

# Early Cambrian seawater chemistry from fluid inclusions in halite from Siberian evaporites

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Received 18 September 2003; received in revised form 27 December 2004; accepted 22 February 2005

## Abstract

Thirty nine samples of Lower Cambrian marine sedimentary halite with zoned primary fluid inclusions were analyzed using the UMCA method introduced by Petrichenko (1973) [Petrichenko, O.I., 1973. *Metody doslidzhennya u mineralakh galogennykh porid*. Naukova Dumka, Kyiv, 91 pp.] in order to determine the contents of  $K^+$ ,  $Mg^{2+}$ ,  $SO_4^{2-}$  and  $Ca^{2+}$  ions and to interpret the composition of parent seawater. The analyzed samples were from the giant salt basin of eastern Siberia where five major phases of salt deposition can be distinguished, in the Late Vendian (Danilovo) and Early Cambrian (Usolye, Belsk, Angara, and Litvintsevo) basins. Our samples are all from Early Cambrian basins although the largest data set comes from the Angara Basin. The results indicate that Early Cambrian parent seawater was similar in all studied basins and was characterized by lower  $Mg^{2+}$  and  $SO_4^{2-}$ , and higher  $Ca^{2+}$  concentrations relative to modern seawater; the concentration of  $K^+$  in Early Cambrian seawater was similar to that of modern seawater. Accordingly, the seawater in the entire Early Cambrian was  $Ca^{2+}$ -rich and  $SO_4^{2-}$ -poor. The change of composition of seawater—from  $SO_4^{2-}$ -rich,  $Ca^{2+}$ -poor in the latest Neoproterozoic to  $Ca^{2+}$ -rich,  $SO_4^{2-}$ -poor recorded throughout the Early Cambrian—probably occurred within a relatively short time span during the earliest Cambrian (Nemakit-Daldynian) time and caused a rise in  $Ca^{2+}$  concentrations in the shelf seas leading to the onset of biocalcification and then the Cambrian explosion.

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**Keywords:** Cambrian; Chemistry; Halite; Siberia; Fluid inclusions; Evaporites

## 1. Introduction

Although marine salinity has remained relatively stable during the Phanerozoic (Holland, 1984) and thus marine salinity in the Cambrian was approximately the same as present-day seawater (Johnson and Goldstein, 1993), the composition of fluid inclusions in primary-bedded marine halite reveals

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that the chemical composition of marine brines has oscillated significantly between the Na–K–Mg–Ca–Cl (Ca-rich) type and the Na–K–Mg–Cl–SO<sub>4</sub> (SO<sub>4</sub>-rich) type over geologic time (Kovalevich et al., 1998; Lowenstein et al., 2001; Brennan and Lowenstein, 2002; Horita et al., 2002; Kovalevych et al., 2002a,b). The importance of information derived from the composition of fluid inclusions in halite for the interpretation of parent seawater composition is now generally accepted (Zimmermann, 2001). The study of fluid inclusions in chevron halite crystals of the Ara Formation in Oman (544–543 My) indicated that latest Proterozoic seawater was rich in Mg<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> (Horita et al., 2002) and that it was characterized by a relatively high Mg<sup>2+</sup>/Ca<sup>2+</sup> ratio (Lowenstein et al., 2001; Horita et al., 2002). In turn, the study of fluid inclusions in several halite samples of the Angara Formation (ca. 515 My) in eastern Siberia showed that late Early Cambrian seawater was Ca<sup>2+</sup>-rich, and that the substantial increase in Ca<sup>2+</sup> concentration was accompanied by a decrease in other ions (especially SO<sub>4</sub><sup>2-</sup>) (Lowenstein et al., 2001; Horita et al., 2002; Brennan et al., 2004).

Brennan et al. (2004) suggested that this significant change in the major-ion chemistry of seawater played an important role in the Cambrian explosion, which occurred 530–520 million years ago (Valentine, 2002). Our set of halite samples covers much of the Lower Cambrian and thus the aim of this paper is to determine the major ion chemical composition of Early Cambrian seawater from analyses of fluid inclusions in halites of eastern Siberia using the method of Petrichenko (1973).

## 2. Geological setting

Salt deposits of Late Neoproterozoic to Early Cambrian age in East Siberia cover an extensive territory (ca. 2 million km<sup>2</sup>) located to the northwest of Lake Baikal, and delineated by the Lena river to the east and the Yenisey river to the west (Fig. 1); in the north, the salt limit is located 250 km north of the Nizhnyaya Tunguska river. The thickness of the Vendian–Lower Cambrian succession is 2.0–2.5 km in the southern, western, and central parts of the basin, and 1.3–1.5 km in the northeastern part (Nepa-Vilyui). Paleogeographical data (Pisarchik et al.,

1975) as well as a great total volume of Upper Vendian–Lower Cambrian evaporites of East Siberia (785,000 km<sup>3</sup>—Zharkov, 1984) are regarded as indications of a marine origin for the Siberian salt giant. It is characterized by the occurrence of 14 regional marker carbonate units and 15 salt units (Chechel et al., 1977; Zharkov, 1984, with references therein). Five major phases of salt deposition can be distinguished, in the Late Vendian (Danilovo) and Early Cambrian (Usolye, Belsk, Angara, and Litvintsevo) basins (Fig. 2; Chechel et al., 1977; Zharkov, 1984; Kuznetsov et al., 2000). It should be mentioned that the Vendian–Cambrian boundary is not the internationally accepted Neoproterozoic–Cambrian boundary, and thus the Late Vendian (Danilovo) basin is Nemakit-Daldynian, i.e. the earliest Cambrian.

Each evaporite cycle of the Early Cambrian was characterized by a progressive decrease in the salt-forming area and an increase in the shallow-water part of the basin, as well as a sharp transition from carbonate horizons to rock salt: sulfate deposits contained between them only rarely reach 2 m in thickness. Halite precipitation coincided with maximum rates of subsidence, and there was an interrelationship between subsidence and the degree of restriction of brine exchange with connected basins. The onset of halite precipitation was almost instantaneous throughout the basin, while the change to less saline conditions that resulted in deposition of sulfate-carbonate deposits was gradual.

The area of halite deposition in the Late Vendian late Danilovo basin (in the older literature known as the Irkut basin) was 10,000 km<sup>2</sup>, and the average thickness of evaporite deposits is 20 m (Zharkov, 1981). The area of the Usolye salt basin reached 2 million km<sup>2</sup>, and the average thickness of deposited salt is 200 m (Zharkov, 1981). Four major phases of halite precipitation occurred, and, episodically, potassium salts (carnallite and sylvite) were deposited in the upper part of stratigraphic section. The area of the Belsk salt basin was 1.3 million km<sup>2</sup>, and the average thickness of salt deposits is 100 m (Zharkov, 1981). The Angara salt basin occupies 1.2 million km<sup>2</sup> and the salt thickness is 15–450 m (about 100 m on average; Zharkov, 1981; Mashovich et al., 1991). Potassium-bearing deposits occur in different stratigraphic levels; the total thickness of the potash salt complex (composed of carnallite and/or sylvinit) in

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