

CHERT IN CONTINENTAL EVAPORITES, EBRO BASIN, SPAIN:  
DISTRIBUTION AND SIGNIFICANCE <sup>(1)</sup>

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INTRODUCTION

The presence of authigenic silica in Phanerozoic marine formations is a well-known fact. Silica generally occurs as nodular or banded-nodular lithofacies, characteristic of replacive processes, that are emplaced on a variety of host-rocks such as carbonates, marls, fine-grained siliciclastics, etc. Authigenic silica is rare in evaporite formations, however. Hence, silica occurrences are unknown in sulphate and chloride formations of the great marine evaporitic basins of the past, and references to chert nodules replacing Ca-sulphates have rarely been reported. These replacements occur in evaporite sequences displaying marine to continental transitional conditions or in marine formations which undergo ephemeral evaporitic episodes. The growth of authigenic quartz crystals replacing sulphates is much more frequent, although volume-wise these replacements represent unimportant occurrences. On the other hand, laminated chert is frequent in the pre-evaporitic units of the basins related to upwelling and diatomite deposits.

On the contrary, although nodular chert is limited to the pre-evaporitic units and the low-solubility facies (Ca-sulphates, some alkaline carbonates, etc), it is extensively developed in non-marine evaporites.

CHERT DISTRIBUTION IN THE EVAPORITE FORMATIONS OF THE EBRO BASIN

The Ebro basin is a good example of a Tertiary basin including both marine and non-marine evaporite formations. In this basin, nodular chert is lacking in the two Eocene marine evaporite formations (Lutetian Beuda Gypsum and Priabonian South-Pyrenean Potash Basin) but is abundant in the continental formations. The latter have been divided into two categories (Ortí *et al.*, 1989) according to their palaeogeographic distribution and sedimentary features: marginal sulphate systems and central chloride-sulphate systems.

Nodular chert is practically absent in the central systems which are large evaporitic bodies deposited from highly concentrated brines. On the other hand, it is widely distributed in the small sulphate bodies located along both SE (Catalan Coastal Ranges) and SW (Iberian Chain) margins of the basin. In these marginal bodies chert replaces Ca-sulphate and also, locally, the associated carbonate. Chert replacements consist of nodules, lenses and meganodules, the latter showing a diameter larger than 50 cm. Hence, a chert belt may be distinguished as having developed in the marginal evaporite lacustrine system. In this belt, the abundance as well as the scarcity of nodules is difficult to explain. Locally, a limited number of small chert nodules may be found in some evaporite units of transitional characteristics between the two above-mentioned categories (St. Martí de Tous Gypsum, in the Catalan zone) and in the externalmost part of some central evaporitic units (Gelsa quarries, in Zaragoza Gypsum Fm.).

Regardless of their age, which ranges from Upper Paleocene to Lower Miocene, these marginal evaporite bodies lack chlorides and sodium sulphates and are interpreted to have been precipitated from low concentrated brines. Within these units, very shallow lacustrine episodes -in which microlenticular primary gypsum precipitates- alternate with playa stages in which there occurs interstitial development of both replacive and displacive nodular anhydrite. Frequently, such Ca-sulphate bodies change, laterally or vertically, into carbonate units displaying evaporitic features in which nodular chert is also present.

#### CHERT PETROGRAPHY AND ISOTOPIC COMPOSITION

About 20 representative samples taken along this chert belt have been studied in thin section and by XR diffraction. Of these, ten samples were selected for isotopic studies. XR diffraction shows quartz as the only important silicate phase. However, it seems likely that another  $\text{SiO}_2$  phase: moganite (fibrous microstructure and positive elongation character (length-slow); Flörke *et al.*, 1984) occurs in most samples.

Petrographically, this chert is composed of: a) microcrystalline quartz (10 to 50  $\mu\text{m}$ ) fabric, b) length-slow chalcedonic aggregates (lutecite and quartzine in minor proportion; also moganite?), c) blocky fabric of cementing quartz (several hundreds of micrometers), and d) some chalcedonic films. Only rarely do both positive and negative chalcedonic generations alternate in spherulites. Lutecite pseudomorphs, after microlenticular gypsum crystals, are generalized. Mixed fabric built up by microcrystalline quartz and imperfect lutecite aggregates are frequent. Though opal has not been found, it could have been an original silica phase because some peloidal textures constituted by microquartz are

noticeable, and almost cryptocrystalline quartz textures surround the pseudomorphs.

Concerning the  $\delta^{18}\text{O}_{\text{SMOW}}$  results of the selected chert samples, the six belonging to the evaporitic units of the SE (Catalan Coastal Ranges) margin -Eocene to basal Oligocene- display very close values: between 28.5 and 29.8‰ (mean 28.9  $\pm$  0.5,  $1\sigma$ , n=6 : standard error 0.2‰); while the four belonging to the SW (Iberian Chain) margin -Miocene- display a wider range of values: from 26.1 to 32.6‰ (identical mean value, 28.9  $\pm$  2.9,  $1\sigma$ , n=4 : s.e. 1.5‰). According to Hoefs (1987),  $\delta^{18}\text{O}$  values of marine cherts of different ages may contain records of several facts: temperature, isotopic composition of the ocean water and diagenetic history. Very little literature concerning the oxygen isotopic composition of continental chert is available. Recorded values in the Ebro basin samples do not differ significantly from the contemporary oceanic values (Anderson and Arthur, 1983), despite their non-marine origin. Because of the influence of meteoric waters on the genesis of this chert, a greater concentration of light isotope could be expected. But two factors at least may influence the final enrichment in heavy isotope: 1) the important isotopic fractionation determinant for silica precipitation, and 2) water bodies that have suffered strong evaporation tend to show positive  $\delta^{18}\text{O}$  values, particularly those waters with low initial ionic concentration (Pierre, 1986).

#### SILICIFICATION PROCESS

Silicification as described above is here considered as an early diagenetic process operating within the shallow lake and playa sulphatic sediments in relation with the hydrochemistry of the interstitial brines. In general, typical morphologies of silcrete horizons or sequences formed along the shore of shallow lakes and playas (Bustillo and Capitán, 1990) are lacking. Nevertheless, some sites exist along this belt (the zone to the S of Pozuelo de Aragón) where chert is apparently replacing marly or lutitic host sediments and displaying morphologies resembling crusts.

As for pin-pointing the exact time the process was produced there is evidence that the silicification was a very early diagenetic phenomenon since primary gypsum was replaced prior to its transformation into anhydrite during early diagenesis. It should be pointed out, moreover, that: a) some sedimentary structures such as bioturbation or lamination have been preserved as silicified features which would have been destroyed easily by anhydritization; b) deformation within the unlithified gypsum sediment produced by the growth of anhydrite meganodules has also affected some chert nodules and lenses.

Silica concentration could be explained either from: a) lacustrine evaporation, which could be an efficient mechanism for both silica and Mg enrichment in interstitial waters (Jones et al., 1967); b) clay mineral transformations (palygorskite and trioctahedral (Mg-rich) smectites forming from detrital clays; Inglès et al., 1991) which suggest that significant amounts of silica were present in the environment, either from detrital clay dissolution or from an external source. An only partial consumption of total dissolved silica for palygorskite or smectites formation would allow the SiO<sub>2</sub> excess to be precipitated into opal nodules.

Changes of pH values (caused by rapid dilution of brines or by intermittent photosynthetic activity) are a major mechanism, widely accepted in the literature of sedimentary chert, responsible for the precipitation of unusually high amounts of amorphous silica from lake waters. We have no evidences as to the way this could have taken place in our case and no diatomites or other sediments which could suggest a significant silica content in the open waters have been found in the sedimentary record of these sulphate lakes till now. The mixing of evaporitic lacustrine and dilute stream waters could be, nevertheless, an additional mechanism to consider.

In conclusion, at the moment we can only assume that 1) the silica precipitation in the lacustrine belt is apparently related to evaporation and low salinity conditions, and 2) the gypsum replacement by the chert was produced from interstitial waters in early diagenesis.

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