silica, adularia, sericite, pyrite and carbonate minerals.

Metamorphic basement rocks are generally barren, but are variably altered to sericite, chlorite, clay minerals, and pyrite-hematite assemblages in a ductile-brittle transition zone, below the detachment. However, at one of the prospects, i.e. Surnak, this transition zone is displaced to deeper crustal levels, within the metamorphic basement rocks, and the later rock units are also mineralized, which is explained by an increased permeability of connected observable structures along listric faults.

		HOST ROCK	ADJACENT LITHOLOGIES	STRUCTURAL SETTING	ALTERATION & MINERALOGY	TEXTURES	SPECULATED Au DEPOSITION
KRUMOVGRAD AREA	ADA TEPE	Tectonically affected coarse grained conglomerates (Shavar formation)	Weakly altered amphibolites and gneisses	Detachment zone and E-W vertical fractures	Intense silica and potasic, later cabonate Electrum and disseminated pyrite	Bladed and banded crustiform veins, replacement textures, Hydrothermal breccia	**Intense boiling, fluid mixing, fluid-rock interaction, reduction by coal**
	KUKLITZA	Fine grained conglomerates with sandy matrix	Weakly altered amphibolites	Detachment zone and SE-NW oriented fractures	Intense silica , argilic along the veins Electrum and disseminated pyrite	Bladed and banded crustiform- colloform veins	**Boiling and fluid mixing**
	KUPEL	Coarse grained conglomerates (Shavar formation)	Weakly altered amphibolites	N-S and NE-SW oriented strctures	Silica and hematitic alteration	Jointing, replacement textures, breccia with hamatite matrix	**Fluid - rock interaction**
	SURNAK	Black, fine grained sandstones and amphibolites	Tectonic breccias of Shavar formation	Bounded by N-S striking listric faults	Silica and carbonate along veins Abundant pyrite	Jointing, replacement textures	**Fluid - rock interaction, reduction by coal, fluid mixing**
	SKALAK	Medium to fine grained conglomerates	Tectonic breccias of Shavar formation	Minor E-W fractures	Strong silica	Jointing, replacement textures	**Fluid - rock interaction, fluid mixing**
	ROSINO	Black, fine grained sandstones and siltstones Cataclastic contact zone	Granitic rocks with network of joints	Kechros thrust fault and SE-NW structures	Silica and carbonate alteration Abundant pyrite, some galena and sphalerite	Ankerite and silica veins, abundant hydrothermal breccia with pyrite matrix	**Fluid - rock interaction, reduction by coal, fluid mixing**
	STREMTZI	Conglomerates and sandstones , local coal bearing layers	Volcanic rocks, marls and limestones	E-W oriented faults	Early silica and later carbonate	Chalcedony and barite veins, some bladed texture	**Fluid mixing, local boiling, reduction by coal**

Table 1. Comparison between the studied gold deposits and prospects based on deposit structure, alteration, ore textures and mineralogy. On the basis of these relationships, it is likely that gold may have been deposited as a consequence of different physical-chemical processes in the various deposits and prospects.

On the basis of the alteration mineralogy and textural relationships, it is possible that gold may have been deposited as a consequence of different physical-chemical processes in the various prospects. These characteristics are summarized in Table 1. The abundant bladed quartz pseudomorphs replacing platy calcite suggest boiling in different prospects, including at Ada Tepe, Kuklitsa and Kupel. However, in cases of other prospects, such as Rosino, Surnak, Kremenitz and Skalak, boiling textures are scarce to absent, and intense fluid-rock interaction may be responsible for gold mineralization, possibly due to pH and Eh variations of the gold-transporting fluid. In two prospects, i.e. Ada Tepe and Surnak, areas enriched in organic carbon were identified, which correlate with high Au grades, due probably to the intense local reduction of the hydrothermal fluids.

Thermodynamic and oxygen isotope constraints

Two-phase, liquid-vapour phase fluid inclusions were identified in early stage carbonates from the sub-vertical veins at Ada Tepe. The preliminary microthermometric results show that deposition of this calcite took place at temperatures about 180-210 °C (Fig. 3.) from very dilute fluids.

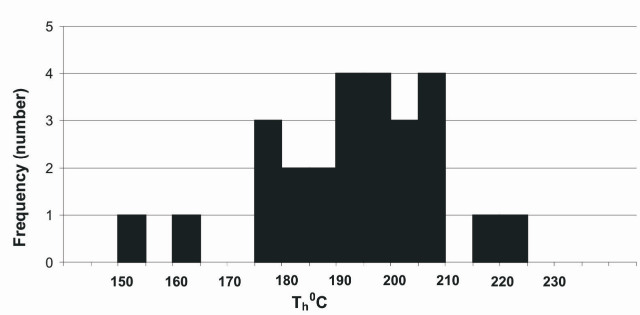

Figure 3. Histogram of homogenization temperatures from carbonate hosted fluid inclusions at Ada Tepe.

Preliminary $\delta^{18}O$ values (vs. V-SMOW) range between 11.2 and 13.5‰ in quartz samples, and between 9.2‰ and 10.0‰ in adularia dominated samples from the Ada Tepe deposit. The calculated $\delta^{18}O$ values (vs. V-SMOW) of water in equilibrium with analyzed quartz and adularia samples are about -3.6 to 0.1‰.

These isotopic compositions can be interpreted as typical for mineralizing fluids with a dominantly magmatic/metamorphic character, or a surficial fluid that has been equilibrated with magmatic and metamorphic rocks, especially if we consider the very dilute nature of the fluids on the basis of microthermometric fluid inclusion data.

Precipitation mechanism and sulfur isotope results

Ore textures suggest several gold deposition processes, including: cooling and boiling of the ore fluid, dilution, oxidation or other changes caused by mixing of two fluids, or wall rock reactions such as reduction of fluids by organic matter or sulfidation. If gold is transported in hydrothermal solutions as a gold bisulfide complex, a decrease in H_2S content may cause gold precipitation. A decrease in H_2S content may be caused by precipitation of sulfide minerals or mixing with a H_2S-poor solution (e.g., shallow ground water). The reduction of fluids is favored by organic matter and ferrous-bearing minerals.

The importance of sulfidation and the gold transport as a bisulfide complex are indicated by: 1) petrographic evidence which suggest that sulfidation of host rock iron was an important process (Fig. 4); 2) mass transfer studies which show that sulfur was one of the most abundant elements introduced by hydrothermal fluids, whereas iron contents remained nearly constant; 3) the low salinity of measured fluid inclusions and 4) high Au/Ag ratios in electrum. These observations are consistent with chemical reaction path modelling, which shows that sulfidation can result in ore grades observed in the sedimentary-rock hosted gold deposits (Shenberger and Barnes, 1989 and Gammons, 1997).

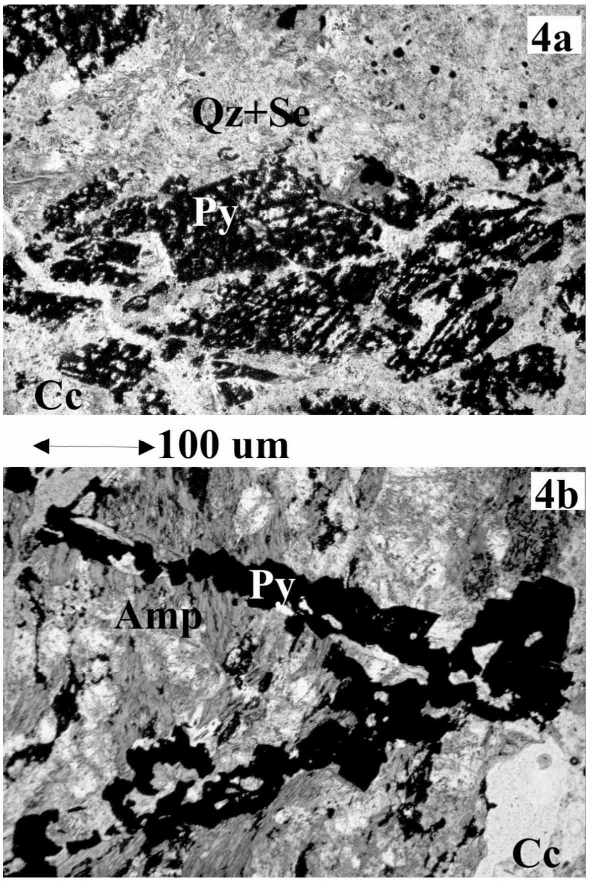

Figure 4. Pyrite forming as replacement of amphiboles along cleavages (4a) and in fractures within amphiboles (4b), demonstrating that the major process controlling the precipitation of pyrite is sulfidation of host rock iron. (Amp – amphibole, Py – pyrite, Cc – carbonate, Qz+Se – quartz and sericite). Samples are from Skalak and Ada Tepe.

Increased understanding of the source of sulfur and mechanism of H_2S generation may help to discriminate between the various models and fluid sources proposed for the deposits. Therefore, sulfur isotopic studies were conducted on pyrite samples from the different prospects. Figure 5 shows the range of isotopic compositions obtained for the pyrite samples. The calculated isotopic composition of H_2S in the ore fluids at 200 ºC might be 2-3 ‰ lower to the one of the minerals with strong metal-sulfur bonds like pyrite, in which ^{34}S is enriched (Ohmoto and Rye, 1979).

The wide range of sulfur isotopic composition (Fig. 5.) suggests a variety of sources for the sedimentary-rock hosted gold deposits of the Eastern Rhodopes. One deposit show a narrow range: probably the Sedefche deposit (South of Zvezdel, Fig. 1) could be explained by distal-disseminated model (Sillitoe and Bonham, 1990), where the magmatism provided the major source of H_2S.

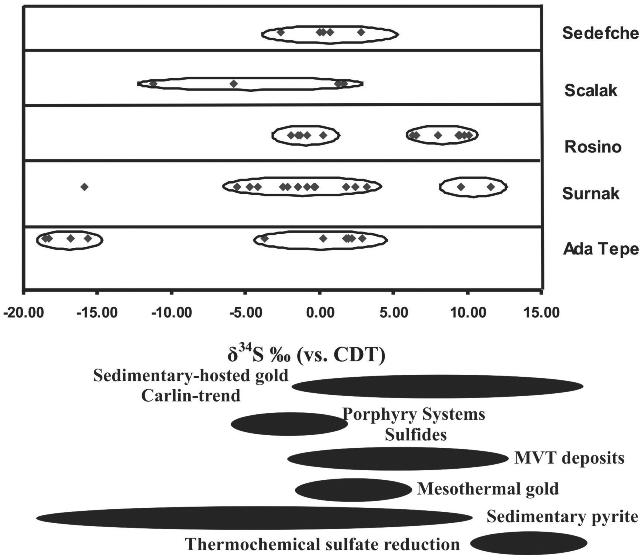

Figure 5. Sulfur isotopic data from Eastern Rhodopian sedimentary-rock hosted gold deposits relative to important references (Ohmoto and Rye, 1979; Cline et al, 2005).

Discussion: potential sulfur sources and mechanism of H_2S generation

Interpretation of sulfur isotope results from the deposits requires consideration of the isotopic composition of potential sulfur sources and mechanism of H_2S generation. Given that gold was transported as a bisulfide complex, knowledge of the sites of H_2S generation and migration pathways is important to gather information on the source of gold.

High H_2S concentration could promote high gold solubility, based on the well known reaction (Gammons and Barnes, 1989):

$$\mathbf{Au(s) + 2\ H_2S(aq) + 0.25O_2(g) = Au(HS)_2^- + H^+ + 0.5H_2O}$$

Figure 6 compares the mobility of gold versus silver as bisulfide complexes at 200 ºC (temperature from the fluid inclusion results at Ada Tepe) and shows that: 1) the higher the H_2S content, the higher the gold solubility; and 2) the higher the H_2S content, the higher the Au/Ag solubility ratio.

Shikazono and Shimizu (1987) demonstrated for the auriferous and gold-silver deposits of Japan that the Ag/Au ratios of native gold and electrum might be controlled by several factors such as temperature, pH, sulfur activity and Ag/Au concentration in fluid. On the other hand, they derived a relationship between these variables showing that the Ag/Au ratio is useful in estimating geochemical variables (sulfur activity, temperature, etc).

Most sedimentary rock-hosted epithermal deposits in the Eastern Rhodopes have Au/Ag ratios ranging between 4 and 5. Therefore, assuming that the metal ratios of the deposits reflect the metal ratios of the fluids from which they formed, this implies that H_2S concentrations in the fluids ranged between 10^{-3} and 0.1 molal.

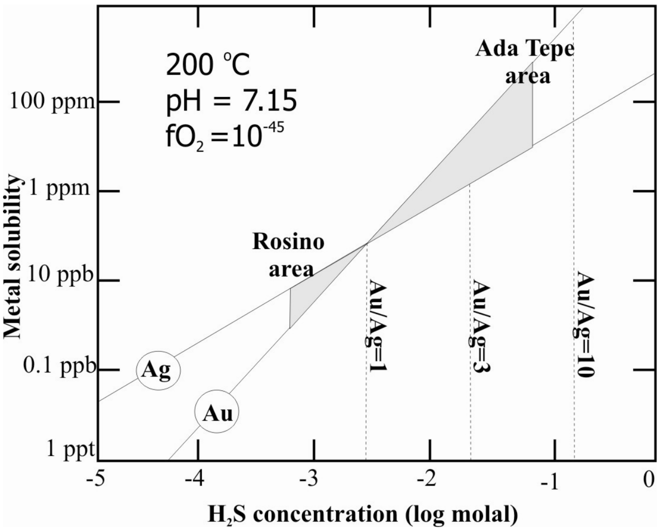

Figure 6. Diagram summarizing the solubility of gold and silver as a function of H_2S content. The shaded region shows the range in Au/Ag metal concentrations and sulfide content suggested for the Eastern Rhodopian sedimentary rock-hosted epithermal gold deposits. Solubility data from Gammons and Barnes (1989), Shenberger and Barnes (1989) and Gammons (1997).

Few mechanisms could be highlighted that can generate enough quantities of H_2S:

a) influx of magmatic H_2S;
b) release of H_2S during metamorphism of sulfide-rich country rocks;
c) dissolution of sedimentary pyrite
d) bacterial (30-110 °C) and thermochemical sulfate reduction (150-200 °C)

Dissolution of sedimentary pyrite could be responsible especially for the light sulfur isotopic fluid components (Ada Tepe, Skalak, Fig. 5.). The abundant framboidal pyrite at Stremtsi (Fig. 1.) also underlines this (C. Noverraz, personal communication, 2006, M.Sc. thesis in progress). However, only pyrite dissolution cannot explain the unusually high H_2S contents that appear to be necessary for the formation of the sedimentary rock-hosted gold deposits and the large range of $\delta^{34}S$ values of pyrite presented above.

The presence of deep sourced H_2S is also supported by the oxygen isotope data. However, considering that no magmatic reservoir contemporaneous with the formation of the sedimentary rock-hosted epithermal deposits has been identified so far and the fact of low sulfide content of the metamorphic basement requires an alternative mechanism.

Studies on other sedimentary rock-hosted deposits (e.q. Carlin-trend, Gammons, 1997, Cline *et al*, 2005) highlighted the importance of thermochemical sulfate reduction. This process could be considered especially in generation of heavy isotopic components in the case of Rosino and Surnak (Fig. 5.). Thermochemical sulfate reduction refers to the process by which buried organic matter (kerogen or other organic compounds) reduces sulfate to hydrogen sulfide. The occurrence in the stratigraphic column of sedimentary rocks rich in organic matter and sulfates evidences the possibility of this process.

Further sulfur, oxygen and carbon isotope studies are needed to characterize the significance of sedimentary-meteoric sources and to identify deep sourced fluids as a source of sulfur and gold. In conclusion, the fluid inclusion and stable isotope data are consistent with a magmatic/metamorphic fluid source, or a surficial fluid that has been extensively reequilibrated with magmatic and metamorphic rocks. Sulfur isotope data suggest that dissolution of sedimentary pyrite and thermochemical sulfate reduction are additional sulfur sources.

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