



Fluid inclusions in halite from marine salt deposits: are they real micro-droplets of ancient seawater?

Volodymyr KOVALEVYCH and Serhiy VOVNYUK



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Evaluation of data sets on inclusion brine compositions in halite from the Phanerozoic marine evaporite deposits used for the reconstruction of ancient seawater chemistry shows that brine analysis of primary inclusions from primary marine halite (in the case of proper genetic type determination) undoubtedly indicate two megacycles in secular variation of seawater chemistry during the Phanerozoic. It is also shown that inside primary halite, inclusions formed at later stages of deposit formation locally occur. Erroneous attribution of such inclusions to primary ones is the main reason for deviations observed in most data sets. It is also obvious that fluid inclusions in clear (recrystallized) halite are unsuitable for the reconstruction of ancient seawater chemistry. Brines from inclusions properly determined as primary in primary bedded halite are micro-droplets of concentrated ancient seawater.

Volodymyr Kovalevych and Serhiy Vovnyuk, Institute of Geology and Geochemistry of Combustible Minerals, National Academy of Sciences of Ukraine, Naukova 3A, 79060 Lviv, Ukraine, e-mail: igggk@mail.lviv.ua (received: December 03, 2009; accepted: August 25, 2010).

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INTRODUCTION

The idea of steady-state (or close to it) in seawater chemical composition over the past 1000 m.y. prevailed in geological literature until the end of the 20th century (e.g., Valiashko, 1962; Borchert and Muir, 1964; Braitsch, 1971; Garrels and Mackenzie, 1971; Holland, 1984) although some authors suggested probable variations of seawater chemistry based on known (and quantitatively described) or predicted changes in different geological processes and on the composition of evaporite and carbonate rocks (Ronov, 1980; Fischer, 1984; Yanshin, 1988; Spencer and Hardie, 1990; Hardie, 1996). During last few decades, geologists started to use the results of study of individual brine inclusion droplets in halite from evaporite formations to solve this problem for the Phanerozoic. The brines of primary inclusions in primary (sedimentary) halite were considered to be trapped microdroplets of evaporite basin brines, i.e. brines similar in composition to concentrated contemporaneous seawater (Holser, 1963; Petrychenko, 1973; Lazar and Holland, 1988; Petrichenko, 1988; Roedder, 1984) and their analyses have resulted in several quantitatively similar models of secular variations in evaporite basin brines and in seawater chemistry (Kovalevich, 1988; Kovalevich *et al.*, 1998; Zimmermann,

2000; Lowenstein *et al.*, 2001, 2003; Horita *et al.*, 2002). It was concluded that secular variations in seawater chemistry were controlled primarily by fluctuations in the mid-ocean ridge hydrothermal brine flux, which in turn have been driven by fluctuations in the rate of ocean crust production (Spencer and Hardie, 1990; Hardie, 1996).

Despite significant progress in reconstruction of secular variations in evaporite basin brines and seawater chemistry, some aspects such as: substantiation of genetic types of fluid inclusion suitable for analysis; comparability of results obtained by different methods and different authors; methodology of calculations of seawater composition based on data on composition of halite-hosted fluid inclusions; and scales of local factors impacting on the chemical composition of seawater during its passage to restricted evaporite basins or during its evaporation in the basins, still remain a topic of discussion, (Kovalevich *et al.*, 1998, 2005, 2009; Zimmermann, 2000, 2001; Ayora *et al.*, 2001; Lowenstein *et al.*, 2001, 2003; Horita *et al.*, 2002; Holland, 2003; Cendón *et al.*, 2003, 2004, 2008; García-Veigas *et al.*, 2009).

In this paper we focus on the main evidence in favour of the concept of significant secular variations in seawater chemistry during the Phanerozoic, since selection of the initial concept is very important for interpretation of the analytical data. In par-

ticular, the estimate of local factors impacting on basin brine composition (evaluated from fluid inclusions in marine halite) depends mainly on which seawater (modern or ancient) is used as the standard for comparison. There are brine inclusion data in halite that have to be excluded from evaluation of ancient seawater chemistry, because the halite in question is a nonmarine deposit, or because it comes from a part of the evaporite section where seawater was not the main source for salt precipitates, as defined based on palaeogeographical and geochemical data, including the bromine content of the halite (see, for example, Ayora *et al.*, 1994; Zimmermann, 2000; Cendón *et al.*, 2004). Then we will concentrate on the problems of substantiation of the genetic type of fluid inclusions suitable for seawater chemistry evaluation. The necessity of detailed consideration of this problem results from the findings of later and secondary inclusions inside many primary textures of halite (chevron) inclusions. These post-sedimentary inclusions sometimes differ in chemical composition (Kovalevych *et al.*, 2002a, 2009; Vovnyuk and Kovalevych, 2007). We will also make a brief comparative description of the main methods of inclusion brine analysis.

VALIDITY OF CONCEPT OF SECULAR VARIATION IN SEAWATER CHEMISTRY

THE NATURE AND SCALE OF VARIATIONS

Modern ideas concerning variations in evaporite basin brines and seawater chemistry during the Phanerozoic can be described by quantitative models based on the results of halite-hosted fluid inclusion studies published in recent decades (Kovalevich, 1988; Kovalevich *et al.*, 1998; Zimmermann, 2000; Lowenstein *et al.*, 2001, 2003; Horita *et al.*, 2002). According to these data, during the Phanerozoic there were two long-term cycles of variations in chemical composition of seawater and (correspondingly) evaporite basin brines. During each of those cycles, basin brines and seawater dominantly of Na-K-Mg-Ca-Cl (Ca-rich) type changed to a Na-K-Mg-Cl-SO₄ (SO₄-rich) type.

The curve of secular variations of Ca vs. SO₄ concentrations in evaporite basin brines clearly reflects these changes (Fig. 1). The curve is a modification of an earlier published curve (Kovalevich *et al.*, 1998) and it includes data taken from summary papers (Zimmermann *et al.*, 2000; Lowenstein *et al.*, 2001; Horita *et al.*, 2002) and also from many papers devoted to individual basins (Brennan and Lowenstein, 2002; Brennan *et al.*, 2004; Cendón *et al.*, 2004, 2008; Kovalevych *et al.*, 2002a, b, 2003, 2006b, c, 2009; Lowenstein *et al.*, 2003, 2005; Petrychenko and Peryt, 2004; Petrychenko *et al.*, 2005). The individual curve for two components reflects a real chemical composition of brines evaporated prior to the potash facies, when brines, depending on their chemical type, contain either Ca or SO₄. This curve shape allows us to conclude that variations in Ca and SO₄ concentrations in Phanerozoic seawater were synchronous and inversely proportional.

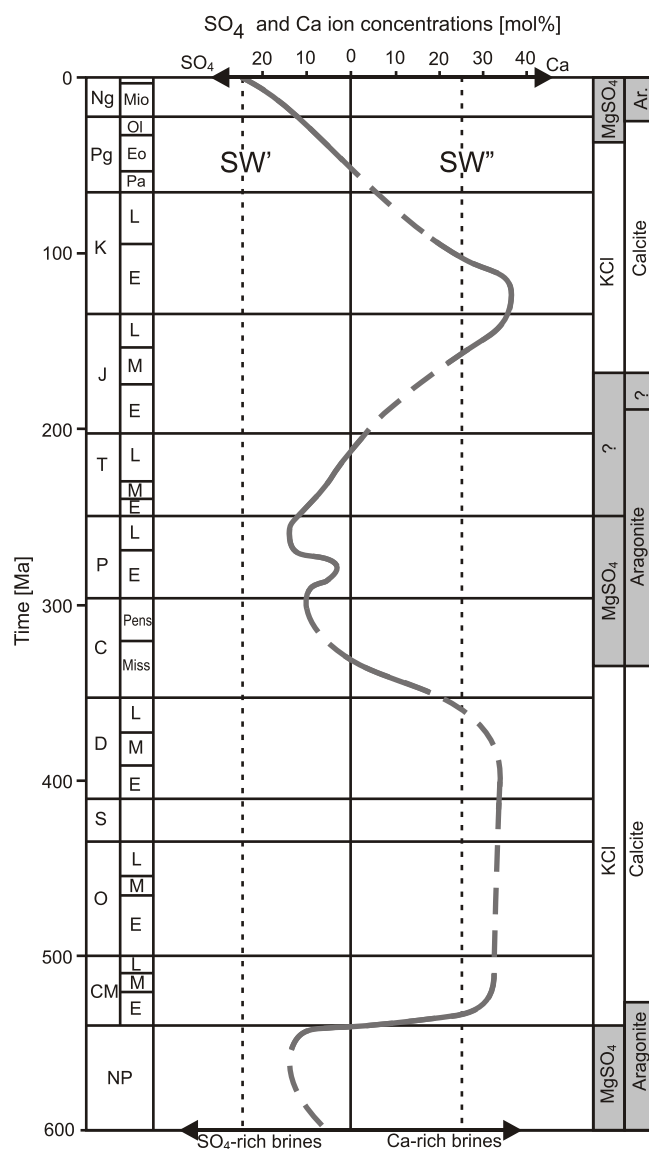


Fig. 1. Secular variation in Ca and SO₄ concentrations (in Jänecke units, mol%) of evaporite basin brines during the Phanerozoic estimated from fluid inclusions in marine halite

Solid line is our best estimate of age curve based on analyses of primary fluid inclusions. Dashed line – parts where the curve could be built only approximately due to wide scatter, suspect authenticity or absence of data. Axis line separates basin brines into two chemical types: SO₄-rich (to the left) and Ca-rich (to the right). Also plotted are (two columns on right) temporal distribution of primary Phanerozoic nonskeletal carbonate minerals (calcite vs. aragonite; Sandberg, 1983) and potash evaporites (MgSO₄-rich vs. KCl-rich; Hardie, 1996). SW' – modern evaporated seawater prior to potash facies; SW'' – ancient evaporated seawater of Ca-rich type (with Ca concentration equal to SO₄ concentration in evaporated modern seawater); NP – Neoproterozoic, CM – Cambrian, O – Ordovician, S – Silurian, D – Devonian, C – Carboniferous, P – Permian, T – Triassic, J – Jurassic, K – Cretaceous, Pg – Paleogene: Pa – Paleocene, Eo – Eocene, Ol – Oligocene; Ng – Neogene: Mio – Miocene; E – early, M – middle, L – late

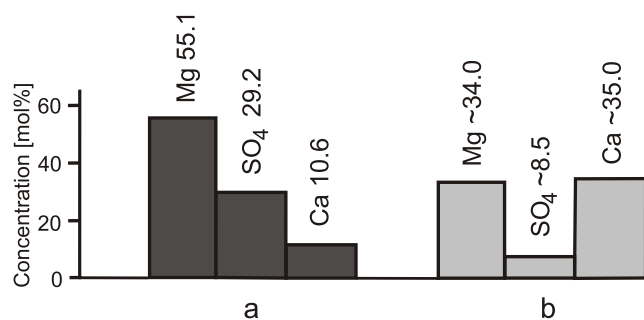


Fig. 2. Comparison of Mg, SO₄ and Ca concentrations in modern seawater of SO₄-rich type (a – after Holland, 1984) and ancient seawater of Ca-rich type (b – calculated after Kovalevych *et al.*, 1998; Lowenstein *et al.*, 2001, 2003; Horita *et al.*, 2002), as two extreme versions of seawater in the Phanerozoic

It is assumed that Na and Cl contents (which made up about 90% of total ion content in both of seawater chemical types) did not change significantly, and K content was stable

Secular variations of all major ion (Na, Cl, K, Mg, Ca and SO₄) concentrations in seawater calculated on the basis of the data on the composition of fluid inclusions in marine halite are published (Lowenstein *et al.*, 2001, 2003; Horita *et al.*, 2002). These data show a direct correlation of Na and Mg with SO₄, and Cl with Ca concentrations, although relative changes in the concentration of each ion are substantially different. It was assumed that the overall salinity of seawater and K concentration did not change. Extreme compositions of two types of seawater: the modern SO₄-rich type, characterized by highest SO₄ concentration and calculated ancient seawater of Ca-rich type, characterized by the highest Ca concentration, are shown in Figure 2.

Na and Cl were, evidently, the major components of ancient seawater during the Phanerozoic, making up to 90% of the total ion concentration. Secular variations of these two ions were relatively small and they are still insufficiently studied; therefore, they are not shown in Figure 2. Thus, the secular variations of seawater chemistry discussed were formed mostly by changes in relative concentration of Ca, SO₄ and Mg ions, although these ions were less than 10% of the total ion concentration. The Ca ion concentration in ancient seawater could increase (with synchronous SO₄ decrease) by up to three (or a little more) times compared to their concentration in modern seawater. During the Phanerozoic, both these ions were constantly present in seawater regardless of its chemical type and calcium sulphate deposits are present in all ancient evaporite formations of marine origin. Sufficient differences in the mineralogy and chemistry of marine evaporites become apparent only when the brine concentration reaches facies of K-Mg salts precipitation. At these facies, in the case of brines of Ca-rich type, K-Mg salts of chloride type (KCl at Fig. 1) precipitate, whilst in the case of brines of SO₄-rich type, the sulphate K-Mg salts (MgSO₄ at Fig. 1) precipitate. The periods of precipitation of these two types of salt can be correlated well with periods of the existence of corresponding types of seawater (Fig. 1; Hardie, 1996; Lowenstein *et al.*, 2001, 2003).

The Mg concentration in ancient seawater was in direct relation with SO₄ concentration and in inverse relationship with Ca concentration. This kind of relation caused significant changes of the Mg/Ca ratio in seawater. According to the re-

sults of study of halite-hosted inclusions this ratio in seawater was below ~2.0 at periods of Ca-rich seawater and at periods of SO₄-rich seawater it was above ~2.0 reaching 5.2 (a value typical of modern seawater; Lowenstein *et al.*, 2001, 2003; Timofeeff *et al.*, 2006). This ratio thus varied approximately between 1.0 and 5.2. The value of the Mg/Ca ratio in seawater evidently had a decisive importance for marine carbonate precipitation and it explains the nature of periods of so-called “argonite seas” and “calcite seas” (Sandberg, 1983; Hardie, 1996; Lowenstein *et al.*, 2001, 2003) which are synchronous with periods when potash deposits are characterized by MgSO₄ and KCl salts respectively (see Fig. 1).

Thus, secular variation of seawater chemistry in the Phanerozoic is evaluated mostly from changes in the relative concentration of Ca, SO₄ and Mg ions. Despite their relatively low content, variations in their relative concentrations caused significant changes in the mineralogy of marine carbonates and evaporites.

EVIDENCE IN FAVOUR OF THE IDEA OF SECULAR VARIATION IN SEAWATER CHEMISTRY

Cases in favour of the idea of significant secular variation in seawater chemistry are widely discussed (Yanshin, 1988; Spencer and Hardie, 1990; Kovalevich, 1990; Hardie, 1996; Kovalevich *et al.*, 1998; Lowenstein *et al.*, 2001, 2003; Horita *et al.*, 2002; Holland, 2003; Kovalevych *et al.*, 2006a; Timofeeff *et al.*, 2006). The following arguments seem to speak for the variation most convincingly:

1. There is a clear stratigraphic control of changes in evaporite basin brine chemistry evaluated from fluid inclusions in marine halite regardless of the palaeogeographic and tectonic conditions of salt formation, intensity of water-rock interaction and runoff amount. For example, in the Neogene, when seawater was unambiguously of SO₄-rich type, brines of all marine evaporite basins also were only of this type.

2. The changes in the major-element chemistry of ancient seawater correlate in time with variations in the mineralogies of marine nonskeletal limestones and potash evaporites, with variations of isotopic composition of some elements and many other geological processes in the Phanerozoic.

3. There is apparent lack of extensive contemporaneous dolomite in many evaporite basins, that casts doubt on the importance of dolomitization in parent brine composition.

COMPARATIVE DESCRIPTION OF ANALYTICAL METHODS

Available data for the composition of fluid inclusions in halite are obtained mostly with three methods: (1) ultramicrochemical analysis (UMCA) introduced by Petrychenko (1973), (2) microextraction followed by ion chromatography (Lazar and Holland, 1988) or by inductively coupled plasma mass spectrometry (ICP-MS; von Borstel *et al.*, 2000), (3) Cryo-SEM-EDS (Ayora and Fontarnau, 1990; Ayora *et al.*, 1994; see also Timofeeff *et al.*, 2000). Inasmuch as detailed description of these methods is widely published, we will concen-

trate on their comparative characteristics, and in particular on the possibility of the use of each method for analysis of primary inclusions, which usually do not exceed 150 μm .

UMCA is the main method used by us. It allows the major ions (except for Na and Cl) in brine inclusions to be determined: K, Mg, Ca and SO_4 ions (see Petrychenko and Peryt, 2004, for detailed discussion). The analytical error of this method is 15–23% (for Mg and K) and 37–43% (for SO_4 and Ca). To reduce errors, a number of analyses of each component in inclusion brines need to be carried out. Two to three repeated analyses decrease the error to 16–17% (Petrychenko, 1973). Generally inclusions $>40 \mu\text{m}$ in size were used for chemical analyses. The UMCA method is the only technique that allows observation of the behavior of inclusions ($>40 \mu\text{m}$) in halite during their opening by a needle under the microscope. This establishes the approximate pressure in inclusions (high or low), and approximate gas concentration in the brines. These features are very important for the genetic characterization of inclusion types (Roedder, 1984; Kovalevych *et al.*, 2002a, 2009).

The method of microextraction followed by ion chromatography or by inductively coupled plasma mass spectrometry is distinguished by the most precise determination of major constituents (with a precision of 2 to 5%) and some trace elements (Br, Li), though with a precision of 3 to 15%. However, this method is only applicable to large fluid inclusions ($>200 \mu\text{m}$ in diameter), which are rare in chevron halite.

The Cryo-SEM-EDS methods permits the determination of Na, K, Mg, Ca, SO_4 and Cl in frozen fluid inclusions greater than $\sim 15 \mu\text{m}$ in size, which is an important advantage because chevron textures are often built up with inclusions smaller than $40 \mu\text{m}$. Other advantages are a relatively small analytical error (below 10%) and the possibility to run many analyses of the same opened inclusion. The method does not allow us to observe the analysed inclusion in transmitted light or to estimate the inner pressure; the determination of genetic type of the inclusion studied remains problematic.

One more method (LA-ICP-MS) exists, which allows analysis of fluid inclusions bigger than $20 \mu\text{m}$ with high accuracy (Shepherd *et al.*, 1998). Its use is limited because it only defines the relative concentrations of elements. But good results can be obtained when this method is used together with Cryo-SEM-EDS.

GENETIC TYPES OF HALITE HOSTED FLUID INCLUSIONS

The detailed investigations of salt deposition in modern salt lakes gave the key to understanding the features of halite crystal growth and fluid inclusion formation (Valiashko, 1951, 1962; Dellwig, 1955; Shearman, 1970; Lowenstein and Hardie, 1985). Most of the halite texture revealed built up with fluid inclusions, and also solitary inclusions in clear halite from salt lakes, appeared to be similar to those in ancient halite, helping to understanding their origin. (Wardlaw and Schwerdtner, 1966; Petrychenko, 1973; Petrychenko, 1977; Roedder, 1984; Lowenstein and Hardie, 1985). However, the genetic classification of fluid inclusions in halite remains problematic except

as regards primary inclusions in primary bedded (sedimentary) halite (Petrychenko, 1973; Roedder, 1984). In this paper we also use such ambiguous terms as “inclusions in recrystallized halite”. Sometimes we divide these into “early diagenetic” or “late diagenetic”, taking into account data on the inner pressure and chemistry of these inclusions. We also use the term “secondary inclusions” but only in case of their relation to healed faults in crystals.

PRIMARY INCLUSIONS IN PRIMARY HALITE

Rock salt deposits, either modern or ancient, if not disturbed by salt tectonics, very often consist of interbedded annual layers of grainy halite. The average thickness of layers is 5–8 cm, with grains from several millimetres to several centimetres in size. Annual layers usually are separated by thin layers of anhydrite, terrigenous or carbonate rocks. Annual layers are often subdivided into seasonal/periodic layers which differ in texture, admixtures and grain shape and size. There are three halite grain textures outlined by fluid inclusions: 1 – pyramidal hoppers, plates and/or rafts; 2 – chevrons; and 3 – cubic hoppers. The first of these – skeletal halite crystals – originated at the brine/air interface. The second one – chevrons – are bottom-growth halite crystals with one cube vertex oriented upwards; they form a layer of vertically oriented elongated (up to few centimetres) halite crystals, clearly visible in cross-sections of annual halite layers (Fig. 3A). The third texture – cubic hoppers – formed at boundary of two brines of different density and saturation (Raup, 1970; Kovalevich, 1978). The inclusions from the first and the third textures are formed in specific conditions, and thus cannot be used to reconstruct brine composition of halite facies of seawater saturation. The brines in these inclusions can differ in major ion ratios from near-bottom brines, but these inclusions are suitable for distinguishing between two chemical types of brine (Kovalevich, 1990).

Chevron texture is most widely distributed in primary bedded halite. Inclusions in chevron halite normally are one-phase (liquid). They are microdroplets of brine trapped during crystal growth. Inclusions are arranged in bands located parallel to crystal growth faces. In thin plates of halite cut out parallel to cleavage one can observe bands located in two perpendicular directions. These bands form the chevron texture; the chevron top shows the growth direction (Fig. 3A, B). Inclusions are of negative cubic crystal shape with sides oriented parallel to faces of the host crystal. Inclusions usually do not exceed $150 \mu\text{m}$ (cube edge).

The internal structure of chevrons can vary significantly even within the same sample. They may or may not have clear rhythmic banding (Figs. 3B and 4A), and locally the sides of chevron can be outlined by inclusions that differ in size (Fig. 4B). Also chevrons can differ in inclusion size and distribution – normally they are formed with inclusions of similar size (either relatively small or larger; Fig. 4C), but one can also observe chevrons with rare large inclusions on a background of numerous smaller ones (Fig. 4D) or with gradual increase of inclusion size from chevron axis outwards (Fig. 4E). Locally, a chevron carries traces of partial dissolution thus recording breaks in crystal growth (Fig. 4F). In potassium-bearing zones,

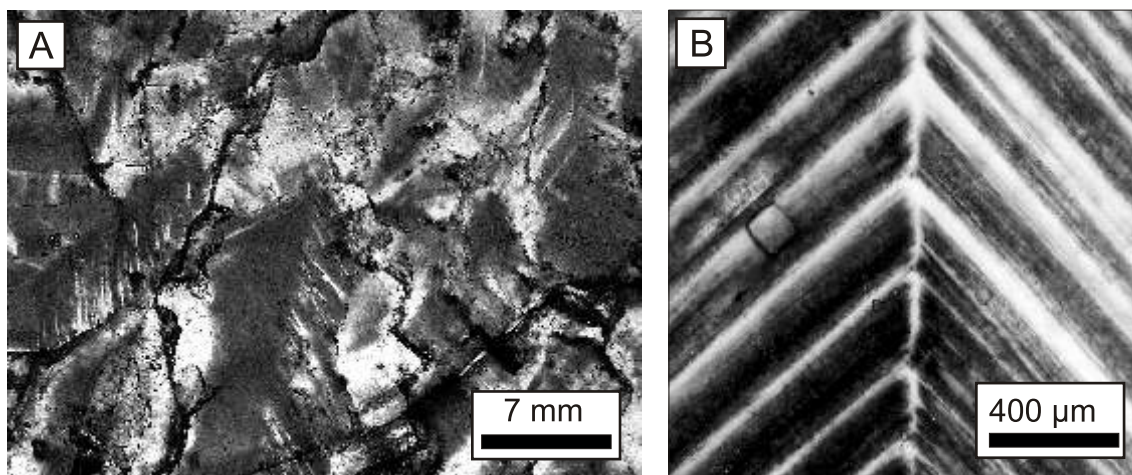


Fig. 3. Thin section photographs of vertically oriented chevron crystals

A – bedding perpendicular (and growth direction parallel – upward) cut through chevron halite grains which are elongated along the [110] axis, lower Permian Solikamsk Basin, Russia. Underlying Salt Member; **B** – fragment of chevron texture with rhythmic banding outlined by tiny primary brine inclusions, lower Permian Dnipro-Donets Basin, Ukraine. Slovyans'k Suite, Nadbryantsiv Bed, Volodars'k Mine

inclusions in chevrons often contain daughter crystals of sylvite or carnallite (Fig. 5A). Numerous photos of different chevrons have been published by Petrychenko (1973; Petrichenko, 1977). Here is important to note that all primary inclusions in chevrons (unless they are anomalously large or contain daughter crystals) are suitable for the reconstruction of the ancient seawater chemistry. In some evaporite deposits, all inclusions in chevrons contain gas bubbles, i.e. are two-phase (Fig. 5B). The gas phase in initially liquid inclusions trapped at the sedimentary stage can appear due to stretching or partial cracking of the inclusions after their heating to above 50°C, as shown by experiments on artificial and natural halite (Petrychenko, 1973; Holdaway, 1974; Roedder, 1984). The use of such inclusions for seawater chemistry reconstruction is discussed in the literature and it is variously accepted (Kovalevych *et al.*, 2002a, 2009; Vovnyuk, 2007) or denied (Horita *et al.*, 2002) by different authors. Discussions result from the assumption that the chemical composition of brines in these inclusions was changed due to depressurizing during their stretching or partial cracking. This resulted from inclusion brine studies of chevron halite from deposits that have different inclusion phase compositions in various parts (in one part of the deposit inclusions are single-phase liquid and in the other they also contain a gas phase). As these instances are from the Neogene of Transcarpathia (Kityk *et al.*, 1983; Shaidetska, 1997) and from the Permian and Triassic of Western Europe (Kovalevych *et al.*, 2002a, b, 2009; Vovnyuk, 2007) we assume that salt deposit overheating to relatively low temperatures (100–120°C) did not result in brine chemistry changes significant enough to be recognized by existing methods. In fact, the analyses showed identical brine compositions (major ion ratios) in these two types of inclusions in each deposit. Inclusion brines with a gas phase from Messinian salts of the Red Sea showed a chemical composition very close to that of modern seawater, which also indicates that this type of inclusion is suitable for ancient seawater chemistry reconstruction (Kovalevich *et al.*, 1997; Horita *et al.*, 2002). Before using

two-phase inclusions for ancient seawater chemistry evaluation it is important to make sure that the liquid/gas phase ratio is equal in all inclusions from a given sample and that the inner pressure is relatively low (i.e., it is close to atmospheric – in such a case the gas bubble volume will not exceed 1% of the inclusion volume).

A very interesting phenomenon can be recorded in chevron halite from the overheated deposits – a migration of inclusions along a thermal gradient (Roedder, 1984). Larger inclusions move faster towards higher temperatures and on their way they “eat” smaller inclusions, leaving a trace formed of clear inclusion-free halite (Fig. 5C). Obviously such an inclusion can merge with inclusions of other genetic types resulting in change of its brine composition.

There are the records of tectonic impact in chevron halite from most ancient salt deposits, such as chevron axis displacement along healed microfaults (Fig. 5D) or individual healed faults visible as chains of inclusions crossing the chevron in irregular directions (Fig. 5E). Sometimes, later, a post-sedimentary origin of individual inclusions located inside chevrons is shown by the presence of a xenogenic phase, oil or bitumen for example (see Fig. 5C). This is why the best way to avoid probable errors is to choose for study, if possible, only ideal chevrons, without any visible trace of deformation or migration, free of healed faults and built up with inclusions of regular cubic shape and similar size.

INCLUSIONS IN RECRYSTALLIZED HALITE

It is difficult to find very well-preserved chevrons in many ancient evaporites. This is explained by halite's ability to recrystallize easily at early stages of diagenesis and during later post-sedimentary stages, in conditions of increasing pressure and temperature or tectonism. As the result of recrystallization, halite grains become clear and inclusion-free. Locally this process affects only peripheral parts of the grain, leaving a relic of

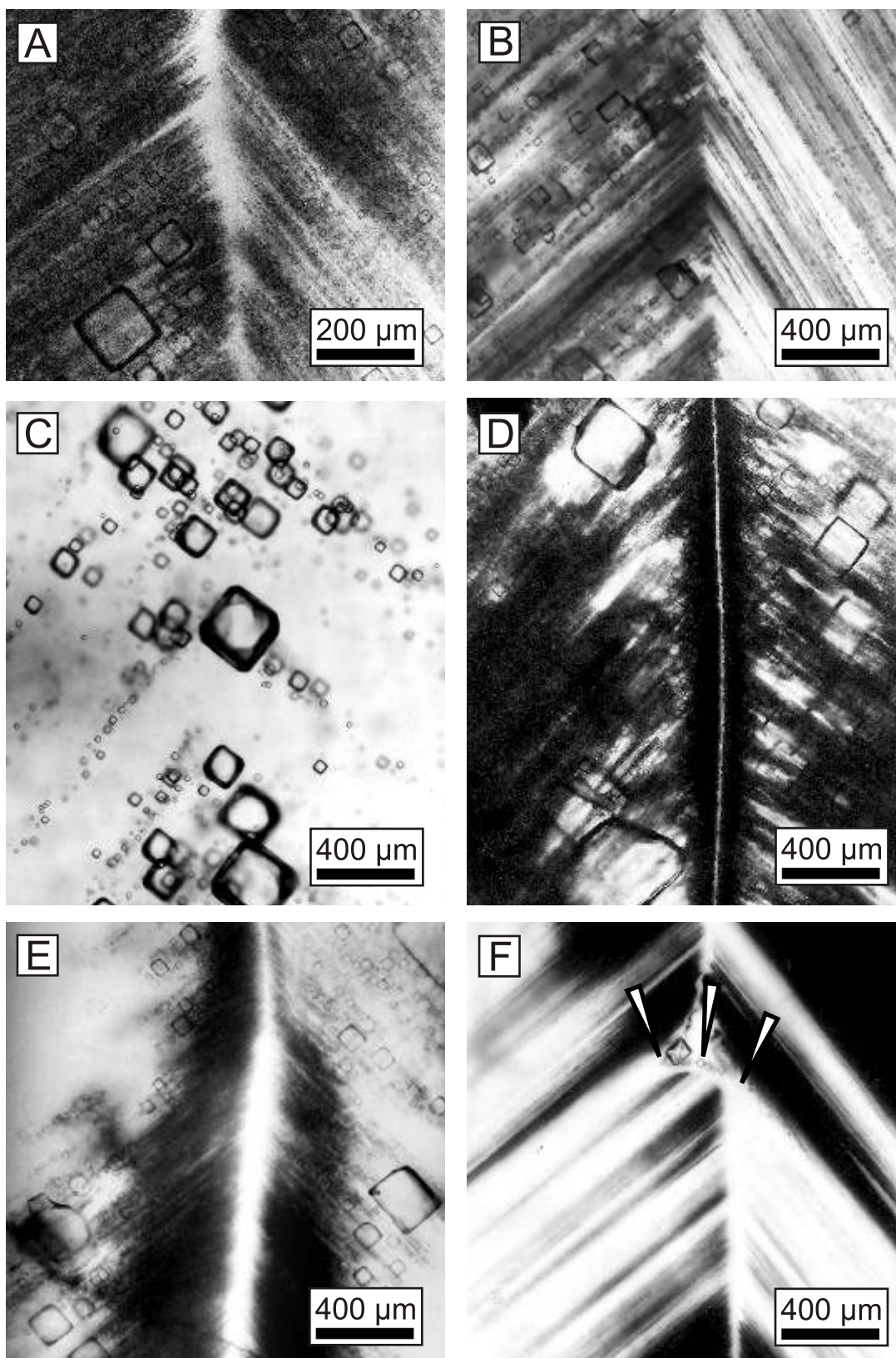


Fig. 4. Chevron textures with different inner structure

A – chevron texture outlined by tiny and relatively large primary fluid inclusions (without rhythmic banding), lower Permian Dnipro-Donets Basin, Ukraine, Slovyans’k Suite, Bryantsiv Bed, Sverdlov Mine; **B** – fragment of chevron texture outlined by differently sized primary brine inclusions, smaller in the right part of the texture and larger in its left part, Carpathian Foredeep, Poland, Bochnia deposit, Badenian; **C** – poorly visible chevron texture outlined by a few relatively large fluid inclusions, upper Permian Delaware Basin, USA, Salado Formation, WIPP Storage, 655.3 m; **D** – chevron texture with rare large primary brine inclusions on a background of numerous small ones, lower Permian Dnipro-Donets Basin, Ukraine, Slovyans’k Suite, Bryantsiv Bed, Sverdlov Mine; **E** – chevron texture with gradual increase of inclusion size from chevron axis outwards, Eocene Navarra Basin, Spain, Biurrun borehole, sample Bi-415; **F** – fragment of chevron halite crystal with a trace of dissolution (arrowed) during the crystal growth, upper Permian (Zechstein) Basin, Miłoszewo ONZ1 borehole, depth 1293.0 m (Oldest Halite Na1)

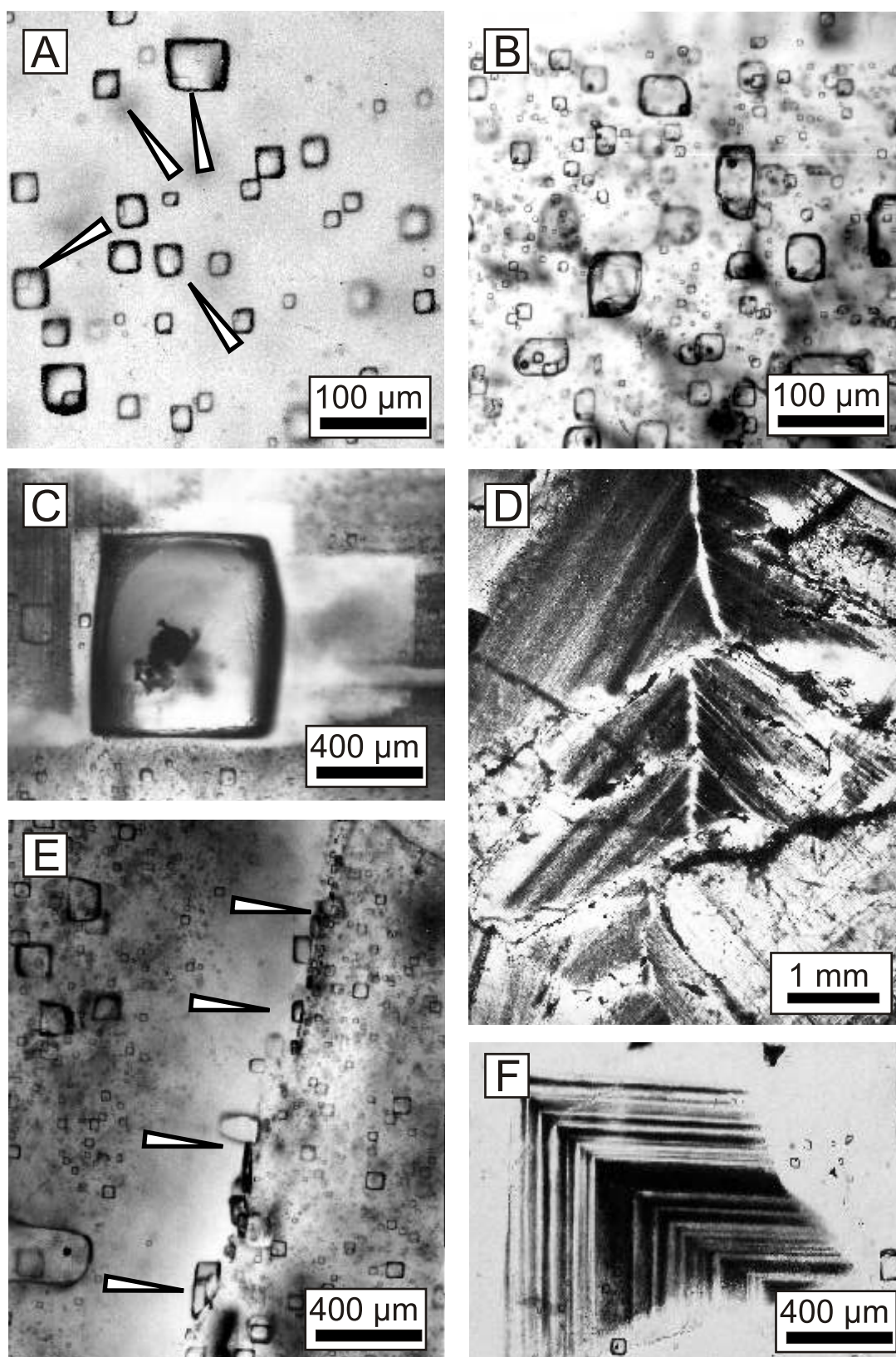


Fig. 5. Primary (sedimentary) and postsedimentary fluid inclusions within, or adjacent to, chevron halite

A – primary fluid inclusions with daughter crystals of sylvite (arrowed) in a growth band of chevron halite, upper Permian (Zechstein) Basin, West Poland, Older Halite, Na₂, Lelechów 4 borehole, depth 1066.7 m; **B** – fragment of chevron texture outlined by two-phase (liquid + gas) primary inclusions, gas bubbles (black) are well seen in larger inclusions, Messinian halite from the Red Sea (DSDP site 225; sample 23-225-29-3,101-103); **C** – anomalously large secondary fluid inclusion with trails of its migration within a growth band of chevron halite, bitumen particles and oil droplet (black) covered by bitumen crust are visible in the central part of the large inclusion, lower Permian Solikamsk Basin, Russia, Potash member; **D** – chevron texture of halite disturbed by microfaults, upper Permian (Zechstein) Basin (Oldest Halite, Na1 of Peri-Baltic area), Poland, Zdrada IG 6 borehole, depth 867.5 m; **E** – healed microfault (arrowed) crossing a growth band of chevron halite, secondary brine inclusions located along the fracture are of irregular or elongated shape, inclusion-free zone of transparent recrystallized halite is visible parallel to the fault, Carpathian Foredeep, Poland, Bochnia deposit, Badenian; **F** – relic of chevron texture in the middle part of a halite grain surrounded by solitary gas-brine inclusions in transparent halite, upper Permian (Zechstein) Basin, West Poland, Chartów 2 borehole, depth 2724.0 m (Basal Anhydrite A2)

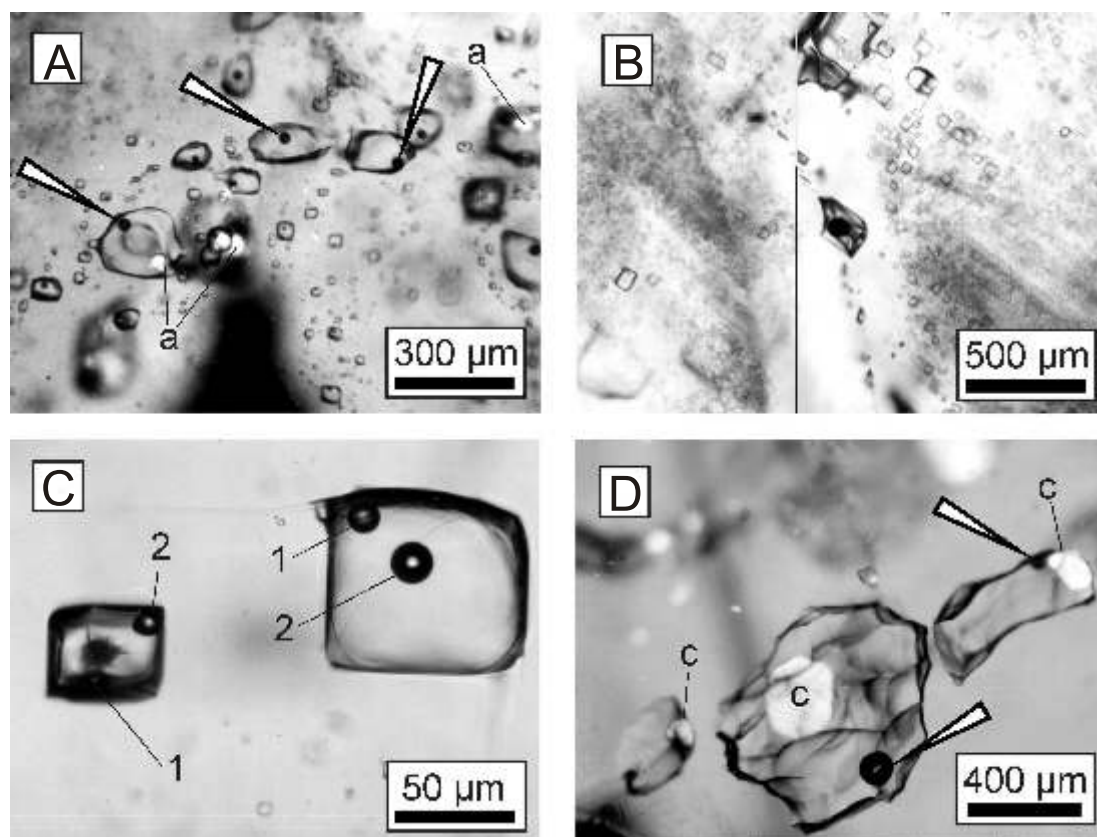


Fig. 6. Fluid inclusions of different phase composition in recrystallized halite

A – group of variably-sized liquid inclusions with gas bubbles (arrowed) in recrystallized halite. Anisotropic crystals (a) (anhydrite ?) occur in some of the inclusions. Many inclusions, especially large ones, are of irregular or slightly elongated shape. Also, a chain of some inclusions related probably to a healed crack can be traced. Lower Cambrian, Eastern Officer Basin, South Australia, Manya 6 borehole, depth 1329.7–1349.8 m, crossed polars; **B** – large solitary fluid inclusions of irregular shape with apparent relation to a healed fracture along the boundary between two halite grains. Lower Cambrian East Siberia Basin, Russia, Tyret' Deposit, complex V; **C** – solitary three-phase inclusion with a bitumen globule (1) and a gas bubble (2), in transparent halite crystal from the salt succession overlying a hydrocarbon accumulation, upper Permian (Zechstein) Basin West Poland, Barnówko 5 borehole, depth 3063.1 m (Basal Anhydrite A2); **D** – large solitary fluid inclusions (in recrystallized halite) with gas bubbles (arrowed) and carnallite crystals (c), crossed polars, Upper Ordovician Canning Basin, Western Australia, Gingerah Hill 1 borehole, depth 1345.8–1345.9 m

chevron texture in the central part of the grain; a relic is surrounded by transparent clear halite (Fig. 5F). But often, mostly in salt domes, rock salt consists of grains of clear, fully recrystallized halite. Grain shape became elongated along bedding, and sometimes lenses of transparent giant-crystalline halite appear. In recrystallized halite, fluid inclusions also occur, but they are relatively rare, solitary or in small groups (Fig. 6A–D). Only sometimes their relation to healed faults is visible (Fig. 6B). Individual inclusions, locally reaching several millimetres in size, usually have irregular shapes. Often inside these inclusions anhydrite daughter crystals or gas bubbles are observed (see Fig. 6A–D). In potassium-bearing zones postsedimentary inclusions may contain sylvite or carnallite daughter crystals, and when salt strata are located close to hydrocarbon deposits oil droplets or bitumen globules may occur (Fig. 6C, D; Kovalevych *et al.*, 2008).

The above-described variety of halite-hosted postsedimentary inclusions can be located inside a chevron texture and thus they are very difficult to determine inasmuch as healed faults are not always visible, and the shape of these inclusions can be close to the shape of primary inclusions. Therefore, the determination of the genetic type of such inclusions should be

based on other criteria, such as inner pressure, brine saturation with gases, phase composition, and the chemical compositions of brine and gases. Primary inclusions, formed at the sedimentary stage, are characterized by low pressure (close to atmospheric) and their brine composition is close to those of other primary inclusions from the same deposit (or from the other deposits of the same age). The chemistry of gases dissolved in postsedimentary inclusion brines is often characterized by an elevated methane content. Thus, there is a set of criteria for the primary origin of fluid inclusions in halite, but they require detailed research into both chevrons and individual inclusions. Unfortunately, convincing evidence of the primary origin of studied inclusions are rather the exception than the rule in the literature, and in some cases the primary origin of inclusions is based only on their location inside chevrons.

In evaporite deposits where primary inclusions contain a gas phase due to overheating, the later postsedimentary inclusions will also have this, but these inclusions will differ from primary ones by elevated inner pressure. Sometimes the opening of such inclusions provokes the momentary “boiling up” of brines or even their ejection.

EVALUATION OF DATA SETS AND CONCLUSIONS

Analytical data available in literature have been obtained by different authors and by different methods. Evidently all these data are close to the true ion composition in inclusions (within analytical errors), inasmuch as all the methods were verified on artificial brines or on inclusions in modern halite of known brine composition. Furthermore, analytical data authenticity is shown by recent studies conducted using two methods (UMCA and Cryo-SEM-EDS) on the same samples (Kovalevych *et al.*, 2005), and also by identical results, obtained by different authors (and different methods) for the same formations or the formations of the same age (see, for instance, Kovalevich *et al.*, 1998; Zimmermann, 2000; Horita *et al.*, 2002). This is shown also by regular pattern of secular variations of major ion ratios in Phanerozoic evaporite basin brines (Kovalevich *et al.*, 1998; Lowenstein *et al.*, 2001, 2003; Horita *et al.*, 2002).

Errors in analyses of individual inclusions or groups of inclusions usually occur due to erroneous genetic type determination. This especially concerns large inclusions (>250 µm across) when they are considered primary. Inclusion brine composition in the same halite crystal can differ depending on inclusion genetic type (Kovalevych and Hauber, 2000; Kovalevych *et al.*, 2002b, 2009). Apparently these individual errors cause the variability in published data sets. These differences become evident during analysis of nearly all data sets, ir-

respective of method used or age of studied evaporite deposits, although they become particularly apparent when large inclusions were studied. These individual errors inside large sets of data on primary inclusion brines usually do not impact average values used for global conclusions. The average values based on small numbers of analyses should be considered with care when they do not fit the known pattern of chemical evolution of basin brines. For evaluation of small deviations between evaporite deposits that are close in age it is needed to have a considerable number of analytical results and only those inclusions that are undoubtedly primary can be used for analyses.

These criteria for analytical data evaluation are based on the assumption that evaporite basin brines did not undergo significant changes of major ion ratios during halite precipitation (up to K-Mg salt facies) when seawater was the main source for salt precipitation. Primary inclusions in primary bedded halite are real relics of concentrated seawater or are very close to it as regards major ion composition. Despite the impact of local factors, data on inclusion brine composition in marine halite are representative for evaluation of two cycles in chemical evolution of seawater during the Phanerozoic and for detailed reconstructions of some time periods.

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