Hydromagnesite precipitation in the saline Lake Dujiali, central Qinghai-Tibetan Plateau : Constraints on hydromagnesite precipitation from hydrochemistry and stable isotopes

Lin Yongjie^{a,b}, Zheng Mianping^{a,b*}, Ye Chuanyong^b

a. School of Earth Sciences and Mineral Resources, China University of Geosciences, Beijing 100083, China

b. MLR Key Laboratory of Saline Lake Resources and Environment, Institute of Mineral Resource, CAGS, Beijing 100037, China

Abstract

The mineral hydromagnesite, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, is a common form of hydrated Mg-carbonate in alkaline lakes, yet the processes involved in its formation are not well understood. This study focuses on Dujiali Lake, in the central Qinghai-Tibetan Plateau (QTP), which is one of the few environments on the earth's surface with extensive Holocene precipitation of hydromagnesite. The hydrogeochemistry of surface waters, and the mineralogical, stable isotope ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$), and radiogenic isotope content of hydromagnesite deposits were analyzed to investigate formation mechanisms. The chemical composition of surface water around Dujiali Lake evolved from the rock-weathering-type waters of T1 (Ca-Mg- HCO_3 water type) to more concentrated sodic waters of T2 (Na- SO_4 -Cl water type) due to evaporation. XRD results show that the mineralogical composition of samples is pure hydromagnesite. Analysis of oxygen isotopes in the hydromagnesite indicates that supergene formation with authigenic carbonate crystallization from evaporation water is the dominant precipitation process. Combined carbon-oxygen isotope analysis suggests atmospheric CO_2 provided a carbon source for the precipitation of hydromagnesite. These findings suggest that hydromagnesite precipitation at Lake Dujiali is mainly inorganic in nature, and the greenhouse gas, CO_2 , is trapped and stored in the hydromagnesite directly from the atmosphere. AMS radiocarbon dating of samples indicates CO_2 was sequestered between 5845 ± 30 to 6090 ± 25 cal a BP in the Dujiali Lake hydromagnesite deposit. The study contributes to improved understanding of hydromagnesite formation in modern and ancient playas.

*Corresponding author at: Institute of Mineral Resources, Chinese Academy of Geological Sciences, NO.26, Baiwanzhuang street, 100037 Beijing, China.
E-mail address: zhengmp2010@126.com

Keywords: Hydromagnesite, Hydrochemistry, Stable isotopes, Evaporative sedimentation, Salt lake, Qinghai-Tibetan Plateau

1. Introduction

Hydromagnesite has long been known as a low-temperature hydrothermal mineral occurring in veinlets of serpentine, and it is relatively common in natural environments where it is found as an alteration product of mafic and ultramafic rocks such as basalt and serpentinite (Green and Young, 2006; Akhtar *et al.*, 2009). Hydromagnesite is considered to be the third most common carbonate mineral in karstic caves, where it forms speleothems, or is found on top of aragonite concretions, or as a component of “moonmilk” (Fischbeck and Müller, 1971; Hill and Forti, 1997; Northup *et al.*, 2001). It is deposited from Mg-rich waters that have seeped through the sedimentary rock. In addition, hydromagnesite has also been found in many alkaline lakes in the world, where it presents a particular interest as a biomineral that precipitates in microbial mats and stromatolites in alkaline lakes, such as Lake Specchio di Venere in Italy, Salda Lake in Turkey, British Columbia lakes, Alchichica Lake in Mexico (e.g. Renaut and long, 1989; Thompson *et al.*, 1990; Braithwaite and Zedef, 1994; Power *et al.*, 2007; Kaźmierczak *et al.*, 2009; Cangemi *et al.*, 2016), or is stratabound in lakes such as Pangkog tso, Selin Co, and Dujiali lakes in Tibet (Zheng *et al.*, 1989, 1997). The hydromagnesite mineralogy of modern and ancient playas is variable and complex, consequently there continue to be uncertainties. The genesis of sedimentary hydromagnesite in modern saline lakes, including the role of microorganisms in hydromagnesite precipitation, the temperature at which hydromagnesite forms, and its carbon source, constitutes a “hydromagnesite problem”, which unlike the “dolomite problem”, has so far attracted little attention from geologists.

Recently, however, hydromagnesite has attracted a great deal of interest for its potential capacity to store CO₂ by mineral carbonation. Although it is commonly accepted and well documented that the source of Mg²⁺ in recent or subrecent hydromagnesite is Mg-rich ultramafic and basaltic rocks (e.g., Coshell *et al.*, 1998; Wilson *et al.*, 2009a, 2009b, 2011; Power *et al.*, 2009, 2014), the source and pathway of carbon in such deposits has been the subject to continuing debate (Zedef *et al.*, 2000; Power *et al.*, 2009;). Combined use of the isotopes $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ has been applied in several studies of the development of hydromagnesite formations, and in

verifying and monitoring sequestration of atmospheric CO₂. Most of studies focus on hydromagnesite derived as meteoric or hydrothermal alteration products of ultramafic rocks (e.g. Hansen *et al.*, 2005; Boschi *et al.*, 2009; Wilson *et al.*, 2009a, 2009b; Wilson *et al.*, 2010; Wilson *et al.*, 2011; Oskierski *et al.*, 2013; Oskierski *et al.*, 2016), and a number of explanations have been proposed for this type of occurrence. Carbonate precipitation can be fostered either by physical-chemical or metabolic processes such as photosynthesis and sulfate reduction (Cangemi *et al.*, 2016). However, from the limited study of hydromagnesite in saline lakes, deposition appears to be associated with microbial activity (Braithwaite and Zedef, 1996; Power *et al.*, 2009, 2014; Cangemi *et al.*, 2016). Braithwaite and Zedef (1996) proposed bio-mediated precipitation of hydromagnesite with atmospheric origin for Salda Lake, Turkey. In addition, Power *et al.* (2009, 2014) suggested bio-mediated hydromagnesite precipitation in lakes in British Columbia, Canada as a biogeochemical model for CO₂ sequestration at the watershed scale.

Hydromagnesite is the most widespread form of hydrated Mg-carbonate in the Quaternary saline lakes of the Qinghai-Tibetan Plateau (QTP). Dujiali Lake, in the central QTP, is one of the few modern environments on the earth's surface that has experienced extensive hydromagnesite precipitation during the Holocene, and it constitutes a considerable resource of high purity hydromagnesite. In this study, we analyze the hydrogeochemistry of surface waters, and the mineralogical, stable isotope ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$), and radiocarbon isotope content of the Dujiali hydromagnesite deposits to investigate its formation mechanism.

2. Geologic setting

Dujiali Lake is located in the central QTP, China (32°05'20"N, 88°42'10"E; Fig. 1). The modern lake has a surface area of 80 km² and is at an elevation of 4524 m above sea level (asl). The Dujiali Lake area is characterized by a strong continental climate, with an annual mean temperature of -1 °C, annual precipitation of approximately 200 mm, and an annual evaporation loss of approximately 2400 mm. It is a semi-closed endorheic basin that is mainly recharged by meteoric water and groundwater, with a seasonal river supply in the southwest of the lake. The hydrochemistry of the lake is carbonate dominated, with a lake water pH of 8.8 and salinity of 114.17 g/l (Zheng *et al.*, 2002). In recent years, river discharge has increased and the lake is inundated year-round.

Structurally, the lake is located at the center of the Banggong-Nujiang suture zone, within a Cenozoic tectonic faulted basin. The lake basin is a downwarped subbasin derived from the ancient Selin Co basin, which lies in the north Lhasa Terrane that includes more than 3000 m of upward-coarsening Lower Cretaceous Strata. The margins of the subbasin are mainly covered by Jurassic and Cretaceous limestone, tertiary glutenite and mudstone, and within it are multi-stepped lake terraces, covered by Quaternary sandy gravel, silty clay and salt deposits.

3. Sampling and methods

3.1 Sample collection

In a field survey in March 2015 we sampled hydromagnesite deposits, which were characterized by extreme whiteness, in the first lake terrace in the northwest of Dujiali salt lake. The lake terrace is subparallel to the land surface and up to 10 m thick above the present lake surface (Fig. 2A). Seven samples were taken from a profile (DPSP01) through the hydromagnesite deposit, after removal of the weathered surface crust (Fig. 2B). The samples were equidistantly spaced at different lamellar horizon, and numbered 01 (bottom) to 07 (top).

In addition, a total of 10 surface water samples were collected from the study area in March 2015; sampling locations are depicted in Fig. 1. Six lake water samples were collected from the downstream around the Dujiali Lake. Three stream water samples obtained from the close to the Dujiali Lake. One seep water sample is obtained from the loose Quaternary sediments close to the Dujiali Lake.

3.2 Analytical techniques

3.2.1 Hydrochemistry

Standard analytical methods of the Analysis Group, Qinghai Saline Lake Institute and Chinese Academy of Science (1988) were employed for the water samples. The concentrations of K^+ , Na^+ , Li^+ , Mg^{2+} , and Ca^{2+} were determined by atomic absorption spectrophotometry using a WFX-120 atomic absorption spectrophotometer (Beijing Rayleigh Analytical Instrument Group., Beijing, China), which has a precision of 0.5%. Cl^- was analyzed using the $AgNO_3$ volumetric titration method, with a precision of 0.1%. CO_3^{2-} and HCO_3^- concentrations were determined by titration with 0.1 mol/L HCl, using methyl orange and phenolphthalein as a double indicator, with a precision of 0.3%. SO_4^{2-} was analyzed using the gravimetric method with $BaCl_2$, with a precision of 0.01%. The borate concentration was evaluated by titration with 0.05 mol/L NaOH in the presence of mannitol and using phenolphthalein as the indicator,

with a precision of 0.3% (Analysis Group, Qinghai Saline Lake Institute, Chinese Academy of Sciences, 1988; Gao *et al.*, 2012). Total dissolved solids (TDS) were calculated by summing all ions and subtracting half of the HCO_3^- . All analyses were carried out at the Analytical Laboratory of the Research & Development Center of Saline Lake and Epithermal Deposits, Chinese Academy of Geological Sciences (CAGS), Beijing.

3.2.2 X-ray diffraction

Seven samples from the hydromagnesite profile DJSP01 were ground into 200-mesh powder, smear mounted onto petrographic slides with anhydrous ethanol, and allowed to dry at room temperature. X-ray diffraction was carried out by the Key Laboratory of Saline Lake Resources and Environment, Ministry of Land and Resources, Beijing, using a Rigaku MiniFlex 600 X-ray diffractometer. The long fine-focus Cu X-ray tube was operated at 40 kV and 15 mA, using a take-off angle of 6° . Data were collected from $3\text{--}70^\circ 2\theta$ using a step size of 0.02° . The major crystalline mineral phases were identified with reference to the International Centre for Diffraction Data database using the program JADE.

3.2.3 Stable carbon and oxygen isotopes

Seven powdered samples from profile DPSP01 (100-mesh, 0.5 to 1 mg) were analyzed for their stable carbon and oxygen isotopic compositions using a Finnigan MAT 253 mass spectrometer coupled with a Thermo Finnigan GasBench II system at the Institute of Mineral Resources, CAGS. Carbonate micro-samples were loaded manually into 12 ml round-bottomed borosilicate Exetainers. The Exetainers are automatically flushed with grade 5 helium (flow rate of ml/min) by penetration of the septa with a double-holed needle. Subsequently, four to six drops of phosphoric acid were added to each sample, which were then placed on an aluminum tray and heated to 72°C for 24 h. The emitted CO_2 was separated from other volatile components using a gas chromatographic column heated to 72°C , and then passed into the mass spectrometer through an open split (see Spötl and Vennemann (2003) for further details). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data are reported as per mil deviations relative to the VPDB reference, and the external precision of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ is better than 0.1‰.

3.2.4 Radiocarbon dating

Two samples were selected for radiocarbon dating, from the bottom and top of the profile (DJSP0101 and DJSP0107, respectively). Gravel and other debris were

picked out of the hydromagnesite samples with tweezers and they were then acid washed with 0.1 N HCl to eliminate carbonates. When the surface of the sample had acid eroded by about 1/3, they were rinsed with ultrapure water to near neutral, and oven dried at low temperature.

About 20 mg of the treated sample were transferred into a carbonate acid hydrolysis device with 1 ml of phosphate acid and was connected to a graphite line. They were then pumped to remove the absorbed atmosphere on the sample surface and flame-sealed. Soil and charcoal samples were combusted in a quartz tube muffle furnace at 160 °C for over 16 hours and 900 °C for 16 hours, respectively, to release the carbon. The CO₂ was purified and was converted into graphite over iron at 550 °C in the presence of H₂. The ¹⁴C analyzes were carried out at the updated NEC Compact PKUAMS facility at the Institute of Heavy Ion Physics, Peking University, which is dedicated to ¹⁴C measurements with a maximum terminal voltage of 0.6 MV and a 40-sample multi-Cathode SNICS ion source. The ¹⁴C values are reported as conventional 14C yr after correction for isotopic fractionation and normalization to ¹³C (-25‰) using the ¹³C term measured directly with the accelerator. The ¹⁴C errors of each date include statistical uncertainties based on ¹⁴C counts, standard and ¹⁴C background targets, and machine random error. Calendar dates were calculated using OxCal v4.2 (Ramsey, 2009). The quoted age is in radiocarbon years using the Libby half-life of 5568 years and the uncertainties are reported as 1σ.

4. Results and discussion

4.1 Water hydrochemistry

The physiochemical characteristics of the investigated water samples are presented in Table 1. The abundance of major ions expressed in mg/L followed a general pattern of Na⁺>K⁺>Mg²⁺>Ca²⁺ for cations and Cl⁻>SO₄²⁻>CO₃²⁻>HCO₃⁻>B₄O₇²⁻ for anions. On a Chadha (1999) geochemical classification diagram, the water samples were shown to represented two hydrogeochemical water facies (Fig. 3): Type 1 (T1: Ca-Mg-HCO₃ water; e.g., seep water and stream water), and Type 2 (T2: Na-SO₄-Cl water; e.g., lake water). T1 waters were usually fresh with TDS ranging from 319.39 to 699.73 mg/L. They were slightly alkaline (pH=7.37–8.16), and characterized by higher concentrations of weak acidic anions (mainly HCO₃) than strong acidic anions (Cl+SO₄), and higher concentrations of alkali earth elements (Ca+Mg) than alkali elements (Na+K). Dujiali Lake water samples fell into the T2 water type. They were characterized by very high

TDS and pH compared to seep water and stream water (Table 1). Based on the Chadha diagram, surface water in the Dujiali Lake area has evolved from Ca-Mg-HCO₃ (T1) type to Na-SO₄-Cl type (T2).

Mineral equilibrium and saturation indices can be used to predict the reactive mineralogy (Deutsch, 1997). The saturation index (SI) is defined as the decadic logarithm of the quotient of the ion activity product and the mass balance constant (Kaźmierczak *et al.*, 2011). The SI of aragonite, calcite, dolomite, magnesite, artinite, huntite, nesquehonite, and hydromagnesite for the studied water samples is given in Table 2. The results show that the T1 waters are undersaturated with respect to artinite, huntite, magnesite, hydromagnesite, and magnesite, and the T2 waters are supersaturated with respect to huntite, magnesite, and artinite. Despite their tremendous supersaturation, these carbonates are not as abundant as might be expected. The SI calculation shows that Dujiali Lake water is near saturation for hydromagnesite. Comparably high hydromagnesite supersaturation has been reported for Lake Alchichica, Mexico and Lake Specchio di Vennere, Italy (Kaźmierczak *et al.*, 2011; Cangemi, *et al.*, 2016). Cangemi *et al.* (2016) supposed that hydromagnesite saturation depends on the temperature at the base of the saturation, switching from undersaturation during cold months to supersaturation when lake waters warm up in the summer season.

The chemical evolution of water in terms of evaporation and mineral precipitation is described in Fig. 4. Concentrations of many dissolved species are contrasted against those of chloride. The diagrams are drawn in an attempt to evaluate the extent to which the lake waters formed by simple evaporation, based on the reasonable hypothesis that, in the lake's salinity range, chloride behaves as a conservative element. As such, Fig. 4 supports both: (1) the genetic link between lake water and make-up water (seep water and stream water); and (2) the conservative behavior of the elements Na, K, Li, Br, Sr, SO₄. These elements, along with Br, do not participate in mineral precipitation, and behave conservatively as their element/chloride ratios are independent of salinity. In contrast, the alkaline earth element Ca is strongly depleted in lake water compared with the seep water and stream water, which may suggest an efficient removal of the element from solution due to the carbonate phase. In addition, the distributions of Mg vs. Cl substantiate an efficient mineral sink for Mg elements, most probably as magnesium carbonate. Gibbs (1970) developed a plot of TDS vs. the weight ratio of Na/(Na+Ca) which could be

used to provide information on the relative importance of three major natural mechanisms for controlling world surface water chemistry: (a) atmospheric precipitation; (b) rock dominance; and (c) evaporation-crystallization process. In the present study, the Gibbs plot indicates that seep water and stream water are primarily controlled by rock weathering, with only one sample (DJS03) lying outside of the diagrammatic range, but also near the rock weathering area (Fig. 5). Lake water samples and intercrystalline brine had high Na/(Na+Ca) ratios and TDS concentrations, suggesting lake water is primarily influenced by the evaporation-crystallization process (Fig. 5). Evapocentration of ions is important for driving carbonate precipitation in playas. The chemical composition of surface water around Dujiali Lake evolved from the rock-weathering-type waters of T1 to more concentrated sodic waters due to evaporation. In addition, the levels of Na⁺, Cl⁻, and TDS, and the Mg/Ca ratio, are higher than those found in upstream waters. In addition, the increase in Na⁺, Cl⁻, and SO₄²⁻ in the lake is mainly due to solute accumulation by evaporation, while the depletion of Ca²⁺ and HCO₃⁻ could reflect carbonate mineral precipitation. Zheng et al. (2002) discuss samples Z1 and Z2, which were collected from Dujiali Lake in the 1970s when it was a playa. The playa was very alkaline, with a Mg/Ca ratio of approximately 50:1 and a Mg concentration as low as 5.0 mg/L. These geochemical conditions are favorable for abundant precipitation of magnesium carbonate minerals.

4.2 Mineralogy

Analysis of the XRD data identified pure hydromagnesite [Mg₅(CO₃)₄(OH)₂·4H₂O], with no other mineral phases revealed.

4.3 Radiocarbon analysis

Sample DJSP0107 yielded a corrected age of 5845±30 cal a BP, and sample DJSP0101 yield a corrected age of 6090±25 cal a BP. These results are in accordance with stratigraphic order, i.e., sample DJSP 0107 was from the top of the profile and DJSP0101 from the bottom.

4.4 Carbon and oxygen isotopes

The δ¹³C and δ¹⁸O values of the hydromagnesite samples are presented in Table 3 and Fig. 6. The δ¹⁸O_{V-PDB} values are all highly positive, ranging from +4.1 to +5.2 ‰, which corresponds to a δ¹⁸O_{V-SMOW} range of 35.14 to 36.27 ‰ (Coplen *et al.*, 1983). The δ¹³C_{V-PDB} values are also all highly positive, and fall within a narrow range of 5.3 to 6.5 ‰ with an average of 5.94 ‰. No significant correlation exists between

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ when all data are considered ($R^2=0.1069$).

The high $\delta^{18}\text{O}$ values of the samples are similar to the $\delta^{18}\text{O}$ range for hydromagnesite-rich deposits in modern evaporitic environments (Braithwaite and Zedef, 1996; Oskierski *et al.*, 2013), and clearly indicate that lake water precipitating hydromagnesite at Dujiali is subject to rapid evaporation. Wilson (2010) established a kinetic control on the oxygen isotopic composition of experimental solutions, which demonstrates the utility of oxygen isotopes for identifying processes occurring during mineral precipitation. In this case significant evaporation drives ^{18}O -enrichment during mineral precipitation. Further evidence for the prevalence of inorganic precipitation processes is provided by positive $\delta^{18}\text{O}$ values, suggesting authigenic crystallization of carbonates from evaporating lake waters. During the evaporation process progressive ^{18}O enrichment in the dissolved phase would preferentially remove the lighter ^{16}O into water vapor, and allow the crystallization of carbonates with progressively increasing $\delta^{18}\text{O}$ (Clark and Fritz, 1997; Cangemi *et al.*, 2016).

A range of studies have used $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data to identify the sources of carbon tapped in the precipitation of carbonate minerals (e.g., Weber and Woodhead, 1970; O'Neil and Barnes, 1971; Fallick *et al.*, 1991; Wilson *et al.*, 2009a). Earlier studies indicated that carbonate deposits with different origins occupy different fields on a plot of $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ (Aharon, 1988; Fallick *et al.*, 1991; Zedef *et al.*, 2000; Power *et al.*, 2009, 2014; Wilson *et al.*, 2009a; Oskierski *et al.*, 2013). Modern precipitation of hydromagnesite has also been documented in Salda Lake, western Turkey by Braithwaite and Zedef (1996). Based on stable isotopes, they inferred that the carbon dioxide necessary to form hydromagnesite in Salda Lake was probably of atmospheric origin. The $\delta^{13}\text{C}_{\text{V-PDB}}$ values in this study are all highly positive, and slightly higher than those for the modern hydromagnesite deposits in Salda Lake, which all yield positive values, and are interpreted in terms of equilibration with atmospheric CO_2 (Fig. 6) (Braithwaite and Zedef, 1996).

Different isotopic signatures and fingerprints of carbon sources also can be established based on isotope fractionation in exchange equilibrium (Wilson *et al.*, 2010; Oskierski *et al.*, 2013). While isotope fractionation during dissolution of $\text{CO}_2(\text{g})$ and between aqueous carbon species has been characterized in a number of studies (e.g. Mook *et al.*, 1974; Romanek *et al.*, 1992; Zhang *et al.*, 1994; Halas *et al.*, 1997; Wilson *et al.*, 2010), interpretation of the stable isotopic compositions of hydrated Mg-carbonate minerals is hampered by an incomplete knowledge of isotopic

fractionation between CO₂ gas, dissolved inorganic carbon (DIC), and minerals (Wilson et al., 2010). There are no published equilibrium fractionation factors for carbon isotopic exchange between hydrated Mg-carbonate minerals and CO₂ gas or aqueous carbonate species. Wilson (2010) presented stable isotopic data from Mg-carbonate precipitation experiments. Using the measured $\delta^{13}\text{C}$ value for laboratory CO₂ gas of -8 ± 1 ‰ (VPDB), the kinetic diffusion effect proposed by O'Neil and Barnes (1971) would produce aqueous bicarbonate with $\delta^{13}\text{C}$ DIC $\approx$ -20 to -18 ‰ (VPDB), which is consistent with the initial carbon isotopic composition of DIC in the experiment (i.e., -19.3 to -19.2 ‰, VPDB). The DIC $\delta^{13}\text{C}$ values become increasingly positive with time. This trend toward enrichment in ¹³C is consistent with either very slow diffusion of atmospheric CO₂ into solution or degassing of light CO₂ from solution. Theoretical values of $\delta^{13}\text{C}$ for hydrated magnesium carbonates have also been calculated, assuming atmospheric CO₂ has a $\delta^{13}\text{C}$ of -9 to -7 ‰ (Clark and Fritz, 1997). Hydromagnesite precipitated in equilibrium with atmospheric CO₂ (with $\delta^{13}\text{C}$ of -7.0 to -9.0 ‰) is characterized by $\delta^{13}\text{C}$ between 1.2 and 7.6 ‰ (Clark and Fritz, 1997).

The lack of covariance of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ for hydromagnesite samples could be due to differing conditions at the lake water-atmosphere interface, and relate to the exceptional nature of carbonate precipitation events and to the limited lake volume. Furthermore, it could indicate a more complex control on carbon and oxygen isotope fractionation, during a stage when abundant hydromagnesite formation only took place in isolated instances.

5. Conclusion

In this study, we analyzed stable ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) and radiogenic (¹⁴C) isotopes from representative sedimentary hydromagnesite deposits in Dujiali Lake, QTP, and investigated the mechanism of hydromagnesite formation. The chemical composition of surface waters around Dujiali Lake evolved from a rock weathering type with Ca-Mg-HCO₃ to a more concentrated sodic Na-SO₄-Cl water type as a result of evaporation. Carbon and oxygen isotopic data indicated a supergene formation in which authigenic carbonate crystallization from evaporation water is the dominant precipitation process. High $\delta^{18}\text{O}$ signatures of hydromagnesite reflect significant evaporation, which has likely been the trigger of hydromagnesite precipitation on the

supersaturated surface alkaline waters. The $\delta^{13}\text{C}$ - $\delta^{18}\text{O}$ values imply that atmospheric CO_2 provided a carbon source for the precipitation of hydromagnesite. In addition, the hydromagnesite precipitation is mainly inorganic in nature and it has trapped and stored the greenhouse gas, CO_2 , directly from the atmosphere. Given that the hydromagnesite deposits have been stable over thousands of years, in a carbon storage scenario, artificial sinks of anthropogenic CO_2 that mimic the conditions of Dujiali Lake would be stable long enough to reduce atmospheric CO_2 concentrations and combat global climate change. Detailed analyses of hydromagnesite sediments in Dujiali Lake provide an improved understanding of the modes of sediment deposition and environmental conditions at the time of deposition.

Acknowledgements

This research was supported by the National Science Foundation of China (U1407207 and 41603048).

References

- Aharon, P., 1988. A stable-isotope study of magnesites from the Rum Jungle Uranium Field, Australia: Implications for the origin of strata-bound massive magnesites. *Chemical Geology* 69(1–2), 127–145.
- Akhtar, T., Shireen, K., Bashir, E., Naseem, S., 2009. Characteristics of ultramafic rocks and associated magnesite deposits, Nal Area, Khuzdar, Balochistan, Pakistan. *Journal of Geology & Mining Research* 1(2), 034–041.
- Boschi C, Dini A, Dallai L, Ruggieri, G, Gianelli, G., 2009. Enhanced CO₂ -mineral sequestration by cyclic hydraulic fracturing and Si-rich fluid infiltration into serpentinites at Malenrata (Tuscany, Italy). *Chemical Geology* 265(1–2):209–226.
- Braithwaite, C.J.R., Zedef, V., 1994. Living hydromagnesite stromatolites from Turkey. *Sedimentary Geology* 92(92), 1–5.
- Braithwaite, C.J.R., Zedef, V., 1996. Hydromagnesite stromatolites, sediments in an alkaline lake, Salda Gölü, Turkey. *Journal of Sedimentary Research* 66(5):991–1002.
- Cangemi, M., Censi, P., Reimer, A., D'Alessandro, W., Hause-Reitner, D., Madonia, P., Oliveri, Ygor., Pecoraino, G., Reitner, J., 2016. Carbonate precipitation in the alkaline lake Specchio di Venere (Pantelleria Island, Italy) and the possible role of microbial mats. *Applied Geochemistry* 67, 168–176.
- Chadha, D. K., 1999. A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data. *Hydrogeology Journal* 7(7):431–439.
- Clark, I.D., Fritz, P., 1997. *Environmental Isotopes in Hydrology*. CRC Press (328 pp.).
- Coshell, L., Rosen, M. R., Mcnamara, K. J., 1998. Hydromagnesite replacement of biomineralized aragonite in a new location of Holocene stromatolites, Lake Walyungup, Western Australia. *Sedimentology* 45(45):1005–1018.
- Coplen T B, Kendall C, Hoppo J., 1983. Comparison of stable isotope reference samples. *Nature* 302(5905):236–238.
- Deutsch, W. J., 1997. *Groundwater geochemistry: fundamentals and applications to contamination*. Lewis Publishers, Florida, Boca Raton.
- Fallick, A.E., Ilich, M., Russell, M.J., 1991. A stable isotope study of the magnesite deposits associated with the Alpine-type ultramafic rocks of Yugoslavia. *Economic Geology* 86(4), 847–861.
- Fischbeck, R., Müller, G., 1971. Monohydrocalcite, hydromagnesite, nesquehonite, dolomite, aragonite, and calcite in speleothems of the Fränkische Schweiz, Western Germany. *Contributions to Mineralogy & Petrology* 33(2), 87–92.
- Gao, F., Zheng, M.P., Song, P.S., Bu, L.Z., Wang Y. S., 2012. The 273.15-K-Isothermal Evaporation Experiment of Lithium Brine from the Zhabei Salt Lake, Tibet, and its Geochemical Significance. *Aquatic Geochemistry* 18(4):343–356.
- Gibbs, R. J., 1970. Mechanisms controlling world water chemistry. *Science* 170(3962):1088–1090.
- Green, D.I., Young, B., 2006. Hydromagnesite and dypingite from the Northern Pennine Orefield, Northern England. *Proceedings-Yorkshire Geological Society* 56(2), 151–154.
- Halas, S., Szaran, J., Niezgoda, H., 1997. Experimental determination of carbon isotope equilibrium fractionation between dissolved carbonate and carbon dioxide. *Geochimica Et Cosmochimica Acta* 61(13):2691–2695.
- Hansen, L. D., Dipple, G. M., Gordon, T. M., Kellett, D.A., 2005. Carbonated Serpentine (Listwanite) at Atlin, British Columbia: A Geological Analogue to Carbon Dioxide Sequestration. *Canadian Mineralogist* 43(1):225–239.
- Hill, C., Forti, P., 1997. *Cave Minerals of the World*, 2nd edn. Huntsville, AL:National Speleological Society.
- Kaźmierczak, J., Altermann, W., Kremer, B., Kempe, S., Eriksson, P. G., 2009. Mass occurrence of benthic coccoid cyanobacteria and their role in the production of Neoproterozoic carbonates of South Africa. *Precambrian Research* 173(1–4), 79–92.
- Kaźmierczak, J., Kempe, S., Kremer, B., López-García, P., Moreira, D., Tavera, R., 2011. Hydrochemistry and microbialites of the alkaline crater lake Alchichica, Mexico. *Facies* 57(4):543–570.
- Mook, W. G., Bommerson, J. C., Staverman, W. H., 1974. Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. *Earth & Planetary Science Letters* 22(2):169–176.
- Northup, E., Kathleen, H., Lavoie, D., 2001. Geomicrobiology of caves: a review. *Geomicrobiology Journal* 18, 199–222.
- O'Neil, J.R., Barnes, I., 1971. C¹³ and O¹⁸ compositions in some fresh-water carbonates associated with ultramafic rocks and serpentinites: western United States. *Geochimica Et Cosmochimica Acta*

- 35(7), 687-697.
- Oskierski, H.C., Dlugogorski, B.Z., Jacobsen, G., 2013. Sequestration of atmospheric CO₂ in chrysotile mine tailings of the Woodsreef Asbestos Mine, Australia: quantitative mineralogy, isotopic fingerprinting and carbonation rates. *Chemical Geology* 358, 156-169.
- Oskierski H C, Dlugogorski B Z, Oliver T K, Jacobsen, G., 2016. Chemical and isotopic signatures of waters associated with the carbonation of ultramafic mine tailings, Woodsreef Asbestos Mine, Australia. *Chemical Geology* 436:11-23.
- Power, I.M., Wilson, S.A., Thom, J.M., Dipple, G.M., Southam, G., 2007. Biologically induced mineralization of dypingite by cyanobacteria from an alkaline wetland near Atlin, British Columbia, Canada. *Geochemical Transactions* 8(2), 229-247.
- Power, I.M., Wilson, S.A., Thom, J.M., Dipple, G.M., Gabites, J.E., Southam, G., 2009. The hydromagnesite playas of Atlin, British Columbia, Canada: A biogeochemical model for CO₂ sequestration. *Chemical Geology* 260(12), 286-300.
- Power, I.M., Wilson, S.A., Harrison, A.L., Dipple G.M., Mccutcheon, J., Southam, G., Kenward, P.A., 2014. A depositional model for hydromagnesite–magnesite playas near Atlin, British Columbia, Canada. *Sedimentology* 61, 1701-1733.
- Ramsey, C.B., 2009. Bayesian Analysis of Radiocarbon Dates. *Radiocarbon* 51(1), 337-360.
- Renaut, R.W., Long, P.R., 1989. Sedimentology of the saline lakes of the Cariboo Plateau, Interior British Columbia, Canada. *Sedimentary Geology* 64(4), 239–264.
- Romanek, C. S., Grossman, E. L., Morse, J. W., 1992. Carbon isotopic fractionation in synthetic aragonite and calcite: Effects of temperature and precipitation rate. *Geochimica Et Cosmochimica Acta* 56(1):419-430.
- Spötl, C., Vennemann, T.W., 2003. Continuous-flow isotope ratio mass spectrometric analysis of carbonate minerals. *Rapid Commun. Mass Spectrom.* 17, 1004–1006.
- Thompson, J.B., Ferris, F.G., 1990. Cyanobacterial precipitation of gypsum, calcite, and magnesite from natural alkaline lake water. *Geology* 18(10), 995.
- Weber, J.N., Woodhead, P.M.J., 1970. Carbon and Oxygen Isotope Fractionation in the Skeletal Carbonate of Reef-Building Corals. *Chemical Geology* 6, 93-117.
- Wilson, S.A., Dipple, G.M., Power, I.M., M.Thom, J., Anderson, R.G., Raudsepp, M., Gabites, J., Southam, G., 2009a. Carbon Dioxide Fixation within Mine Wastes of Ultramafic-Hosted Ore Deposits: Examples from the Clinton Creek and Cassiar Chrysotile Deposits, Canada. *Economic Geology* 104(1), 95-112.
- Wilson, S.A., Raudsepp, M., Dipple, G.M., 2009b. Quantifying carbon fixation in trace minerals from processed kimberlite: a comparative study of quantitative methods using X-ray powder diffraction data with applications to the Diavik Diamond Mine, Northwest Territories. *Can. Applied Geochemistry* 24, 2312–2331.
- Wilson, S. A., Barker. S. L., Dipple, G.M., Atudorei, V., 2010. Isotopic disequilibrium during uptake of atmospheric CO₂ into mine process waters: implications for CO₂ sequestration. *Environmental Science & Technology* 44(24), 9522-9529.
- Wilson, S.A., Dipple, G.M., Power, I.M., Barker, S.L.L., Fallon, S.J., Southam, G., 2011. Subarctic weathering of mineral wastes provides a sink for atmospheric CO₂. *Environmental Science & Technology* 45, 7727–7736.
- Zedef, V., Russell, M. J., Fallick, A. E., Hall A.J., 2000. Genesis of vein stockwork and sedimentary magnesite and hydromagnesite deposits in the ultramafic terranes of southwestern Turkey: A stable isotope study. *Economic Geology* 95(2):131-134.
- Zhang, J., Quay, P. D., Wilbur, D. O., 1995. Carbon isotope fractionation during gas-water exchange and dissolution of CO₂. *Geochimica Et Cosmochimica Acta* 59(1):107-114.
- Zheng Mianping, Xiang Jun and Wei Xinjun, 1989. Saline Lake on the Qinghai-Xizang (Tibet) Plateau. Beijing: Science Press, 1–431 (in Chinese).
- Zheng Mianping, 1997. An Introduction to Saline Lakes on the Qinghai-Tibet Plateau. Springer Netherlands, 1–294.
- Zheng Xiyu, Zhang Minggang, Dong Jihe, Gao Zhanghong, Xu Chang, Han Zhiming, Zhang Baozhen, Sun Dapeng, Wang Kejun, 1995. Salt Lakes in Inner Mongolia. Beijing: Science Press, 196–218, 229–247 (in Chinese).

Table 1 General parameters and major ion chemistry of the water in Dujiali Lake area

NO.	Li ⁺	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	F ⁻	Cl ⁻	Br ⁻	HCO ₃ ⁻	OH ⁻	CO ₃ ²⁻	SO ₄ ²⁻	B ₄ O ₇ ²⁻	pH	TDS	Mg/Ca	Water
DJS01	0.3	81.0	9.9	30.8	81.2	0.4	0.8	21.8	0.0	442.3	0.0	36.0	56.8	11.6	7.5	556.2	0.4	seep
DJS02	0.2	47.0	4.8	30.2	67.0	0.3	0.0	14.5	0.0	391.6	0.0	9.0	24.3	27.2	7.4	424.3	0.5	stream
DJS03	0.4	152.0	10.0	58.2	22.0	0.0	0.5	54.5	0.0	391.6	0.0	52.8	139.9	9.7	8.2	699.7	2.7	stream
DJS04	0.2	58.0	4.1	8.8	44.2	0.3	0.1	22.7	0.0	206.2	0.0	6.0	58.4	11.3	7.8	319.4	0.2	stream
DJZS01	2.2	1820.0	129.0	42.4	9.6	0.1	1.6	563.7	0.4	320.3	0.0	705.0	1962.5	141.7	9.6	5541.5	4.4	lake
DJZS02	1.0	407.0	52.0	49.0	17.8	0.0	0.7	158.2	0.1	146.4	0.0	204.0	472.5	41.9	9.0	1478.8	2.8	lake
DJZS03	2.2	2080.0	130.0	63.2	9.2	0.0	1.0	554.6	0.4	549.0	0.0	900.0	2020.1	135.8	9.5	6176.6	6.9	lake
DJZS04	5.2	2600.0	166.0	62.4	10.4	0.1	2.0	723.7	0.6	488.0	0.0	960.0	2983.3	156.8	9.6	7919.3	6.0	lake
DJZS05	9.0	3120.0	248.0	48.6	15.0	0.1	1.2	2272.8	1.4	1082.8	0.0	450.0	2404.6	188.2	8.8	9311.2	3.2	lake
DJZS06	2.1	1660.0	108.0	29.0	6.8	0.0	1.2	461.8	0.5	259.3	0.0	720.0	1644.8	116.4	9.7	4882.8	4.3	lake
DJZS0201	5.1	1560.0	199.0	90.0	8.4	0.1	1.0	1400.1	—	305.0	0.0	520.0	788.8	148.8	—	4876.8	10.7	lake
DJZS0202	5.5	2200.0	160.0	68.0	8.6	0.1	0.0	1157.6	—	593.1	0.0	316.7	2399.6	140.1	—	6758.7	7.9	lake
Z1	150.0	51000.0	7855.0	32.6	0.0	<1	—	41323.7	38.4	187.6	—	11893.4	36960.0	3709.7	—	153058.5	—	lake
Z2	112.0	40500.0	3415.0	5.0	0.1	<2	—	16310.0	9.4	3266.0	—	6225.0	42850.0	1486.7	—	112578.8	50	intercry bri

Note: The data of the sample Z1 and Z2 were cited from Zheng et al.,2002.

All variable are given in mg/L.

Dashes(—) denote no data.

Table 2 Saturation indices of various carbonate minerals of Dujiali Lake water

Sample	SI aragonite	SI Artinite	SI calcite	SI dolomite	SI huntite	SI hydromagnesite	SI nesquehonite	SI magnesite
DJS01	0.33	-5.68	0.48	1.93	-1.61	-10.48	-3.19	-0.17
DJS02	0.13	-5.99	0.27	1.6	-2.2	-11.8	-3.31	-0.3
DJS03	0.36	-3.17	0.51	2.83	1.03	-5.37	-2.32	0.7
DJS04	0.1	-6.11	0.24	1.17	-3.42	-12.8	-3.71	-0.69
DJZS01	0.64	-0.37	0.79	3.61	2.8	-1.08	-1.82	1.19
DJZS02	0.47	-1.65	0.61	3.03	1.43	-3.55	-2.22	0.8
DJZS03	0.75	-0.1	0.89	4.03	3.85	0.14	-1.51	1.51
DJZS04	0.74	-0.04	0.89	3.95	3.61	-0.04	-1.59	1.43
DJZS05	0.71	-2	0.86	3.62	2.69	-2.89	-1.89	1.13
DJZS06	0.5	-0.47	0.64	3.3	2.17	-1.65	-1.98	1.04

Fig.1. Map showing sampling locations around Dujiali lake.

Fig.2. A photographs of the hydromagnesite deposits in Dujiali lake. (A) Profile DJSP01(red line), in which hydromagnesite sediments were extensively precipitated over 10 m above the present lake surface. (B) 7 samples of profile DPSP01 were equidistantly taken at different lamellar horizon after removeing the weathered crust.

Fig .3. Classification of hydrogeochemical water types from the waters of the Dujiali Lake area (Chadha, 1999)

Fig.4. Binary diagrams of dissolved, conservative and non-conservative species vs. Cl concentration. Green colours mark samples represent seep water, blue colours samples represent stream water, red colours mark represent lake water. Trend lines for increasing concentrations of conservative species upon evaporation are given in grey. Red lines denote the trends of mixing and loss of species by mineral precipitation in the lake.

Fig.5 Gibbs plot showing the mechanisms controlling the major ion composition of the water in Dujiali Lake area. Dujiali Lake water is mainly controlled by evaporation-crystallization process.

Fig.6. Plot of $\delta^{13}\text{C}_{(\text{PDB})}$ vs. $\delta^{18}\text{O}_{(\text{SMOW})}$ data the Dujiali lake hydromagnesite. There are compared with similar data for hydromagnesite from Salda Lake in Turkey(Braithwaite and Zedef, 1996).