

Apparent stable isotope heterogeneities in gangue carbonates of the Mississippi Valley-type Zn-Pb deposit of San Vicente, central Peru

J. Spangenberg¹, Z.D. Sharp², and L. Fontboté¹

¹ Département de Minéralogie, Université de Genève, 13, rue des Maraîchers, CH-1211 Genève 4, Switzerland
 ² Institut de Minéralogie, Université de Lausanne, CH-1015 Lausanne, Switzerland

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Abstract. The aim of the present communication is to emphasize that some variations of the measured δ^{13} C and δ^{18} O values are *apparent*, and due to analytical interferences caused by the presence of sulfur and organosulfur compounds in the analyzed carbonates. This is particularly relevant for isotopic studies on carbonate-hosted mineral deposits, where the nearly ubiquitous association of the host carbonates with organic matter and sulfides can certainly affect the metallogenetic interpretations. In this work two methods were used to overcome the disturbing effects of sulfides and organic matter: (1) sample pretreatment following the method proposed by Charef and Sheppard (1984), combining the oxidation of organic matter with sodium hypochlorite and trapping of the sulfur species with silver phosphate; and (2) laser-based microprobe extraction. Apparent isotopic variations in sparry dolomite from a single hand sample of zebra ore from the MVT Zn-Pb deposit, San Vicente, central Peru, are as large as $6\% \delta^{13}$ C and $4\% \delta^{18}$ O. These variations are reduced to several tenths of a per mil when the samples are pretreated. A careful examination of the effects of treatment with NaOCl and/or Ag₃PO₄ in relation to the concentration of sulfide inclusions indicates that the main disturbing effects for δ^{13} C values are the presence of sulfur species and organic matter, whereas the δ^{18} O values are mainly affected by the presence of sulfides. Fine- and medium-grained replacement carbonates from MVT and other sediment-hosted base metal deposits are potentially the most affected during isotope analysis, due to the common presence of organic matter and sulfides. Using in situ laser microprobe techniques, it is possible to determine isotopic variations at a sub-millimeter scale. Our results show that laser extraction analysis allows a more precise sampling of the carbonate minerals, and minimizes contamination of the sample with sulfides and to some extent with intergrown organic matter. However, there is an isotopic shift associated with the laser extraction technique, of the order of 0.5–1‰ for δ^{13} C and δ^{18} O values.

Changes in the stable isotope composition of host and gangue carbonates of Mississippi Valley-type (MVT) Pb-Zn deposits are mainly explained as an effect of changing fluid composition, temperature, water/rock ratio, or some combination of these effects (e.g. Hall and Friedman 1969; Pinckney and Rye 1972; Sverjensky 1981; Hannah and Stein 1984; Machel 1987; Gregg and Shelton 1989; Rowan and Leach 1989; Frank and Lohman 1986; Ghazban et al. 1990). In general, it has been observed that with advancing diagenetic stages, the carbon and oxygen isotope ratios are lowered (Machel 1987; Banner et al. 1988; Kaufman et al. 1990, 1991; Fontboté and Gorzawski 1990; Moritz et al. 1993).

In the course of an ongoing investigation on the geochemical zonation in gangue carbonates of the Mississippi Valley-type Zn-Pb district San Vicente, central Peru, we attempt to trace potential small carbon and oxygen isotopic variations (e.g. less than 2%) at the deposit and the district scale that could reflect basinal brine migration. For this purpose, defined carbonate generations have been sampled and analyzed from different parts of the district. Preliminary results confirm the general tendency toward lower isotope ratios with advancing diagenetic stages, but reveal variations within single hand specimens of the same order as those observed over the entire deposit (in the range of -4.1 to $2\% \delta^{13}$ C and -10.3 to -5.9% δ^{18} O, see Fontboté and Gorzawski 1990). These major isotopic heterogeneities at hand specimen scale may preclude the recognition of subtle isotopic variations at orebody, deposit, or district scale.

The aim of the present communication is to demonstrate that some of the variations of the measured δ^{13} C and δ^{18} O may be *apparent*, and due to analytical interferences caused by the presence of sulfides and organic matter in the analyzed carbonates. Sulfides and organic matter, which are abundant in most carbonate-hosted base metal deposits, can strongly affect the carbon and oxygen isotope analyses (e.g. Smith and Croxford 1975; Weber et al. 1976; Rye and Williams 1981; Charef and Sheppard 1984), and may account for the large isotopic variations at a small scale. We want to emphasize the need for controlling the influence of organic, organosulfur, and sulfur species of the measured δ^{13} C and δ^{18} O values of carbonates. This is particularly relevant for isotopic studies on carbonate-hosted mineral deposits, where the nearly ubiquitous association of the host carbonates with organic matter and sulfides can certainly affect the metallogenetic interpretations.

In this work two methods were used to overcome the disturbing effects of sulfides and organic matter: (1) sample pretreatment following the method proposed by Charef and Sheppard (1984), combining the oxidation of organic matter with sodium hypochlorite and trapping of the sulfur species with silver phosphate; and (2) laser-based microprobe extraction.

The isotopic variations at the centimeter to sub-millimeter scale were evaluated with a combination of a systematic detailed sampling using conventional and *in situ* laser methods. Treatment for organic matter and sulfur allows us to recognize slight variations of isotopic ratios (i.e. less than 0.5%) in a defined generation of the host carbonates in San Vicente through the ore-bodies, ore deposits, or ore district, which otherwise might be overlooked.

Geologic background

The geology and genetic aspects of the San Vicente Zn-Pb deposit, including Sr, C, and O isotope studies in the carbonate gangue

minerals, are discussed in Fontboté and Gorzawski (1990) and Moritz et al. (1993). The ore occurs as lens-shaped bodies, generally concordant with the bedding, and displays a characteristic rhythmic banding, known as zebra rock or diagenetic crystallization rhythmites (Fontboté and Gorzawski 1990; Fontboté 1993). The main ore minerals, sphalerite and galena, are interbanded with white sparry dolomite and grey replacement dolomite. Three distinct dolomite types occur in the host rocks: dark-grey replacement dolomite, ore-stage sparry dolomite, and late-stage void-filling dolomite.

The early stage replacement dolomite, referred to as generation I in Fontboté and Gorzawski (1990), is a very fine- to mediumgrained, dark-grey dolomite, with abundant inclusions of organic

 Table 1. Range of organic carbon and sulfur contents of gangue carbonates in the San Vicente MVT deposit. The number of analyzed samples (by LECO pyrolisis) is given in parentheses

Carbonate generation	C _{org} (wt. %)	S (wt. %)	
Dark replacement	0.09-5.2	0.13-2.1	
White sparry dolomite (5)	< 0.01–0.09	0.07-0.08	
Late filling carbonate (3)	< 0.01-0.05	< 0.01-0.02	



Fig. 1. Representative hand sample (FSV-924) of zebra ore showing the sampled sites. Detail of the *in situ* laser microsampled area. Individual bands (*letters*) and specific analysis locations (*numbers*) correspond with sample names in tables

matter. In some ore-bearing samples this stage I dolomite is completely replaced by sphalerite and, less commonly, by galena. The total organic carbon and sulfur contents in this dark replacement dolomite are up to 5.2 wt.% and 2.1 wt.%, respectively (Table 1).

The sparry dolomite consists of coarse or very coarse, subhedral, light-grey to white or light-brown dolomite, and corresponds to generation II of Fontboté and Gorzawski (1990). This dolomite type occurs as cement in moldic and vuggy porosity, or as bands between the dark replacement dolomite, giving the characteristic rhythmic banding of the zebra rock (Fig. 1). Zonal crystal growth can often be recognized as a simple color difference, due to a low amount of disseminated sulfides (up to 0.08 wt.% total sulfur) and organic matter (up to 0.09 wt.% total organic carbon). The precipitation of sparry dolomite is interpreted as a late diagenetic event, having formed from highly saline basinal brines (Fontboté and Gorzawski 1990; Moritz et al. 1993). Sphalerite mineralization is mainly paragenetically associated with this sparry dolomite generation.

Late-stage open-space-filling dolomite is a coarse- to very coarsegrained, milky-white, xenomorphic dolomite, virtually free of organic matter and sulfides (Table 1). It occludes voids in white sparry dolomite, and correlates with the generation III dolomite of Fonteboté and Gorzawski (1990). Locally, this late-stage diagenetic crystallization generation consist of calcite, galena, or bitumen instead of dolomite. In the samples selected for this study the filling carbonate is exclusively dolomite.

Analytical procedures

Three different analytical procedures have been compared: (1) conventional acid CO₂-extraction without pretreatment: (2) conventional CO₂-extraction with sodium hypochlorite and silver phosphate pretreatment; and (3) *in situ* laser microprobe CO₂-extraction without treatment. Treatment of laser-extracted CO₂ with silver phosphate was attempted, but a successful method was not found.

Conventional method

Individual dolomite types were selectively sampled from roughly polished slabs using a drilling device. The holes of a diameter of about 1-3 mm were aligned along profiles covering the different dolomite generations.

All isotope analyses were carried out at the Laboratory of Isotopic Geochemistry at the University of Lausanne. Carbon and oxygen isotope analyses were performed following standard carbon dioxide extraction techniques of McCrea (1950). Approximately 10 mg of fine-grained dolomite was dissolved in vacuum at 50 °C by 100% phosphoric acid. The released carbon dioxide was trapped in liquid nitrogen and cleaned by means of a fractionate sublimation using a dry ice-ethanol mixture. The gas was measured on a Finnigan[®] MAT-251 mass spectrometer. Data were corrected for fractionation using the carbonate-acid fractionation factor for dolomite of 1.01065 (Rosenbaum and Sheppard 1986) and are expressed conventionally in the δ notation as the variation in per mil relative to the PDB standard. Analytical reproducibility, reported as standard deviations of replicate analyses of the laboratory working standard Binn Dolomite, is better than $\pm 0.05\%$ for carbon and $\pm 0.1\%$ for oxygen.

Sodium hypochlorite and silver phosphate pretreatment

Earlier publications report the oxidation of organic matter by sodium hypochlorite (e.g. Weber et al. 1976; Land et al. 1977) and the removal of acid-volatile sulfur compounds by a silver phosphate pretreatment (e.g. Smith and Croxford 1975; Rye and Williams 1981). We have used the pretreatment procedure proposed by Charef and Sheppard (1984) to minimize the effects of organosulfur

 Table 2. Average and standard deviation of conventional carbon and oxygen isotope analyses of laboratory standard Binn Dolomite.

Pretreatment (n)	δ^{13} C‰ PDB	δ^{18} O ‰ PDB
None (21)	1.55 (0.04)	- 9.41 (0.10)
NaOCl + Ag_3PO_4 (8)	1.61 (0.03)	- 9.46 (0.06)
Ag_3PO_4 (8)	1.61 (0.05)	- 9.48 (0.10)

species. It consists of the combined oxidation of organic matter by sodium hypochlorite (NaOCl) followed by silver phosphate (Ag_3PO_4) treatment of the phosphoric acid evolved gas.

The powdered samples were reacted with 5% fresh NaOCl solution for 15 h at room temperature, filtered, washed several times with distilled water, and dried at 80 °C for 4 h. The gas released by the phosphoric acid was exposed to coarsely powdered Ag_3PO_4 at room temperature for 10 min to eliminate the evolved H_2S . The Ag_3PO_4 was dried at 150 °C for 30 min and left in the vacuum line for at least another 30 min prior to extraction.

No significant differences of the isotope ratios of the laboratory dolomite standard were observed by using the Ag_3PO_4 - or the combined NaOCl + Ag_3PO_4 pretreatment, within the analytical precision of $\pm 0.05\%$ for $\delta^{13}C$ and $\pm 0.1\%$ for $\delta^{18}O$ (Table 2). As stated by Charef and Sheppard (1984), the sodium hypochlorite treatment does not necessarily remove all types of organic carbon in the carbonate samples, but it certainly destabilizes all 'active' organosulfur compounds, sensitive to oxidation by the 5% NaOCl solution, leaving only stable organic carbon species.

In situ laser microprobe determination

In situ laser measurements, following the procedure of Sharp (1992) were made at the University of Lausanne to study the isotopic zonation at sub-millimeter scale across a single 1-cm-thick band of white sparry dolomite. The CO₂-extractions were carried out at 100% laser power (20 W). Twenty laser shots, each of 30 ms duration, performed in two closely neighboring sites, produced 150-200 µm-diameter holes (Fig. 1). The evolved CO₂ was trapped with liquid N₂, cryogenically purified, and then transferred on-line to the mass spectrometer for isotopic analysis. The precision of the oxygen and carbon isotope ratios reported for homogeneous samples is better than $\pm 0.1\%$ and $\pm 0.2\%$, respectively (Sharp 1992).

The procedure for the *in situ* measurements with Ag_3PO_4 treatment were identical to the conventional *in situ* method except that a cold finger with Ag_3PO_4 was included in the extraction line. The Ag_3PO_4 treatment was similar to that described for conventional analyses. Various methods of heating and degassing of the Ag_3PO_4 were attempted in order to remove the isotopic shift caused by the phosphate interaction; none was found to alleviate the problem.

Results and discussion

Two representative ore-bearing hand specimens with megascopically recognizable different dolomite crystallization generations from the San Vicente mine have been analyzed in detail. The isotopic analyses of a zebra ore sample with typical rhythmic banding are given in Fig. 1 and Tables 3 and 4. Three sets of analyses are compared: conventional acid extraction method without pretreatment, with pretreatment, and laser extraction.

A comparison between the results of the conventional isotopic analyses with and without pretreatment (Fig. 2 and Table 4) shows a dramatic difference. The use of the combined NaOCl + Ag_3PO_4 pretreatment for the

Sample name	δ^{13} C‰ PDB		$\frac{\delta^{18}O_{\infty}^{*}PDB}{Pretreatment}$			
	Pretreatment					
	None	NaOCl + Ag ₃ PO ₄	Ag ₃ PO ₄	None	$NaOCl + Ag_3PO_4$	Ag ₃ PO ₄
		Dark rep	lacement dolomi	te		
G1	7.9	0.0	1.1	- 7.0	- 8.7	- 8.3
I1	1.5	0.8	1.2	- 7.9	-8.1	- 8.5
K1	2.0	0.7		- 8.4	- 8.9	
G3	8.4	0.3	1.3	- 6.3	- 8.7	- 8.6
13	1.7	1.1		- 7.2	- 7.7	
14	1.4	0.7		- 8.4	- 8.5	
G2		0.4			- 8.9	
12		0.4			-8.0	
K2		1.0			- 8.6	
Average	3.8	0.6	1.2	- 7.5	-8.4	- 8.5
(1σ)	(3.4)	(0.4)	(0.1)	(0.8)	(0.4)	(0.2)
		Light-gro	ey sparry dolomi	te		
C1	2.0		0.8	- 7.1		- 7.8
D1	1.3	0.7	0.7	- 8.0	- 8.0	- 9.1
E1	18.7 ^b	0.5	0.7	- 4.1	-8.0	- 8.0
F1	15	1.1	1.3	-8.2	- 8.1	- 8.3
HI	13	1.0	1.3	-8.2	- 8.3	- 8.2
11	14	1.0	1.3	- 7.6	-8.1	- 7.7
1.2	15	110	1.3	- 7.8		- 8.1
C3	13	0.7	1.2	- 7.9	- 9.4	8.1
D2	54	0.7	1.2	- 6.5	- 8.1	- 7.7
E2	31	0.8	1.0	- 5.2	- 8.0	- 7.7
F2	13	0.9	1.0	- 8.7	- 9.1	- 9.3
H2	1.5		0.8			- 9.0
12			1.2			8.4
A1			1.2			-8.2
B1			1.2			- 8.8
C4			1.1			- 8.1
D3			0.7			-8.5
F3			1.5			8.4
НЗ			1.3			- 8.4
H4			1.2			7.8
HS			1.0			- 8.3
14			1.3			-8.2
Average	2.0	0.8	1.1	- 7.2	- 8.3	- 8.3
(1σ)	(1.3)	(0.2)	(0.3)	(1.4)	(0.5)	(0.4)
		White late-sta	ige void-filling do	olomite		
L1	1.1		1.0	- 11.5		- 11.6
$\overline{C2}$	1.3		1.1	- 10.8		- 11.3
13	1.7		1.1	- 10.0		- 11.2
J4	/		1.1			- 11.1
Average	1.4		1.1	-10.8		- 11.3
(1σ)	(0.3)		(0.1)	(0.7)		(0.2)

Table 3. Variation of δ^{13} C and δ^{18} O values of gangue dolomites of a zebra ore sample^a with method of pretreatment

^a Sample FSV-924 from San Vicente N mine, level 1570, local coordinates 20602 N and 19797 E

^b Value excluded from average and from Fig. 2

replacement dolomite and of the Ag₃PO₄ trap for the sparry dolomite and late-stage void-filling dolomite eliminates most of the heterogeneities found in the non-treated samples. Without pretreatment, the dark replacement dolomite displays a strong variation of δ^{13} C (between 1.4 and 8.4‰) and δ^{18} O (between - 8.4 and - 6.3‰). The two most erratic δ^{13} C values (7.9‰ and 8.4‰) are probably mainly due to the presence of sulfur species as shown by the strong decrease of the values achieved with the Ag₃PO₄-only treatment. In these same two samples the oxygen isotope ratios are clearly lowered with the Ag_3PO_4 pretreatment. The use of the combined pretreatment decreases slightly but consistently the $\delta^{13}C$ values and has no clear influence on the $\delta^{18}O$ values, suggesting that the main disturbing effects for the carbon isotopic ratios are due to the presence of organic matter and sulfur whereas the oxygen isotope ratios are disturbed mainly by the presence of sulfides.

The light-grey sparry dolomite is virtually free of organic matter but bears variable amounts of sulfides. Accordingly, important differences are already achieved with the Ag_3PO_4 -only treatment, with the help of which, for

Table 4. In situ stable isotope-analyses of the zebra ore sample using a laser extraction technique

Analysis number ^a		δ^{13} C ‰ PDB	δ^{18} O ‰ PDB	
	Dark replacement dolomite			
$\frac{1}{2}$	LC43-15 LC43-3 LC43-4	1.5 1.3 1.4 (0.1)	-7.4 -7.3 -7.4 (0.1)	
Light-grey sparry dolomite				
4 5 6 7 8 10 13	LC43-5 LC43-6 LC43-9 LC43-8 LC43-10 LC43-12 ^b LC43-2 rage(1g)	1.1 0.9 0.8 0.7 0.8 1.5 1.3 1.0 (0 3)	- 6.3 - 7.6 - 7.9 - 7.2 - 7.9 - 7.9 - 7.9 - 7.9 - 7.9	
White late-stage void-filling dolomite				
9 11 12 ave	LC43-11° LC43-14 LC43-13° rage (1σ)	0.5 0.3 0.6 0.5 (0.2)	$-10.6 \\ -11.1 \\ -10.3 \\ -10.7 (0.4)$	

^a Location of the analysed microsamples are shown in Fig. 1 ^b Sample site rich in sphalerite

^e Possibly contaminated by sparry dolomite

instance, instead of the erratically heavy δ^{13} C value of 18.7% a ratio of 0.7% is obtained. The results show that the treatment with NaOCl is not necessary for this dolomite generation.

The use of the above described pretreatment produces less important changes in the isotopic values of the very clean void-filling dolomite, but eliminates the still significant disturbances (see Table 3 and Fig. 1).

Variations in the δ^{13} C and δ^{18} O values at a submillimeter scale were evaluated with the in situ laser extraction technique. The range in the δ^{18} O values for the dark replacement dolomite and light-grey sparry dolomite are small (-7.9 to -7.2%, except for one anomalously high value at the contact between these two carbonate generations, Table 4). As expected, the δ^{18} O values for the late-stage dolomite are $3\%_{00}^{\circ}$ lighter than the earlier dolomite generations. The δ^{13} C values for the sparry dol omite are in good agreement with the conventional pretreated analyses, while the $\delta^{13}C$ values for the dark replacement dolomite are closer to the unpretreated values. The late-stage void-filling dolomite is depleted in ¹³C relative to the conventional analyses.



Fig. 2. Variations of δ^{13} C (a) and δ^{18} O (b) values in replacement dolomite, sparry dolomite and late-stage void-filling dolomite of a zebra ore hand sample (FSV-924) using conventional acid extrac-

tion with and without pretreatment. Distances are referred to the lower edge of the sample, as illustrated in Fig. 1

Dolomite generation (Sample FSV-924)	Analytical procedure	δ^{13} C‰PDB	δ^{18} O‰ PDB
Dark replacement dolomite	Conventional NaOCl + Ag_3PO_4 Ag_3PO_4 In situ	3.8 (3.4) 0.6 (0.4) 1.2 (0.3) 1.4 (0.1)	$\begin{array}{r} -7.5 (0.8) \\ -8.4 (0.4) \\ -8.5 (0.2) \\ -7.4 (0.1) \end{array}$
Light-grey sparry dolomite	Conventional NaOCl + Ag ₃ PO ₄ Ag ₃ PO ₄ In situ	2.0 (1.3) 0.8 (0.2) 1.1 (0.3) 1.0 (0.3)	$\begin{array}{r} -7.2 & (1.4) \\ -8.3 & (0.5) \\ -8.3 & (0.4) \\ -7.5 & (0.6) \end{array}$
White late-stage void-filling dolomite	Conventional NaOCl + Ag ₃ PO ₄ Ag ₃ PO ₄ In situ	1.4 (0.3) 1.1 (0.1) 0.5 (0.2)	- 10.8 (0.7) - 11.3 (0.2) - 10.7 (0.4)

Table 5. Summary of the average δ^{13} C and δ^{18} O values and 1σ of the gangue dolomite analyzed with different procedure

Table 6. Isotopic composition of the different stage dolomites of an ore sample^a using the combined pretreatment

Sample name	δ^{13} C ‰ PDB	δ^{18} O ‰ PDB	
Dark replacement dolomite ^b			
A1	1.4	- 8.3	
A2	1.3	- 8.2	
B 1	1.0	- 9.2	
B2	1.2	-8.8	
average (1σ)	1.2 (0.2)	- 8.6 (0.5)	
Light-grey sparry dolomite ^c			
C1	0.7	-10.8	
C2	0.6	-10.7	
D1	0.4	-10.6	
D2	0.5	-10.8	
D3	1.0	-10.2	
D4	0.7	-11.1	
D5	0.5	- 11.8	
D6	0.9	-11.2	
D7	0.8	-11.1	
D8	1.0	-10.4	
D9	1.0	-10.4	
average (1σ)	0.7 (0.2)	- 10.8 (0.5)	
White late-stage void-filling dolomite ^c			
E1	0.0	- 10.9	
E2	-0.2	- 12.5	
E4	0.1	- 12.4	
E3	0.1	- 12.2	
average (1σ)	0.0 (0.1)	- 12.0 (0.7)	

^a Sample FSV-919 from San Vicente N mine, level 1570, local coordinates 20561.5 N and 19795 E

^b NaOCl + Ag₃PO₄ - pretreatment

 $^{\circ}$ Only Ag₃PO₄ – pretreatment

The following conclusions can be drawn regarding the *in situ* laser analyses of sulfides- and organic matter-rich carbonates (Table 5): (1) in samples rich in organic matter (e.g. dark replacement dolomite) the δ^{13} C and δ^{18} O values are equivalent to conventional analyses, but different from samples pretreated to remove the disturbing effects of sulfur species and organic contaminants; (2) in samples rich only in sulfides (e.g. light-grey sparry dolomite) the δ^{13} C values are elevated by ~ 1‰ to those obtained with pretreatment; (3) the lower δ^{13} C values for the late-stage dolomite may reflect



Fig. 3. Hydraulic breccia (sample FSV-919) with grey-white sparry dolomite (C and D) surrounding the dark replacement dolomite (A and B), and milky-white dolomite (E) filling the open spaces

kinetic fractionation effects common to all laser analyses (Sharp 1992) or may be explained by a more precise micro-sampling than can be obtained with conventional drilling; (4) simple Ag_3PO_4 treatment does not alleviate the problem of sulfur contamination.

The results of a second representative hand specimen are presented in Table 6 and Fig. 3. The combined NaOCl and Ag_3PO_4 pretreatment was used for the analyses of the dark replacement dolomite. The sparry dolomite and the late-stage filling dolomite were only subjected to the pretreatment with Ag_3PO_4 . Consistent clear trends without erratic values are illustrated, for example, in profiles D–E and E'–A across the three dolomite generations (Fig. 4). The white sparry dolomite exhibits significantly lighter



Fig. 4. Cross section (D-E and E'-A, see Fig. 3) of carbon and oxygen isotope ratios, covering dark replacement dolomite (NaOCl + Ag₃PO₄ pretreatment), grey-white sparry dolomite and late-stage void-filling dolomite (both Ag₃PO₄ pretreatment)

 δ^{13} C and δ^{18} O values than the early stage replacement dolomite, and heavier values than the paragenetically later open-space-filling dolomite. The decreasing isotopic ratios with increasing distance relative to the replacement dolomite may be explained by changes in the water to rock ratio, having precipitated the late-stage dolomite from an isotopic lighter fluid with a smaller contribution from the original replacement dolomite.

Conclusions

1. Our results show that small-scale isotopic variations in the MVT gangue carbonates of San Vicente deposit are mainly due to the presence of sulfides in the carbonate sample, and that the associated organic matter plays a minor role.

2. The combined sodium hypochlorite and silver phosphate pretreatment, proposed by Charef and Sheppard (1984) is necessary for the accurate isotopic analysis of samples containing organic matter and sulfides, i.e. most fine- and medium-grained carbonate samples from MVT and other sediment-hosted base metal deposits.

3. For the isotopic analyses of white sparry and openspace-filling dolomite, which are virtually free of organic matter, the treatment with silver phosphate is sufficient.

4. Using this methodology the total variation of the δ^{13} C and δ^{18} O values of a defined carbonate generation in

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a hand specimen can be lowered to the global analytical and sampling error, i.e. not larger than ± 0.1 to 0.4%. Without this pretreatment an additional error in the range of +1 to + 2‰, and occasionally up to + 10‰ may be introduced.

5. There is an isotopic shift associated with the *in situ* laser techniques. The δ^{13} C and δ^{18} O values are elevated relative to conventional pretreated samples by 0.5 to 1‰. The *in situ* method yields reproducible results. These data indicate that there is no appreciable isotopic variations at the sub-millimeter scale within any of the three carbonate generations.

6. In the samples studied in the present work, the variations of the stable isotope compositions within and between bands of a defined carbonate generation are very small (± 0.1 to 0.4% δ^{13} C and 0.2 to 0.7% δ^{18} O), suggesting uniform chemical and physicochemical conditions during precipitation of a given carbonate generation, at least at a centimeter scale.

7. The pretreatment methodology allows us to recognize subtle isotopic variations in the gangue carbonates that can be relevant for tracing basinal fluid pathways, and that would otherwise go unnoticed without pretreatment.

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Editorial handling: K. Shelton