



# Oxygen isotopes in authigenic quartz from massive salt deposits



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## ABSTRACT

We describe a new geochemical tool that could provide temperatures of ancient basins in which massive evaporites were deposited: the oxygen isotope composition of fine crystalline quartz found in large halite bodies. Such quartz is well preserved from post-depositional alterations and it can be relatively easily separated. For the purpose of this study, five halite samples were selected from four various evaporite basins, spanning in age from the Early Cambrian to the Late Jurassic. The obtained isotope temperatures refer to locations where evaporites were deposited, i.e. in subtropical zones of the Earth, as it may be estimated from continental distribution during Phanerozoic times. Reasonable temperatures are obtained, with an assumption for the  $\delta^{18}\text{O}$  of brines ranging from  $-1\%$  to  $0\%$  during halite deposition. The assumption of higher  $\delta^{18}\text{O}$  values leads to unrealistic temperatures, higher than the homogenization temperatures of fluid inclusions in halite.

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## 1. Introduction

For more than half a century oxygen isotope measurements become a powerful geochemical tool used to determine temperatures of ancient oceans. An updated review of major paleotemperature techniques (Lea, 2014) considers various proxies of paleoclimate based on isotope determination of  $\delta^{18}\text{O}$  and  $\delta^{44}\text{Ca}$  of different marine biogenic phases (foraminifera, reef corals, diatoms etc.) and also on their elemental composition such as Mg content and Sr content. However those proxies are not suitable to determine paleotemperatures of evaporite basins.

Another problem which emerges from isotopic studies is the evolution of isotopic compositions of ocean water. Hoefs (1981) argued that the amount of oxygen in the ocean is massive compared to other significant elements such as sulfur, carbon and strontium. The change in the  $\delta^{18}\text{O}$  of ocean water needs processing of large amounts of oxygen with an isotopic composition which is very different from that of ocean water. For example a lowering of  $\delta^{18}\text{O}$  of present-day ocean by  $1\%$  would require melting of all the ice caps, the main reservoir of isotopically light water. Muehlenbachs and Clayton (1976) argued that the oceanic  $\delta^{18}\text{O}$  had relatively been constant because the enrichment of ocean water in  $^{18}\text{O}$  by high-temperature hydrothermal alteration

of mid-ocean ridge basalts was compensated by low-temperature weathering of the oceanic crust.

Karhu and Epstein (1986) were able to calculate the  $\delta^{18}\text{O}$  of ocean water, from the Late Cambrian to Eocene, on the basis of oxygen isotope records in coexisting cherts and phosphates. They obtained  $\delta^{18}\text{O}$  values somewhat below  $-1\%$ , which is in agreement with the above mass balance considerations. Their data support the idea that the observed  $\delta^{18}\text{O}$  variations of marine cherts were caused by secular variation of water temperature, but not by the isotopic composition of oceanic water.

Recent study by Pope et al. (2012) also confirmed that Archean ocean had similar oxygen isotope composition, though its  $\delta\text{D}$  was considerably different (by at most  $25\%$  vs. VSMOW) and up to  $26\%$  it was more voluminous. The authors argued that “throughout geologic time the oxygen mass budget was likely conserved within these Earth system reservoirs, but hydrogen’s was not, as it can escape to space.”

Here we describe a new geochemical proxy that provides temperatures of ancient brines from which evaporites were deposited. The oxygen isotope composition was determined on finely crystalline quartz found in large halite bodies. Such quartz is not affected by post-depositional alteration and can be separated relatively easily. The temperatures are determined from measured  $\delta^{18}\text{O}$  of quartz and either assumed or determined  $\delta^{18}\text{O}$  of water from the study homogenization temperatures of liquid inclusions in adjacent halite crystals. Our preliminary oxygen isotope measurements of authigenic quartz from selected

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massive halite deposits provide reasonable estimates of their crystallization temperatures.

## 2. Material and methods

For the purpose of this study five halite samples were selected from four various evaporite basins, spanning the Early Cambrian to Late Jurassic. All the samples were taken from cores at various depths (Table 1). The rock salt samples (30–50 g) were dissolved in distilled water and after decanting soluble chlorides, the water-insoluble residue was dried and sieved. The authigenic minerals were identified by their idiomorphic form (cf. Braitsch, 1971).

Euhedral quartz crystals in salt are evidently of very early secondary origin and if one includes the time span until the end of the particular evaporitic cyclothem, they can be considered syngenetic (Sonnenfeld, 1984, pp. 248–249, with references therein). Chevron texture is most widely distributed in primary bedded halite. Chipley and Kyser (1994) concluded that chemical and isotopic compositions from fluid inclusions in some chevron halites indicate that chevron halite may form in the subsurface or, less likely, recrystallize without destruction of its delicate texture. A post-sedimentary origin of individual inclusions located inside chevrons is shown by the presence of a xenogenic phase, oil or bitumen for example (Kovalevych & Vovnyuk, 2010). In addition, there are the records of tectonic impact in many chevron halite and therefore, as indicated by Kovalevych and Vovnyuk (2010), to avoid probable errors 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, have been chosen for the study. The quartz samples were extracted from cores in the Polish Geological Institute, Warsaw, and were analyzed in Stable Isotope Laboratory at the University of Graz.

One quartz sample (Fig. 1, Sample 1) was separated from Lower Cambrian salt deposits of the eastern Officer Basin, Australia. These evaporites were deposited in open marine environments (Kovalevych et al., 2006b). The salts mainly occur in the lower part of the Oulduburra Formation in Manya 6 borehole and are interbedded with layered carbonates and calcareous siltstones. The salt, up to 5 m thick, is translucent to transparent or dark-coloured due to the presence of organic matter. In the uppermost Oulduburra formation salt layers are thinner. Poor preservation of the fluid inclusions, especially the rarity of primary inclusions and predominant two-phase (gas–fluid) composition of inclusions in the diagenetic halite, indicates an intensive post-depositional recrystallisation of the salt deposits (Kovalevych et al., 2006b). Authigenic quartz is often present and varies up to 15% of the total water-insoluble residue. The quartz is colourless, pink and white, and occurs in the form of transparent bipyramidal-prismatic or translucent aggregates with corroded surface (Kovalevych et al., 2006b).

The next sample (Fig. 1, Sample 2) is from the upper salt formation within the Carribuddy Group in the Canning Basin of Western Australia. A recent stratigraphical scheme for the Canning Basin assumes that this salt unit, the Mallowa Salt, is of the latest Ordovician

age (Kovalevych et al., 2006a). Williams (1991) described a 477 m stratigraphic interval of the Mallowa Salt from Gingerah Hill-1 (the well bot-tomed out in the Mallowa Salt) that consists of rock salt interbedded with sparse red-brown (less commonly grey to black) beds of anhydrite and dolomite. Numerous cycles, indicative of upward-shallowing deposition in a desiccating basin were recognized and reported. The halite crystals usually occur as a mosaic of interlocking grains (5–20 mm in diameter) and primary chevron crystals being occasionally present (Williams, 1991). Sample 2 is a pink crust with admixture of pelitic matter. Analyses of primary and early diagenetic fluid inclusions in the halite indicate a Ca-rich composition and high concentration of parent brines in the basin, which were close to sylvite and carnallite precipitation equilibria (Kovalevych et al., 2006a).

Two samples (Fig. 1, Samples 3 and 4) were selected from the Upper Triassic deposit located in western-central Poland. The salt occurs in the Lower Gypsum Beds, which are of Early Carnian age and were deposited in an intracontinental Southern Permian Basin (Doornenbal & Stevenson, eds, 2010). The bromide content of halite indicates its partial or total recycling, with minor marine origin preserved (Gajewska et al., 1985). Recent interpretations based on seismic data strongly suggest that at that time the Upper Permian Zechstein salt was relatively close to the surface and eventually extruded onto the basin floor (Krzywiec, 2004); thus recycled Zechstein salt may have generated the Keuper salt. Samples 3 and 4 are rosy and/or yellowish, with large bipyramidal-prismatic, sometimes flattened, crystals.

One sample (Fig. 1, Sample 5) was taken from the Kimmeridgian (Upper Jurassic) rock salt of Predobrogea (western Ukraine). These evaporites were deposited along the south-western slope of the East European Platform. The sedimentary profile comprises interbedded dolomites, dolomitic limestones, anhydrite and siliciclastic rocks, and in Predobrogea (near Izmail) it also consists of gypsum and salt rocks (Khmelevska, 1997). The thickness of the salt rock represented by white, grey, or pink medium- and coarse-grained halite, is 78 m (Tiuremina & Khmelevska, 1990). The NaCl content in the rock salt is 93–98%, and in addition authigenic anhydrite, calcite, dolomite, quartz, celestite, fluorite, and pyrite minerals occur. The salt is composed of sedimentary and recrystallized halite. The recrystallization took place under the influence of residual chloride solutions that were buried in soft sediment. Sample 5 is a colourless rosette-like quartz with a chalcedony core. Among the authigenic minerals in the water-insoluble part of rock salt, anhydrite prevails and dolomite is common.

All the described salts were deposited at low latitudes: the Early Cambrian and Late Ordovician from Australia at 15–30°N, the Late Triassic from Poland at 32°N, and the Late Jurassic from Ukraine at 36°N (Golonka, 2000).

Stable isotope measurements were done at the Karl-Franz University, Graz, on a Finnigan MAT Delta plus mass spectrometer on O<sub>2</sub> gas. Oxygen for isotope analysis was extracted from quartz heated with a 20 W CO<sub>2</sub>-laser by reaction with BrF<sub>5</sub> following the technique of Sharp (1990). The δ<sup>18</sup>O values of quartz samples were measured with a reproducibility of ±0.1‰ and normalized to the NBS-28 standard.

**Table 1**

The list of investigated quartz samples and inferred crystallization temperatures. T<sub>h</sub> is homogenization temperature of fluid inclusions in halite, nd = not determined.

Sample no.	Age	Provenance	Borehole	Depth [m]	δ <sup>18</sup> O [‰]		T <sub>crystal</sub> [°C]	T <sub>h</sub> [°C]	δ <sup>18</sup> O [‰] of water from T <sub>h</sub>
					Quartz	Water			
1	Early Cambrian ~540 Ma	Australia	Manya 6	1329.7	24.0	-1.0	76.2	80	-0.1
						0.0	82.4		
2	Late Ordovician ~450 Ma	Australia	Gingerah Hill-1	1246.6	23.4	-1.0	79.8	62	-3.8
						-4.0	62.4		
						-1.0	46.3		
3	Late Triassic ~225 Ma	Poland	Rdutów 2	3121	29.8	0.0	51.0	nd	
						-1.0	40.2		
4	Late Triassic ~225 Ma	Poland	Krośńiewice IG1	3148.0	31.2	-1.0	40.2	~55	~-2.6
						0.0	44.6		
						-1.0	34.8		
5	Late Jurassic ~152 Ma	Ukraine	1c	526.7	32.5	0.0	39.1	~40	~0.7
						-1.0	34.8		

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