Zoned sulphur isotope signatures at the Mississippi Valley-type Touissit - Bou Beker - El Abed District (Morocco-Algeria) - Evidence for thermochemical sulphate reduction and mixing of sulphur sources

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ABSTRACT: In the Touissit - Bou Beker - El Abed MVT district the distribution of δ^{34}S values of the main stage mineralization can be essentially interpreted as the result of mixing between a heavy and a light δ^{34}S reservoir. The results suggest that thermochemical reduction of Triassic sulphate and, possibly, pyrites disseminated in the sedimentary sequence (and/or leaching of basement sulphides) constitute the sources of the two sulphur types. A zonation with δ^{34}S values for main stage sphalerite and galena increasing systematically eastwards has been recognized at the district scale. Temperatures calculated from coexisting sphalerite-galena pairs range from 70 ºC to 135 ºC and are in good agreement with geological and fluid inclusion data.

1 INTRODUCTION

In the northeastern part of Morocco and adjacent Algeria occurs probably the largest Mississippi Valley-type (MVT) district documented in Africa known as the Touissit - Bou Beker - El Abed (TBE) mining district (Bouabdellah 1993, Touahri 1991). The proposed genetic model considers hot basinal brines (100ºC, 10-15wt% NaCl) passing through Triassic and Infra-Liassic clastic and evaporitic units to reach the immediately overlying Aalenobajocian (middle Jurassic) dolomitic strata of the basin margin (Bouabdellah 1993, Bouabdellah et al. 1996). Mineralization is thought to take place during Oligo-Miocene compressional deformation and uplift and to have involved thermochemical sulphate reduction by hydrocarbons

In order to verify the validity of such a hypothesis, we conducted a regional sulphur isotope study on the sulphides and sulphates of the Moroccan deposits complemented by selected samples from El Abed. In a further evaluation of evaporite sources for these MVT deposits, we have analyzed gypsum from several locations in the TBE. These data provide insights into: (1) the source of sulphur; (2) the nature of processes involved in ore formation (i.e., biogenic versus thermochemical reduction of sulphate); and (3) the temperature of mineralization.

2 GEOLOGICAL SETTING

Mississippi Valley-type deposits of the TBE mining district are located in the NE of 'La chaîne des Horsts' within the Meseto-Atlasic domain of northeastern Morocco and adjacent Algeria (Fig.1). The TBE district represents one of the world's great Pb/Zn concentrations in carbonate strata and produced between 1926 and 1997 about 67 million metric tons of ore averaging 7 % Pb and 3 % Zn. In addition, the deposits contain silver (up to 600 g/t) and locally copper as by products. The district stretches 16 x 4 km in an ENE-WSW direction and encloses five major deposits of which four (Bou Beker, Touissit, Mekta and Beddiane) are located in Morocco and the fifth (El Abed) in Algeria. More than 30 sub-economic prospects are also known. Major deposits of the district lie in the large Missouine graben which trends northeasterly, bounded on the north and south successively by the horsts of Chebicat El Hamra and Menjel El Akhal (Fig. 1). Lead ore predominates in the western part of the district, whereas zinc is more important in the Algerian portion to the east.

In the TBE mining district, field relationships and modal mineralogical analyses show that the lithologies in the ore environment can be grouped into two stratigraphic and lithotectonic units (Fig. 2). A Palaeozoic basement of presumed Visean age is uncomfortably overlain by a relatively thin sequence of strata ranging in age from the Infraliassic to Callovo-Oxfordian. Mesozoic strata begin with a thin (2m) sequence of conglomerates and limestones of Infra-Liassic age, followed by a 25 metre-thicksequence of alternating dolomitic strata with interbeds of marls and clays of Aalenobajocian age. The Aalenobajocian strata (including the ore-hosting units) are in turn overlain uncomformably by a suc
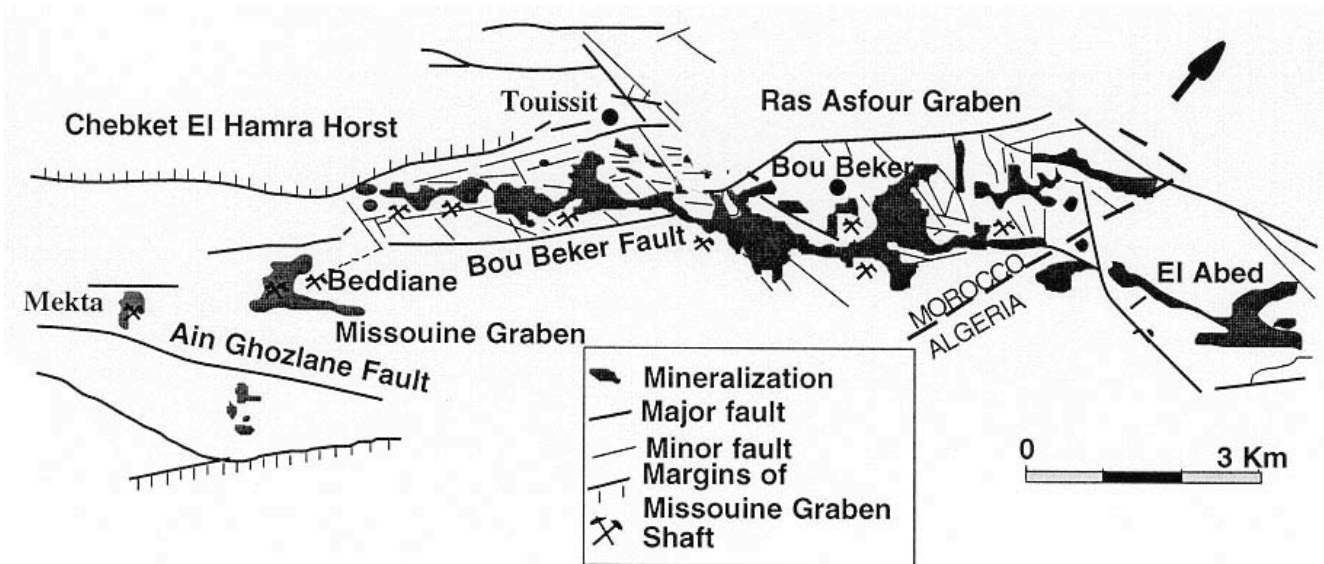
Figure 1 - Structural map of the Touissit - Bou Beker - El Abed district.

cession of sandstones, marls and carbonates of Upper Bajocian age known locally as the 'toit jaune'. The latter generally represents the hanging wall of economic mineralization, and grades upward into a 2 metre-thick ferruginous oolitic unit of Bathonian age. A thick impermeable formation consisting of-shales and carbonate rocks of Callovo-Oxfordian age completes the lithostratigraphic column. Ore

Figure 2 - Stratigraphic column of the Touissit - Bou Beker - El Abed district with localisation of Zn, Pb and Cu mineralizations.

bodies are exclusively concentrated within Aaleno-bajocian dolomites. Mineralization occurs as open space filling (veins, karst, collapse-breccias and internal sediments) and as replacement of more porous dolomite beds. A significant part of the ore occurs as zebra ore. Ore minerals are dominated by sulphides such as sphalerite, galena, pyrite, chalcopyrite, tetrahedrite and, to a lesser extent, marcasite.

Structurally, the TBE mining district is dominated by two major fault systems (Fig. 1): a dominant ENE-WSW-trending system consisting of extensional faults resulting in a piano key-like horst-and-graben structure, and a minor NNW-SSE-trending system. This deformation and the timing of the two fault systems are discussed by Dupuy (1984) and Torbi (1988).

3 RESULTS AND DISCUSSION

Sulphur isotope compositions were determined for 13 samples of sphalerite, 13 samples of galena and 3 samples of pyrite. In a further evaluation of evaporite sources for the MVT deposits investigated in this study, we have analyzed 8 samples of gypsum from several locations. The analyses were performed at the University of Lausanne using the on-line elemental analyser (Carlo Erba 1108) -continuous flow-isotope ratio mass spectrometer (Finnigan Mat Delta S). The analytical uncertainty (2σ) was ± 0.2 ‰. The data are reported as per mil (‰) deviations relative to the Canyon Diablo Troilite (CDT) standard. The main stage sulphur isotope values exhibit a range from 0.9 to 7.4 ‰ for galena and from 6.6 to 11.9 ‰ for sphalerite (Table 1 and Fig. 3). Th heaviest $\delta^{34}S$ values are seen in the easternmost deposit (El Abed) where $\delta^{34}S$ sphalerite values range from 10.6 ‰ to 11.9 ‰. Touahri (1991) reported similar
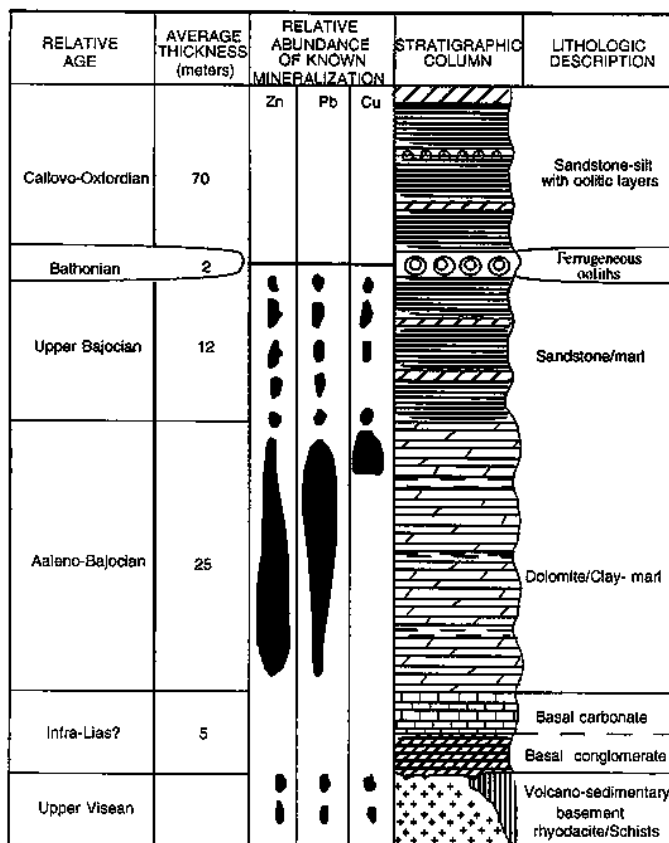
Table 1 - $\delta^{34}S$ values (‰ vs. CDT) of sulphides from the Touissit - Bou Beker - El Abed district.

	Sample #	Mineral	$\delta^{34}S$	Sample #	Mineral	$\delta^{34}S$
Mekta	MT2	galena[*]	1.9	BB1	galena[*]	3.9
	MT5	galena[*]	2.9	BB4	galena[*]	3.6
	MT7	galena[*]	0.9	BB5	galena[*]	3.6
	MEKTASP1	sphalerite[*]	6.6	BBSP-1	sphalerite[*]	9.1
	MEKTASP2	sphalerite[*]	9.0	BB2	galena[**]	-4.3
	MEKTASP4	sphalerite[*]	8.6	BBGAL	galena[**]	-4.4
				BBPY2	pyrite[***]	-17.8
Beddiane	BEDC1	galena[*]	3.1	BBPY3	pyrite[***]	-18.4
	BEDC2	galena[*]	4.0	BBPY4	pyrite[***]	-18.8
	BEDK6	sphalerite[*]	8.3			
	BEDK7	sphalerite[*]	7.4	EAB1	galena[*]	7.4
	BEDK8	sphalerite[*]	7.8	EAB2	galena[*]	6.6
	K1	sphalerite[*]	8.2	EAB3	galena[*]	7.0
	K2	sphalerite[*]	8.4	EAB4	sphalerite[*]	11.1
	K4	sphalerite[*]	8.5	EAB6	sphalerite[*]	11.9
				EAB7	sphalerite[*]	10.6

[*] main ore stage.

[**] late galena generation.

[***] pyrite disseminated in the basal limestones and overlying dolostones.

Figure 3 - $\delta^{34}S$ values of main stage sulphides, late galena, and Triassic gypsum from the Touissit - Bou Beker - El Abed district.

values for the main mineralization of El Abed. The lightest $\delta^{34}S$ values are found in the westernmost deposit of Mekta where sphalerite varies from 6.6 ‰ to 9.0 ‰. The deposits of Touissit and Beddiane, located in the centre of the district, show intermediate values with $\delta^{34}S$ sphalerite ranging between 7.4 ‰ and 9.1 ‰. $\delta^{34}S$ values of main stage galena show a similar decrease westwards (El Abed, 6.6 ‰ to 7.4 ‰; Bou Beker, 3.6 ‰ to 3.9 ‰; Beddiane 3.1 ‰ to 4.0 ‰; Mekta, 0.9 ‰ to 2.9 ‰). A paragenetically later galena generation occurring as fine disseminations in crystalline dolomites located stratigraphically higher in the lithostratigraphic column, a type of mineralization of minor importance, is characterized by light $\delta^{34}S$ values (-4.4 ‰ and -4.3 ‰).

The $\delta^{34}S$ values of gypsum, varying from 12.2 ‰ to 14.6 ‰ (not included in Table 1), fall within the ranges expected for Triassic through Late Jurassic marine evaporites (Claypool et al. 1980). This indicates a marine signature of the sulphur.

The distribution of the $\delta^{34}S$ values of the Touissit-Bou Beker-El Abed main stage sulphide minerals can be essentially interpreted as the result of mixing between a heavy and a light $\delta^{34}S$ reservoir. The heavy source had a stronger contribution in the eastern part of the district (El Abed) and the light source in the western part (Mekta). The central part of the district typified by Toussit and Bou Beker reflects an intermediate situation. Within each deposit, the narrow ranges of the main stage values and the fact that $\delta^{34}S$ sphalerite > $\delta^{34}S$ galena suggest an efficient homogenization of the H_2S of the ore-forming fluid and that precipitation of the sulphides occurred close to isotopic equilibrium. The light $\delta^{34}S$ values of late galena in Bou Beker suggest an increasing contribution from the light sulphur source subsequent to the

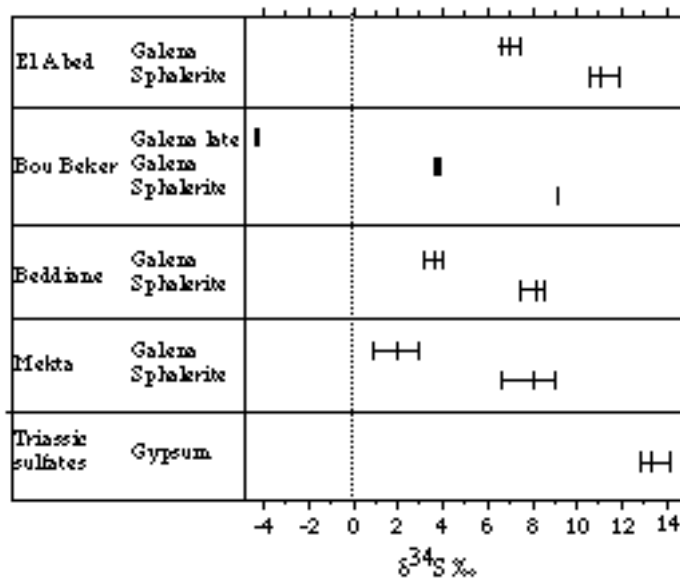main stage mineralization (this explanation can also be applied to some light $\delta^{34}S$ values for galena in "karst mineralization" reported by Touahri 1991).

Pyrite disseminated in the sedimentary sequence, mainly in the basal limestones and the overlying dolomitic strata, yields $\delta^{34}S$ values between -18.8 ‰ and -17.8 ‰ (Table 1) and is a possible source of light sulphur. Alternatively, light sulphur could be leached from basement rocks which constitute a probable metal source according to ore and rock lead isotope ratios (M. Chiaradia, Geneva, written comm.). This alternative would require an acid brine (see below).

Thermochemical reduction of Triassic sulphate is the most probable source of the heavy sulphur. It has been well documented that the reduction of sulphates by reaction with hydrocarbons could produce H_2S with the same isotopic ratio as the sulphate or up to 15 ‰ lighter, depending on the temperature and the amount of sulphate reduced (Jones et al. 1996). Whereas bacterial reduction produces sulphides with $\delta^{34}S$ values 40 ± 20 ‰ less than the parent sulphate, thermochemical sulphate reduction involves little or no net fractionation, although steps in the process could involve fractionation (Ohmoto et al. 1990, Goldhaber & Nicholson 1993). Regardless of the absolute amount, fractionation will produce sulphide with a $\delta^{34}S$ value lower than or similar to that of the parent sulphate (Jones et al. 1996).

In the TBE mining district, the close association of ore with dolomitic facies rich in organic matter as well as the light carbon isotope values of gangue carbonates led, Bouabdellah (1993) and Bouabdellah et al. (1996) to suggest that hydrocarbons acted as a reductant of sulphate. This is also supported by the following evidence indicating that during minerali-

zation temperatures were high enough to allow thermochemical sulphate reduction. Field observations show that coarse crystalline dolomites (CCD) which host economic orebodies crosscut stylolitization indicating that the formation of CCD occurred after burial (Bouabdellah 1993). On the other hand, organic petrography studies of macerals (exinite, vitrinite and inertinite), amorphous kerogen, and solid bitumen underline the high maturity of organic matter which has exceeded the oil window in areas spatially associated with economic orebodies (Bouabdellah 1993). Gathering together these observations, we may conclude that in the TBE mining district, mineralization occurred at temperatures > 100 ºC. Temperatures calculated from coexisting sphalerite-galena pairs (contiguous crystals) using fractionation factors recommended by Ohmoto & Rye (1979) range from 70 ºC to 135 ºC. These temperatures are in good agreement with homogenization temperatures deduced from fluid inclusions in sphalerite and saddle dolomite (Dupy 1984, Makhoukhi 1993, Bouabdellah 1993).

The sulfur isotope results are consistent with Oligo-Miocene migration of brines transporting metals leached from basement rocks which encountered, trapped in Aaleno-Bajocian dolomites, H_2S derived from thermochemical reduction of sulphate. The structural control and widespread dissolution suggest that the brines were acid and that they were transported into the basin along fractures without much interaction with the carbonate host rock.

4 CONCLUSIONS

(1) $\delta^{34}S$ values of sphalerite and galena in the main mineralization phase increase eastwards at the district scale.
(2) Within each deposit, the homogeneity of the values and the fact that $\delta^{34}S$ sphalerite > $\delta^{34}S$ galena suggest an efficient homogenization of the H_2S of the ore-forming fluid and that isotopic fractionation of the mineralization occurred close to equilibrium.
(3) The distribution of the $\delta^{34}S$ values of the Touissit-Bou Beker-El Abed main stage mineralization can be essentially interpreted as the result of mixing between a heavy and a light $\delta^{34}S$ reservoir. Thermochemical reduction of Triassic sulphates is the most probable source of heavy sulphur. Pyrite disseminated in the sedimentary sequence constitute a probable source of light sulphur. Leaching of basement sulphides represent an alternative source of light sulphur.
(4) Temperatures calculated from coexisting sphalerite-galena pairs, ranging from 70 ºC to 135 ºC are in good agreement with homogenization temperatures deduced from fluid inclusion data, the geological context, and the maturation of organic matter.

(5) Precipitation of ore-grade sulphides in the TBE mining district occurred when metal-bearing fluids arrive at "traps" rich in H_2S derived largely from thermochemical reduction of Triassic sulphates mixed to different degrees with light reduced sulphur. The "traps" are characterized by being rich in organic matter showing a maturation beyond the oil window.

5 ACKNOWLEDGEMENTS

REFERENCES

Bouabdellah, M. 1993. Metallogenesis of a Mississippi Valley-type district: case of the Touissit - Bou Beker mining district, Northeastern Morocco. *Unpub. Ph.D. thesis Ecole Poly. de Montréal*: 367 (in French).

Bouabdellah, M., Y. Héroux, & A.C. Brown, 1996. Pétrographie et altération de la matière organique du gisement de plomb-zinc-cuivre de Beddiane, district de Touissit - Bou Beker, Maroc nord oriental. *Can. J. Earth Sci. 33*: 1363-1374.

Claypool, G.E., I.R. Holser, H. Kaplan, H. Sakai & K. Zak, 1980. The ages curves of sulphur and oxygen isotopes in marine sulphate and their mutual interpretations. *Chem. Geol. 28*: 199-260.

Dupuy, J. 1984. Etude du gîte plombifère de Oued Mekta (Maroc Oriental); essai d'explication de la répartition des métaux (Pb, Zn, Cu, Ba) dans le district de Touissit-Bou Beker. *Unpubl. Ph.D. thesis Univ. Orléans*: 268.

Goldhaber, M. & A.D. Nicholson, 1993. Thermochemical sulphate reduction as a source of sedimentary H_2S [abs.]: *Geol. Soc. of Am.- Abstracts with Programs 25(6)*: 21-22.

Jones, H.D., S.E. Kesler, F.C. Furman, & J.R. Kyle, 1996. Sulphur isotope geochemistry of Southern Appalachian Mississippi Valley-Type Deposits. *Econ. Geol 91*: 355-367.

Makhoukhi, S. 1993. Le gisement de plomb de Beddiane (Maroc Oriental): gîtologie et éléments de modélisation d'une minéralisation de type Mississippi Valley. *Unpubl. Ph.D. thesis Ecole Normale Supérieure de Paris*: 124.

Ohmoto, H. & R.O. Rye, 1979. Isotopes of sulphur and carbon. *In: H.L. Barnes (ed.), Geochemistry of hydrothermal ore deposits*. 509-567.

Ohmoto, H., C.J. Kaiser, & K.A. Geer, 1990. Systematics of sulphur isotopes in recent marine sediments and ancient sediment-hosted base metal deposits. *In. H.K. Herbert & S.E. Ho (eds.) Proceedings of the conference on stable isotopes and fluid processes in mineralization*: 70-120.

Torbi, A. 1988. Analyse structurale et étude de la fracturation du socle hercynien et de sa couverture dans les Monts du SE d'Oujda, Méséta Orientale, Maroc. *Unpub. Ph.D. thesis, Univ. de Poitiers*: 186.

Touahri, B. 1991. Géochimie et métallogénie des minéralisations à plomb et zinc du Nord de l'Algérie. *Mémoires-Offices National de la Géologie, 4*: 168.