GEOCHEMISTRY AND MINERAL ASSEMBLAGES OF THE MEDITERRANEAN EVAPORITE DEPOSITS : THE TUZLA ROCK - SALT DEPOSIT IN BOSNIA - HERCEGOVINA

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Abstract

The evaporitic deposit of the Tuzla salt basin in Bosnia-Hercegovina is treated in terms of the regional Mediterranean evaporite formations. The geological and tectonic processes leading to the breakup of the Tethyan ocean during the middle and upper Miocene have caused a sequence of dessication and marine transgression periods which have resulted in the formation of extensive evaporite deposits along the continental margins of the Paratethyan and Mediterranean Seas. The lithofacial, mineralogical and geochemical characteristics of the Tuzla evaporite series show a similar pattern with the Gessoso-Solifera Messinian series in Sicily and set the requisite framework for a complex investigation of the depositional environments of Mediterranean evaporites.

Key-words : basin formation, diapirs, evaporites, geochemistry, mineralogy

Introduction

Evaporites in the Mediterranean region occur in a variety of environmental settings. Depositional environments range from coastal intertidal and supratidal zones (sebkhas), small coastal or atoll-type lagoons, deeper marine basins and sub-sealevel basins with marine inflow, to non-marine interior freshwater and saline lakes. The paleogeographic and tectonic settings include continental margins and shelves, interior cratonic basins and rifted continental slopes. The passage from one evaporitic sub-environment to another is often not obvious, as in the case of the carbonate deposits or sedimentary facies in less dynamic regions. The inherent diversity of the evaporitic series is further complicated by diagenetic processes. Moreover, some of the products of late diagenesis exhibit outward similarities to textures actually developed during sedimentation, including early diagenetic features which developed from and may be superposed on any characteristic facies of the depositional environment.

Mediterranean evaporites older than Tertiary age are comparatively rare. This appears to be a consequence of Miocene plate tectonic activity which created regions of relatively restricted marine sedimentation - the Mediterranean and the Paratethyan Seas, which evolved from the Tethyan ocean. Rapid changes in marine depositional environments seem to have occurred in the Mediterranean region during the middle Miocene. Following a peak in marine sedimentation during the early Badenian, there was widespread dessication in the Carpathian foredeep and eastern intramontane basins followed by a number of short marine transgressions. This event, decribed as the "middle Miocene salinity crisis", was caused by the closing of the marine seaway to the Indo-Pacific oceans and gave rise to the brackish water beds of the Karagangian stage of the eastern Paratethys and Mediterranean Seas (1). The subsequent and far-reaching transgression flooded the entire area of the central and eastern Paratethys during the late Badenian stage and covered the evaporitic series with radiolarian and pteropod marls, with a wide variety of lateral equivalent facies depending on the geological and stratigraphic setting of the small local basins which formed after the breakdown of the Paratethys intracontinental sea.

The origin of Mediterranean evaporites should also be assessed in view of the formation and occurrence of seafloor brines. A recent study reports brines from the Discovery basin in the eastern Mediterranean which have the highest salinity ever found in the marine environment (2). These brines, formed by dissolution of bischofite ($MgCl_2.6H_2O$), give the first clear evidence for bischofite formation during the the Miocene salinity crisis, when the eastern Mediterranean evaporated near to dryness.

The Tuzla evaporite series

The salt deposit of Tuzla is located in the north-eastern part of Bosnia-Hercegovina and is the largest rock salt reservoir in the Balkan peninsula, with estimated reserves of ca. 170 million tons of salt. The essentially stratified salt-dome type deposit is of mid-Miocene age and consists of a sedimentary sequence of banded halite and anhydrite. Despite the rather well investigated geological setting of the area, the depositional environment in which these evaporites formed is still uncertain. Early investigations of the Tuzla salt basin indicate that halite crystallization has occurred cyclically –several times, as the basin became shallower during the Styrian orogenetic phase (3). Anhydrous and hydrated salts were deposited on tertiary dolomites and marls. The geochemistry of coexisting brines and their saturation states imply that the formation environment may be interpreted in terms of the mixing-zone model, rather than as an end-member marine or salt lake deposits (4,5). On the other hand, the close relationship of the evaporite series with the associated dolomitic limestones as well as evidence of progressive dolomitization, may reflect their possible formation under evaporative, non-evaporative or seepage-reflux conditions (6). The described framework shows some similarities with the depositional environment of the Messinian deposits of Sicily which may serve as a sedimentary model for the extensive Messinian evaporite deposits throughout the Mediterranean basin (7).

The mineral assemblage and trace element distribution

The mineral association of the Tuzla rock-salt series consists of halite, thenardite and anhydrite. The $a(H_2O)$ indicator couple is thenardite-mirabilite. Several accessory minerals, including northupite, are present in varying amounts. The assemblage, as well as possible lithotype indicator minerals have been studied in detail (4,8).

An earlier investigation into the thermodynamics of northupite precipitation from brines percolating the halite strata (10) using the equilibrium computer code SOLMINEQ.88 showed that the major ion composition of the saline waters are consistent with either primary (formed by seawater evaporation) or secondary brines (formed by dissolution of evaporites). However, trace element concentrations can be used to differentiate between the two brine types since Li, Br and B do not form evaporite minerals during seawater evaporation.

In the paragenesis, a new mineral - named tuzlaite to honour the occurrence - with a pentaborate sheet structure has been discovered in the marls laterally equivalent to the evaporites (9). The conditions of its formations and thermodynamic stability are still unclear, but there are indications that diagenetic changes could have affected the nucleation kinetics of the normal succession of borate minerals in the sequence, resulting in the precipitation of tuzlaite.

Another highly interesting feature of the host rock, especially the lateral equivalents of the evaporite series is the content and distribution of microelements in these sediments. A preliminary instrumental neutron activation analysis (INAA) study of marls and the tuzlaite mineral indicate that several transition group metals (Fe, Cr, Ni) are related to sulfides present in the marls as pyrite. These are a consequence of the syn- and postdiagenetic conditions of low redox potential which is often associated with seepage reflux. Strontium shows an interesting distribution pattern both in tuzlaite and the proximal and distant marls. Strontium replaces calcium in the tuzlaite structure and has Kd values of about 2 compared to those of the proximal marl rock and of about 5 for the distant marls, indicating probable Sr absorption from the parent marl series.

Elements of the lanthanide series (REE's) also display significant interrelationships, both in the tuzlaite mineral and the host rock. The crystal structure of tuzlaite strongly influences the concentration and distribution of individual lanthanide elments, so that REE concentrations in the marls are up to a hundred times greater than in the tuzlaite. This mineral displays a peculiar negative Eu and Yb anomaly and a positive Tb anomaly, contrary to the marls which have no pronounced anomalies. The distribution of REE's in the proximal marls shows the same overall pattern as in the distant northupite-containing marl