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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