Thermodynamics of formation and stability of Northupite in the Tuzla salt deposit in Bosnia and Herzegovina

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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, teepleite 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, $Na_2CO_3.MgCO_3.NaCl$ or $Na_3Mg(CO_3)_2Cl$ is a rare mineral, and apart from Tuzla - which now is a classic occurence 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 $\mu°RT^{-1} = 989.6$ (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 gcm^{-3}, concentrations in g/L)

NaCl	Ca	Mg	Cl	SO_4	HCO_3	H_2S
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 :

a) departure of the present day brine from ancient brine/seawater composition, and/or
b) 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 occurence 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.

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Sedimentary processes in the Petit Rhone Canyon and the Rhone upper fan inferred from Sar profiles

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As part of the "Processus sédimentaires sur les pentes et Instabilités" research project of IFREMER, a geophysical survey using the SAR french side-scan sonar (Système Acoustique Remorqué), the multibeam echosounder EM-12 and a SIG 600 KJ sparker, was carried out in January 1992, in the Gulf of Lions (South of France)(Fig. A-B). The goals of the survey were to characterize, by their seismic and side scan sonar signatures, the instability processes of a young passive continental margin and to study their relation with the high frequency cycles of sea level changes. The studied area includes the shelf break, the slope and the upper domain of the Rhône deep sea fan.

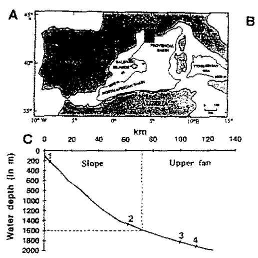
The morphology and architecture of the Rhône deep sea fan has already been described from sea-beam and superficial seismic data by BELLAICHE *et all.*, (1983), DROZ (1983) and DROZ and BELLAICHE (1985). These authors differentiated the continental slope located between the shelf break (-180 m) and the isobath -1600 m and the upper fan located between 1350-1600 to 2000 m depth (Fig. C), with a main valley and associated sedimentary levees. On the slope, the Petit Rhône canyon is considered as the main vector for sedimentary supply towards the deep sea fan and then considered mainly as an erosional domain . The study of new SAR profiles across the Petit Rhône canyon, on the slope, and across the main valley of the upper fan shows that the sedimentary processes that occur in the area are not so simple.

The Petit Rhône canyon has a U section 3.5 km wide and 250 m deep on the upper slope (SR 50 profile, fig. D. l), and becomes narrower and shallower downslope (see TR 24 profile, fig. D.2). A unit characterized by discontinuous high amplitude reflections overlains a basal unconformity. As displayed on the TR 24 profile this unit is thicker on each side of the Petit Rhône canyon.

These deposits demonstrate the existence of depositional processes in a domain previously considered as an erosional domain.

The TR 7 and TR 36 profiles (Figs. D.3, D.4), across the upper fan domain show the main valley with a flat bottom and an inner minor V valley shaped, few hundred metres wide and 70 m deep forming like terrace features. The main valley is infilled by the unit characterized by discontinuous high amplitude reflections (with interbeded transparent zones) which onlap the basal unconformity. On the TR 7 profile, this unit is confined in the main valley, whereas downwards (by exemple on the TR 36 profile) it also constitutes the eastern border of the main valley. Despite the absence of cores permetting us the datation of the upper unit and the basal unconformity, we suppose that the upper unit on the slope and the upper fan domain must be contemporaneous.

The formation of a basal unconformity in the canyon and the main valley might result from sea level fluctuations, whereas the presence of the upper unit on both sides of the Petit Rhône canyon and infilling of the main valley remains puzzling. In the main valley, it could be the result of (1) infilling of the main channel with slumps and channel facies as suggested by the presence of interbedded transparent facies followed latter by the incision of the minor valley, or (2) overflow deposition from the minor valley, as suggest by KTR7 and KTR8 cores obtained during the TRANSRHO survey which show a succession of fine turbidites which are interpreted as typical levee facies, or even a combination of these two mechanisms.



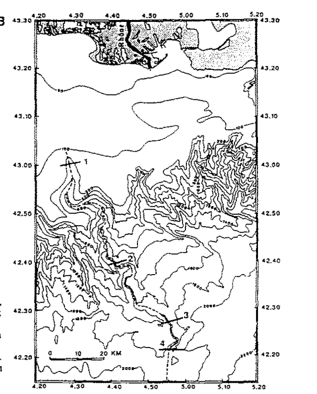
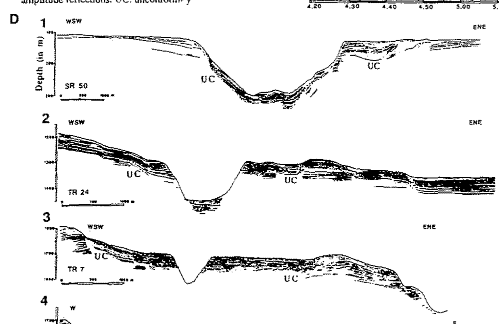


FIGURE CAPTIONS.

A - Location of the studied area.
B - Bathymetric map of the studied area off the Rhône mouth, showing the location of the bathymetric profile (fig. C: dashed line) and the SAR profiles shown in D.
C - Bathymetric profile of the Petit Rhône Canyon and the main valley with the location of the SAR profiles shown in D.
D - Line-drawings of selected 3.5 kHz subbottom SAR profiles. Stipple: upper unit characterized by discontinuous high amplitude reflections. UC: unconformity



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