Origin of the late Cretaceous potash-bearing evaporites in the Vientiane Basin of Laos: $\delta^{11}$B evidence from borates

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The evaporites on the Khorat Plateau comprise one of the largest potash deposits in the world, and their origin has long been a controversial problem. Based on boron isotope measurements from borate as a good indicator to distinguish marine and nonmarine evaporites, the borates of potash layers were identified and the results were used to indicate the source of evaporites in the study area as representative of the whole Khorat Plateau. The results show that the main borates include boracite and hilgardite. The boracites occur as crystals and ooids with minor amounts of hilgardite aggregates. The range of $\delta^{11}$B values is from $+21.30\%$ to $+32.94\%$ (averaging $+29.74\%$) and falls in the range of marine borates. The $\delta^{11}$B values in the potash layer are seemingly variable because of the influence of fluvial influx when salts were precipitating. Although the composition of seawater has possibly been modified, the evidence from boron isotopic composition implies that the evaporites in the study area or in the whole Khorat Plateau are marine deposits.

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1. Introduction

The late Cretaceous Maha Sarakham Formation (also known as the Tagon Formation in the Vientiane Basin) potash deposit is one of the largest potash deposits in the world (Hite and Japakasetr, 1979; Fan, 2000). Before the 1990s, a large amount of exploration had been carried out in the region because of the economic benefits of potash. Since then, additional work has been conducted mainly for their scientific reasons (Utha-Aroon, 1993). One of the unsolved problems is the origin of evaporites in this area. Through studies on bromine contents and their changes, Hite and Japakasetr (1979) thought that the salts were derived from seawater. Sulfur isotopes from anhydrites (El Tabakh et al., 1999) falling in the range of marine evaporites implied their seawater origin. Evidence from boron isotope composition in fluid inclusions of halite showed that it differed significantly from that of continental evaporites and is very close to that of salts precipitated from evapo-concentrated seawater (Tan et al., 2010). Based on the lack of evidence suggesting transgression, some authors insisted that the Maha Sarakham Formation is not of marine origin (Utha-Aroon, 1993; Meesook, 2000; Racey and Goodall, 2009).

Comparing the depositional characteristics of the Sergipe Basin of Brazil, the Congo–Gabon Basin of Africa, and basins on the Khorat Plateau, Garrett (1996) concluded that the formation was deposited in a terrestrial but not a marine environment. Warren (1999) commented that the Khorat and the Sakon Nakhon Basins lack MgSO$_4$ salt, indicating a likelihood for a continental or basinal brine source.

Since about 2000, a large amount of geologic exploration has been carried out to find more potash in the Vientiane Basin of Laos. Borehole FJ is one of many boreholes in this area. Although the borehole does not reach the bottom of the Tagon Formation, the complete potash layer has been obtained. Therefore, a complete succession of potash samples in borehole FJ was selected as a study object and the insoluble minerals, which include many borates, were obtained. Through studies on the borates, we attempted to use the boron isotopic composition of borates to reveal the origin of potash-bearing evaporites on the Khorat Plateau. Because of the significantly different range of marine and nonmarine borates (averaging $+25 \pm 4\%$ and $-7 \pm 10\%$, respectively), the boron isotopic composition of borates has widely been used to distinguish marine and nonmarine sedimentary environments or the origin of fluids from which they precipitate in many evaporite deposits (Swihart et al., 1986; Oi et al., 1989; Vengosh et al., 1992; Grice et al., 2005; Tan et al., 2010). In this paper, we also attempted to characterize the changes of boron isotopic composition and discuss its influencing factors.
2. Geology

2.1. Regional geology

The Khorat Plateau, which lies in northeast Thailand and central Laos of Southeast Asia, is a part of Indochina terrane and divided into the Khorat Basin to the south and the Sakon Nakhon Basin to the north by the Phu Pan Anticline. Tectonically, the plateau is bounded to the west by the Nan Suture (also called Nan Uttaradit Suture) and the Sukhothai Arc and Sibumasu Terranes, and to the north by the Song Ma Suture and the South China Terrane (Sone and Metcalfe, 2008; Metcalfe, 2011).

Along with the Paleo-Tethys oceanic floor northwards subducting beneath Indochina, the processes of separation, amalgamation and accretion successively took place among the Sibumasu Terrane, Sukhothai back-arc basin and Indochina Terrane from the Early Permian to the Triassic (Sone and Metcalfe, 2008; Metcalfe, 2011). By the early Late Triassic, the collision of the Sibumau Terrane with the continental Sukhothai Arc of western Indochina indicates the closure of the Palaeo-Tethys Ocean (Sone and Metcalfe, 2008). The Sakon Nakhon and Khorat basins on the Khorat Plateau are the result of late-stage tectonic relaxation or extension following the collision (Metcalfe, 1988). In two basins, the nonmarine Khorat Group with a thickness up to 5 km was deposited (Fig. 1; El Tabakh et al., 1999). The Khorat Group sediments is overlain by the Maha Sarakhan Formation of which sedimentary characteristics has been detailedly described by Japakasetr and Workman (1981). During the early Paleocene, an estimated erosion of about 3000 m of the Khorat sediments is produced and the NW–SE trending Phu Phan anticlinorium in the central part of the Khorat Plateau formed (Cooper et al., 1989; Mouret, 1994). Recently, Morley (2012) indicates that the Cenozoic folds are not located only over normal faults inverted during the Cenozoic, but also over old compressional features (e.g. in the Permian).

The Thongmang mining area is located in the northern Vientiane Basin of Laos, which belongs to the northwest part of the Sakon Nakhon Basin (Fig. 2A). As a part or a subbasin of Sakon Nakhon Basin, the Vientiane Basin has a tectonic and evolution history highly consistent with the whole Khorat Plateau. Borehole FJ is one of total 14 boreholes drilled in the mining area (Fig. 2B). Besides fault F8, which trends west–east (Fig. 1A), there is no significant fault to influence the area. Stratigraphic analyses in the Vientiane Basin show that the Tagon Formation is divided into three evaporite-clastic cycles—Upper Member, Middle Member, and Lower Member, similar to other places on the Khorat Plateau. The potash seams are atop the evaporites of the Lower Member.

2.2. Lithology of borehole FJ

The strata of borehole FJ are divided into two parts: upper Quaternary sediments and lower late Cretaceous sediments; most of the Tertiary sediments may have been lost (Fig. 3A). The Quaternary sediments mainly consist of unconsolidated fluvial reddish and greenish silty clay and heretofore are unnamed. The Tertiary sediments comprise a suite of evaporite-clastic sediments and only two complete cycles of Lower Member and Middle Member of the Tagon Formation have been found. The Upper Member has probably been leached by meteoric water, and the salts (halite or anhydrite) were dissolved completely.

The Middle Member contains a sequence of rock salt and clastic layer. The clastic layer is reddish brown silty mudstone. The greater thickness of the clastic unit of the Middle Member indicates that the clastic unit of the Upper Member was partly included. The rock salt is composed of semitransparent and transparent halite, in which a few anhydrites were often found.
The Lower Member is of importance because of the existence of potash within it. It also has two parts: a potash-evaporites unit and a clastic unit. The clastic unit mainly is reddish brown silty mudstone or mudstone in which some orange carnallite or halite veins were found. The potash deposit lies atop the upper part of the potash-evaporite unit and the soluble minerals are dominantly colorless or pink carnallite and transparent halites, but locally much honey tachyhydrite occurs. The borehole FJ was terminated when still in salt of the Lower Member but the potash layer has been penetrated throughout.

3. Materials and methods

3.1. Sampling and processing procedure

According to the combining characteristics of soluble salts (carnallite, tachyhydrite, halite, etc.), fourteen samples obtained by grooving method in the core were collected from the bottom of the borehole to the top of the potash layer (Fig. 3B). The gross weight of salt samples ranges from about 150–400 g. Owing to the low content of the insoluble components in evaporites, a longer core is required to obtain a large enough quantity for every insoluble mineral sample. Generally, the sampling interval in the potash layer is about 5–10 m, and it is about 20–30 m in the rock salt. All samples were dissolved in 5 L beakers 4 or 5 times to remove the soluble salts thoroughly. After that, the obtained insolubles were rinsed with ethanol and dried at 40 °C in an oven. After these procedures, the final insoluble samples have a weight range of about 0.4–3.8 g.

Additionally, the criteria of sampling are as follows: (1) the samples in halite layers and potash layers were collected separately; (2) the different potash types (sylvite layers, carnallite layers and carnallite layers with much tachyhydrite) were sampled separately; (3) in the layers with similar assemblage of minerals, the samples were collected by virtue of the changes of bromine content; and (4) the amount of insoluble samples must be enough
to satisfy the requirement of analyses of mineralogy and boron isotope. The purpose to make these regulations is to discuss the difference of boron isotope composition in different salt layers.

3.2. Observation and X-ray diffraction determination of insoluble minerals

The insoluble samples were observed under a microscope and pictures were taken with a digital camera. The main aspects of observation include the optical properties of minerals and the appearance features of crystals. The minerals are also identified using a polarizing microscope. The components of insoluble minerals are determined by X-ray diffraction method (XRD).

3.3. Analyses of boron isotopes

The samples were decomposed with a mixture of Na₂CO₃ and K₂CO₃ (Wang et al., 2000). Boron in the sample was then purified by ion exchange with Amberlite IRA 743 resin and a mixture of cation-exchange resin (H⁺ form) and anion-exchange resin (ion exchanger, HCO₃⁻ form). The boron isotopic measurement procedure is the same as that described by Xiao et al. (1988). The measurement of boron isotopes was done using a Triton mass spectrometer (TIMS) at the Qinghai Institute of Salt Lakes, Chinese Academy of Sciences. The ¹¹B/¹⁰B ratio of NBS SRM 951 was determined repeatedly to be 4.05662 ± 0.00078 (2σ = 0.02%, n = 9). The isotopic composition of boron in the samples is expressed as a per mil deviation relative to the NBS SRM 951 boric acid standard (Table 1).

4. Results

4.1. Main insoluble borates

Analyses of XRD and microscope images showed that the main insoluble minerals comprise anhydrite, borates, carbonates, and quartz. Anhydrite and borates are the dominant minerals. The borates include boracite and hilgardite (Fig. 4). Boracite occurs as crystals and grains. The boracite crystals are cubic, tetrahedral, and generally 0.1–1.5 mm in size (Fig. 4A). In fact, the boracite grains should accurately be called ooids because they show concentric or radial microfabrics, or the coexistence of both (Flügel, 2010). These ooids are often less than 2 mm in size and most of them are radial. Studies on carbonate ooids implied that the radial-fibrous structure of ancient ooids is considered to be primary (Flügel, 2010). Hence these boracite ooids are also a good indicator of primary borate. Hilgardite is another important borate but the abundance in samples is not as high as boracite. The occurrences of hilgardite are usually translucent or cream aggregates comprised of very small crystals (Fig. 4C). These borates are the materials used to measure the boron isotopes in this study.
4.2. Boron isotopic composition

The boron isotopic composition results are shown in Table 1. The range of $\delta^{11}$B values varies from +21.30‰ to +32.94‰, with an average of +29.74‰. In halite layers, the $\delta^{11}$B values show small variations from +30.68‰ to +30.94‰. However, in potash layers, their values (+21.30‰ to +32.94‰) seem to vary significantly. In the light of conspicuously different isotopic composition of boron in marine and nonmarine minerals, the $\delta^{11}$B values from borates in this study are very close to those from marine evaporitic borates (Fig. 5). Hence the source of potash-bearing evaporites in the Vientiane Basin should be from seawater. Although the Vientiane Basin is only a part of the Khorat Plateau, it could be reasonably speculated that these evaporites in basins of the whole plateau are marine deposits.

4.3. Changes of boron isotopes in profile

There is a fluctuation of the $\delta^{11}$B value in the profile of borehole FJ and the values are divided into three stages from the bottom to the top (Fig. 6):

I. The early stage (from FJ-14 to FJ-12): In the early stage, the host rock is mainly rock salt. In three samples, the $\delta^{11}$B values (+30.68‰ to +30.94‰) gradually increase upward with brine continuously concentrating.

II. The middle stage (from FJ-11 to FJ-02): In the middle stage, the host rock is mainly carnallite with locally much tachyhydrite. The $\delta^{11}$B values change sharply. At the beginning of the stage, the $\delta^{11}$B value of sample FJ-11 is even lower than that of samples at the early stage. Some terrestrial muscovites are found on the bottom of the potash layer in borehole T1 and borehole T2, which is near borehole FJ. Therefore the lower $\delta^{11}$B value of FJ-11 possibly is related to the fluvial flux.

Later in the stage, the $\delta^{11}$B value of sample FJ-10 suddenly increases and then decreases gradually with depth until the upper part of the potash layer. During this period, a lot of potassium–magnesium salts precipitate.

At the end of the stage, the $\delta^{11}$B value of sample FJ-02 has the lowest value (+21.30‰) in the whole profile. Perhaps shrinkage of the salt pond and fluvial influx are the main reasons of the phenomena.

III. The late stage: the $\delta^{11}$B peak value (+32.94‰) occurs and only a few boracites are found at the late stage. The high $\delta^{11}$B value possibly implies that these boracites precipitated in a stable intercrystalline brine environment and have experienced an advanced evaporation stage.

5. Discussion

Because of the absence of MgSO$_4$ salts and voluminous sulfate (e.g. gypsum or anhydrite) and carbonate, as well as the existence of tachyhydrite, the evaporites on the Khorat Plateau were called “abnormal evaporites” and the thermal fluid rich in CaCl$_2$ has mixed with normal seawater, similar to the cases in the Sergipe Basin, Brazil, and the Congo–Gabon Basin, Africa (Braitsch, 1971; Borchert, 1977; Hardie, 1990). Recent studies on the main components of Cretaceous seawater showed that the seawater initially had a lower Mg/Ca ratio compared with other ages because of
the high rates of ocean crust production related to fierce volcanic activity at the MORs (mid-ocean ridges) in the Cretaceous (Timofeeff et al., 2006; Lowenstein and Timofeeff, 2008). MOR activity involves circulation of hot seawater through oceanic basalts and during this process, Na\(^+\), Mg\(^{2+}\), and SO\(_4\)\(^{2-}\) are exchanged from seawater to oceanic rock and Ca\(^{2+}\) and K\(^+\) are lost from basalts to seawater (Timofeeff et al., 2006). By these activities and reactivities, more Ca\(^{2+}\) entered into the seawater and the metamorphism of normal Cretaceous seawater happened.

Many reports have been made on borates in marine formations and, on the basis of their $\delta^{11}$B values, at least part of the boron in these minerals originated from seawater (Garrett, 1998). Normal seawater contains about 4.6 ppm boron. Evaporating experiments showed that the range of boron in the end liquor of seawater is about 200–400 ppm (Zherebtsova and Volkova, 1966; Valevev et al., 1973; Vengosh et al., 1992). Valevrev et al. (1973) found that borates could not precipitate from seawater until the concentration was 2500–4000 ppm and they speculated that boron-supplemented seawater could precipitate boracite during the final period of salt and potash-crystallization if residence times were long.

Neither tachyhydrite nor boracite could precipitate from the normal seawater (Valevrev et al., 1973; Herrmann et al., 1973; Hardie, 1990; El Tabakh et al., 1999) and additional boron could enter the seawater from terrestrial or geothermal sources or originally deposited boron could have been redissolved, concentrated, and reprecipitated (Garrett, 1998). As the result of terrestrial input and ion exchanges, the component of seawater was metamorphosed into the abnormal seawater, which was rich in calcium and boron.

The experimental evaporation of Mediterranean seawater showed that the $\delta^{11}$B values of both the evaporated sea water and salts increased with evaporation (Vengosh et al., 1992). Whereas the fluctuant change of $\delta^{11}$B values observed in this study possibly implied that some following reasons caused the result. As the evaporite basin restriction increased, the originally marine inputs changed to continental or marine-modified inputs (Cendón et al., 2008). This means that the nonmarine input or influx would enter the salt pond at the late stage of halogenesis. Much muscovite was found in the upper and middle parts of potash layers in some boreholes in study area. The thickness of layers containing this mineral is about 13 m, 14 m, 45 m and 33 m in borehole T1, T2, T4 and T5, respectively. Taking account of those extensively developed lacustrine deltas during halogenesis in Thongmang area, which is adjacent to the north rim of Vientiane Basin (Guo et al., 2005), it is not surprising that so much terrestrial muscovite was found in potash layers. These evidences suggest that a terrestrial input or riverine water had entered into the salt basin when the potash deposits were precipitating. The lower $\delta^{11}$B values possibly have a close relationship with the influence of nonmarine input or fluvial influx.

It is very possible that the fresh water rich in lighter $^{10}$B induced the lower $\delta^{11}$B values when these evaporites were precipitating. Although some geochemical evidence suggests that the evaporation is a continuous process (Hite and Japakasetr, 1979; El Tabakh et al., 1999), due to not being significantly subject to dissolution and recrystallization, the Br content in salts was little influenced but the $\delta^{11}$B values were to a great extent affected by the freshwater into salt basins. These values which still fall within the range of marine borates in this study indicate that the supply of the freshwater is not high enough to substantially alter the boron isotopic composition of the seawater (Swihart et al., 1986). At the same time, the existence of boracite ooids also suggests that the borates in borehole FJ should not be affected by riverine water. Otherwise, these ooids could not exist in the potash layer and would dissolve and recrystallize. Consequently, whether the seawater has been modified or supplied by deep-seated geothermal fluid or terrestrial inputs, the boron isotopic compositions of borates from potash-bearing evaporite deposits in the area should reflect the boron isotopic composition of late Cretaceous seawater.

6. Conclusions

The borates in the potash layer of borehole FJ are abundant and two borates (boracite and hilgardite) were identified. The boracites occur as crystals and ooids. The former are commonly cubic, tetrahedral crystals. The latter often show concentric or radial microfabrics, or the coexistence of both. According to studies on ooids of carbonates and other minerals, these boracite ooids are possibly primary.
The range of δ11B values is from +21.30‰ to +32.94‰, averaging +29.74‰. In potash layers, the δ11B values were seemingly variable because of the influence of fluvial influx. Although the chemical signature of seawater was modified by volcanism or structure movements in the Cretaceous, the evidence from boron isotopic composition indicates that the source of potash-bearing evaporites in the Vientiane Basin should be derived from seawater.

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