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CARBON ISOTOPIC ANALYSIS IN MEXICO: A PROGRESS REPORT ON SOME MEXICAN ORE DEPOSITS AND METAMORPHIC ROCKS

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RESUMEN

Se presentan algunos resultados preliminares del análisis isotópico de carbono en carbonatos de ganga de diferentes tipos de yacimientos, así como en rocas metamórficas. Las muestras analizadas provienen de: el depósito paleokárstico de La Purísima en Coahuila, el yacimiento epitermal de metales preciosos de El Barqueño en Jalisco, la breccia de cobre de La Sorpresa en Jalisco, el yacimiento de skarn de Pb-Zn-W de Zimapán en Hidalgo, el yacimiento de pórfido de cobre de La Verde en Michoacán y rocas metamórficas de alto grado de Oaxaca. La composición isotópica de $\delta^{13}C$ de estos carbonatos varía dentro de los intervalos esperados (*i.e.* –10 a 0 por millar) para cada tipo de yacimiento y roca metamórfica.

ABSTRACT

Preliminary results of carbon isotopic analysis on carbonate gangue minerals from different types of ore deposits and metamorphic rocks are presented. The analyzed samples came from: the paleokarstic deposit of La Purísima, Coahuila; the epithermal precious metal deposit of El Barqueño, Jalisco; a copper breccia ore from La Sorpresa, Jalisco; the Pb-Zn-W skarn deposit of Zimapán, Hidalgo; a porphyry copper deposit of La verde, Michoacán and high grade metamorphic rocks from Oaxaca. The $\delta^{13}C$ isotopic composition of these carbonates varies within the expected ranges (*i.e.* -10 to 0 per mil), for each type of ore deposit and metamorphic rock.

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INTRODUCTION

Carbon-13 isotopic analysis has a widespread use in many fields as a climatological indicator, or as a natural organic carbon tracer (Fritz and Fontes, 1980). Moreover this analysis has provided useful data on the origin of carbon (Robinson, 1974) and the evolution of carbonate deposits (Robinson, 1975), and can also be used as a useful tracer in mining prospection. In México, carbon-13 analysis data is limited to the work of Rye and Ohmoto (1974) and Rye (1966), on hydrothermal calcites from La Providencia lead-zinc deposit. This informational gap has been caused mainly by the lack of a laboratory in México able to do rutinary carbon isotopic analyses. The main objective of this communication is to present the carbon-13 data, obtained at the Instituto de Física UNAM new facilities, associated with the following carbonate deposits: La Purísima (paleokarst), El Barqueño (epithermal veins), La Sorpresa (copper breccia), Zimapán (skarn), La Verde (porphyry copper) and high grade metamorphic rocks from Oaxaca (Fig. 1). Then we will compare these results with the published data on similar deposits (Ohmoto and Rye, 1979).

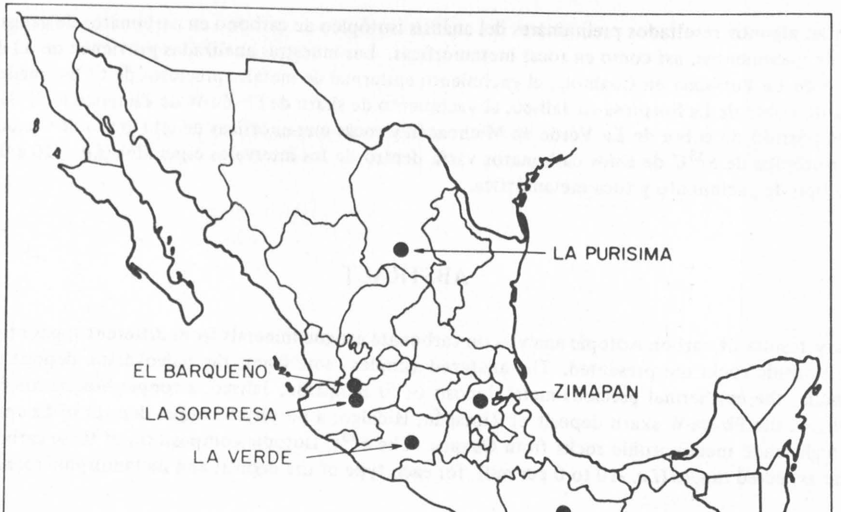

Fig. 1. Map showing the sampled areas in México.

The ore deposits studied are located in geological environments with rather different conditions for thermal and pressure evolution. This difference makes it possible to compare the main isotopic features of each environment.

The data presented in this communication will be the point of departure for a major research program of the isotopic features of the different paragenetic phases of the areas under study.

EXPERIMENTAL TECHNIQUE

The experimental procedure employed was the following (Coplen, 1983): twenty mg of a carbonate sample were reacted at 25°C with 100% H_3PO_4 to liberate CO_2 in a high vacuum preparation manifold in the following sequence: the carbonate sample was crushed in an agata mortar and allocated in the bottom of the reacting flask. Two ml 100% H_3PO_4 were poured in the arm of the reacting flask with the aid of a folded pipette and then mixed, prior to evacuation at high vacuum. After the reaction was completed, evolved CO_2 were removed and dried with U-traps and sequential use of ethil alcohol-dry ice mixture and liquid nitrogen. Then, the CO_2 was sent through flasks towards a three-collector-type mass spectrometer (Finnigan Mat 250) to perform the carbon isotopic analysis. The 100% H_3PO_4 was prepared by slowly disolving 1 000 g of P_2O_5 in 2 150 g of 85% H_3PO_4 in a 2-1 beaker. Ten mg CrO_3 were added and the solution was covered and heated at 200°C for 7 h. Three ml of H_2O_2 were added and the solution was heated up to 220°C for additional 4 h. After cooling overnight, the acid was stored in glass bottles with caps containing conical plastic inserts for tight sealing. Specific gravity should be between 1.90 and 1.92; otherwise more P_2O_5 (or water) was added as required, and the process was repeated beginning with heating for 7 h.

Carbon isotopic analyses of carbonate samples are presented in Table 1 expressed in delta units (‰), *i.e.*, per mil deviation from the PDB Standard (belemnitella americana from the Cretaceous Peedee-formation, South Carolina). Delta units are defined by the formula:

$$\delta^{13}C = \left\{ \frac{(^{13}C/^{12}C)\ \text{sample} - (^{13}C/^{12}C)\ \text{std}}{(^{13}C/^{12}C)\ \text{std}} \right\} 10^3$$

Direct mass spectrometric readings were corrected by Oxygen-17 contributing to collectors. The correction applied to our working standard was $\delta^{13}C = 1.0676\ \delta^{45} - 0.0338\delta^{46}$ determined using N.B.S. – 16 standard. The precision was better than 0.1 ‰.

All measurements were done by duplicate.

TABLA I

CARBON ISOTOPIC ANALYSIS

DEPOSITS	SAMPLE	$\delta^{13}C$ (o/oo)	$\overline{\delta^{13}C}$ (o/oo)	σ_{n-1}
	La Verde-1	-6.1		
Porphyry	La Verde-2	-6.3		
Copper	La Verde-3	-4.5	-5.1	1.8
(La Verde, Mich.)	La Verde-4	-2.1		
	La Verde-5	-6.1		
	La Sorpresa-1	-3.7		
	La Sorpresa-2	-3.7		
	La Sorpresa-3	-3.6		
	La Sorpresa-4	-3.0		
Copper	La Sorpresa-5	-3.4		
Breccia	La Sorpresa-6	-1.9	-2.7	1.0
(La Sorpresa, Jal.)	La Sorpresa-7	-1.9		
	La Sorpresa-8	-1.6		
	La Sorpresa-9	-1.4		
	La Sorpresa-10	-1.2		
	La Sorpresa-11	-3.8		
	El Barqueño-1	-4.9		
	El Barqueño-2	-4.9		
Epithermal	El Barqueño-3	-4.7		
Veins	El Barqueño-4	-4.6	-4.9	0.2
(El Barqueño, Jal.)	El Barqueño-5	-5.2		
	El Barqueño-6	-5.1		
	El Barqueño-7	-5.2		
	Zimapán-1	-6.5		
	Zimapán-2	-6.4		
Skarns	Zimapán-3	-5.9		
(Zimapán, Hgo.)	Zimapán-4	-9.0	-6.3	1.7
	Zimapán-5	-3.8		
	Zimapán-6	-7.6		
	Zimapán-7	-4.9		

Table 1 (Continued)

Paleokarstic (La Purísima, Coah.)	La Purísima-1	0.9		
	La Purísima-2	1.4		
	La Purísima-3	1.6		
	La Purísima-4	1.1		
	La Purísima-5	1.5		
	La Purísima-6	1.1		
	La Purísima-7	1.3		
	La Purísima-8	1.1		
	La Purísima-9	2.0	1.2	0.3
	La Purísima-10	1.3		
	La Purísima-11	1.2		
	La Purísima-12	1.0		
	La Purísima-13	0.7		
	La Purísima-14	1.2		
	La Purísima-15	0.9		
High Grade Metamorphic Rocks (Oaxacan Complex)	Oaxaca-1	0.3		
	Oaxaca-2	0.3		
	Oaxaca-3	0.3		
	Oaxaca-4	0.1		
	Oaxaca-5	-1.6	-0.8	1.0
	Oaxaca-6	-2.1		
	Oaxaca-7	-1.6		
	Oaxaca-8	-1.6		
	Oaxaca-9	-0.9		

GEOLOGICAL AND ISOTOPIC FEATURES OF SAMPLED AREAS

I) The paleokarstic deposit of Sierra de La Purísima is emplaced in cavities of lower-cretaceous reef limestones. The ore mineralogy consists of Pb-Zn sulfides and $BaSO_4$, while gangue mineralogy is dominated by calcite (González, 1984); limestone is dolomitized and the fluid present in calcite gangue minerals have salinities of 7.48 to 22.4% (NaCl) and temperatures of ±50°C, as shown by uniphasic fluid inclusions. Carbon isotopic analysis of calcite gangue exhibit values ranging from 0.71 to 1.49‰.

II) The hydrothermal veins of El Barqueño Minning District are characterized by their low Pb-Zn content and high gold concentration (3 to 10 g/Ton). Alvarez and Rosas (1984) studied fluid inclusions in gangue minerals and showed that the temperature of formation in this deposit ranges from 157°C to 374°C, with salinities from 0.5 to 7.5% (NaCl). Carbon isotopic content in last mineralization stage ranges from – 4.6 to – 5.2‰.

III) La Sorpresa is a copper breccia emplaced in Tertiary granitoids and andesites. The hydrothermal alteration is shown by limited potassic alteration and extensive propylitization and tourmalinisation (Martínez, 1984). The copper is accompanied by a gangue of quartz and calcite. Carbon isotopic gangue values range from + 3.7 to − 1.2°/oo. Sulphur isotopic studies and fluid inclusion determinations performed by González-Partida and Arnold (in preparation) showed elevated temperatures and saturated salinities in the mineralizing fluids.

IV) The Zimapán Mining District has a large part of its mineralization in chimneys. The paragneiss studied by microthermometry indicates that the pyrrhotite-copper phase was formed between 430°C to 230°C, the lead zinc phase between 340°C to 230°C and a last event superimposed to the former ones, characterized by sulphosalts and fluorite-calcite gangue, formed between 340°C and 100°C. High salinities and complex chlorides were also detected (González-Partida, 1984). The calcites of the last event showed carbon-13 values ranging from − 9.0 to − 3.8°/oo.

V) La Verde porphyry copper deposit of middle tertiary age (Damon *et al.*, 1983) presents an alteration zonning consisting of a pervasive potassic stockwork, surrounded by extensive propylitization, accompanied by late calcite veins (Martiny, 1987). The hydrothermal fluids of the paragneiss studied by González-Partida and Arnold (in preparation) present temperatures of formation that range from 760°C within the potassic zone, to 148°C in the late calcite gangue veins. Carbon isotopic analyses from samples coming from last mineralization stage yielded Carbon-13 values ranging from − 6.0 to − 2.0°/o.

VI) Marbles from the metamorphic rocks of Oaxaca included within the Oaxacan Complex form thin bands parallel to foliation, seldom showing discordant relationships within a sequence of paragneiss of quartz feldspar to pellitic composition. Generally the marble bands are intercalated with hornblendites and metamorphic augite, scapolite or wollastonite-quartz limy shales (Keith and Ortega, 1975). They have been classified as cipolin marbles due to its high content of phlogopite and ferromagnesian minerals, that according to Ortega (1977) were formed in granulite facies (±750°) from impure limestones showing evidences of anatexis. ^{13}C values of cipolin marbles ranges from − 0.9 to 0.3°/oo, which correspond to the expected values obtained elsewhere for these kind of rocks (Faure, 1977).

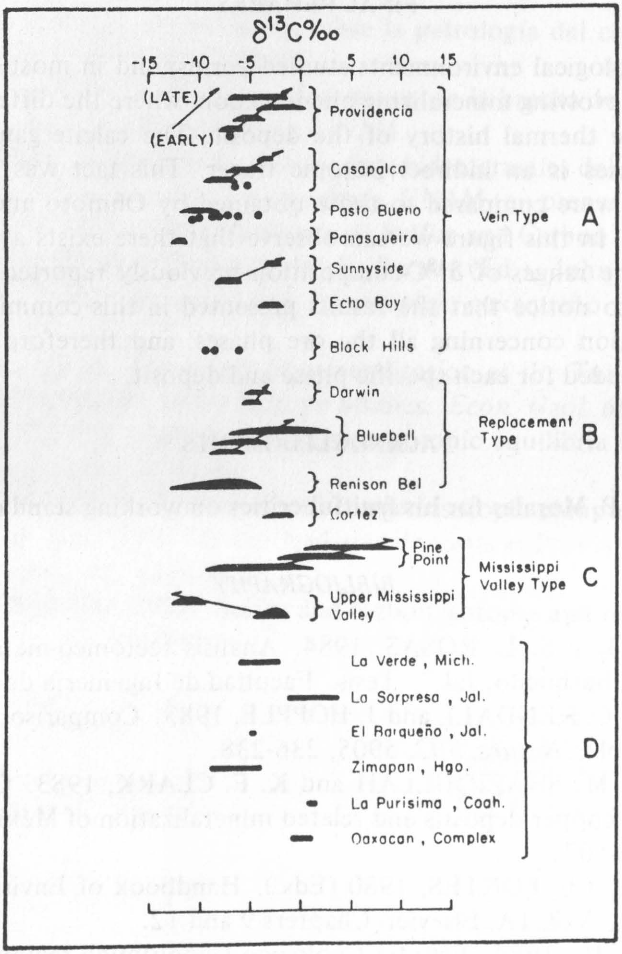

Fig. 2. Comparison of previously reported measured ranges (Ohmoto and Rye, 1979) of the early to late phases of mineralization of:

A) middle to low temperature hydrothermal deposits (vein type),

B) high temperature hydrothermal deposits (remplacement type),

C) non hydrothermal, paleokarstic deposits (Mississippi Valley type) and

D) measured ranges for deposits studied in this report. Although our sampling did not permit to differentiate from early and late carbonate depositions, the measured ranges have a good coincidence.

FINAL REMARKS

The different geological environments studied correspond in most cases to a single stage of a whole evolving mineralizing phenomenon, where the different paragenetic phases reflect the thermal history of the deposit. The calcite gangue that accompanies these phases is an indirect isotopic tracer. This fact was indeed observed when our results were compared to those obtained by Ohmoto and Rye (1979), as shown in Fig. 2. In this figure we can observe that there exists a very good agreement between the ranges of $\delta^{13}C$-composition previously reported and our results. It is important to notice that the results presented in this communication do not contain information concerning all the ore phases, and therefore further isotopic studies will be needed for each specific phase and deposit.

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