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Chemical composition of seawater in Neoproterozoic: Results of fluid inclusion study of halite from Salt Range (Pakistan) and Amadeus Basin (Australia)

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Abstract

Data on chemical composition of brines in primary inclusions of marine halites and on mineralogy of marine evaporites and carbonates lead to the conclusion that during the Phanerozoic two long-term cycles of chemical composition of seawater existed. During each of those cycles, seawater dominantly a Na-K-Mg-Ca-Cl (Ca-rich) type changed to a Na-K-Mg-Cl-SO_4 (SO_4-rich) type. Recrystallised halite from the uppermost Neoproterozoic Salt Range Formation (ca. 545 Ma) in Pakistan, contains solitary inclusions indicating SO_4-rich brines. This supports the concept derived from the study on primary fluid inclusions from the Neoproterozoic Ara Formation of Oman; SO_4-rich seawater existed during latest Neoproterozoic time (ca. 545 Ma). In contrast, samples of recrystallised halite from the Bitter Springs Formation (840–830 Ma) in Australia contain inclusion brines that are entirely Ca-rich, indicating that basin brines and seawater were Ca-rich during deposition of central Australian evaporites. These combined data supported by the timing of aragonite and calcite seas suggest that during the Proterozoic, significant oscillations of the chemical composition of marine brines, and seawater, occurred, which are similar to those known to exist during the Phanerozoic. It is suggested that Ca-rich seawater dominated for a substantial period of time (more than 200 Ma), at 650 Ma, this was replaced by SO_4-rich seawater, finally returning to Ca-rich seawater at 530 Ma.

Keywords: Neoproterozoic; Geochemistry; Halite; Australia; Pakistan; Fluid inclusions; Evaporites

1. Introduction

The most important quantitative characteristics of changes in chemical composition of ancient seawater, are measured by analysis of primary inclusions within sedimentary halite from marine evaporite formations (Kovalevich, 1988; Kovalevich et al., 1998; Lowenstein et al., 2001, 2003; Horita et al., 2002). Previous studies have shown that during the Cambrian-Carboniferous and Jurassic-Palaeogene times, seawater was a Na-K-Mg-Ca-Cl (Ca-rich) type (e.g. Kovalevich et al., 1998; Brennan and Lowenstein, 2002; Brennan et al., 2004; Petrychenko and Peryt, 2004; Petrychenko et al., 2005), while during the Permian-Triassic (and Neogene times), seawater was a Na-K-Mg-Cl-SO_4 (SO_4-rich) type (e.g. Kovalevych et al., 2002a,b; Lowenstein et al., 2005;

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Zimmermann, 2000). The timing of those chemical phases of seawater coincides with changes in seafloor spreading rates, global sea level, and the primary mineralogies of marine limestones and evaporites (Spencer and Hardie, 1990; Hardie, 1996). On the basis of studies of marine carbonates, Hardie (2003) concluded that similar changes occurred during the Precambrian.

Although primary inclusions are undoubtedly preferred to reconstruct the chemical composition of ancient seawater, it is possible to extract some information from secondary fluid inclusions. Previous studies (Bein et al., 1991; Roedder et al., 1987; Kovalevich et al., 1998) showed that recrystallised halite originally precipitated from SO_4-rich brines could contain inclusions of two chemical assemblages—SO_4-rich and Ca-rich. Therefore, the occurrence of secondary SO_4-rich inclusions also indicates that basin brines and seawater were SO_4-rich. In turn, entirely Ca-rich secondary inclusions suggest that basin brines and seawater were Ca-rich. It should be stressed that the study of secondary inclusions does not allow for estimation the ion ratios of contemporaneous brines and seawater.

The study of fluid inclusions in chevron halite crystals from the Neoproterozoic Ara Formation of Oman (544–543 Ma) indicated that Latest Neoproterozoic seawater was SO_4-rich (Lowenstein et al., 2001; Horita et al., 2002). In this study we present the results of analyses of fluid inclusions and Br content in six samples of uppermost Neoproterozoic Salt Range Formation of Pakistan (coeval with the Ara Formation of Oman) and in four samples from the older (840–830 Ma), evaporites of the Amadeus Basin, Australia. The aim of this study is to ascertain the original chemical characteristics of parent brines of evaporite basins and thus of the contemporaneous, Neoproterozoic seawater.

It should be mentioned that an alternative methodological approach and interpretation of fluid inclusions in marine halite exists; advocating that recorded sulfate depletion in the brines of particular evaporite basins can be due to dolomitization or to the addition of a $CaCl_2$-rich solution (e.g. Ayora et al., 2001). The concept of secular variation in the composition of the ocean applied by us in this paper is based on the following evidence presented elsewhere (Kovalevich et al., 1998; Lowenstein et al., 2001, 2003; Horita et al., 2002; Holland, 2003):

1. the compositional changes of brines in primary fluid inclusions in marine halite show clear stratigraphic control;
2. brines of all Neogene marine evaporite basins that were characterized by SO_4-rich parent seawater, are of the SO_4-rich type;
3. evaporite basins of the same age and located on various continents show the same or similar chemical composition; and the varied intensity of sulfate depletion in coeval basins (as recorded by Ayora et al., 2001) can be explained by the influence of local factors (such as water–rock interactions and inflow of non-marine water;
4. apparent lack of extensive contemporaneous dolomite in many evaporite basins casts doubt on the importance of dolomitization in parent brine composition.

2. Geological setting

2.1. Salt Range

The Salt Range is considered to be the youngest and southernmost compressional structure within the Himalayan foreland and represents an emergent thrust front along which, the Potwar Plateau has been translated southward (Fig. 1; Grelaud et al., 2002). The Salt Range and Potwar Plateau have a surface extent of approximately 27,000 km^2. The Salt Range is a complex salt anticlinorium (Gee, 1989), with well-expressed salt diapirism. In the substrate of the Salt Range, Precambrian metamorphic and magmatic rocks occur (outcropping 80 km south of Salt Range). A borehole 280 km south of Salt Range contains a 900 m thick section of metamorphic/magmatic rocks, below the Salt Range Formation (Gee, 1989).

The Upper Neoproterozoic Salt Range Formation consists of salt, gypsum, dolomite, claystones and sandstones that were deposited in a sedimentary cycle beginning with an evaporite facies, through an alternating nonmarine–marine deposition and then finally into a second evaporitic facies (Attaullah and Javed, 1979; Ghauri, 1979). Such restricted marine-deposits occur in southern Oman, Iran and northwest India and are regarded as coeval (Stöcklin, 1986), being formed under similar tectono-depositional conditions (Peters et al., 1995).

Samples from the Khewra salt mine in the Salt Range (Fig. 1), where a total thickness of salt beds is about 150 m were examined as part of this study. Halokinetic salt movement has made it impossible to place the samples on a stratigraphic column, as they no longer sit in correct stratigraphic position. The salt is transparent, white, pink, reddish to beef-colour red.

2.2. Amadeus Basin

The Amadeus Basin in the southern Northern Territory is approximately 170,000 km^2 in areal extent

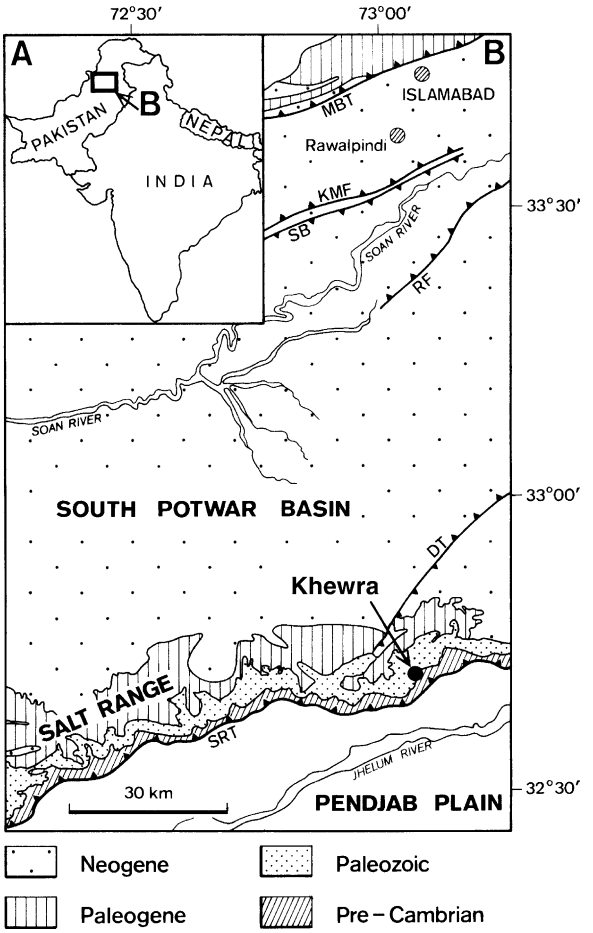

Fig. 1. Geological map of eastern Salt Range and Potwar Plateau (after Greland et al., 2002) showing the location of the Khevra Mine. MBT = Main Boundary Thrust, KMF = Khari Murat Fault, DT = Domeli Thrust, SRT = Salt Range Thrust, RF = Riwat Fault, SB = Soan Backthrust.

(Fig. 2). It is at the heart of a series of intracratonic basins on the Australian continent that share their origins in the break up of the supercontinent Rodinia at about 1 Ga. Strong stratigraphic ties have been made between these basins, which include the Officer, Ngalia and Georgina Basins, leading to them being referred to collectively as the Central Australian Rift System (Dyson, I.A., personal comm., 2005; Walter et al., 1995).

Mapping by NTGS geologists in the Petermann Ranges area on the southwestern margin of the Amadeus Basin, has confirmed the presence of bimodal volcanics and sediments that represent the onset of rifting and basin formation. The Amadeus Basin succession begins with sheet-like, tidally influenced deposits of the Heavitree Quartzite. A subsequent increase in accommodation space led to the deposition of thick, shallow marine, and in parts, anoxic rocks of the Bitter Springs Formation.

The Bitter Springs Formation contains variable volumes of basal evaporites and salt that form the foundation for halotectonic structures observed throughout the Amadeus Basin (Korsch and Kennard, 1991). The main evaporitic unit is the Gillen member, which, where the best outcrops occur, can be subdivided into at least five shallowing-upward units. Two of these units show signs of having had halite beds that have been removed by solution. These individual cycles may relate to the regular occurrence of salt units and the repetition of anhydrite/gypsum, halite, and anhydrite dolomite units as identified in petroleum wells (Lindsay, 1987; Wells and Kenewell, 1972). Halite intersected in petroleum wells is generally very coarsely crystalline and usually gray or pink in colour. The unit invariably includes suspended fragments of laminated anhydrite and organic rich dolomite, suggesting that it has been considerably modified by salt tectonics (Dyson and Marshall, 2005). A basin-wide hiatus at the top of the formation coincided with structural evolution in the basin. This hiatus was followed by deposition of a succession of glacial and interglacial deposits including representatives of the Sturtian (Areyonga Formation) and Marinoan (Olympic Formation) glaciations.

Deposition through the latest Neoproterozoic is dominated by marine-influenced clastics and carbonates of the Pertatataka, Winnall and Julie Formations (Fig. 3). Movement associated with the Petermann Orogeny (520–580 Ma) rearranged basin palaeogeography and further localised sedimentation, introducing foreland basin-style deposition to the southwest and extensive fluvial tongues of Arumbera Sandstone to the north and east. While clastics continued to be deposited in the south and west, the overlying Cambrian succession of the Chandler and Giles Creek Formations in the north and east is dominated by marine and marginal marine deposits of dolomite and evaporitic mudstone that incorporate organic-rich facies.

3. Materials

In total, 10 samples of Neoproterozoic rock salt from the Salt Range Formation and Bitter Springs Formation were studied (sample locations shown in Fig. 4). Short petrographic characteristics of samples are shown in Tables 1 and 2. Textures of all studied samples of rock salt vary from medium-grained (grain sizes 3–10 mm) to very coarse-grained (up to 5 cm in size). Most samples are rose in colour, or show rose spots due to the admixture of clay material. Elongated halite grains in some samples, indicate strong influence that halokinetic processes have had in the halite minerals internal structure.

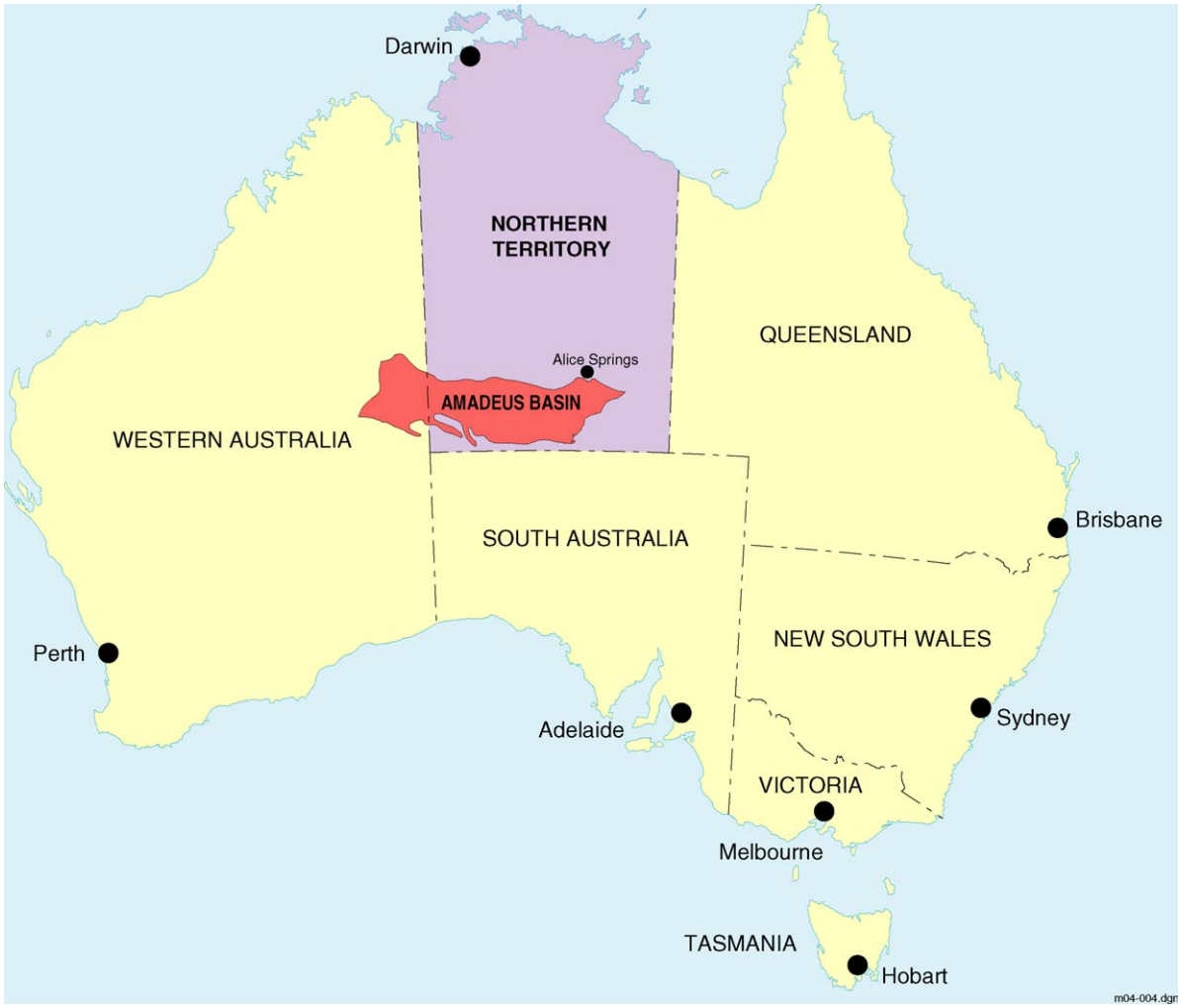

Fig. 2. Location of the Amadeus Basin.

In samples 4-P and 9-P from the Salt Range Formation, admixtures of K-Mg sulfate minerals: kieserite, polyhalite, kainite, leonite occur. In several samples the Bitter Springs Formation contains anhydrite nodules and dolomite clasts.

Primary sedimentary structures with fluid inclusions are not present in all samples studied.

Four halite samples (of six studied), from the Salt Range Formation, contained solitary fluid inclusions. The inclusions are commonly irregular in shape

Table 1
List of salt samples from the Khewra mine penetrated the Upper Neoproterozoic Salt Range Formation in the east-central part of the Salt Range, Pakistan

Sample	Characteristics	Br (ppm)
2-P	Light coarse-grained (up to 2 cm) rock salt with rose spots	54
4-P	Rose medium-grained rock salt with elongated grains, ocelli (up to 2 cm cross) of transparent halite and admixture of K-Mg minerals	52
5-P	Light medium-grained (up to 1 cm) rock salt with rosy spots	35
7-P	Rosy medium-grained (3–10 mm) rock salt	62
9-P	Light medium-grained (up to 10 mm) rock salt with rosy spots, elongated grains and admixture of K-Mg minerals	79
10-P	Clear, transparent, coarse-grained rock salt showing massive texture	34

Table 2
List of salt samples from the boreholes penetrated the Upper Proterozoic Bitter Springs Formation, Amadeus Basin, Australia

Sample	Borehole	Depth (m)	Characteristics	Br (ppm)
1/04	Ooramina 1	1595.3	Light rosy very coarse-grained rock salt with admixture of anhydrite and clasts (up to 3 cm) of brown dolomite	18
3/04	Mount Charlotte 1	1871.5	Rosy medium-grained rock salt with elongated grains (up to 1 cm), anhydrite nodule and dolomite clasts (up to 2 cm)	99
4/04	Mount Charlotte 1	1946.5	Similar medium-grained rock salt	102
5/04	Mount Liebing 1 (Well 1261), No. Core 31	95.6–95.7	Yellow-rosy medium-grained (3–8 mm) rock salt with anhydrite nodule and dolomite fragments (up to 1 cm)	132

and 20–800 μm in size. In one instance, a fluid inclusion 1.5 mm in size was found. Generally, the number of recorded inclusions is small: in every sample (about 500 g) approximately 3–30 inclusions were identifiable. The inclusions are variable: single-phase (fluid; Fig. 5A), and two-phase (fluid with sylvite daughter crystals; Fig. 5B). Some inclusions contain gas bubbles, or elongated anisotropic crys-

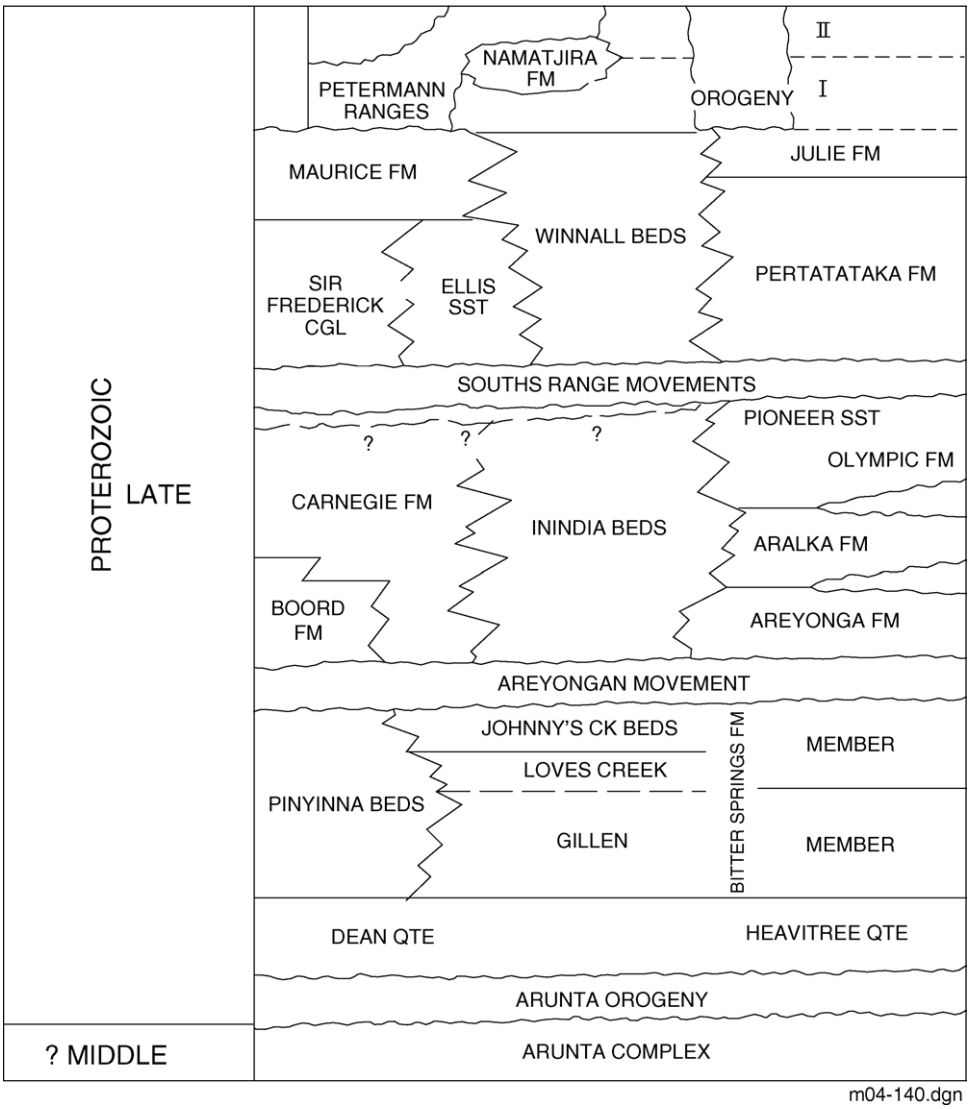

Fig. 3. Upper Proterozoic stratigraphy of the Amadeus Basin.

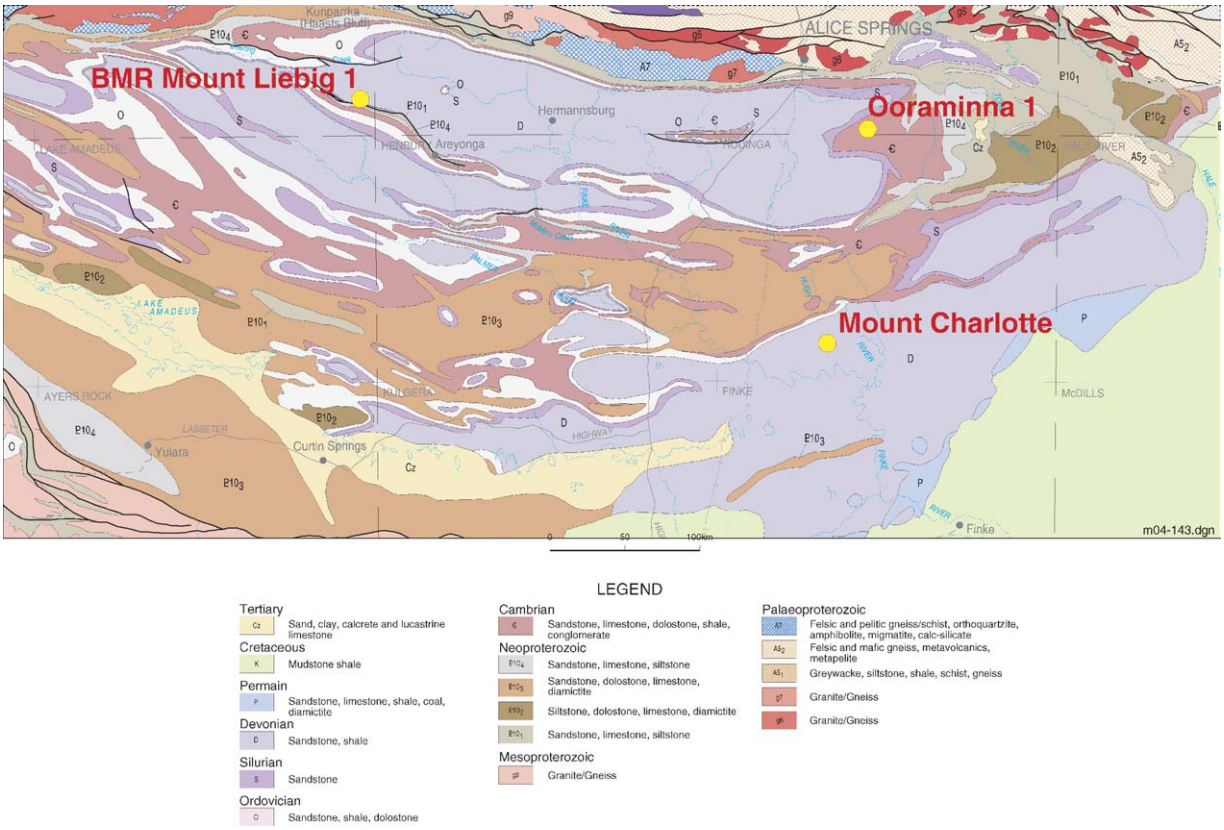

Fig. 4. Location of studied boreholes.

tals (of anhydrite?), possibly related to healed fractures.

In all samples, single-phase gas inclusions are present. Sample 10-P contains abundant gas inclusions, which relate to healed fractures diagonal to the crystal face (Fig. 5C). There are two groups of inclusions in terms of size: small (<20 μm), and large (from 20 to 150 μm, and rarely up to 300 μm). Small inclusions are usually cubic or close to cubic, and large are irregular in shape (although include elements of a cubic habit).

Geometrically similar solitary fluid inclusions were found in two samples (of four examined) from the Bitter Springs Formation. Two-phase gas-fluid inclusions predominate (Fig. 5D) within these samples. In some inclusions, small anisotropic crystals (anhydrite?) were identified. In one sample (5/04) several three-phase inclusions, containing brine, gas bubbles and sylvite daughter crystals, were observed (Fig. 5E). In the same sample (5/04) large (up to 200 μm), single-phase gas inclusions were found, which have a cubic shape. After dissolving in water, insoluble residue such as authigenic anhydrite crystals, dolomite and quartz were found. Quartz crystals (approximately 1 mm long) have one well-faced pyramidal apex and contain individual two-phase (gas-fluid) inclusions 10–25 μm in size.

4. Methods

Multiple techniques were utilised for this study, including petrographic, fluid inclusion and bromine analysis. As part of the attempt to record fluid inclusions in halite (pattern of distribution, size, and phase composition), thin plates (1–5 mm, depending on degree of transparency of crystal) were taken along the halite cleavage with a knife. These plates were put in a glycerine-filled flat glass cuvette under the microscope for photomicrographing.

All brine inclusions in the samples were analysed by the ultra microchemical analysis technique (UMCA), introduced by Petrichenko (1973). This method allows the major ions in brine inclusions to be determined: K, Mg, Ca and SO_4 ions, except Na and Cl. Although several other techniques have become available for the analysis of individual fluid inclusions in halite (Lazar and Holland, 1988; Ayora et al., 1994; Shepherd et al., 1998; Timofeeff et al., 2000), the UMCA method is the only

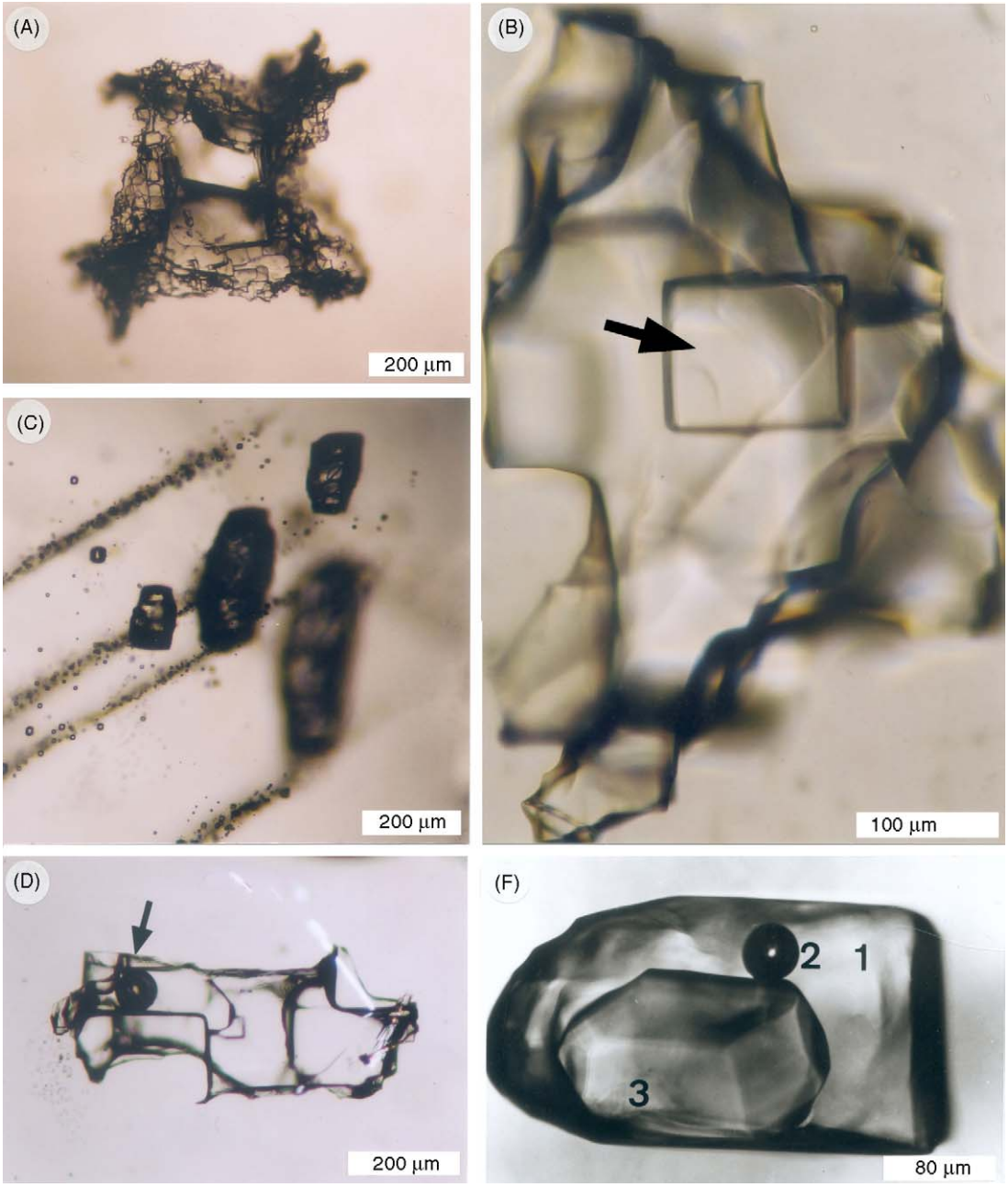

Fig. 5. Photographs of characteristic fluid inclusions in recrystallized halite; (A) Single-phase fluid inclusion of irregular shape; (B) Two-phase (brine + sylvite daughter crystal, arrowed) inclusion of irregular shape. (C) Small and large gas inclusions along healed fractures, oriented diagonal to cleavage face of halite crystals; small inclusions are cubic and big ones are irregular; (D) Two-phase (brine + gas bubble, arrowed) inclusion of irregular shape; (E) Three-phase (1: brine, 2: gas, 3: sylvite daughter crystal) inclusion. (A–C) Upper Neoproterozoic Salt Range Formation, Khewra salt mine, Pakistan; (D–E) Upper Proterozoic Bitter Springs Formation of the Amadeus Basin, Australia. (D) Borehole Ooramina 1, depth 1595.3 m; (E) Borehole Mount Liebing 1, depth 109.2 m).

technique that allows observation of the behaviour of inclusions (≥40 μm), in sedimentary halite, during their opening by a needle under the microscope. This establishes the approximate pressure in inclusions (high or low), and approximate degree of gas concentration in the brines. These features of brine inclusions are very important for the genetic characterization of inclusion types (Kovalevych et al., 2002a). Recent comparative studies of the same samples by UMCA and Cryogenic Scanning Electron Microscopy and Energy Dispersive Spec-

troscopy (Cryo-SEM-EDS), showed that the results of both methods are consistent and equivalent (Kovalevych et al., 2005). A study on primary fluid inclusions in the Middle Miocene Badenian of Poland, utilised both these methods, and gave similar results (Galamay et al., 1997; García-Veigas et al., 1997; Kovalevich and Petrichenko, 1997; Cendón et al., 2004).

In the UMCA method, halite is dissolved with a thin jet of water to within a few tens of micrometers of the inclusion walls. After the halite crystal is dried, the inclusion is opened. Inclusion fluid is then extracted with a conical capillary tube (3–5 μm in diameter), and a reagent is added to determine the solutes within the inclusion fluid (see Petrychenko and Peryt, 2004, for details). The capillary is then sealed and centrifuged. The volume of precipitate formed during this process is measured and compared to that formed from a standard solution. The analytical error of the applied method is 15–23% (for Mg and K) and 37–43% (for SO_4 and Ca), as differing density of the precipitates in capillaries is related to the speed (and temperature) of the reactive-solution, as well as the size of the precipitating crystals. To reduce errors, a number of analyses of each component in inclusion brines need to be (and were) carried out; two to three repeated analyses of the same type (same phase composition; typically one to three inclusions) significantly decrease the error to 16–17% (Petrichenko, 1973). It is impossible to reconstruct the quantitative composition of contemporaneous seawater from inclusions occurring in recrystallized halite and therefore the object of the study is to determine the basic chemical type of brines in each respective formation. The analytical error and number (repetition) of analyses were thus not critical, and the content of each element was measured 1–2 times. The minimum quantity of ions needed (in g/L): 0.8 g/L for K, 1.0 g/L for Mg, 0.9 g/L for Ca, and 0.5 g/L for sulfate ions (the lower values are semi-quantitative). Generally, the inclusions >40 μm are used for chemical analyses.

The homogenisation temperature of inclusions with gas phase and/or sylvite daughter crystals is measured under the microscope in a special thermochamber. For this purpose, halite plates 1–2 mm thick and approximately 5 mm × 5 mm in area, are cut; those plates contained as many inclusions as possible for simultaneous homogenisation. Fluid inclusions (20–70 μm), from each 'salt plate' are heated in a stepwise fashion until homogenisation was reached. Heating runs near the homogenisation temperature were performed at the rate of 0.2 °C/min. The error of determination of homogenisation temperature is approximately 1 °C.

The chemical composition of inclusion gases is established with the use of a mass spectrometric method (Kaluzhnyy et al., 1974). A mass spectrometer MKh-1303, containing a special electromagnetic vacuum mortar jointed to the spectrometer, made it possible to analyse gas contained in the inclusions. The attached ion counter SI-01 increased the sensitivity of the method by two orders of magnitude. The weight of each analysed sample is ideally 0.5–3.0 g. The absolute error was found to vary between 0.1 and 3.3%, and the relative error varied between 1.2 and 36.5% (Kaluzhnyy et al., 1974).

A determination of bromine values in halite is done with the sequence fluorescence spectrometer XRF (using a Philips PW 2400 spectrometer), with calibration curves based on natural halite standards. The clearest halite crystals (i.e. devoid of visible admixture of clay material) are chosen for analyses. The error of bromine determination is approximately 3%. During sample preparation, 6 g of sample and 1.5 g of wax is pressed into a pellet (40 mm in diameter).

5. Results

5.1. Salt Range Formation, Pakistan

Measured bromine contents in halite are within a very narrow range—from 34 to 79 ppm (see Table 1). The maximum value (79 ppm) is in sample 9-P. This sample contained an admixture of K-Mg minerals. The minimum value (34 ppm, sample 10-P) is in transparent coarse-grained salt.

During opening of inclusions for the analysis, a sharp increase in the size of gas bubbles was observed in some inclusions. This clearly indicates the increased pressure and gas saturation of brines.

With respect to chemical composition, brines of all studied inclusions are a Na-K-Mg-Cl-SO_4 (SO_4-rich) type (Table 3). In some samples, groups of inclusions (depending on phase composition) showed considerable variation with respect to relative ion concentrations. Usually single-phase inclusions show lower contents of K, Mg and SO_4 ions compared to three-phase inclusions.

For three-phase inclusions (samples 4-P and 9-P), homogenisation temperatures measured (10 measurements for each sample), show a considerable variation (from 55 to 100 °C).

Gas inclusions in all halite samples showed high-pressure values. During dissolution in water, gas inclusions in halite crystals exploded with a loud crack. A sample containing many of these 'explosive' inclusions was further analysed by a chemical mass-spectrometric analysis of gas (Table 4). The result showed that nitrogen clearly predominates, with carbon dioxide only representing a few percent.

Table 3
Chemical composition (in g/l) of inclusion brines in recrystallised halite from the Neoproterozoic marine evaporites; number of analyses (in brackets); and average chemical composition

Sample	Inclusion type	K	Mg	Ca	SO_4
Khewra salt mine of the Salt Range Formation, Pakistan					
4-P	(a) Single-phase (brine)	6.7; 7.5; 9.3; 10.7 (4) 8.5	24.2; 30.1; 31.4; 34.7 (4) 30.1	–	7.0; 8.2; 9.7; 9.9 (4) 8.7
	(b) Three-phase (gas + brine + sylvite)	25.7; 26.4; 36.0; 36.3; 39.0 (5) 32.7	74.1; 77.3; 86.8; 89.2; 108.1 (5) 87.1	–	39.2; 40.3; 41.7; 42.0; 56.6 (5) 44.0
7-P	Single-phase (brine)	14.1; 16.3 (2) 15.2	25.0; 31.2; 32.8; 34.4 (4) 30.9	–	11.3; 14.8 (2) 13.1
9-P	(a) Single-phase (brine)	32.1; 32.3; 40.4; 46.2 (4) 37.7	82.6; 88.8; 94.0; 100.5 (4) 91.5	–	20.2; 26.7; 28.5 (3) 25.1
	(b) Three-phase (gas + brine + sylvite)	30.0; 33.7; 37.3 (3) 33.6	100.0; 104.0; 104.4 (3) 102.8	–	59.7; 69.0; 76.2; 76.8 (4) 70.4
10-P	Single-phase (brine)	18.7; 21.2; 26.7 (3) 22.2	69.9; 71.8; 89.9 (3) 77.2	–	17.2; 18.4; 22.8 (3) 19.4
The Bitter Springs Formation of the Amadeus Basin, Australia					
1/04	two-phase (gas + brine)	6.8; 8.3 (2) 7.5	7.6; 8.6 (2) 8.1	52.1; 52.7; 57.2 (3) 54.0	–
5/04	(a) Two-phase (gas + brine)	(1) 12.7	(1) 70.7	(1) 128.7	–
	b) Three-phase (gas + brine + sylvite)	(1) 30.0	(1) 17.5	(1) 65.5	–
Concentrated modern seawater (after McCaffrey et al., 1987)					
At the beginning of halite precipitation		3.92	12.6	0.22	17.6
At the beginning of magnesium sulphate precipitation		26.10	65.9	–	115.0

Table 4
Gas composition (in vol.%) in Neoproterozoic salts from the Salt Range Formation (sample 10-P) and the Bitter Springs Formation (sample 5/04)

Sample	N_2	CO_2	H_2
10-P	95.5	3.5	1.0
5/04	88.9	9.7	1.4

5.2. Bitter Springs Formation

Bromine contents in all samples of halite show a wide range of values—from 18 to 132 ppm (see Table 2). There is a clear relationship between bromine content and petrographic characteristics of the samples. Low bromine contents were recorded in halite from the very coarse-grained rock salt, and high bromine contents from the medium-grained rock salt. The highest value was found in sample 5/04 (which contains fluid inclusions with sylvite daughter crystals).

Inside fluid inclusions, elevated gas pressures (and saturations) were measured. The highest pressure was observed in inclusions from very coarse-grained halite (sample 1/04). During the opening of inclusions with a needle, the brine was "boiled" by a strong gas expulsion.

The chemical composition of brine inclusions (see Table 3), showed a Na-K-Mg-Ca-Cl (Ca-rich) affinity. Considerable differences were recorded in ion concentrations (and ratios), of inclusions having varying phase compositions in the sample 5/04. Similar differences occur between two-phase inclusions in samples 1/04 and 5/04.

Homogenisation temperatures were measured in three-phase inclusions within halite, and in three-phase inclusions in authigenic quartz from sample 5/04. During the heating of halite slides with three-phase inclusions (10 measurements), sylvite crystals dissolved (at 60–62 °C) and subsequently the gas phase disappeared (at 108–112 °C). The homogenisation of inclusions in authigenic quartz (three measurements) was in the temperature range 140–150 °C.

Gas inclusions with high pressure were found in only one sample. The chemical composition of those inclusions is quite similar to the gas composition in Salt Ridge Formation salts (cf. Table 4).

6. Interpretation and discussion

6.1. Salt Range Formation

The reconstruction of palaeogeographic conditions for salt accumulation in a large number of Middle Asia

basins (including the Salt Range Formation), support their marine origin (Stöcklin, 1986; Horita et al., 2002). In the Salt Range, evaporites characterizing precipitation from continental brines (Hardie, 1984) are lacking. The Br concentration in halite (34–79 ppm) is lower than the values characteristic of halite precipitated from seawater (65–270 ppm—Holser, 1979). This decrease in concentration can result from the reworking of older evaporites, influx of dilute seawater, the mixing of meteoric and seawater, and from the influence of gypsum-dehydration water (cf. Schröder et al., 2003). Taken together, mineralogy and bromine geochemistry of evaporites indicate a seawater source for the evaporitic brines.

A lack of zoned sedimentary structures in halite, formed by primary fluid inclusions, and the increased pressure, plus the high gas saturation of brines of solitary inclusions, are interpreted to represent completely recrystallised rock salt under conditions of increased temperature, pressure and, evidently, halokinesis.

The high pressure inside inclusions has made it impossible to interpret homogenisation temperatures (as some inclusions could be dehermetized any time during the history). By considering experimental data (Kovalevich, 1976), it is possible to approximate a homogenisation temperature from inclusions with sylvite daughter crystals. It can be inferred that the studied salt series was heated to temperatures in the 55–75 °C range, and possibly higher. The gas saturation of buried brines, given relative gas compositions (mostly N_2 and CO_2; see Table 4), was due to the decay of dispersed organic matter.

The bromine contents of halite in general are much lower (37–79 ppm), than the theoretical content within halite of marine origin. First halite crystals, precipitated from concentrated marine water, contain around 75 ppm Br. At the beginning of potassic salt deposition its content increases to 270 ppm (Valiashko, 1956; Holser, 1966, 1979). As inclusions with sylvite daughter crystals occur in most studied halite samples it could be suggested that they precipitated from very concentrated brines, close to the onset of potassic salt deposition. Therefore, it could be expected that the Br content in studied samples was originally about 200 ppm. The cause of low Br contents could be syndepositional remobilization of salt. It is also possible that fluid inclusions with high brine concentration, and sylvite daughter crystals, do not characterize the phase of salt deposition but instead infer subsequent processes of salt recrystallisation and interaction with burial brines that have elevated K, Mg and SO_4 ion contents.

Our results make it impossible to reconstruct the ratios of those ions, neither in basin brines nor in the contemporaneous seawater. However, the chemical type of inclusion brines (SO_4-rich) without any doubt is inherited from basin brines. Only salts crystallized from SO_4-rich parent brines have secondary inclusions of the same chemical type (Kovalevich et al., 1998), whereas salts formed from Ca-rich brines, do not have secondary SO_4-rich inclusions.

The recorded variation of K, Mg and SO_4 ions in inclusion brines clearly record results of brine–rock interaction during various post-depositional stages of salt recrystallisation. Comparing our results with data on modern seawater chemistry (see Table 3), it can be inferred that brines concentrated during the initial and final stages of halite precipitation are represented. However, in all cases the content of SO_4 ion was either slightly or considerably lower than its equivalent concentration in modern seawater.

6.2. Bitter Springs Formation, Australia

Palaeogeographic reconstruction models of the Amadeus Basin indicate a marine genesis of the salts in the Bitter Springs Formation. Conditions suitable for evaporite deposition appear to have occurred after relative seal level reached its maximum in the lower half of the Gillen Member and began to fall again. It was noted by Lindsay (1987), that eustatic sea-level changes controlled the flow of seawater across the barrier formed by the peripheral bulge, causing cyclical deposition of evaporites. Data on bromine content in halite of three samples (99–132 ppm) can be regarded as support for its marine origin. In one sample of very coarse-grained halite, very low Br values (18 ppm) were found, and such coarse crystals could possibly have been formed as a result of multiple recrystallisation events.

Data from inclusion openings indicates complete recrystallisation of salts occurred in conditions of high pressure and high gas saturation brines. There is no doubt that salt recrystallisation occurred in conditions of increased temperature, evidenced by a gas phase in fluid inclusions examined.

The homogenisation temperature within three-phase inclusions in the sample 5/04 (60–62 °C and 108–112 °C) should be regarded as very approximate (given presence of high pressure in inclusions). The homogenisation temperature of inclusions in authigenic quartz from sample 5/04 (140–150 °C) is more reliable as the inclusions are hermetic.

Brines of all studied inclusions are characterized by high Ca contents and an absence of SO_4. An important variation in ion content was controlled by brine–rock interaction in burial conditions during salt recrystalli-

sation (as in salts from Pakistan). Sample 5/04 had the highest concentrations of all ions (K, Mg, Ca) within inclusion brines, with high bromine contents and sylvite daughter crystals.

Considering measured data and the lack of SO_4-rich brines in any inclusion in recrystallised halite of the Bitter Springs Formation we can hypothesise that during salt deposition, brines (and thus seawater) were Ca-rich.

7. Evolution of chemical composition of seawater in Late Proterozoic

When attempting to evaluate the composition of seawater during the Late Proterozoic, it is important to take into consideration the presence of $MgSO_4$ salts within the uppermost Neoproterozoic evaporites from the Salt Range, Hanseran Evaporite Group (Jones, 1970).

The presence of sulfate potash salts within marine evaporites supports the SO_4-rich parent seawater as indicated by a clear stratigraphic co-occurrence of sulfate potash salts, and SO_4-rich inclusion brines during the entire Phanerozoic (Hardie, 1996; Kovalevich et al., 1998). The inclusion brines reported in this paper that reach the level of sylvite saturation level, do not allow for the quantitative estimation of the contemporaneous seawater (see Zimmermann, 2001, for discussion). However, it is inferred that the chemical type of inclusion brines in primary marine halite is the same as in parent seawater (Kovalevich et al., 1998; Lowenstein et al., 2001; Horita et al., 2002). In the case of recrystallised halite the interpretation is still possible, therefore we conclude that during the deposition of the Salt Range Formation the seawater was SO_4-rich and during the deposition of the Bitter Springs Formation it was Ca-rich.

New data on fluid inclusions allows reconstruction of seawater type, in two very short time intervals of Late Neoproterozoic history that are separated by a long (almost 300 Ma) time interval from which data is lacking. Taking into consideration the mineralogy of carbonates (Hardie, 2003) and changes of seawater composition during Phanerozoic (Kovalevich, 1988; Kovalevich et al., 1998; Lowenstein et al., 2001, 2003; Horita et al., 2002), it is possible to estimate the lengths of time that characterized the Ca-rich and SO_4-rich seawater phases during the Neoproterozoic.

SO_4-rich seawater, recorded by studies of inclusions in uppermost Neoproterozoic of the Ara Formation in Oman (Lowenstein et al., 2001; Horita et al., 2002), and in coeval recrystallised halite of the Salt Range Formation, lasted until Nemakit-Daldynian time, 543–530 Ma, when it changed to become Ca-rich (Petrychenko et al., 2005). There is no doubt that this SO_4-rich phase lasted for a long time, presumably comparable for the length of the next, younger phase of SO_4-rich seawater that was spanning the Late Carboniferous to the beginning of Jurassic (Kovalevich et al., 1998). The Neoproterozoic SO_4-rich phase was initiated about 650 Ma. It was probably preceded by a longer phase of Ca-rich seawater. This conclusion is supported by data from the Bitter Springs Formation (about 830–840 Ma). It should be mentioned that the next, younger phase of Ca-rich seawater lasted about 230 Ma (from Early Cambrian till the Late Carboniferous) and the youngest Ca-rich phase was even shorter (about 175 Ma—from Jurassic till Palaeogene).

8. Conclusions

Fluid inclusions in samples of recrystallised halite from the uppermost Neoproterozoic Salt Range Formation in Pakistan were found to contain SO_4-rich brines. As secondary inclusions of the same chemical type only occur in salts crystallized from SO_4-rich brines, this demonstrates the presence of SO_4-rich seawater during deposition. Samples of recrystallised halite from the considerably older Bitter Springs Formation (840–830 Ma) in Australia, contain inclusion brines entirely Ca-rich. In salts formed from Ca-rich brines, secondary inclusions with SO_4-rich brines do not occur. Thus, Ca-rich type of inclusion brines in the halite from the Bitter Springs Formation suggests that basin brines and seawater were Ca-rich. The Ca-rich seawater present during deposition of the Bitter Springs Formation was replaced by SO_4-rich seawater at approximately 650 Ma. It is estimated that the next change in seawater chemistry took place at 530 Ma, where seawater changed from SO_4-rich to Ca-rich. The timing of those changes is in agreement with the duration suggested during the Phanerozoic, and supported by the timing of aragonite and calcite seas established by Hardie (2003) for the Late Neoproterozoic.

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References

Attaullah Khan, M., Javed Khan, M., 1979. Stratigraphy of the Banghanwala Formation, Khewra Gorge, Khewra, Jhelum District, Punjab, Pakistan. Bull. Centre Excel. Geol. Univ. Peshawar 12, 21–31.

Ayora, C., Cendón, D.I., Taberner, C., Pueyo, J.J., 2001. Brine-mineral reactions in evaporite basins: implications for the composition of ancient oceans. Geology 29, 251–254.

Ayora, C., García-Veigas, J., Pueyo, J.J., 1994. X-ray microanalysis of fluid inclusions and its application to the geochemical modeling of evaporite basins. Geochim. Cosmochim. Acta 58, 43–55.

Bein, A., Hovorka, S.D., Fisher, R.S., Roedder, E., 1991. Fluid inclusions in bedded Permian halite, Palo Duro Basin, Texas: evidence for modification of seawater in evaporite brine-pools and subsequent early diagenesis. J. Sediment. Petrol. 61, 1–14.

Brennan, S.T., Lowenstein, T.K., 2002. The major-ion composition of Silurian seawater. Geochim. Cosmochim. Acta 66, 2683–2700.

Brennan, S.T., Lowenstein, T.K., Horita, J., 2004. Seawater chemistry and the advent of biocalcification. Geology 32, 473–476.

Cendón, C.I., Peryt, T.M., Ayora, C., Pueyo, J.J., Taberner, C., 2004. The importance of recycling processes in the Middle Miocene Badenian evaporite basin (Carpathian foredeep): palaeoenvironmental implications. Palaeogeogr. Palaeoclimatol. Palaeoecol. 212, 141–158.

Dyson, I.A., Marshall T.R., 2005. The influence of salt tectonics on Neoproterozoic to Early Palaeozoic sedimentation, Amadeus Basin. Central Australian Basin Symposium.

Galamay, A.R., Bukowski, K., Przybyło, J., 1997. Chemical composition and origin of brines in the Badenian evaporite basin of the Carpathian Foredeep: fluid inclusion data from Wieliczka (Poland). Slovak Geol. Mag. 3, 165–171.

García-Veigas, J., Rosell, L., Garlicki, A., 1997. Petrology and geochemistry (fluid inclusions) of Miocene halite rock salts (Badenian Poland). Slovak Geol. Mag. 3, 181–186.

Gee, E.R., 1989. Overview of the geology and structure of the Salt Range, with observations on related areas of northern Pakistan. Geol. Soc. Am. Special Papers 232, 95–112.

Ghauri Khan, A.A., 1979. Sedimentary structures of the Jutana Dolomite and the Banghanwala Formation. Bull. Centre Excel. Geol. Univ. Peshawar 12, 1–10.

Grelaud, S., Sassi, W., de Lamotte, D.F., Jaswal, T., Roure, F., 2002. Kinematics of eastern Salt Range and South Potwar Basin (Pakistan): a new scenario. Mar. Petrol. Geol. 19, 1127–1139.

Hardie, L.A., 1984. Evaporites: marine or nonmarine? Am. J. Sc. 284, 193–240.

Hardie, L.A., 1996. Secular variations in seawater chemistry: an explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporites over the past 600 my. Geology 24, 279–283.

Hardie, L.A., 2003. Secular variations in Precambrian seawater chemistry and the timing of Precambrian aragonite seas and calcite seas. Geology 31, 785–788.

Holland, H.D., 2003. The geologic history of seawater. Treatise on Geochemistry 6, 583–625.

Holser, W.T., 1966. Bromide geochemistry of salt rocks. In: Rau, J.L. (Ed.), Second Symposium on Salt. N. Ohio Geol. Soc., Cleveland, vol. 1, 248–275.

Holser, W.T., 1979. Trace elements and isotopes in evaporites. Rev. Mineral 6, 295–346.

Horita, J., Zimmermann, H., Holland, H.D., 2002. Chemical evolution of seawater during the Phanerozoic: implications from the record of marine evaporites. Geochim. Cosmochim. Acta 66, 3733–3756.

Jones, C.L., 1970. Potash in halitic evaporites, Salt Range, West Pakistan. U.S.G.S. Prof. Paper 700D.

Kaluzhnyy, V.A., Svoren, I.M., Platonova, E.L., 1974. Sostav gaza fluidnykh vklucheniy i voprosy obnaruzheniya vodoroda v nikh. Doklady AN SSSR 219, 973–975.

Korsch, R.J., Kennard, J.M. (Eds.), 1991. In: Bureau of Mineral Resources, Australia, Bulletin, 594, p. 236.

Kovalevich, V.M., 1976. Fiziko-khimicheskiye usloviya formirovaniya soley Stebnikskogo kaliynogo mestorozhdeniya. Kiev, Naukova Dumka, 100.

Kovalevich, V.M., 1988. Phanerozoic evolution of ocean water composition. Geochem. Intern. 25, 20–27.

Kovalevich, V.M., Petrichenko, O.I., 1997. Chemical composition of brines in Miocene evaporite basins of Carpathian region. Slovak Geol. Mag. 3, 173–180.

Kovalevich, V.M., Peryt, T.M., Petrichenko, O.I., 1998. Secular variation in seawater chemistry during the Phanerozoic as indicated by brine inclusions in halite. J. Geol. 106, 695–712.

Kovalevych, V.M., Peryt, T.M., Carmona, V., Sydor, D.V., Vovnyuk, S.V., Halas, S., 2002a. Evolution of Permian seawater: evidence from fluid inclusions in halite. N. Jb. Mineral. Abh. 178, 27–62.

Kovalevych, V., Peryt, T.M., Beer, W., Geluk, M., Halas, S., 2002b. Geochemistry of Early Triassic seawater as indicated by study of the Röt halite in the Netherlands, Germany, and Poland. Chem. Geol. 182, 549–563.

Kovalevych, V.M., Carmona, V., Pueyo, J.J., Peryt, T.M., 2005. Ultramicrochemical Analyses (UMCA) and Cryogenic Scanning Electron Microscopy (Cryo-SEM-EDS) of brines in halite-hosted fluid inclusions: a comparative study of analytical data. Geochem. Intern. 43, 268–276.

Lazar, B., Holland, H., 1988. The analysis of fluid inclusions in halite. Geochim. Cosmochim. Acta 52, 485–490.

Lindsay, J.F., 1987. Upper Proterozoic evaporites in the Amadeus basin, central Australia, and their role in basin tectonics. Geol. Soc. Am. Bull. 99, 852–865.

Lowenstein, T.K., Timofeeff, M.N., Brennan, S.T., Hardie, L.A., Demicco, R.V., 2001. Oscillations in Phanerozoic seawater chemistry: evidence from fluid inclusions. Science 294, 1086–1088.

Lowenstein, T.K., Hardie, L.A., Timofeeff, M.N., Demicco, R.V., 2003. Secular variation in seawater chemistry and the origin of calcium chloride basinal brines. Geology 31, 857–860.

Lowenstein, T.K., Timofeeff, M.N., Kovalevych, V.M., Horita, J., 2005. The major-ion composition of Permian seawater. Geochim. Cosmochim. Acta 69, 1701–1719.

McCaffrey, M.A., Lazar, B., Holland, H.D., 1987. The evaporation path of seawater and the coprecipitation of Br− and K+ with halite. J. Sediment. Petrol. 57, 928–937.

Peters, K.E., Clark, M.E., Das Gupta, U., McCaffrey, M.A., Lee, C.Y., 1995. Recognition of an Infracambrian source rock based on biomarkers in the Baghewala-1 oil. India. Am. Assoc. Pet. Geol. Bull. 79, 1481–1494.

Petrichenko, O.I., 1973. Metody doslidzhennya vkluchen u mineralakh galogennykh porid. Kyiv, Naukova Dumka, 92.

Petrychenko, O.Y., Peryt, T.M., 2004. Geochemical conditions of deposition in the Upper Devonian Prypiac' and Dnipro-Donets evaporite basins (Belarus and Ukraine). J. Geol. 112, 577–592.

Petrychenko, O.Y., Peryt, T.M., Chechel, E.I., 2005. Early Cambrian seawater chemistry from fluid inclusion in halite from Siberian evaporites. Chem. Geol. 219, 149–161.

Roedder, E., d'Angelo, W.M., Dorzapf, A.F., Aruscovage, P.J., 1987. Composition of fluid inclusions in Permian salt beds, Palo Duro Basin, Texas, USA. Chem. Geol. 61, 79–90.

Schröder, S., Schreiber, B.C., Amthor, J.E., Matter, A., 2003. A depositional model for the terminal Neoproterozoic-Early Cambrian Ara Group evaporates in south Oman. Sedimentology 50, 879–898.

Shepherd, T.J., Ayora, C., Cendón, D.I., Chenery, S.R., Moissette, A., 1998. Quantitative solute analysis of fluid inclusions in halite by LA-ICP-MS and cryo-SEM-EDS: complementary microbeam techniques. Eur. J. Mineral. 10, 1097–1108.

Spencer, R.J., Hardie, L.A., 1990. Control of seawater composition by mixing of river waters and mid-ocean ridge hydrothermal brines. Geochem. Soc. Spec. Publ. 19, 409–419.

Stöcklin, J., 1986. The Vendian-Lower Cambrian salt basins of Iran, Oman and Pakistan: stratigraphy, correlations, paleogeography. Sciences de la Terre 47, 329–345.

Timofeeff, M.N., Lowenstein, T.K., Blackburn, W.H., 2000. ESEM-EDS: an improved technique for major element chemical analyses of fluid inclusions. Chem. Geol. 164, 171–182.

Valiashko, M.G., 1956. Geochemistry of bromide in the processes of salt deposition and the use of the bromide content as a genetic and prospecting tool. Geochemistry USSR 6, 570–587.

Walter, M.R., Veever, J.J., Calver, C.R., Grey, K., 1995. Neoproterozoic stratigraphy of the Centralian superbasin, Australia. Precambrian Res. 73, 173–195.

Wells, A.T., Kenewell, P.J., 1972. Evaporite drilling in the Amadeus basin: Goyder Pass, Gardiner Range and Lake Amadeus, Northern Territory. In: Bureau of Mineral Resources, Geology and Geophysics record 1972/36, 230 pp.

Zimmermann, H., 2000. Tertiary seawater chemistry—implications from primary fluid inclusions in marine halite. Am. J. Sci. 300, 723–767.

Zimmermann, H., 2001. On the origin of fluids included in Phanerozoic marine halite—basic interpretation strategies. Geochim. Cosmochim. Acta 65, 35–45.