High $\delta^{34}S$ in pyrite from magnetite-rich beds in the Urbana Limestone (eastern Sierra Morena).

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ABSTRACT

Anomalous high $\delta^{34}S$ (+39.7 o/oo and +45.5 o/oo) in pyrites from iron-beds in the Urbana Limestone are interpreted as a result of biogenic reduction of pore water sulphate in a system closed to H_2S and SO_4^{2-} and upwards migration of the remaining aqueous sulphate very depleted in ^{32}S. The isotopic compositions of sulphur of pyrites from the Urbana Limestone, as well as those from Bancos Mixtos and Chavera Shales ($\delta^{34}S$ = +8.3 o/oo and -13.6 o/oo, respectively) are consistent with the sedimentary environment assumed for these formations.

RESUMEN

Valores $\delta^{34}S$ anormalmente altos (+39.7 o/oo and 45.5 o/oo) observados en niveles ricos en magnetita y/o pirita en la Caliza Urbana son interpretados como el resultado de la reducción biogénica del sulfato en fase acuosa en el sedimento, en un sistema cerrado a H_2S y SO_4^{2-} y una migración subsecuente del sulfato acuoso remanente muy empobrecido en ^{32}S. Los valores $\delta^{34}S$ observados en piritas de la Caliza Urbana, así como los de aquellas de los Bancos Mixtos y de las Pizarras Chavera son coherentes con el ambiente sedimentario interpretado para estas formaciones.

Key Words: *sulphur isotopes, pyrite, magnetite, iron beds, Urbana Limestone.*

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Introduction

Pyrite found in pyrite- and magnetite-rich beds in the Urbana Limestone outcropping in eastern Sierra Morena displays anomalous high $\delta^{34}S$ values above the assumed $\delta^{34}S$ of the coeval Ordovician sea water (+27 o/oo after Claypool *et al.*, 1980). Moreover, the occurrence of the heaviest $\delta^{34}S$ values at top of the set is inconsistent with the isotopic variations observed in modern sediments, where the light compositions are found close to the water-sediment interface (e.g. Vinogradov *et al.*, 1962; Goldhaber and Klapan, 1980).

In the present contribution, we will examine the physico-chemical processes that could produce the observed isotopic anomalies.

Magnetite-pyrite beds in the Urbana Limestone

The studied section of the Urbana Limestone (early Ashgillian) is exposed at La Despreciada quarry, near Aldeaquemada (Jaén). It is made up of amalgamated sequences of decimetric and rare metric beds in accretional sets with reactivation surfaces and bimodal cross-laminae. The whole exposure (about 12 m. thick) is interpreted as nearshore tide-influenced clastic carbonate deposits (Lillo, 1992).

A thin discontinuous bed of centimetric thickness formed by magnetite (dominant), pyrite, quartz (authigenic and detrital), siderite and minor berthieroid iron silicate is found in the lower portion of the exposure (Fig. 1). That iron bed is located a few cm. below a sedimentary reactivation surface. Magnetite and pyrite are mostly euhedral, pyrite in crystals up to one cm. size. Siderite is present as matrix. Berthierod silicate appears in euhedral grains which can be deformed, surrounding the coarser grains of pyrite and magnetite. The presence of magnetite is limited to this bed but pyrite occurs (associated with accessory white mica) some cm. below, being relatively abundant in discontinuous lenses up to 3 cm. thick at 50 cm. below that 'magnetite bed'.

Geochemical data

Two pyrite samples from the 'pyrite bed' and from the 'magnetite bed' were analysed for sulphur isotopes, yielding $\delta^{34}S$ = +39.7 o/oo and $\delta^{34}S$ = +45.4 o/

Formation		$\delta^{34}S$ o/oo
Urbana Limestone	Magnetite bed	+ 45.4
	Pirite bed	+ 39.7
	Lumachelle	+ 16.5
Bancos Mixtos (Mixed Beds)		+ 8.3
Chavera Shales		-13.6

Table 1. Sulphur isotope data of sedimentary pyrites

Tabla 1.- Datos de isótopos de azufre de piritas sedimentarias

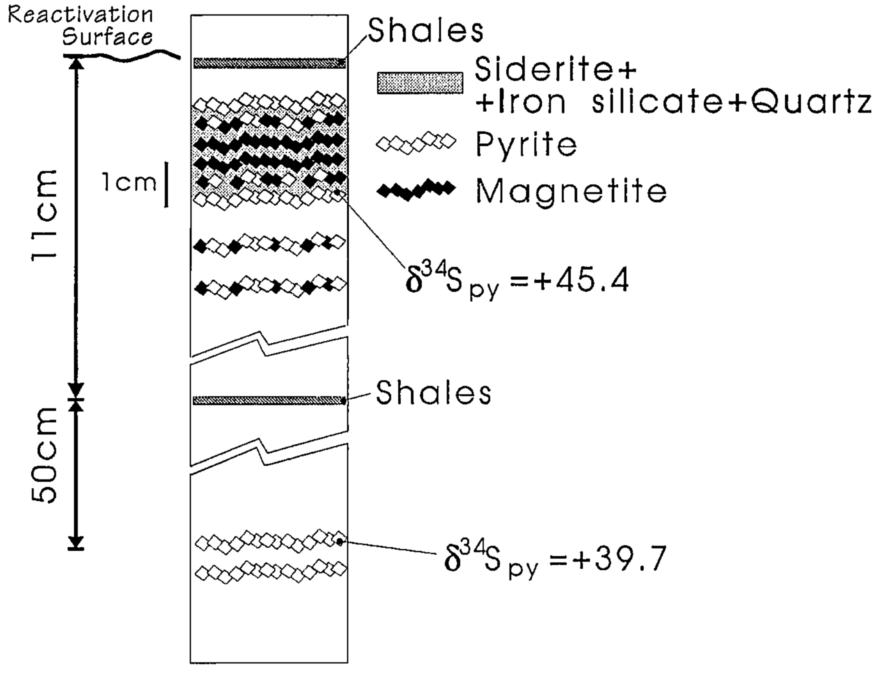

Fig 1.- Skecth depicting the disposition and mineral association of magnetite and pyrite beds in the Urbana Limestone at La Despreciada quarry (Aldeaquemada, Jaén).

Fig. 1.- Esquema mostrando la disposición y asociación mineral de niveles de pirita y magnetita en la Caliza Urbana en la corta La Despreciada (Aldeaquemada, Jaén)

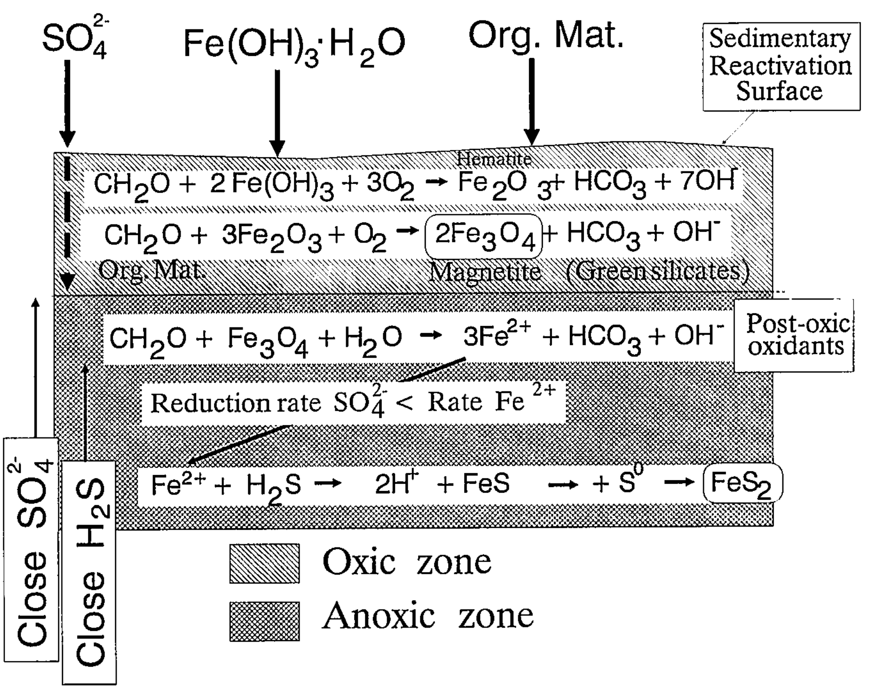

Fig. 2.- Geochemical model for the formation of sedimentary iron minerals in the Urbana Limestone.

Fig. 2.- Modelo geoquímico 'para la formación de minerales sedimentarios de hierro en la Caliza Urbana

oo, respectively (Fig.1). Another pyrite sample from a 'lumachelle' in the Urbana Limestone at different location (El Centenillo) gave a $\delta^{34}S$ value of +16.5 o/oo.

A sample from the underlying Bancos Mixtos formation and another sample from the overlying Chavera Shales have been analysed, yielding $\delta^{34}S$ = +8.3 o/oo and $\delta^{34}S$ = -13.6 o/oo, respectively (Table 1).

Origin of the magnetite-pyrite beds. Formation of pyrite with very high $\delta^{34}S$ values

Magnetite found in metasediments may be formed by metamorphic reactions or alternatively, it may precipitate at 'syngenetic-early diagenetic' conditions as shown by Garrels and Christ (1965) (Fig. 2). In most of the ironstones, magnetite is found in mineral equilibrium with siderite and/or iron silicate (e.g. berthierite) and a syngenetic-early diagenetic origin is commonly accepted if there are not unambiguous evidences to support the metamorphic origin (Brown, 1943). Similarly, pyrite, siderite and iron silicate can be stable at conditions encountered within the sediment (Curtis and Spears, 1968).

Pyrite formation in sediments is usually early diagenetic, as a result of the reaction of H_2S generated by bacterial reduction of the sulphate in pore water with reactive iron from minerals present in the sediment (Berner, 1970) (Fig. 2). In 'normal' marine sediments (those deposited in oxygenated bottom waters), the bacterial reduction of sulphate occurs in anoxic conditions, usually some cm. below the water-sediment interface.

The bacteriogenic sulphide subsequently reacts with the iron present as Fe^{2+} species (formed in post-oxic reactions) to produce metastable iron monosulphides that transform to pyrite (Fig. 2). In a closed system to SO_4^{2-} (which is the environment expected in the anoxic zone of 'normal' nearshore marine sediments), the remaining sulphate in pore water will be progressively depleted in ^{32}S (Goldhaber and Kaplan, 1980; Raiswell, 1982 among others). When the supply of iron is limited, the system is open to H_2S as it remains in the system as aqueous specie. Alternatively, when an excess of reactive iron exists relative to the availability of aqueous sulphide (e.g. when the bacterial activity is limited by low amounts of readily metabolisable organic matter), the system is closed to H_2S: the aqueous sulphide is continuously removed to form pyrite. In that case, the sequence of pyrite deposition reflects a trend towards heavier $\delta^{34}S$ values. Theoretically, if a Rayleigh distillation process is assumed, the $\delta^{34}S$ value of sulphur incorporated in the latest formed pyrites may be higher than the original values of sulphate in sea water (Fig. 3).

Then, a previous ^{32}S depletion of SO_4^{2-} in pore water is required to explain the observed values. Note in fig. 3 that the $\delta^{34}S$ values from pyrites formed in open systems to H^2S are expected to be lower than those from closed systems and the $\delta^{34}S$ value of sea water. Therefore, sedimentary pyrites

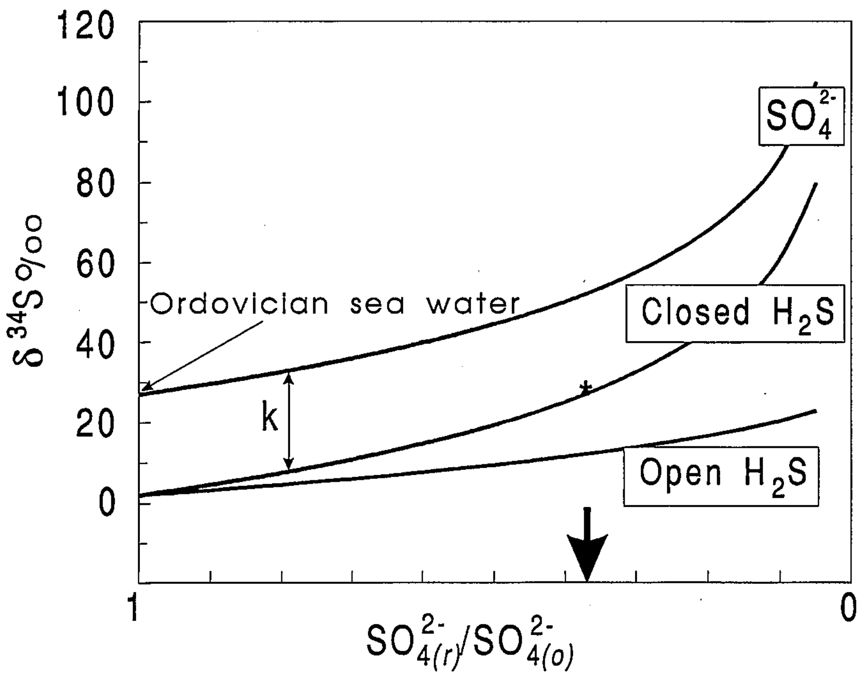

Fig. 3.- Variations of $\delta^{34}S$ values of residual sulphate and sulphide produced in a system closed to SO^{2-}_4. Curves calculated from the expressions proposed by Ohmoto and Rye (1979) assuming a Rayleigh distillation process. k is kinetic factor (1.025). Assumed starting composition of sulphate in Ordovician sea water: +27 o/oo. $SO^{2-}_{4(r)}$/(r)/$SO^{2-}_{4(O)}$ fraction of the remaining sulphate. Arrow indicates the fraction of sulphate from which the δ^{34}_{SH2S} > +27 o/oo .

Fig. 3.- Variaciones de $d^{34}S$ de sulfato y sulfuro residuales producidas en un sistema cerrado a SO^{2-}_4. Curvas calculadas a partir de las expresiones propuestas por Ohmoto y Rye (1979) asumiendo un proceso Rayleigh de destilación. k es el factor cinético (1.025). Se ha asumido una composición de partidade sulfato en el agua de mar del Ordovícico de +27 o/oo. $SO^{2-}_{4(r)}$/(r)/$SO^{2-}_{4(O)}$ fracción de sulfato remanente. La flecha indica la fracción de sulfato a partir de la cual d^{34}_{SH2S} > +27 o/oo .

with anomalous high $\delta^{34}S$ values above the $\delta^{34}S$ values of the coeval sea water (as the pyrites from the magnetite-pyrite beds in the Urbana Fm.) formed in an anoxic environment, a system closed to SO_4^{-2} and H_2S, during the early diagenesis of a 'normal' marine sediment.

If the sedimentary reactivation surface reflects a stage of winnowing or low rate of sediment deposition, then the occurrence of the heaviest isotopic values at top of the set is inconsistent with the variations of $\delta^{34}S$ values reported from modern sediments, where the light compositions are found close to the water-sediment interface (e.g. Vinogradov *et al.*, 1962; Goldhaber and Kaplan, 1980). The stratigraphical 'inversion' of the $\delta^{34}S$ values in this section of the Urbana Limestone Fm. can be understood if the nature of these shallow-water sediments is considered. They deposited in a tidal nearshore environment, where the rate of sedimentation is high enough to produce a rapid compaction and subsequent vertical-upwards movement of the pore water in a well-sorted and relatively homogeneous sediment. This process leads to the relocation of the 'heavy' pore water (generated in the anoxic zone during the early stage of low rate of sedimentation) at higher stratigraphic levels; the former oxic zone becomes rapidly an anoxic, sulphate depleted, iron-rich zone where most of the original organic matter has been already used in oxic reactions. In that environment the formation of sulphide is limited due to the low concentrations of dissolved sulphate and low amount of reactive organic matter, and siderite precipitates (cf. Spears, 1989). The late formation of siderite is supported by textural evidence.

The apparent large and inverse isotopic fractionation does not occur at large scale in the whole Urbana formation as it is indicated by the $\delta^{34}S$ value (+16.5 o/oo.) of pyrite from a 'lumachelle' in El Centenillo. That $\delta^{34}S$ value is reflecting a system closed to SO_4^{2-} but probably open to H_2S with a limited supply of iron. Similar conditions may be assessed for the formation of pyrite in the analised sample from Bancos Mixtos, which yielded $\delta^{34}S$ = +8.2 o/oo, as they are also nearshore sediments (storm deposits close to wave base, after Lillo, 1992). Bacterial reduction of sea water sulphate in a system closed to SO_4^{2-} produces isotopic displacements up to -25 o/oo from the original values of seawater sulphate (Ohmoto and Rye, 1979; Goldhaber and Kaplan, 1980). Thus, the observed $\delta^{34}S$ values in pyrites from the Urbana Limestone and the Bancos Mixtos are very high for sulphide produced from marine sulphate if compared with the $\delta^{34}S$ values observed in pyrites formed in anoxic environments, where a slow rate of sulphate reduction produces large fractionation by kinetic effects, giving as result displacements in the $\delta^{34}S$ values between -40 o/oo and -60 o/oo (Ohmoto and Rye, 1979; Goldhaber and Kaplan, 1980). On this basis, the $\delta^{34}S$ py = -13.6 o/oo yielded by the sample from the Chavera Shales is consistent with pyrite formation in a relatively anoxic environment as expected for shelf muds.

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