

GEOCHEMISTRY AND MINERAL ASSEMBLAGES OF THE MEDITERRANEAN EVAPORITE DEPOSITS

2. BORON HYDROGEOCHEMISTRY IN THE TUZLA DEPOSIT, BOSNIA-HERCEGOVINA

Goran Kniewald^{1*} and Vladimir Bermanec²

¹ Center for Marine and Environmental Research, Rudjer Boskovic Institute, Zagreb, Croatia - kniewald@rudjer.irb.hr

² Department of Mineralogy and Petrology, Faculty of Sciences, University of Zagreb, Croatia - vberman@public.srce.hr

Abstract

The evaporite deposit of Tuzla in Bosnia-Herzegovina 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 containing minerals. This study deals with some aspects of the hydrogeochemistry of boron in the deposit, making use of mineralogical and petrological evidence to define the formation conditions of the boron minerals and the deposit in general.

Keywords – basin formation, diapirs, evaporites, geochemical cycles, mineralogy

Introduction

The evaporite deposit of Tuzla is located in the north-eastern part of Bosnia-Herzegovina and is the largest rock salt reservoir in the Balkan peninsula, with estimated reserves of ca. 170 million tons of salt. Despite the rather well investigated geological setting of the area, there is still no unambiguous evidence as to the depositional environment in which these evaporites formed. The essentially stratified salt-dome type deposit is of mid-Miocene age, hosted in a sedimentary series of banded halite and anhydrite. Early investigations of the Tuzla salt basin have indicated that the halite crystallization process has followed a sequence of several cycles, as the basin became shallower during the Styrian orogenic phase (1). 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 end-member type marine or salt lake deposits (2,3). 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 (4). 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 (5). Several factors influence and determine the formation of evaporitic sediments in subaerial, intratidal and hypersaline basins. Of these, clearly the most significant ones are a) the rate of influx of water; b) the concentration and speciation of ionic and complexed forms in solution; c) the rate of evaporation and d) the physical environment in which precipitation takes place. The interrelationships of these factors, coupled with clearly discernible diagenetic processes resulted in the Tuzla basin in a diverse suite of lateral equivalents of the evaporite series. Several distinct facies can be observed in most of the proximal and distal lateral rock formations. A lack of marine and/or freshwater flora and fauna in all adjacent geological formations further complicates the investigation of prevailing sedimentary cycles and environmental conditions. Changes in the features of the original depositional forms are frequently caused by tectonics, burial and migrating waters and brines.

The mineral association of the Tuzla rock-salt series consists of halite, thenardite and anhydrite. The a(H₂O) 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 (2,6). In the paragenesis, a new mineral - named tuzlaite to honour the occurrence - with a pentaborate sheet structure has been discovered (7). 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. Searlesite is the other boron containing mineral in the deposit.

Hydrogeochemical behaviour of boron in the Tuzla deposit

Boron is a highly dispersed element in nature, averaging 3 ppm in the earths crust and 4.6 ppm in seawater. The few occurrences worldwide with economical-

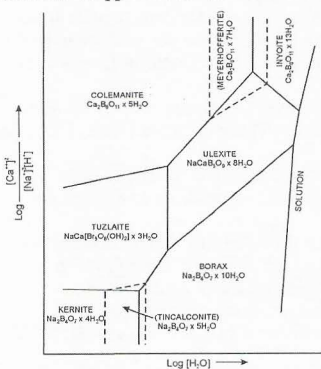


Fig. 1. Activity-activity diagram for the system Na₂O-B₂O₃-H₂O-CaO-B₂O₃-H₂O-H₂O

ly significant concentrations of boron involve local volcanic activity as a source of B (8). Also involved is a standing body of water capable of accumulating boron salts leached from the volcanics. Associated evaporation processes are required to concentrate the solution to the point of precipitation of various boron containing minerals. Impervious evaporite salts (of possibly different origin) form a protective layer and a geochemical barrier that prevents subsequent redissolution. Thus, sodium and calcium borate salts present major economic minerals (borax, kernite, ulexite, colemanite) but also secondary or accessory minerals associated with evaporite salts (tuzlaite, proberite, searlesite).

In agreement with mineralogical and petrological evidence of the tuzlaite-bearing host rock, it can be assumed that this hydrated borate formed initially as a chemical deposit in a saline body of water. Essentially two distinct types of borates form by this mechanism – hydrated sodium borates from alkaline environments high in Na and low in Ca, and hydrated sodium-calcium borates from milieus relatively higher in Ca. These two situations correspond to the conditions for the stability fields of borax and ulexite respectively in activity-activity diagrams, taking into account that the primary borates would be the higher hydrates (10). The relative abundance of Mg²⁺ in a brine or groundwater, at any stage of the paragenetic sequence is a complicating factor, since the actual assemblage formed depends on the ratio (Ca²⁺)/(Mg²⁺) and (H₂O). Consequently, a decrease in the activity of water due to concentration of solution after evaporation of water (or due to the possible influx of a more concentrated solution), or any increase in temperature, would cause the dehydration of the primary borate with the formation of a lower hydrate. Upon eventual burial of a saline water body (lake), the increase in pressure would thermodynamically favour the formation of lower hydrates since these have lower specific volumes. The water formed might be transferred to interstitial pore solutions. Parental fluids for the carbonate (and borate) evaporites may originally have been derived from the evaporation of surface waters fed by geothermal springs associated with local volcanic activity. However, a direct volcanogenic exhalative model for the Tuzla deposit appears unlikely, since borate minerals are too soluble to precipitate directly into a fresh, mixed lacustrine or marine water body associated with unevaporated hydrothermal fluids. In this respect, the Tuzla salt deposit seems to have a comparable formation history with Tertiary lacustrine borates of Bigadic in Turkey, which is the worlds largest sedimentary evaporite deposit (9). On the other hand, the major boron phases of Bigadic are the minerals colemanite and ulexite, deposited as nodules and veins within laminated and tuffaceous sediments of a perennial alkaline salt lake.

Conclusion

The occurrence of banded tuzlaite in the Tuzla salt deposit could indicate short periods of extreme dessiccation and subaerial exposure within the standing water bodies (lakes). The presence of searlesite implies periods of high Si concentrations. Thus, boron-containing minerals such as tuzlaite may have formed as secondary minerals either during burial and dewatering, or as reconversion products of other boron phases exposed to weathering and/or percolating groundwaters. The possible association of the Tuzla evaporite deposit - and its conspicuous suite of boron minerals – with local volcanic activity is still to be tested in terms of boron isotopic signature compatibilities.

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