1 Introduction

Many salt minerals have hydration water in their crystal structure in nature. These waters can provide information on the isotope compositions, the origin and evolution of fluids, and even the hydrological processes during diageneses. Carnallite (K\textsubscript{2}Mg\textsubscript{3}Cl\textsubscript{6}·6H\textsubscript{2}O) is one of the most extensive and voluminous salt minerals in many potash deposits (Garrett, 1996). With respect to studies on gypsum (CaSO\textsubscript{4}·2H\textsubscript{2}O) (Sofer, 1978; Horita, 1989; Hodell et al., 2012), the stable isotope composition of water in chloride mineral hydration water (e.g. carnallite) have not been well studied.

Khorat Plateau is located in northeast Thailand and middle Laos, where large-scale potash deposits have been developed since Late Cretaceous (Maha Sarakham Formation in Thailand; also called Nongbok Formation in Khammouan of middle Laos) in its two sub-basins (Sakon Nakhon Basin to north and Khorat Basin to south). This is one of the largest potash deposits in the world (Fan, 2000). Carnallite is the most potassium minerals in the salt deposit sequences. 58 samples in this study were collected from 5 boreholes drilled in Khammouan, which lies in the eastern rim of Sakon Nakhon Basin.

The method for extraction of hydration water of carnallite established by Tan et al. (2013) was followed. After hydration water was extracted by vacuum heating, an online method using a carbon-reducing furnace connected to a continuous-flow mass spectrometer system (Flash-Ea-MAT253) was utilized to measure hydrogen and oxygen stable isotopic ratios. All isotope data obtained were calibrated by fractionation factor, which is 0.98703 for hydrogen and 1.00632 for oxygen. These calibrated data represent the isotope composition of water in parent brine where the carnallite was deposited. Br content in carnallite was measured by the visible spectrophotometer.

2 Results and Discussions

2.1 Composition of Hydrogen and Oxygen Isotope

In this study, the $\delta^D$ values range from $-37.2^{\circ}$ to $-73.07^{\circ}$, averaging $-45.79^{\circ}$. The $\delta^{18}O$ values vary from 0.95‰ to $-9.43^{\circ}$ and average $-1.71^{\circ}$. Most of data distributed on the right of global meteoric water line (GMWL; Craig, 1961), and only a few of them plot on the left of the line (Fig. 1).

It is obvious that the regression trendline of evolution of seawater (curve C) almost cannot pass through these isotope data of carnallites in study area (Fig. 1). Similarly,
curve D only can pass through a part of these data. Therefore, it seems that the simple evaporation of seawater cannot explain these isotope data of hydration water observed in Fig. 1.

2.2 Origin and Evolution of hydration water

The possible sources of waters for brines in salt basins had been summarized by Knauth and Beeunas (1986). These waters would influence the isotope composition of hydration of carnallite.

High Br content of carnallite (generally more than 3000 ppm) in our study indicates these brines should be derived from seawater rather than evaporation of meteoric waters. Absence of sulfates (e.g. gypsum and anhydrite) excludes the possibility that these waters were from gypsum dehydration. Just as discussed previous, all data plot did not distribute along any seawater evaporation trajectory. It implied that seawater was not its dominant source. As increasing shrinkage of salt pan, the non-marine/continental input would play a more and more important role at the late stage of evapo-concentration of brine in a seawater-feed salt basin (Cendón et al, 2008; García et al., 2013). Based on these analyses mentioned above, it is reasonable to infer that hydration water in carnallite was from mixing of concentrated seawater brine with meteoric water.

With relative to modern seawater, Late Cretaceous seawater had about 5‰ depletion in $\delta^{18}$O (Jafvres et al., 2007). Given the isotope composition of ocean water changing with time but global circulation patterns like today, except for the different intercept, the slope of GMWL would remain at a value of 8 (Hoefs, 2009). In light of these inferences, the evolution trajectory of brine in study area is plotted in Fig. 2. Under extreme arid climate in Late Cretaceous on Khorat Plateau (Meesook, 2000), the evolution of seawater may along Curve E and was very close to curve B (Fig. 2). When the concentrated seawater brine evolved along the curve E and reached to the point H, the mixing of evapo-concentrated seawater with meteoric water occurred in highly restricted salt pan in study area. Point I represented the new isotope composition of water in brines after the mixing. Then these mixed brines evolved along the line F until carnallites were crystallized. The isotope data and their distribution observed in Fig. 2 can be well explained by these complex processes.

3 Conclusions

Oxygen and hydrogen isotope evidence of hydration water in carnallite in this study show that these waters may be sourced from evaporation of concentrated seawater brine mixed with meteoric water. It is speculated that all carnallites in any evaporite deposit are probably not primary, just as concluded by Koehler and Kyser (1996) in their experiments.

Acknowledgements

This research was supported by National Program on Key Basic Research Project of China (973 Program, 2011CB403004) and National Natural Science Foundation of China (41073034, 40903014 and 41173049).

References


