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Cycling of calcite and hydrous metal oxides and chemical changes of major element and REE chemistry in monomictic hardwater lake: Impact on sedimentation

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ABSTRACT

The variation of major and rare earth elements and yttrium (REY) in the monomictic hardwater Lake Tiberias during the wet and dry seasons of the hydrological year was studied in two profiles. The average volume and Cl concentration of the known and unknown saline inflows of 1.6×10^7 m^3 and 1.2×10^9 mol are derived by closing both balances. This brine corresponds to a mixture of 83% of groundwater from Cretaceous aquifers and 17% of very saline deep brine. Taking cycling of calcite in the hypolimnion into account, the settling rate of authigenic calcite is estimated to be 3.3 mol m^{-2} a^{-1}.

In the stratified lake of the dry season dissolved inorganic carbon increases by 490 μM at the thermo-/chemocline due to microbial reduction of $SO_4{}^{2-}$, $NO_3{}^{-}$, chemical reduction of Fe(III) and MnO_2 colloids, and cycling of calcite in the hypolimnion. REY distribution in the stratified water column is dominantly controlled by coprecipitation with calcite, hydrous ferric oxides and MnO_2 in the epilimnion and cycling of these compounds in the hypolimnion. The positive Ce anomaly in the hypolimnetic water is produced by cycling of MnO_2. The simulation of the increase of REY in the hypolimnion reveals that hydrous ferric and manganese oxides only play a negligible role except Ce. Only about 10% of REY from cycled matter enhance REY in solution. Most of the released REY are adsorbed by particular matter and thus settling on the floor of the lake.

Different from Na, U, $SO_4{}^{2-}$ and SiO_2, the other elements, in particular REY, increase in the mixed water column from the top to the lower third and mostly decrease thereafter toward the bottom in the mixed lake during the wet season. The behavior of REY is caused by some cycling of calcite and pH-dependent re-equilibration of REY bound to hydrous ferric and manganese oxides adsorbed by particular matter.

1. Introduction

The behavior of trace metals in aquatic systems has received considerable attention over the past decades. Important insights into the behavior of metals in natural water was developed since the 1950s (Krauskopf, 1956; Jenne, 1968; Turekian, 1977) emphasizing the role of particles in removing highly charged ions by sorption from river-, lake- and seawater. Rare earth elements and Y (henceforth combined to REY) are commonly used as tracers of geochemical processes in aquatic systems. REY are fractionated by coprecipitation with calcite (Tanaka and Kawabe, 2006; Toyama and Terakado, 2014) and by adsorption onto hydrous ferric oxides, HFO (Quinn et al., 2006; Schijf and Marshall, 2011), and δ-MnO_2 (Ohta and Kawabe, 2001; Koeppenkastrop and De Carlo, 1992; De Carlo et al., 1998). These oxides are also present as colloids. Both the ubiquity of these particles and their high specific surface area make them ideal candidates for regulating the concentrations of highly charged tracer metals in aquatic systems. Adsorption by particulate organic matter is considered minor compared with the above colloids and precipitates (Sigg, 1985).

In monomictic lakes warming or cooling of surface water, mixing of surface water with inflowing fresh and saline waters and precipitation of minerals and amorphous matter in surface water lead to halo- or meromixis (Boehrer and Schultze, 2008). Such stratified lakes occur in all climatic zones from polar (Rankin et al., 1999) to humid (Stabel et al., 1986; Küchler-Krischun and Kleiner, 1990; Hodell et al., 1998; Ramisch et al., 1999; Dittrich et al., 2004; Müller et al., 2006), Lake Biwa (Imberger, 1998) and to subtropical/tropical ones (Talling, 1966; Kalff and Watson, 1986; Madoni,

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1990; Katz and Starinsky, 2009). In the Dead Sea, detrital calcite is transformed into aragonite by which Mg and Sr is released (Morse and Bender, 1990; Dittrich and Obst, 2004). In the stratified Lake Tiberias, also known as the Sea of Galilee and Lake Kinneret, part of calcite is dissolved (cycled) in the hypolimnion releasing Mg and Sr (Katz and Nishri, 2013). Cycling of REY-containing precipitates with increasing water depth is known from places in the Atlantic and Pacific Oceans (Elderfield and Greaves, 1982; De Baar et al., 1985; Sholkovitz and Schneider, 1991), Black Sea (Schijf et al., 1991) and the Mediterranean (Schijf et al., 1995). The cycling of MnO_2 in the Orca basin was studied by Van Cappellen et al. (1998). REY distribution was also reported from many lakes in Austria (Stojanovic et al., 2009), and in Malaysia (Sultan and Shazli, 2009).

This study aims at the quantification of mass transfers during stratification of Lake Tiberias in general and for REY in particular. The suite of REY is an excellent tool to study the cycling of authigenic calcite and the scavenging processes. Furthermore, the REY distribution between particles and the hypolimnetic water is compared with the REY distribution of groundwater in limestone and chalk aquifers of the area.

2. Hydrogeological setting

Lake Tiberias is the most important freshwater reservoir in Israel and therefore subject of many hydrochemical studies (Eckert and Trüper, 1993; Nishri et al., 1999; Rimmer, 2000; Rimmer and Gal, 2003; Siebert 2006). It is located in one of the rhomb-shaped, pull-apart basins of the Jordan–Dead Sea Transform also known as the Rift. The maximum depth and the volume of the lake are 47 m and about 4.2×10^9 m^3, respectively. Its peak water level of −209 m (mean sea level, msl.) represents the local erosion base. The water level of the lake varies up to 4 m during the hydrological year depending on rainfall, evaporation and abstraction of water. The average evaporation rate is about 1800 mm/a (Mahrer and Assouline, 1993; Alpert et al., 1997). The major contributor to the lake is the Jordan River. Minor contributions are by ephemeral streams, hibernal rainfalls (600–1200 mm/a), storage of water from the Yarmouk River and the salty offshore springs (Fig. 1). The prevalent clastic nature of the graben-fill (Marcus and Slager, 1985) and the geological structure of both sides of the Rift facilitate flow of fresh groundwater from the Cenomanian–Turonian limestone/dolomite aquifer and the Eocene chalk aquifer towards the lake. These aquifers drain the Eastern Upper and Lower Galilee, the Hula Valley and the Golan Heights.

Both, Ca- and Mg-dominated brines ascend through a system of faults that are associated with the major faults of the Jordan Dead Sea Rift Valley (Nishri et al., 1999). In the vicinity of the lake, these brines emerge, variably mixed with fresh groundwaters, in four spring clusters: the Tiberias Hot Springs, the lacustrine springs of the Fuliya, the Tabgha spring cluster producing the largest quantity of saline water in the area, and the Ha'on cluster along the southern and south-eastern shore (Fig. 1). The brines from the Ha'on cluster are of Mg-Cl type contrasting the aforementioned three clusters, which are of Ca–Cl type (Table 1). The inflow of these brines deteriorated the lake's water quality. After the installation of the salt-water diversion channel (SDC), collecting most of the onshore brines from springs, the chlorinity of the lake water dropped from 400 mg/l in 1964 to an average of 240 mg/l (Nishri et al., 1999). This chlorinity is still high compared with that of the lake's most important contributor, the Jordan River with only 15 mg/l (Table 1). Nevertheless, about $(20–90) \times 10^6$ kg/a of Cl are assumed to enter the lake unmonitored through offshore entries (Stiller et al., 1975; Smith et al., 1989; Stiller, 1994; Siebert, 2006).

The pore water of the lake's sediments reveals Cl concentrations of 2000 ± 860 mg/l at 3 m sediment depth, which linearly declines to the lake's chlorinity at the water/sediment interface (Table 1). The Mg/Ca molar values in deep pore water of 1.1–1.9 is much closer to that of the Ha'on brine (2.5) than to the Tiberias brines (0.32). The Na/Cl value of the Ha'on brine is approached at depths of about 3 m (Möller et al., 2012).

The monomictic hardwater Lake Tiberias is thermally and chemically stratified during May to November into an upper oxygen-rich, warm epilimnion and a cooler, oxygen-poor hypolimnion (Siebert et al., 2009; Katz and Nishri, 2013). With the beginning of the rainy season in November and concomitant cooling of the epilimnion, the lake turns over in December (Katz and Nishri, 2013). With on-set of the thermal stratification in May the thermocline moves downward and the chemocline moves upward, resulting in a separating metalimnion at about 21–22 m water depth.

3. Sampling

Depth-oriented sampling of the water column was performed at the end of the dry seasons in mid-November 2002 at low stand of the stratified lake (lake level at −214.3 m msl.) and at the end of the wet season in March 2004 at high stand of the mixed lake (lake level at −209 m msl.). The water samples were taken from a boat at various stations, among them the stations *Dugit* and *A* (Fig. 1). For sampling of bottom water two silicon tubes were fixed to a stainless steel wire together with a heavy flat weight keeping the sampling tubes vertically and indicating bottom contact. This arrangement enabled contemporaneous sampling at 20 and 70 cm above the sediment/water interface. Only one tube was used for sampling after stepwise pulling up the arrangement of tubes to −25 m. Simultaneously, a similar arrangement with only one tube was used for sampling between the surface and −20 m. On board the tubes were connected to either a multi-head or single-head Masterflex peristaltic pumps temperature, EC, Eh and pH were determined in a flow-through cell by WTW-electrodes (SenTix-PT1000 (pH; temperature); ORP (redox potential), TetraCon-325 (EC)), connected to a WTW 340i multi-parameter instrument (WTW, Germany). In parallel, a pH-, temperature- and Eh-multi-parameter probe (KLL-Q-2, SEBA, Germany) was operated.

The water from each sampling depth passed a capsuled filter (Sartobran, Sartorius, Germany) with a pore size of 0.2 μm attached to the tubes after passing the peristaltic pump. Thus, filtration occurred under pressure. During sampling some exsolution of gases was observed. The water samples from the hypolimnion had always a strong odor of H_2S.

At each depth 30 ml of water was collected for cation and anion analysis into HDPE bottles. The concentration of HCO_3^- was titrated on-board by adjusting 50 ml filtered water samples to pH 4.3 with H_2SO_4 using a digital titrator (Hach, USA). 4.5 liter of filtered water was collected in pre-cleaned HDPE bottles for REY pre-concentration. 1 ml of 100 ppb Tm spike (Merck, Germany) and 8 ml sub-boiled 6 M HCl (Merck, Germany) were added to the filtrate during filtration. Within less than 6 h, these samples were adjusted to pH 2.

For later analyses of stable carbon isotopes, pre-washed solid NaOH pills and $BaCl_2$ were added to precipitate carbonate and sulfate in 1.5 l filtered water samples.

The river Jordan and the ephemeral streams Meshushim, Dalyot and Yehudiya were sampled along with the lake samples. These analyses were supplemented by samples from earlier field campaigns (Möller et al., 2007, 2009). Samples of limestone, chalk and basalt were collected from the area for REY analyses.