

D.TIBLJAS¹, V. BERMANEC¹, Z.Brajkovic² and G.KNIEWALD³

(1) Dep. of Mineralogy and Petrology, Faculty of Science, Univ. of Zagreb, ZAGREB (Croatia)

(2) Tusanj Salt Mine, The Sodaso Company, TUZLA (Bosnia and Herzegovina)

(3) Center for Marine Research Zagreb, "Rudjer Boskovic" Institute, ZAGREB (Croatia)

The Tuzla salt deposit in the central part of northern Bosnia and Herzegovina (Yugoslavia) is a Miocene age salt-dome deposit, whose geological origin is still not fully clear with respect to its marine or non-marine formation (i.e. whether the halite is marine or recycled from dissolution of the rock-salt diapir). The principal saline minerals of the evaporite deposit are halite, anhydrite and thenardite. The mineral assemblage also contains accessory minerals such as northupite, nahcolite, glauberite, probertite, teepelite and bradleyite. Among these, northupite is particularly interesting with regard to its origin and formation and has previously been studied for its trace element content (KNIEWALD *et al.* 1986).

Northupite, $\text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3 \cdot \text{NaCl}$ or $\text{Na}_3\text{Mg}(\text{CO}_3)_2\text{Cl}$ is a rare mineral, and apart from Tuzla - which now is a classic occurrence of northupite - is found only in a few other places in the world. Earlier researchers proposed chemical schemes for its formation involving diagenetic alteration, while more recent studies showed that direct precipitation from brine solutions is also a feasible pathway of formation (VANCINA *et al.* 1986). Although northupite is usually regarded as a typical lacustrine mineral, it can through diagenetic processes be incorporated into marine or mixing-zone sequences. In the Tuzla evaporite deposit northupite occurs in several textural types, ranging from megascopic octahedral crystals in a marl matrix to millimetre-sized brownish crystals (coated with organic matter) imbedded in halite. The Fe(II) enriched ferronorthupite is closely associated with iron sulphides indicating its formation in reducing environments or diagenetic alteration.

Using the equilibrium computer code SOLMINEQ.88 (KHARAKA *et al.* 1988) and the chemical composition of a recent brine percolating through sections of the halite strata (table 1.), the mineral-solution equilibria for northupite formation and dissolution were established. Since the database of SOLMINEQ.88 or other available codes contain no thermochemical values for northupite, its chemical potential was taken as $\mu^\circ_{\text{RT}} = 989.6$ (FELMY and WEARE, 1986). The thermodynamic solubility product of northupite was taken as $\log K = -4.8 \pm 0.3$ at 25 deg C (VANCINA *et al.*, 1986).

Table 1. Chemical composition of a recent brine in the Tuzla evaporite deposit (density 1.207 g cm^{-3} , concentrations in g/L)

NaCl	Ca	Mg	Cl	SO ₄	HCO ₃	H ₂ S
269.3	11.0	4.24	193.2	0.6	2.93	0.0013

The calculated saturation state of the brine, derived from the normalized saturation index, implies that northupite precipitation is thermodynamically feasible. If ancient seawater should on the basis of present day major constituent composition be regarded as undersaturated with respect to northupite, the formation environment can be interpreted in terms of the mixing-zone model.

An inherent problem which has to be considered in geochemical equilibrium modelling of saline mineral assemblages lies in the fact that an entirely non-marine brine can also produce mineral sequences characteristic of modern seawater, since they may contain an identical final invariant salt assemblage. Therefore, in the absence of indicative trace constituent data, the variations between predicted vs. observed mineral sequences associated with the Tuzla northupite may be credited to:

- departure of the present day brine from ancient brine/seawater composition, and/or
- diagenetic alteration of the original marine mineral assemblage.

A final implication of the performed solubility calculations using the SOLMINEQ.88 code is that the comparatively widespread occurrence of northupite in the Tuzla deposit is the result of magnesium carbonate mineral suppression. This would have caused large substantial amount of Mg ions to remain in the brine facilitating northupite formation.

References

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