GEOCHEMISTRY AND MINERAL ASSEMBLAGES OF THE MEDITER-RANEAN EVAPORITE DEPOSITS 4. EUXINIC DEPOSITION OF HEAVY METAL MINERALS IN THE TUZLA SALT DEPOSIT, BOSNIA AND HERCEGOVINA

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Abstract

The evaporite deposit of Tuzla in Bosnia-Hercegovina is the largest rock salt deposit in the Balkan peninsula. In spite of extensive investigations, there is still no final evidence regarding the depositional environment in which it formed. The evaporite series contains a suite of accessory and secondary boron containig minerals, while the lateral equivalents of the rock salt series, in the form of layered marls, contain a suite of heavy metal minerals. Electron microscopic investigations revealed the presence of pyrite and minerals of Hg, Ag, Sb, Sn and U. These findings are dicussed in terms of the diagenetic and dynamic processes of sulfide precipitation at or near redox fronts of euxinic depositional environments of the Tuzla deposit.

Keywords: evaporites, heavy metal minerals, euxinic environments

Introduction

The Tuzla salt deposit is located in the north-eastern part of Bosnia and Hercegovina and is the largest rock salt reservoir on the Balkan peninsula. The essentially stratified salt type deposit is of middle Miocene age, hosted in a sedimentary series of gray marls. In spite of the rather well known geological setting of the occurrence and extensive research of the geochemistry of the host rocks (2,3), there is no unambiguous evidence indicating the depositional environment in which the evaporites formed. The geochemistry of coexisting brines and their saturation states imply that the formation environment may be interpreted in terms of the mixing-zone model, as opposed to the end-member marine or salt-lake type deposits. However, the close relationship of the evaporite series and associated dolomitic limestones, and evidence of progressive dolomitization may account for their formation under evaporative, non-evaporative or seepage reflux conditions (4).

Materials and Methods

The petrographic characteristics of the samples were studied in thin and polished sections, under the optical microscope, both in transmitted and reflected light. Scanning electron microscope images (backscattered electrons mode) were obtained working at 25 keV in a Cambridge Stereoscan S-120 instrument. Qualitative chemical analyses were obtained using a coupled EDS LINK analyser.

Petrographic description of the sulphide-rich marls

The investigated samples of marls contain a suite of sulphides. Pyrite (FeS_2) is very common and forms small crystals (less than 50 microns in diameter). These crystals appear in the following positions: a) rimming euhedral crystals of diagenetic minerals (i.e. northupite), b) as single crystals or clusters disseminated in the marls, c) as thin beds (less than 1 mm in thickness) and d) filling thin veins in the marls, in association with halite and tuzlaite.

All mineral grains are extremely fine, usually lesser than 10 microns, precluding X-ray diffraction identification. They can appear as disseminations (i.e. Fe-poor sphalerite, which occurs as fine disseminations among the searlesite aggregates), the most common occurrence being vein fill-ins. The mineral associations comprise cinnabar, acanthite, silver sulphosalts (possibly, members of the proustite-pyrargyrite series), and tin sulphosalts. These minerals are found included in salt veins, or in cracks into other minerals. They are usually euhedral. Coffinite is also found in veinlets. Finally, barite has also been found as fine disseminations in the marls.

It is interesting to note that no other iron sulfide phases could be identifed. The occurrence of pyrite and barite suggest moderate Eh values in the environment of deposition, and the absence of marcasite suggests moderate pH. The presence of heavy metals in lateral equivalents of the principal rock salt series at Tuzla is an indication of associated syngenetic and postsedimentary volcanic activity in the area of the Tuzla salt deposit. The reduction of sulfate and the formation of an euxinic environment imply the preservation of organic carbon in the marls, which is consistent with a shallow basin sedimentation type of these rocks (5,6).

In the Tuzla deposit, sulfate minerals in the evaporites are not directly responsible for the precipitation of metal sulfides. Euxinic environment in the brine pools above the water-sediment interface is not ultimate prerequisite to ensure favorable condition for sulfate reduction. Sulfate entraining solutions percolating through the marl sediments are reduced in the presence of organic matter to form H_2S by activity of desulfurizing bacteria. High concentration of organics in the sediment, availabe as food for bacterial digestions, ensures low redox potential, mobilisation of divalent iron and precipitation of early diagenetic iron sulfides. Pyrite is the first sulfide phase formed in the sediment. Presence of As, Sb, Hg sulfides suggests prolonged circulation of terrestrial, oxidizing water from the surrounding uphills, probably of lower salinity, leaching base metals and uranium from pyroclastics and siliciclastic rocks. The underground flow is supported by evaporitic pumping and lowering of water tabel in the evaporitic pools. Precipitation occurred directly from the aqueous H_2S species or metasomatic replacement of the early diagenetic iron sulfides.

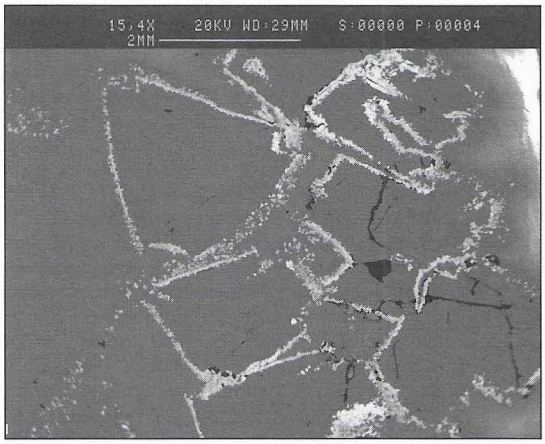

Fig.1. Sulphide grains arround big northupite crystals.

References

1 - Warren, J., 1999, Evaporites - their evolution and economics. Blackwell Science Ltd., Oxford, 438 p.

2 - Kniewald, G., Bermanec, V., Tibljas, D., 1986. On the origin and type of the Tuzla salt deposit in Yugoslavia. *Rapp. Comm. int. Mer Médit.*, 30/2: 72.

3 - Kniewald, G., Bermanec, V., 2001. Geochemistry and mineral assemblages of the Mediterranean evaporite deposits. 2. Boron hydrogeochemistry in the Tuzla deposit in Bosnia-Hercegovina. *Rapp. Comm. int. Mer Médit.*, 36: 9.

4 - Hardie, L.A., Eugster, H.P., 1971. The depositional environment of marine evaporites: a case for shallow, clastic accumulation. *Sedimentology*, 16: 187-220.

5 - Canfield, D.E., 1989. Sulfate reduction and oxic respiration in marine sediments: implications for organic carbon preservation in euxinic environments. *Deep-Sea Res. Part A*, 36: 121-138.

6 - Canfield, D.E., 1994. Factors influencing organic carbon preservation in marine sediments. *Chemical Geology*, 114: 315-329.