

Ordovician seawater composition: evidence from fluid inclusions in halite

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Fluid inclusions in halite can directly record the major composition of evaporated seawater; however, Ordovician halite is very rare. The Ordovician is a key time during the evolution history because profound changes occurred in the planet's ecosystems. Marine life was characterized by a major diversification, the Great Ordovician Biodiversification Event and the Late Ordovician Mass Extinction, the first of the "big five" mass extinctions. However, so far there is no data on the Ordovician seawater. Data from the Ordovician-Silurian boundary were available only. In this study, we report the major compositions from Middle Ordovician halite in China to give the exact composition of Ordovician seawater. The basic ion composition (K^+ , Mg^{2+} , Ca^{2+} , and SO_4^{2-}) of inclusion brines was established with the use of ultramicrochemical analysis. The data on the chemical composition of the brines in the primary inclusions indicated that the brines were of Na-K-Mg-Ca-Cl (Ca-rich) type, and cover a huge gap in the evolution of seawater chemistry. The chemical composition of the primary inclusion brine in halite confirmed the earlier results for the Cambrian and Silurian halite originating from other salt basins and the previous speculation of "calcite sea" during the Ordovician, indicating a higher potassium content in the Lower Paleozoic seawater than in the seawater of other periods of the Phanerozoic.

Key words: Ordovician, fluid inclusions, halite, seawater composition, calcite sea.

INTRODUCTION

The influence of continental, meteoritic waters and groundwaters, as well as other processes, on the change in the composition of marine brines in ancient salt basins is currently discussed (e.g., Klein-BenDavid et al., 2004; Cendón et al., 2008; Garcia-Veigas et al., 2013). There are a number of marine basins, in which the influence of continental factors had a significant impact on the change in the chemical composition of brines (Garcia-Veigas et al., 1995; Ayora et al., 2001; Cendón et al., 2003, 2008). Therefore, the data on the chemical composition of brines of primary inclusions in halite are suitable for the reconstruction of the chemical composition of the Phanerozoic ocean

only when the marine origin of the studied evaporite formations is confirmed by the independent results of palaeogeographic, mineralogical-petrographic and geochemical studies.

To date, models of the chemical composition of the Phanerozoic ocean have been developed based on the chemical composition of the brines of primary inclusions in halite (Kovalevich, 1990; Kovalevich et al., 1998; Lowenstein et al., 2001; Brennan and Lowenstein, 2002; Horita et al., 2002; Kovalevych et al., 2002). These models recognized seawater chemistry variations changing between the Na-K-Mg-Ca-Cl (Ca-rich) type and the Na-K-Mg-Cl-SO₄ (SO₄-rich) type over geologic time. The variations of seawater chemistry in time were correlated with other geological processes on Earth (e.g., changes in seafloor spreading rates, the intensity of magmatic processes, global sea level changes; Horita et al., 2002).

Phanerozoic seawater chemistry oscillated between "calcite sea" (Ca-rich and low-SO₄) type and "aragonite seas" (SO₄-rich and low-Ca) type with the change of primary mineralogy of non-skeletal limestone (Sandberg, 1983). This is confirmed directly by fluid inclusions contained in marine halite (Kovalevich

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et al., 1998; Lowenstein et al., 2001; Horita et al., 2002; Kovalevych and Vovnyuk, 2010; Brennan et al., 2013), while late-stage potash salts in marine evaporites fluctuated between the KCl and MgSO₄ types with the calcite-aragonite oscillations (Hardie, 1996). During “calcite seas” times (Ca-rich), evaporation and precipitation of CaSO₄ completely took all SO₄²⁻ away from the brines during halite formation, leaving Ca²⁺ in excess in brine. Thus, the remnant brines in fluid inclusions of halite are of Na-K-Mg-Ca-Cl (Ca-rich) type, without detectable SO₄²⁻ (Kovalevich et al., 1998; Khmelevska et al., 2000; Petrychenko et al., 2005). The whole time, “aragonite seas” (SO₄-rich and low-Ca), evaporation and precipitation of CaCO₃ and CaSO₄ took all Ca²⁺ away from the brines, leaving SO₄²⁻ in excess during the later brine evolution. As a result, the remnant brines in fluid inclusions of halite are of Na-K-Mg-Cl-SO₄ (SO₄-rich) type without Ca²⁺ (Khmelevska et al., 2000; Lowenstein et al., 2001; Kovalevych et al., 2009).

Alternatively to these models, the change in the Ca/SO₄ ratio was explained as local environmental changes. Thus, several mechanisms have been proposed to explain the removal of sulphate in evaporite basins: bacterial sulphate reduction of dissolved sulphate, sulphate consumption by calcium-rich inflows related to dolomitization of basement carbonates, and input of calcium-rich hydrothermal inflows (Ayora et al., 2001; Cendón et al., 2008; García-Veigas et al., 2011).

Ordovician halite is very rare (Valyashko, 1962; Ronov et al., 1980; Kovalevych et al., 2006b; Fig. 1). Previous data on the Ordovician seawater chemistry come only from the uppermost Ordovician or Upper Ordovician–Lower Silurian deposits of Mallowa Salt in the Canning Basin, Australia (Brennan and Lowenstein, 2002; Horita et al., 2002; Kovalevych et al., 2006b). Their average composition of brines was quite close to

the composition of brines of the Early Cambrian and Late Silurian basins, but a significant difference is lower potassium content of fluid inclusions from Mallowa Salt (Kovalevych et al., 2006b). In this paper, we provide data on the seawater chemistry based on a study of fluid inclusions from Middle Ordovician halite of the Ordos Basin in China, thereby covering the gap in the picture of the seawater chemistry evolution (Kovalevich et al., 1998; Lowenstein et al., 2001; Horita et al., 2002).

GEOLOGICAL SETTING

There are several Ordovician evaporite basins in the North China Platform. One of them is the Ordos Basin – the second largest sedimentary basin in China with an area of ~250,000 km² (Fig. 2). During the Ordovician, the Ordos Basin

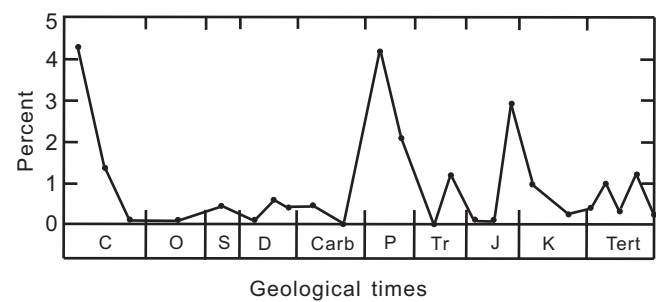


Fig. 1. Variation in abundance of evaporite rocks through Phanerozoic time (after Ronov et al., 1980)

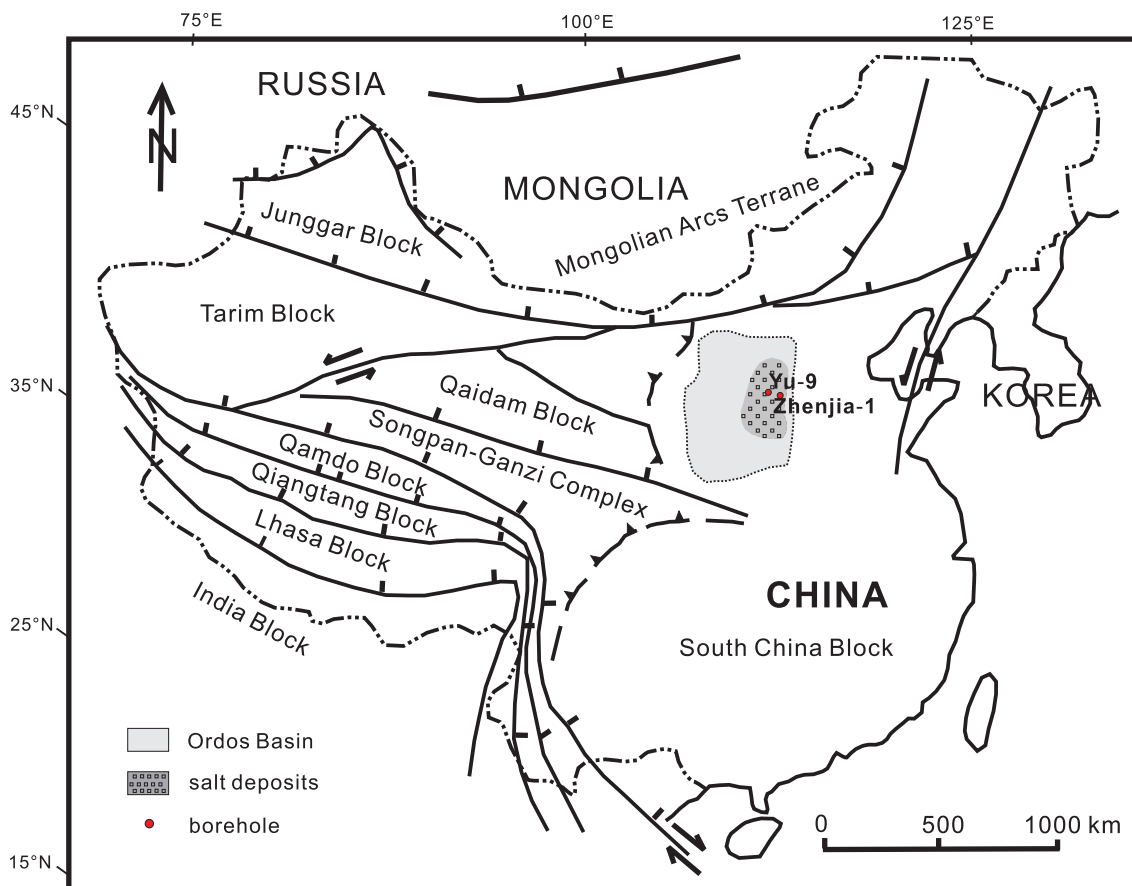


Fig. 2. Location map of the Ordos Basin

developed a gently inclined carbonate platform in a very shallow epicontinental sea, consisting of carbonates and evaporites. The Middle Ordovician evaporites of the Majiagou Formation developed in a restricted, shallow, and hypersaline environment within the Mizhi Depression (Feng et al., 1998; Wang and Al-Aasm, 2002; Yang et al., 2005; Li et al., 2011). The Majiagou Formation contains carbonates and evaporites and can be divided into six members, from Majiagou Member 1 to Majiagou Member 6 (Table 1; Bao et al., 2004). Majiagou 1, 3, 5 members are mainly evaporites, and Majiagou 2, 4, 6 members are mainly carbonates (Table 1).

The $\delta^{34}\text{S}$ values of anhydrite from Ma-5 Member range from +27.1 to +28.0‰ ($n = 5$) (Yao et al., 2010), and coincide with sulphur isotope of marine Late Ordovician evaporites (mean value +25.5‰) (Fox and Videtich, 1997). These evaporites show a “bull’s eye pattern” of facies as not “tear-drop pattern”, so the basin was separated from the outer ocean, within which a limited water exchange existed, not strongly affected by inflow of riverine water (Bao et al., 2004). Our Ordovician halite samples come from the Majiagou Member 5 of the Majiagou Formation from the Yu-9 and Zhenjia-1 boreholes, located in the centre of the basin (Fig. 3).

SAMPLES AND FLUID INCLUSIONS

We have analysed 14 halite samples from two boreholes: Yu-9 ($n = 2$) and Zhenjia-1 ($n = 12$). Of two samples from the Yu-9 borehole – 33[34/61] and 14[2/57] – the latter is nearly devoid of fluid inclusions. Primary and secondary inclusions were revealed in Yu-33 [34/61] (Ma-5 Member, Yu-9 borehole), Zjy-47-21 (Ma-1 Member), and Zjy-24-27 (Ma-6 Member) samples (Zhenjia-1 borehole; Fig. 4).

METHODS

The analysis of individual brine inclusions was carried out by the ultramicrochemical (UMCA) method (or the method of glass capillaries) of Petrichenko (1973). The method can determine the content of major ions (K, Mg, Ca and SO_4) in brine inclusions (except for Na and Cl) with an error of ~20%. The method has been used to analyse the ancient seawater chemistry from fluid inclusions of halite (e.g., Kovalevich et al., 1998; Kovalevich et al., 2002; Galamay et al., 2003; Kovalevych et al., 2005, 2006a, b, 2009; Meng et al., 2014).

Chemical composition of inclusion brine was studied in primary fluid inclusions of Zjy-47-21 sample only (Table 2) because the rest of inclusions were too small for UMCA analysis; only ~50–100 μm inclusions were used for analyses.

The following methodology was applied for establishing Br^- and Cl^- concentrations: firstly, the pure halite samples were dissolved in pure distilled water, followed by oxidation by chloramines T and chromogenesis achieved using fluorescein. In weak acid solutions, a chemical reaction between Br^- and fluorescein produces a strong absorption peak at 510 nm wavelength, which was measured using a V/S7200 spectrophotometer (Tan et al., 2006).

For chlorine isotopic analysis, we carefully selected pure fragments of halite crystals (with Cl^- content ~10 mg/mL) under a stereoscopic microscope. These were dissolved in high-purity water produced by sub-boiling distillation. Secondly, we passed the sample solution through a Ba-resin column to remove inter-

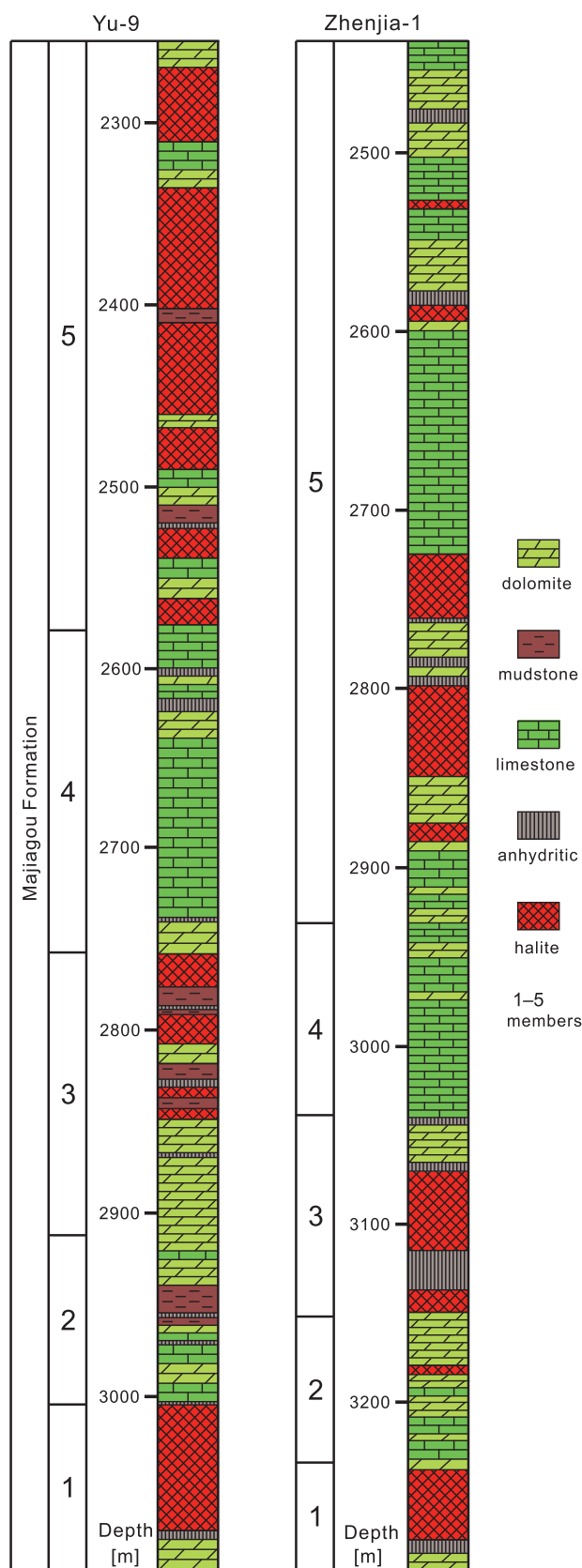


Fig. 3. The lithostratigraphy of drill cores from the Yu-9 and Zhenjia-1 boreholes

Table 1

The stratigraphy of Ordovician carbonate and evaporitic rocks of the eastern Ordos Basin (after Bao et al., 2004)

Stratigraphy			Thickness [m]	Lithology
Geological ages	Formation	Member		
Carboniferous	Benxi			upper part is dark grey mudstone interbedded with coarse-grained lithic quartzose sandstone; basal part is greyish bauxitic mudstone
Ordovician	Majiagou	Ma 6	0–10	micrite, absent in most area of the eastern Ordos Basin
		Ma 5	220–350	upper part is silty dolomite* and micrite, and lower part is halite, anhydrite interbedded with silty dolomite
		Ma 4	120–180	mostly micrite with dolomite
		Ma 3	80–150	silty dolomite, halite and anhydrite
		Ma 2	50–110	silty dolomite, argillaceous dolomite and dolomite containing anhydrite
		Ma 1	20–80	silty dolomite, halite and anhydrite
	Liangjiashan–Yeli		0–150	silty dolomite containing chert beds or nodules
Cambrian	Fengshan			silty dolomite and spatulate** dolostone

*following Ren et al. (2017: fig. 2f)

**in Chinese literature on the Ordos Basin, "spatulate" is used for a characteristic texture (see Lu et al., 2017: fig. 4)

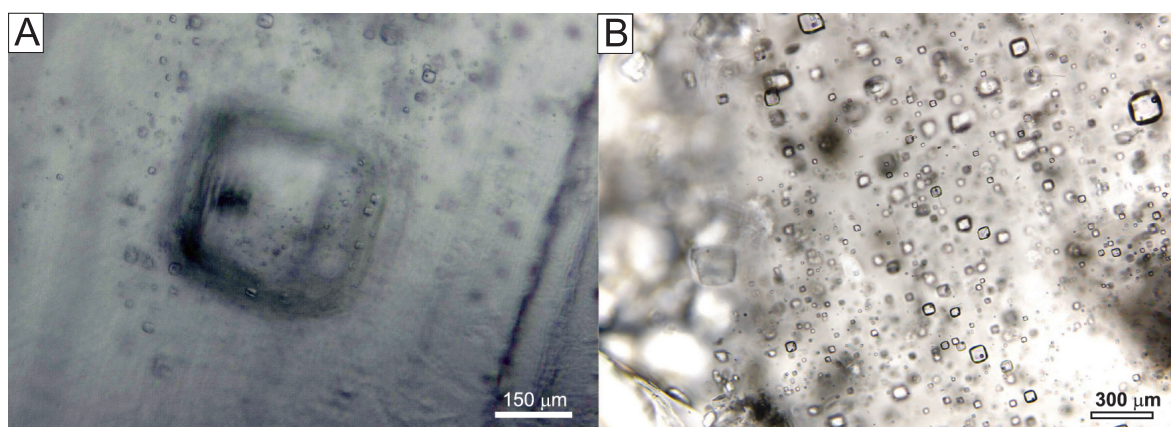


Fig. 4. The remnant primary fluid inclusions in Ordovician halite from the Majiagou Formation of North China

A – halite from the Yu-9 borehole; B – halite from the Zhenjia-1 borehole

Table 2

Concentrations of major components in primary fluid inclusions of Ordovician halite

Sample	Concentration, g/l (mean value in the parentheses)			
	K ⁺	Mg ²⁺	Ca ²⁺	SO ₄ ²⁻
Zjy-47-21	21.4; 23.1; 21.6; 17.3 (20.9)	35.9; 39.2; 48.6; 41.5 (41.3)	49.8; 76.0; 55.4; 74.6; 69.1; 71.6 (66.1)	<0.5
Modern seawater saturated with respect to:				
Halite*	3.9	12.6	0.22	17.6
Sylvite**	33.8	75.7	–	79.1

* after McCaffrey et al. (1987); ** after Valyashko (1962)

fering SO_4^{2-} ions, and subsequently passed it through an H-resin column to remove cations and convert the Cl^- into HCl. Finally, a pure CsCl solution was produced by passing the pure HCl solution through Cs-resin. This could then be analysed by mass spectrometry, using effectively the same methods as described by Vengosh et al. (1989), Xiao and Zhang (1992) and Xiao et al. (1995). Measurements were performed using a VG 354 thermal ionization mass spectrometer (Tan et al., 2006). The determinations of stable chloride isotope content were performed on two halite samples from the Yu-9 borehole (samples 14[2/57] and 33[34/61]).

RESULTS

The tested halite crystals are large and clear. Large fluid inclusions (>100 μm) occur within transparent halite crystals of sample 33[34/61]. In the central parts, they preserve some parallel growth bands interpreted as primary fluid inclusions in chevrons (Fig. 4). On the periphery of chevron halite crystals there are large liquid inclusions. They are arranged without any regularity. Their shapes are close to cubic or irregular and the size varies from 0.2 to 1 mm (Fig. 5). Although these transparent parts of halite can form after sedimentary stage (during diagenesis), the co-existing primary fluid inclusions in the central portions of crystal imply that the halite was recrystallized at a very shallow depth. Homogenization temperature of fluid inclusions of sparry calcite filling pores of dolomites from Majiagou Formation range from 49–74°C, and indicates recrystallization below 170 m (Zhang et al., 1997; Feng et al., 1998).

The major ion composition of inclusion brines has been determined in the primary fluid inclusions of sample Zjy-47-21 (Zhenjia-1 borehole) and in the secondary fluid inclusions of samples Yu-33[34/61] (Yu-9 borehole) and Zjy-24-57 (Zhenjia-1 borehole). In the remaining samples, there were not enough inclusions of suitable sizes to carry out UMCA studies.

The Ca^{2+} and Mg^{2+} concentrations were determined in brines from banded primary fluid inclusions of sample Zjy-47-21. In the brine from six inclusions, the mean Ca^{2+} concentration was 66.1 g/l (from 49.8 to 76.0 g/l). The mean Mg^{2+} con-

centration was 41.3 g/l (from 35.9 to 48.6 g/l), and the mean K^+ concentration was 20.9 g/l (from 17.3 to 23.1 g/l) (Table 2).

The Ca^{2+} and Mg^{2+} concentrations were also determined in brines from large secondary inclusions located in the outer edge of chevron halite crystals. The presence of K-Mg salt minerals in the inclusions provides the evidence of high concentration of parent brines (Table 3). The Ca^{2+} concentration was from 77.8 to 140.4 g/l, Mg^{2+} from 36.2 to 63.2 g/l, and the mean K^+ concentration varied from 20.0 to 35.7 g/l (Table 3).

The Br content in Ordovician halite is from 163 ppm (sample 14[2/57]) to 249 ppm (sample 33[34/61]). The Br content of normal sea-originated halite ranges from 50 to 100 ppm, and increases to a maximum value of 277 ppm at the onset of bittern precipitation (Valyashko, 1956). Thus, the Br contents in the Ordovician imply that the evaporation process can be near to bittern precipitation. It is also confirmed by potash minerals trapped within inclusions.

The $\delta^{37}\text{Cl}$ values obtained for the Ordovician halite were -0.36 and $+0.24\text{‰}$ (Table 4).

DISCUSSION

In halite samples, both primary and secondary inclusions were found. Primary fluid inclusions are microdroplets of brine, trapped during crystal growth. These inclusions were usually arranged in bands located parallel to crystal growth faces (Fig. 4). Secondary fluid inclusions are usually large and can have a cubic shape and occur individually outside the primary structures (Fig. 5A). This kind of large fluid inclusions formed in early stages of diagenesis and their major ion compositions can be similar to those of primary fluid inclusions. There are also secondary large-size and irregular inclusions (Fig. 5B) and they are typical for recrystallized halite (Roedder et al., 1987; Kovalevich et al., 1998).

Previous studies (Roedder et al., 1987; Lazar and Holland, 1988; Bein et al., 1991; Kovalevich et al., 1998) showed that recrystallized halite, which 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 the basin brines and sea-

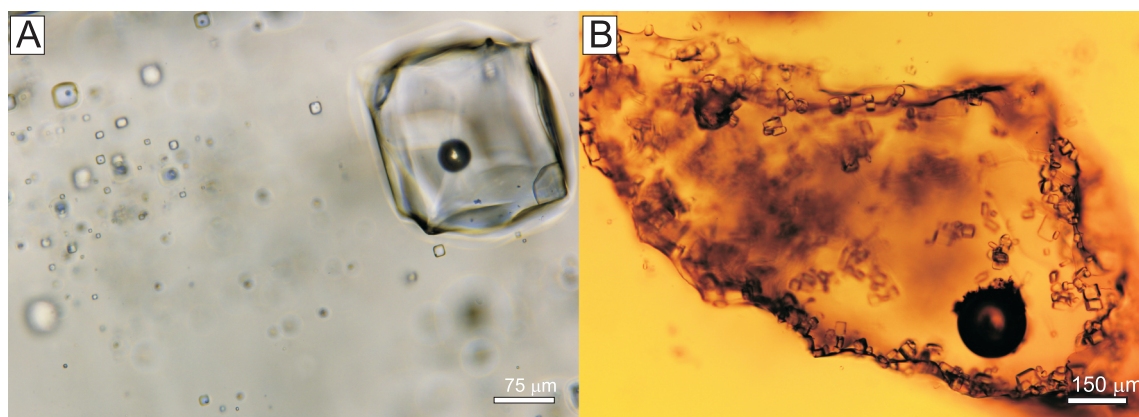


Fig. 5. Secondary fluid inclusions from the Yu-9 borehole

A – inclusion on the periphery of a sedimentary structure of halite; B – large multi-phase inclusion with numerous anisotropic crystals (anhydrite?) within clear, recrystallized halite

Table 3

Concentrations of major components in secondary fluid inclusions of halite from Ordovician halite

Fluid inclusion, No.	Concentration, g/l (mean values in brackets)		Remarks		
	K ⁺	Mg ²⁺	Ca ²⁺	SO ₄ ²⁻	
Yu-9 borehole, sample 33[34/61]					
1	—*	63.2	136.9; 132.5; 151.7 (140.4)	<0.5	inclusion with sylvite daughter crystal
2	—	—	87.9; 75.8 (81.9)	<0.5	gas + liquid inclusions
3	18.6; 21.4 (20.0) 33.0**	—	—	<0.5	sylvite occupies ~1.3 vol% of the inclusion
4	26.6; 22.8 (24.7) 35.7**	—	—	<0.5	sylvite occupies ~1.1 vol% of the inclusion
5	—	42.4; 32.3 (37.4)	124.5; 81.2; 111.5; 118.7; 98.9 (106.9)	<0.5	inclusion with sylvite daughter crystal
6	21.2 31.2**	43.0; 29.3 (36.2)	131.2; 121.0 (126.1)	<0.5	sylvite occupies ~1 vol% of the inclusion
Zhenjia-1 borehole, sample Zjy-24-57					
1	21.2; 22.8 (22.0) 34.0**	37.1	65.5; 73.2; 94.8 (77.8)	<0.5	sylvite occupies ~1.2 vol% of the inclusion

* not determined; ** calculated value, based on volume of sylvite daughter crystal

Table 4

Content of bromine, chloride and $\delta^{37}\text{Cl}$ of the Ordovician halite samples from the Ordos Basin

Sample	$\delta^{37}\text{Cl}$	Error SD (n = 3)	Cl [mass fraction, %]	Br [ppm]
Yu-9 borehole 14[2/57]	0.24	0.15	60.34	163
Yu-9 borehole 33[34/61]	-0.36	0.09	60.31	249

water were SO₄-rich. In turn, entirely Ca-rich secondary inclusions suggest that the basin brines and seawater were Ca-rich. We have to stress that the study of secondary inclusions does not allow for estimation the ion ratios of contemporaneous brines and seawater (Kovalevych et al., 2006a).

The primary mineralogy of non-skeletal carbonate rocks and other evidences imply the Ordovician seawater should be of Na-K-Mg-Ca-Cl (Ca-rich) type and have a high Ca content (Sandberg, 1983; Kovalevich et al., 1998; Lowenstein et al., 2001). The speculation has no other evidence; however, the fluid inclusions in halite can provide the direct evidence.

The Mg²⁺ concentration in ancient seawater was in a direct relation with SO₄²⁻ concentration and in an inverse relation with Ca²⁺ concentration. This kind of relation caused significant changes of the Mg²⁺/Ca²⁺ ratio in seawater. The maximum Mg²⁺/Ca²⁺ ratios for the seawater of "calcite sea" times (rich in Ca and poor in SO₄), such as Cambrian, Silurian, and Cretaceous, were found directly by the measurement of major compositions of fluid inclusions (Kovalevich et al., 1998; Lowenstein et al., 2001). The new data from primary fluid inclusions of Ordovician halite indicate that Middle Ordovician seawater was undoubtedly Ca-rich with the molar ratio Mg²⁺/Ca²⁺ = 1.03 (for medium values). These results are consistent with previous calculations considering the Mg²⁺/Ca²⁺ molar ratio in Ordovician seawater at ~1.0 (Lowenstein et al., 2001).

The $\delta^{37}\text{Cl}$ values of Ordovician halite in this study were -0.36 and +0.24‰. Because all published $\delta^{37}\text{Cl}$ data for marine evaporites fall within a narrow range of 0.0 ± 0.5‰ (Eastoe et al., 2007 with references), we conclude that $\delta^{37}\text{Cl}$ values confirm a marine, origin of Ordovician salts of the Majiagou Formation.

CONCLUSIONS

Fluid inclusions in Ordovician marine halite provide direct evidence of Ca-rich Ordovician seawater (calcite sea) with Na-K-Mg-Ca-Cl composition. This study covers a huge gap on the evolution of seawater chemistry. A series of the bittern precipitates of late-stage potash salts in Ordovician marine evaporites is of KCl type (dominated by sylvite lacking primary MgSO₄ salts). The brines from the secondary inclusions, located in the transparent parts of chevron halite and/or in the peripheries of crystals, showed a higher content of potassium and calcium than the brines from the primary inclusions. Based on our analysis of the chemical composition of the brines of the Cambrian, Ordovician and Silurian salt basins (Table 5), we could assume a higher potassium content in the Lower Paleozoic seawater.

Table 5

Average concentrations of major components in primary fluid inclusions of halite from the Cambrian, Ordovician and Silurian deposits (halite precipitation stage)

Location	Period, time	Age [Ma]	Ion content [g/l]		Jänecke unit [mol %]						N/n*	References
			K ⁺	Mg ²⁺	Ca ²⁺	SO ₄ ²⁻	K	Mg	Ca	SO ₄		
Michigan Basin, Salina Fm., USA	S ₂ , Ludlowian	~420	413** (14.4)	1264** (27.3)	831** (29.7)	0.5	9.0	54.9	36.1	–	41/46	Brennan and Lowenstein (2002)
Ordos Basin, Majiagou Fm., China	O ₂	~470	20.9	41.3	66.1	0.5	7.4	47	45.6	–	1/3	Our data
East Siberian Basin, Angara Fm., Russia	Є ₁ , Toyonian	~516	20.2	35.5	50.1	0.5	8.7	49.2	42.1	–	5/13	Petrichenko et al. (2005)
East Siberian Basin, Belsk Fm., Russia	Є ₁ , Botomanian	~515–519	20.7	46.8	59.1	0.5	7.2	52.6	40.2	–	1/5	Petrichenko et al. (2005)
East Siberian Basin, Usolsk Fm., Russia	Є ₁ , Atdabanian Tommotian	~519–530	23.3	33.9	52.6	0.5	9.9	46.4	43.7	–	5/5	Petrichenko et al. (2005)
Modern seawater concentrated to the beginning of precipitation of:												
Halite	3.9	12.6	0.22	17.6	6.7	68.9	–	24.4				McCaffrey et al. (1987)
Epsomite	26.1	85.9	–	115.0			–					McCaffrey et al. (1987)
Sylvite	33.8	75.7	–	79.1			–					Valyashko (1962)

* N/n – ratio of the number of results included into table (N) to the overall number of studied samples (n)

**Values in millimoles/kg H₂O; in brackets – calculated approximate value in g/l

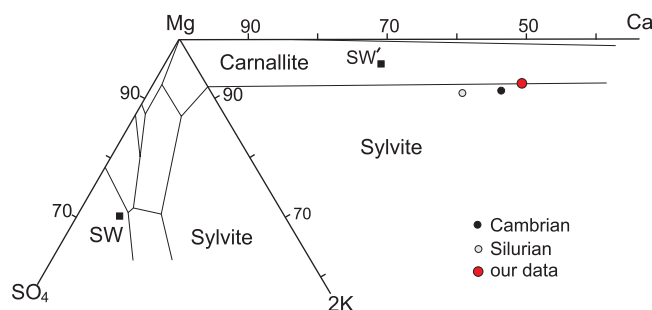


Fig. 6. Compositions of fluid inclusions in halite from Cambrian, Middle Ordovician and Silurian salts in the Mg-2K-SO₄ and Mg-Ca-2K Jänecke diagrams at 25° (diagrams after Eugster et al., 1980: fig. 9)

SW – modern seawater saturated with respect to halite (after McCaffrey et al., 1987), SW' – ancient seawater (Є–C, J–K) saturated with respect to halite (after Kovalevich, 1990)

The $\delta^{37}\text{Cl}$ values of chloride isotopes of Ordovician halite are close to 0.0‰ and can be explained by the precipitation from marine brines. These values are compatible with those measured in earlier studies of other Phanerozoic marine halite. Our results recorded moderately high bromine contents (163 pp and 249 ppm) for primary halite and support the conclusion on the marine genesis of these salts, close to the beginning of bittern crystallization.

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