

Carbonates associated with the Almazan sepiolite-palygorskite deposits (Northern Spain)

J.M. González-López
C. Fernández-Nieto
A. López-Galindo
J. Torres-Ruiz

Dep. Ciencias de la Tierra, Facultad de Ciencias, Univ. Zaragoza, Spain.
Dep. Mineralogía y Petrología and IAGM. Facultad de Ciencias. Univ. Granada - CSIC. Spain.

Introduction

The Almazan sepiolite-palygorskite deposits occur in the easternmost part of the Duero basin. This area consist of Neogene materials made up of a marginal facies of sandstones and poorly evolved conglomerates, and an inner facies of clayey and gypsum-bearing marls covered by the so-called 'Paramo limestones'. Sediment was supplied from the southern border (varieties of Jurassic and Cretaceous limestones, together with sandstones and Triassic marls) and from the eastern border (palaeozoic materials). The study of more of 200 samples reveals that the mineralized interval is made up of neophormed phyllosilicates (sepiolite and palygorskite), detrital silicates (illite, interstratified illite-smectite, beidellite, quartz and feldspars) and carbonates (calcite and dolomite) (Torres-Ruiz *et al.*, 1994). The aim of this paper is the characterization from a mineralogical and geochemical point of view of the carbonate levels in order to elucidate the nature of solutions from which they were formed and their depositional conditions.

Textures

The carbonates show textures corresponding to micrites and dolomicrites. The former contain birdseyes and ostracods and bivalves moulds, and dolomicrites also show veinlets and mudcracks, all of them filled by sparitic crystals of calcite with

grain size ranging from 50 to 100 microns. These textures are typical of carbonates from evaporitic lacustrine environments.

Chemical and isotopic composition

Micrites and sparitic calcite are made up of low-Mg calcite (0–3.6 % mol MgCO_3). Dolomicrites are made up of poorly-ordered non-stoichiometric dolomite (44.06–49.24 % mol MgCO_3) corresponding to low-temperature formation processes.

Table 1 shows the average values of the Na/Ca, Mg/Ca and Sr/Ca molar ratios and the isotopic average values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of micrites and dolomicrites and those corresponding to solutions with which the carbonates were in equilibrium. The Mg/Ca and Sr/Ca molar ratios of the solutions in equilibrium with micritic limestones (after the distribution coefficients of Veizer, 1983) are similar to those found in meteoric waters while the Na/Ca molar ratio is higher. On the other hand, the molar ratios of the solutions in equilibrium with dolomicrites are quite high (around 20 times the value of $M_{\text{Mg}}/M_{\text{Ca}}$ and $M_{\text{Na}}/M_{\text{Ca}}$ and 10 times the value of the $M_{\text{Sr}}/M_{\text{Ca}}$). This fact is consistent with waters having a greater evaporation rate.

The average value of the $\delta^{18}\text{O}$ of the micritic limestones is -7.47‰ PDB. If we consider a range of environmental temperatures between 15° and 25°C it would correspond to calcites precipitated in isotopic equilibrium with waters whose isotopic

TABLE 1.

	Micrites		Dolomicrites	
	Calcite	Waters	Dolomite	Waters
$M_{\text{Na}}/M_{\text{Ca}}$	4.08e-04	16.3	3.50e-03	280
$M_{\text{Mg}}/M_{\text{Ca}}$	1.40e-02	0.39	8.70e-01	8.13
$M_{\text{Sr}}/M_{\text{Ca}}$	2.60e-04	2.00e-03	1.28e-03	1.97e-02
$\delta^{18}\text{O}\text{‰}$	-7.47 (PDB)	-7.71 to -5.43	-3.16 (PDB)	-6.56 to -4.45
$\delta^{13}\text{C}\text{‰}$	-7.49 (PDB)	(SMOW)	-5.36(PDB)	(SMOW)

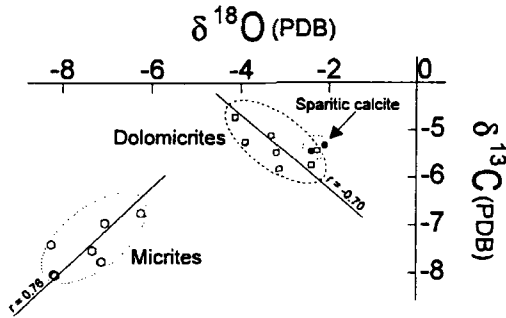


FIG. 1. Isotopic composition of carbonates.

composition ranged from -7.71 to -5.43‰ SMOW (Anderson and Arthur, 1983) and, therefore, they are clearly meteoric in origin. The dolomicrites present an average $\delta^{18}\text{O}$ of -3.16‰ PDB that, for the same temperatures range, should indicate precipitation in isotopic equilibrium with slightly heavier waters, with $\delta^{18}\text{O}$ between -6.56 and -4.45‰ SMOW (Garlick, 1974). The sparitic calcites have a higher $\delta^{18}\text{O}$ (mean of -2.22‰ PDB) and, for the same temperature range, they correspond to waters having a $\delta^{18}\text{O}$ between -2.46 and -0.18‰ SMOW. This represents an enrichment of about 4.5‰ relative to micritic limestones.

The $\delta^{13}\text{C}$ values for the bulk of carbonates range from -7.67 and -4.70‰ . The values are typical from carbonates originated in continental environments strongly affected by highly negative carbon supplies. This kind of carbon is consistent with an edaphic origin under the majority presence of C_3 plants. The micritic limestones present the most negative values (mean of -7.49‰), while dolomicrites and sparitic calcites have average values of -5.25 and -5.38‰ , respectively. These last data are justified by a higher atmospheric CO_2 contribution, probably related with an increase in aridity coincident with lower development of the plant cover.

Micritic limestones show a positive correlation between the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values (Figure 1), which suggests a genesis in an hydrologically closed system, where the effects produced by the

evaporation and residence time dominate the isotopic evolution of the waters (Fritz *et al.*, 1987; Talbot, 1990). In dolomicrites, on the contrary, the isotopic compositions of O and C are negatively correlated, and it would support the primary origin suggested by their textural characteristics, non-stoichiometry and structural data seem to indicate a primary origin for the formation of the micritic limestones and dolomicrites in an evaporitic, hydrologically closed, environment, as well as a meteoric origin of the solutions and an edaphic source for the carbon. In such environment the formation of dolomicrites would correspond with periods of higher evaporation rates.

References

- Anderson, T.F. and Arthur, M.A. (1983) Stable isotopes of oxygen and carbon and their application to sedimentologic and palaeoenvironmental problems. In *Stable Isotopes in Sedimentary Geology* (Eds. M.A. Arthur, T.F. Anderson, I.R. Kaplan, J. Veizer and L.S. Land). Soc. Econ. Paleontol. Mineral., Short Course No. 10, 151 pp.
- Fritz, P, Morgan, A.V., Eicher, U. and McAndrews, J.H. (1987) *Palaeogeogr. Palaeoclimat. Palaeocol.*, **58**, 183–202.
- Garlick, G.D. (1974) The stable isotopes of oxygen, carbon and hydrogen in the marine environment. In *The Sea*, vol 5 (Ed.) E.D. Goldberg, Wiley, New York. 393–425.
- Talbot, M.R. (1990) *Chem. Geol. (Isotope Geoscience Section)*, **80**, 261–79.
- Torres-Ruiz, J., López-Galindo, A., González-López, M. and Delgado, A. (1994) *Geol.*, **112**, 221–45.
- Veizer, J. (1983) Chemical diagenesis of carbonates: theory and application of trace element technique. In *Stable Isotopes in Sedimentary Geology*. (Eds. M.A. Arthur, T.F. Anderson, I.R. Kaplan, J. Veizer and L.S. Land). Soc. Econ. Paleontol. Mineral., Short Course No. 10, 151 pp.

This investigation was supported by the project AMB93-0794 (CICYT)