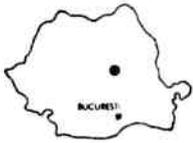# ISOTOPIC COMPOSITION OF OXYGEN, CARBON AND SULPHUR IN SIDERITE ORE DEPOSITS ASSOCIATED TO NEOGENE VOLCANISM IN THE EAST CARPATHIANS – PRELIMINARY DATA.

Alexandru SZAKÁCS, Filofteia GAFTOI

Institutul de Geologie şi Geofizică. Str. Caransebeş 1, 78344 Bucureşti 32.

Abstract: *Isotopic Composition of Oxygen, Carbon and Sulphur in Siderite Ore Deposits associated to Neogene Volcanism in the East Carpathians – Preliminary Data.* The isotopic composition of oxygen and carbon in siderites and of sulphur in associated marcasites, from siderite ore deposits related to the Neogene volcanics in the East Carpathians, has been measured. The obtained $\delta^{18}O$ values (–7.56–9.16 ‰ PDB) are consistent with the meteoric origin of water in the carbonate forming hydrotherms. Siderite formation temperatures (ca. 60^0 C), obtained using Epstein's isotopic thermometer, are in agreement with both mineralogical features of siderites and geothermal data concerning their occurrence areas. The ^{13}C values in the samples from the Harghita Mts can be explained – as in the case of free CO_2 from the actual thermomineral systems in the same area – by thermal decomposition of marine carbonates. The isotopic composition of sulphur from marcasites is consistent with their magmatic origin but also other hypotheses (filtration of hydrotherms through sulphate–bearing formations for instance) may be taken into account.

1. Introduction

By the courtesy of Dr. Wang Zhonggang and Dr. Yu Xueyuan preliminary ^{18}O and ^{13}C data have been obtained in the Institute of Geochemistry – Academia Sinica – from Guiyang (People's Republic of China) on siderite samples collected in the Harghita and Călimani Mts., Romania. Simultaneously Sulphur isotopic composition of marcasite associated to siderite in the Harghita Mts. has been determined in the Institute of Geology and Geophysics, Bucharest.

Informations concerning isotopic composition of Oxygen, Hydrogen and Carbon have recently been obtained for hydrogeological systems in the aria of the Neogene Volcanic chain (Crăciun et al., 1989).

2. Geological and metallogenetical framework

Two major siderite occurrences forming accumulations of economic interest at Lueta–Vlăhiţa and Mădăraş, and a large number of minor occurrences scattered along the western and eastern sides of the volcanic range are known in the Harghita Mts. Small-scale siderite outcrops have also been found within a limited area in the southern part of the Călimani Mts (near Topliţa).

The siderite deposits occur either at the contact zone between Neogene andesitic volcanic rocks and their pre-volcanic basement or within the Volcaniclastic formation produced during the first phase of volcanic evolution. They have been denominated as the "Lueta type" and "Vlăhiţa type" respectively (Peltz et al., 1982).

The deposits essentially consists of sideritized rocks of various original composition: Precambrian metamorphics (at Mădăraş), Neogene sedimentary rocks (at Lueta–Vlăhiţa and Mădăraş) and Neogene volcaniclastics (in all occurrence areas). The mineral paragenesis includes, besides host-rock mineral assemblage, siderite ± opal ± marcasite, as neoformation, the monomineral siderite deposits being however the most frequent ones.

Siderite genesis has largely been debated, the opinions differing from one author to another or even at the same author from one ore type to another. Thus, for instance, Tănăsescu (1967) stressed the hydrothermal origin for the Mădăraş siderites. Peltz et al. (1983) stated different genesis for various ore

types: volcano-sedimentary (Lueta type), volcano-sedimentary + hydrothermal-metasomatic (Vlăhiţa type) and hydrothermal-metasomatic (Chirui type siliceous siderite deposit). Szakács (1988, unpubl. report) assumed a hydrothermal genesis for all types of siderite deposits in the Harghita and South Călimani Mts.

3. Sampling localities

Three siderite samples have been analysed for their stable isotope composition: sample V-1 Vlăhiţa-type sideritized clay, Tîrbuc brook, Băile Homorod (Harghita Mts); sample L-2 Lueta-type sideritised clay, Lueta mine (Harghita Mts.); sample Ro-37 Vlăhiţa-type sideritised clay "soft pebble" from volcaniclastic deposit, Pirîul Popii brook, Topliţa (Călimani Mts). The marcasite samples are localised as follows: sample Fe-29 Vlăhiţa-type ore, borehole 733 Selters m. 232–235, Vlăhiţa; sample Fe-39, Lueta-type ore, Lueta mine; sample Fe-47, Lueta-type ore, borehole 25133 m. 522–524, Mădăraş.[1]

4. Analytical method

Isotopic composition of Oxygen and Carbon has been analysed at the Departament of Isotopic Geochemistry – Academia Sinica – from Guiyang, People's Republic of China by the analysts Qiu Xiuhua and Liu Deping. After testing their mineralogical composition by X-ray diffractometry the samples have been chemically disaggregated by etching with H_3PO_4 100 % at 75^0 C for five hours. ^{18}O and ^{13}C have been measured using a MAT 230-C type mass-spectrometer yielding an instrumental error of 0.04 %. The obtained results are rendered as $\delta^{18}O$ (‰) and $\delta^{13}C$ (‰) values[2] according to the PBD International Standard. $\delta^{18}O$ is given according to the SMOW Standard as well.[3]

Sample processing and analytical method for Sulphur isotope analysis used at the Institute of Geology and Geophysics, Bucharest have already been published (Udubaşa, Gaftoi, 1985). The analytical results are given as $\delta^{34}S$ (‰) according to the CDT International Standard.

---

[1] The sample has been taken off from borehole core kept in the Lithoteque of the Institute of Geology and Geophysics with the contribution of dr. Muşat Gheorghian to whom we are grateful.

[2] The isotopic composition of an element X is rendered as δ_x representing the relative difference between isotopic ratios of the sample and that of the Standard, acording to the formula:
$$\delta_x = \frac{RSample - RStandard}{RStandard} \times 10^3 \text{ (‰)},$$
where R is the isotopic ratio for sample and standard respectively.

[3] The transformation is made using the formula:
$$\delta^{18}O_{SMOW} = 1.03086 \times \delta^{18}O_{PDB} + 30.86$$

5. Analytical results and discussion

5.1. Oxygen isotopes

A narrow range of ^{18}O in CO_2 of the three analysed siderite samples ($\delta^{18}O = -7.56$ to -9.16 ‰PDB) can be observed. This becomes obvious as compared with the wide variation field in different types of carbonatic rocks (+0.6 to +34 ‰, Degens, 1967) suggesting the formation of the discussed siderites under similar conditions of isotopic equilibrium, in similar thermodynamic conditions respectively.

In most natural media the isotopic equilibrium between aqueous solutions and minerals precipitating from them is reached for Oxygen and Hydrogen due to the high rates of their isotopic exchange reactions. Thus minerals usually preserve isotopic composition of the fluid at precipitation temperature (Ohmoto, 1986). For this reason Oxygen and Hydrogen isotopic composition is frequently used for water origin determination in mineralizing solutions. Since the great deal of hydrothermal solutions have been proved to be formed of meteoric water (Sheppard, 1986) and since Crăciun et al. (1989) reached the same conclusion for hydrogeothermal systems associated to the Neogene volcanic areas in Romania, the exogene origin of water in hydrothermal solutions from which the study siderites have been generated, can also be presumed. A simple calculation based upon experimental data concerning ^{18}O fractionation in the calcite-water system (O'Neil et al., 1969) points to the fact that our siderites could be in isotopic equilibrium with a water having $\delta^{18} = +0.93$ ‰ at a temperature of 60^0 C. This value is consistent with the hypotesis of meteoric origin of water in the ore generating hydrotherms.

The higher $\delta^{18}O$ in geothermal systems as compared with unheated local meteoric waters – the so called "oxygen-shift" – is largely explained by heavy isotope enrichment as a result of rections between geothermal waters and percolated crustal rocks. The higher ^{18}O content of our analysed siderites and their generating hydrotherms respectively – assuming isotopic equilibrium between them – with respect to that of waters from the actual geothermal systems of the areas (Crăciun et al., 1989) could be explained by the same mechanism.

The isotopic composition of Oxygen from siderites in base-metal hydrothermal veins at Rudnany (Slovakia) (−11.7‰ PDB) has been interpreted by Cambel et al. (1984) as indicating the magmatic origin of water in the generating hydrotherms.

The Oxygen isotopic geothermometer has been stated by Epstein et al. (1953, fide Sheppard, 1984) and it is widely used especially in sedimentary petrology. It has also been used in the study of thermal conditions of hydrothermal carbonate mineral genesis

(e. g. Cornides et al., 1966). Taking into acount that Epstein's geothermometer has been calibrated for the calcite-water system, its use in our case would not be justified. There are, however, several favourable circumstances for such an attempt even only to test the consistency of the obtained thermic parameter, as order of magnitude, with that suggested by the paragenetic and mineralogical features of the siderite ore. The structural identity of siderite and calcite makes possible the use of the isotopic reaction constants of the latter as already has been done by other authors (Cambel et al., 1984, for instance). Furthermore, the high probability that an isotopic equilibrium state has been reached as suggested by chemical equilibrium inferred from mineralogical studies (Szakács, 1988, 1989, unpubl. reports), the mineralogical and chemical simplicity of the system and the recent age of the ore forming process (Szakács, 1988, unpubl. report) making improbable isotopic exchange reactions subsequent to ore deposition, are all in favour of the use of the isotopic thermometer.

Table 1 presents isotopic temperatures obtained for each sample using Epstein's equation:

$$T (^0C)=16.5-4.3(\delta c-\delta w)+0.14(\delta c-\delta w)^2 \quad [4]$$

were $\delta w \sim 0$. The obtained values of about 60^0C (61.24^0 C in average) are in agreement with both the thermal domain suggested by the mineral paragenesis (siderite + marcasite + opal) and the mineralogical features of siderite (Szakács, 1988, unpubl. report). They are also consistent with regional thermal features in the occurence areas, as reflected in heat-flow anomalies (Veliciu, 1988).

abundance of ^{13}C in the mantle (ca. $-5\%_0$ in average)(Ohmoto, 1986) points to a high participation of the heavy Carbon isotope in the Vlăhiţa siderites exceeding the common values of carbonate rocks.

Carbon, unlike Hydrogen and Oxygen but like Sulphur, tends to preserve its initial isotopic composition during precipitation process of minerals from solutions because the low rate of the isotopic exchange reactions at low temperatures that usually makes impossible isotopic equilibrium to be reached (Ohmoto, 1986). Thus, $\delta^{13}C$ data are interpreted rather in terms of Carbon (CO_2) source than in terms of thermodynamic and chemical conditions of precipitation. Consequently, a possible explanation for high ^{13}C content of Harghita siderites has to be looked for in connection with CO_2 source.

Using published data, Degens (1967, Fig. 2) presented a sketch showing ^{13}C fractination in carbonatic systems from different natural media. In order to explain ^{13}C enrichement in travertines the origin of CO_2 by thermal decomposition of marine limestones has been admitted. The increase of ^{13}C content takes place during CO_2 dissolution in thermal water, the precipitated carbonate from these solutions having $\delta^{13}C$ of ca. $+7 - +8\%_0$. Such a hypotesis is worth considering for the CO_2 origin in the Harghita siderites as well.

Considering $\delta^{13}C$ data Crăciun et al. (1989) presumed Carbon origin in thermal waters of the Pannonian Plain in carbonate deposits. They also assign the isotopic values obtained for free CO_2 on the Tuşnad and Poiana Coşnei mineral waters ($\delta^{13}C = -2.9 - -5.2$

Table 1
Isotopic composition of oxygen and carbon from siderites

No	Sample	Siderite %	$\delta^{16}O \%_0$ PDB	$\delta^{18}S \%_0$ SMOW	$\delta^{13}C \%_0$ PDB	$t(^0C)$
1	RO-37	95	-9.16 ± 0.2	21.42	-0.18 ± 0.2	67.63
2	L-2	90	-7.88 ± 0.2	22.74	$+4.27\pm0.2$	59.07
3	V-1	90	-7.56 ± 0.2	23.07	$+6.81\pm0.2$	57.01
	Average		-8.20	22.41		61.24

5. 2. Carbon isotopes

The two samples from the Harghita Mts. present close positive $\delta^{13}C$ values whereas that from Topliţa shows a low negative value with respect the PDB Standard (Tab. 1). The comparison of these results with the isotopic composition of Carbon in various natural media (ca. $-7\%_0$ for atmospheric CO_2, -2 to $4\%_0$ for marine limestones, $-22\%_0$ in average for organic Carbon in marine environment and $-26 \%_0$ for organic Carbon in terrestrial environment) or with the inferred

$\%_0$) either to the "probably thermal transformation" of certain carbonatic formations or to mixing processes between CO_2 originating in carbonatic rocks with juvenile CO_2 in proportion of 3/1 (p. 35).

The isotopic composition of Carbon in siderites of hydrothermal veins at Rudnany (Slovakia) with an average $\delta^{13}C = -4.2 \%_0$ is interpreted by Cambel et al. (1984) as indicating the mixing of 2/3 deep-seated Carbon (with $\delta^{13}C=-6.5 \%_0$) and 1/3 sedimentary carbon (with $\delta^{13}C = 0 \div +1 \%_0$).

The value of $\delta^{13}C=-0.18 \%_0$ obtained for the Topliţa siderite sample is clearly influenced by the organic Car-

---

[4] δc and δw represent the isotopic composition of Oxygen from carbonate and water respectively.

bon pointed out in the composition of the initial sideritized clay (Szakács, 1988, unpubl. report).

5. 3. Sulphur isotopes

Two of the analysed marcasite samples present positive $\delta^{434}S$ values (+2.32‰ and 1.54 ‰) close to the CDT Standard. The third sample shows a higher positive value (+10.76 ‰) (Tab. 2).

Table 2

Isotopic composition of sulfur from marcasite samples

No	Sample no.	$\delta^{34}S$ ‰ CDT	$^{32}S/^{34}S)_t$
1	Fe–29	+1.54	22.186
2	Fe–30	+2.32	22.169
3	Fe–47	+10.67	21.983

A value of $\delta^{34}S = -3.60$ ‰ has been measured earlier for a marcasite sample occuring within a siderite occurence hosted in a fault clay localised in metamorphic formations near Frumoasa (Ciuc Mts) (Runceanu, Voicu, 1988). This autcrop is considered to be genetically linked with the nearby Harghita Neogene volcanism (Runceanu, Voicu, 1988).

Udubaşa and Gaftoi (1985) presented Sulphur isotopic data for numerous hypogene Neogene ore sulphide deposits from Metaliferi Mts. According to these data $\delta^{34}S$ varies from +1.46 to +3.60 ‰ in pyrites, +0.25 to +4.43 ‰ in sphalerites and –1.52 to + 2.32 ‰ in galenas. The $\delta^{34}S$ values for the Lueta-Vlăhiţa marcasites are placed in the variation domain of pyrites from the Neogene hydrothermal ores in the Metaliferi Mts. The marcasite from Mădăraş displays higher ^{34}S content.

Genetical interpretation possibilities of our analytical results are strongly limited by the lack of information concerning ^{34}S distribution in several associated sulphidic and/or sulphatic phases. The low $\delta^{34}S$ values close to the Standard are usually considered to be consistent with the magmatic origin of Sulphur. Although our Sulphur isotope analyses on marcasite samples from the Harghita Mts are not contrary to a deep-seated (magmatic) origin, other interpretations can also be taken into account, especially if we consider the probable non-magmatic origin of Carbon in siderites as suggested by Carbon isotopic data. Cambel et al. (1984) for instance explained the $\delta^{34}S$ range (–2.0 – +2.5 ‰) measured in pyrites in siderite gangue of the hydrothermal ores at Rudnany (Slovakia) by the deep-seated origin of Sulphur; the high values (+4.5 to +12 ‰) obtained for pyrites in the main ore body are assigned to a possible filtration process of the hydrothermal solutions through sulphate bearing Paleozoic rocks. The influence of a sulphate phase during the generation and movement of ferriferous hydrotherms is not out of question in the Harghita Mts, at Mădăraş especially.

Further detailed isotopic investigations involving larger number of samples, both carbonates and sulphides, would provide more accuracy in genetic studies of siderite deposits associated to the Neogene volcanism in the East Carpathians.

References

Cambel B., Zukov F.I., Timofejevna Savcenko L., Smejkal V. (1984) Isotopic composition of sulphur, carbon and oxygen in minerals of the Rudnany siderite-barite polymetallic ores. *Geologicky Zbornik – Geologica Carpatica*, 35, 1, p. 21–37, Bratislava.

Cornides I., Kiss J., Szeredai L. (1966) A középső-mátrai érctelér képzödési hömérséklete az ^{18}O-izotóp relativ gyakorisága alapján. *Földt. Közl.*, XCVI, 1, p. 43–50, Budapest.

Crăciun P., Barnes I., Bandrabur T. (1989) Stable isotopes in hydrogeothermal structures in Romania. *St. tehn. econ.*, E, 15, p. 17–39, Bucureşti.

Degens E.T. (1967) Stable isotope distribution in carbonates. In: G.V. Chilingar, H.J. Bissel, R.W. Fairbridge (eds.) Carbonate rocks. Elsevier, p. 193–208, Amsterdam.

Ohmoto H. (1986) Stable isotope geochemistry of ore deposits. In: J.W. Valley, H.P. Taylor Jr., J.R. O'Neil (eds.) Stable isotopes in high temperature processes. *Reviews in Mineralogy*, 16, p. 491–559.

O'Neil J. R., Clayton R. N., Mayeda T. K. (1969) Oxygen isotope fractionation in divalent metal carbonates. *Journ. Chem. Phys.*, 51, 12, p. 5547–5558.

Peltz S., Peltz M., Bratosin I., Ianc R. (1982) Contribuţii la cunoaşterea mineralizaţiei de fier asociate vulcanismului neogen din regiunea Lueta-Vlăhiţa-Chirui (judeţul Harghita). *D. S. Inst. Geol. Geofiz.*, LXVI, 2, p. 81–116, Bucureşti.

 – (1983) Iron mineralization associated with the Neogene volcanism in the South-west of the Harghita Mountains (East Carpathians). *An. Inst. Geol. Geofiz.*, XII-th Congress AGCB, LXI, p 233–244, Bucureşti.

Runceanu M., Voicu G. (1988) Date preliminare asupra mineralizaţiei de siderit şi sulfuri de pe pîriul Cere (munţii Ciucului). *D. S. Inst. Geol. Geofiz.*, 74, 2, p. 89–98, Bucureşti.

Sheppard S. M. F. (1984) Isotopic geothermometry. *Thermométrie et barométrie géologique*, 2, p. 349–412, Paris.

 — (1986) Characterization and isotopic variations in natural waters. In: J. W. Valley, H. P. Taylor Jr., J. R. O'Neil (eds.) Stable isotopes in high temperature geological processes. *Reviews in Mineralogy*, 16, p. 165–183.

Tănăsescu L. (1967) Date noi asupra formaţiunilor geologice de adîncime din bazinul Mădăraş şi asupra mineralizaţiei de siderită. *St. tehn. econ.*, Inst. Geol., A, 7, p. 188–204, Bucureşti.

Udubaşa G., Gaftoi F. (1985) Sulphur isotopes of some alpine ore deposits and occurrences from the Metaliferi Mountains, Romania. *D. S. Inst. Geol. Geofiz.*, 70-71/2, p. 141–157, Bucureşti.

Veliciu S. (1988) Contribuţii privind prospecţiunea geotermică a apelor termale cu aplicaţii în R.S. România. *St. tehn. econ.*, Inst. Geol. Geofiz., D, 15, p. 85–201, Bucureşti.