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Isotopic Application in High Saline Conditions

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Abstract

Evaporite minerals record the hydrogeochemical conditions in which they precipitated. And therefore they can be used to reconstruct the paleoclimate and paleoenvironments. Evaporite minerals are also major sources of industrial minerals including gypsum, halite, borates, lithium concentrates, and others. Because of their scientific significance and economic importance, evaporite minerals and their isotopic hydrochemical processes linked to their formation have been the focus of many geologists and paleoclimatologists. This chapter will discuss the application of isotopes of hydrogen, oxygen, sulfur, strontium, and boron in saline conditions. This will include the following: the $\delta^{18}\text{O}$ and δD of hydrated water of gypsum and their paleoclimate since 2.2 Ma in the Qaidam Basin, NE Tibetan Plateau; the $\delta^{18}\text{O}$ and δD of the interlayer water of clay minerals in salar lacustrine sediments; and the $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{34}\text{S}$, and $\delta^{11}\text{B}$ of halite from evaporite deposits in Khorat Plateau, Laos, and Yunnan and their application in the origins of brine.

Keywords: oxygen and hydrogen, Sr isotope, sulfur isotope, boron isotope, salt minerals

1. Introduction

Evaporite minerals record the hydrogeochemical conditions in which they precipitated. And therefore they can be used to reconstruct the paleoclimate and paleoenvironments. Evaporite minerals are also major sources of industrial minerals including gypsum, halite, borates, lithium concentrates, and others. Given their scientific significance and economic importance, evaporite minerals and their isotopic hydrochemical processes linked to their formation have become the focus of many geologists and paleoclimatologists. The Qaidam Basin and Lanping-Simao Basin (LSB) in China and Khorat Basin (KB) and Sakhon Nakhon Basin (SNB) in Thailand and Laos, which have thick sequences of evaporites, have been the focus of study by researcher concerned with its mineral resources, geochemistry, paleoenvironmental evolution, and tectonic uplift [1–3].

Water is nearly ubiquitously in nature. Its isotopic compositions also were recorded in many minerals. In order to identify the past conditions at which sediments formed, many studies focused on the stable isotopes of carbon and oxygen as tracers of environmental conditions. However, we know little about the $\delta^{18}\text{O}$ and δD in saline conditions. On the other hand, halite and gypsum are two common minerals in evaporite deposits. Today, exploited evaporite deposits are most found

in the arid and semiarid deserts of the world (the areas between latitudes 15° and 45° both north and south of the equator). Tectonics, climate, and origins of brine are the prime controls on most evaporite deposits. However, the origins of brine was a big topic for some giant evaporite deposits, for example, the evaporite deposit in Khorat Basin (KB) in Thailand, Sakhon Nakhon Basin (SNB) in Laos, and Lanping-Simao Basin (LSB) in China. Almost all large potash deposits are associated with marine fluids (such as the deposits in Thailand, the United States, Germany, Russia, France, and Brazil), whereas some small potash deposits are with fluids of continental source (such as deposits in the Qaidam Basin, Western Tibet, China) [1, 2]. The isotopes of S, Sr, and B of halite could be very useful in determining the origins of brine. So this chapter will use well-known accepted methods to analyze minerals (halite, gypsum, and clay minerals) and stable isotopes ($\delta^{18}\text{O}$ and δD , $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{34}\text{S}$, and $\delta^{11}\text{B}$) to discuss their application in paleoclimate and origins of brine.

2. The $\delta^{18}\text{O}$ and δD in saline conditions

2.1 Geological setting and the Core SG-1 in the Qaidam Basin, NE Tibetan Plateau

The Qaidam Basin is a Mesozoic-Cenozoic sedimentary basin located on the northern margin of the Tibetan Plateau in China (**Figure 1**). The Asian inland drought basin was formed as the result of intracontinental deformation and plateau uplift due to the collision of the Indian and Eurasian Plates. It is bordered by the Kunlun Mountains to the south, the Qilian Mountains to the northeast, and the Arjin Mountains to the northwest, which have altitudes ranging from 4000 to 4500 m asl to over 5000 m asl. A network of faults exists within the basin [3]. The Paleogene and Neogene strata are widespread and include intrusive rocks. From the Middle Oligocene to the Upper Pliocene, the strata consist of mudstones, calcareous mudstones and marls, intercalating siltstone, very thick gypsum, and rock salt beds in the western basin [4]. Some secondary or subsidiary basins have become well developed since the Middle Pleistocene as a result of slow uplift [1]. Lacustrine sediments in

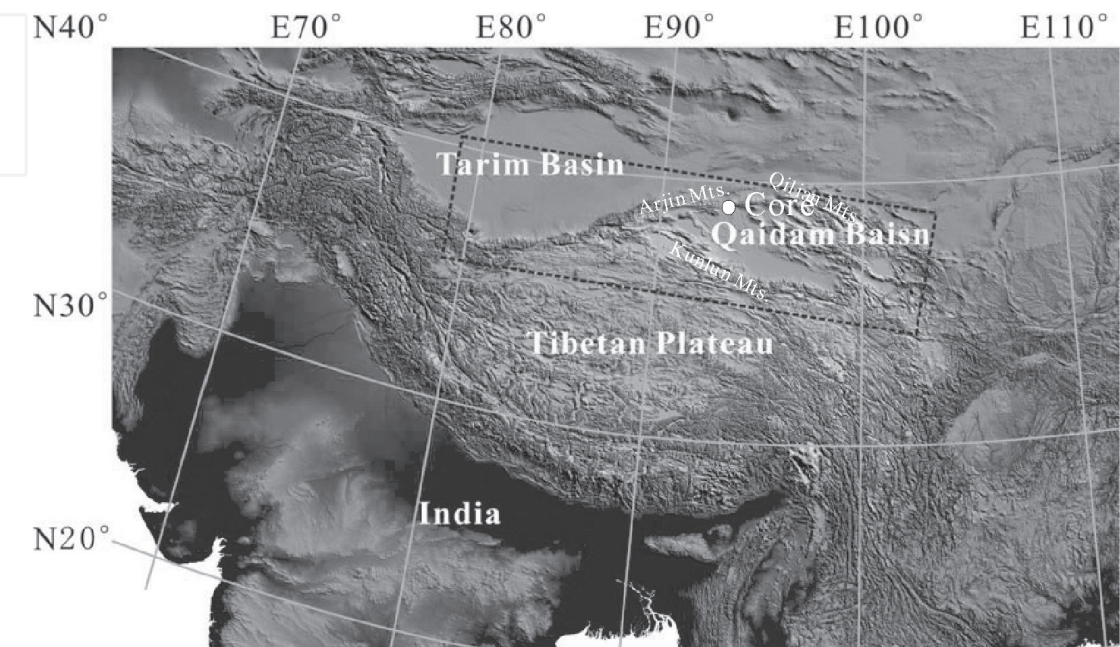


Figure 1.
Map of the Qaidam Basin showing the core site.

the basin cover an area of 30,000 km² with strata up to 700 m thick [4]. Abundant records of palaeo-lake level and paleoclimatic changes are indicated by various proxies, such as pollen, ostracods, evaporite minerals, and isotopic geochemistry [5, 6]. Studies on evaporite minerals and hydrochemistry and geochemistry of salt lakes have been ongoing for about 50 years because of great economic significance [1, 2, 5, 7]. However, no two drainage basins have identical climatic and hydrologic conditions, and even adjacent basins can show striking variations in evaporite mineralogy [8].

The Core SG-1 (38°24'35.3" N, 92°30'32.7" E, 2900 m asl) was located in a playa in the Qahansilatu sub-basin, western Qaidam Basin (**Figure 1**). The core spanned from 2.77 to 0.1 Ma, dated by paleomagnetism and optically stimulated luminescence (OSL) with a sedimentary rate of 26.1–51.5 cm/ka [9]. The sedimentary sequence is composed of clay, clay-silt, and siltstone intercalated with salt layers (mainly halite), marl beds, and thin and/or scattered gypsum crystals, indicating clay-silt and halite-marl depositional cycles (**Figure 2**). The fluctuation between evaporite minerals and carbonaceous clay strata indicates a shift between dry and wet climates. Gypsum and halite make up the majority of the evaporite minerals in the core [11, 12]. During the last ~2.8 Ma, the lake basin evolved from a semi-deep fresh lake to a semi-brackish lake (2.8–2.2 Ma), to a perennial saline lake (2.2–2.0 Ma), to a shallow brackish lake (1.8–1.6 Ma), to a perennial saline lake (1.2–0.6 Ma), to a playa saline lake (0.9–0.6 Ma), and to a saline mudflat (0.6–0.1 Ma) [10] (**Figure 2**). Multi-proxies, such as sedimentary features [10], salt minerals [11], isotope records [13, 14], and rare earth elements [15] of the study area, indicate the long-term persistent aridification of inland Asia since 2.8 Ma.

2.2 Clay minerals and the $\delta^{18}\text{O}$ and δD of their interlayer water

2.2.1 Clay minerals

Clay minerals have been used to reconstruct paleoclimates and environments since Singer’s review in 1984 [16]. It is common that the clay minerals undergo

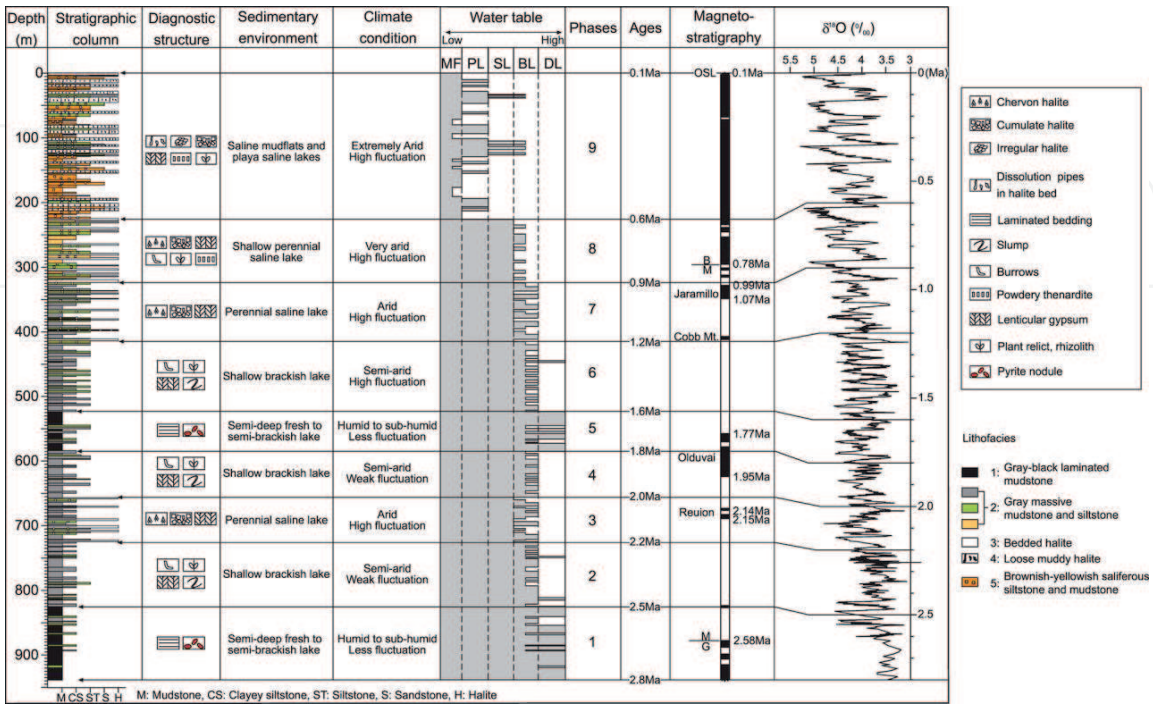


Figure 2. Lithology, sedimentary environment, sediment accumulation rates (SAR), and magnetostratigraphic ages of the Core SG-1 (after Zhang et al. [9] and Wang et al. [10]). DL, semi-deep fresh to semi-brackish lake; BL, shallow brackish lake; SL, perennial saline lake; PL, playa saline lake; and MF, playa saline mudflat.

diagenetic transformations or postdepositional diagenetic changes, and as a result, some paleoclimate information of clays will be overprinted or changed. However, there are still lots of studies to use clay minerals to reconstruct paleoenvironments and paleoclimates. The isotopic exchange rates between the interlayer water of clay minerals and the ambient water are very fast and, in general, are less than a few days. However, in saline conditions, we know little about the isotopic exchange between them.

The clay mineral assemblages in the Core SG-1 are shown in **Figure 3**. The curves of chlorite and illite abundances are similar, but they are different with those of the kaolinite, smectite, and I/Sm (**Figure 3**). The curve of smectite content shows a decreasing trend with decreasing depth, and that of the illite content shows an increasing trend slightly (**Figure 3**). The XRD analyses suggest that the I/Sm in the core exhibits order (R_3 I/Sm) (mixed layer of I/Sm > 80%). R_1 I/Sm is more stable than any other mixed layer I/Sm phase because it has a unique structure, composition, and order [17]. The clay minerals that were identified as R_3 I/Sm by XRD analyses are possible to be mixtures of discrete smectite and R_1 I/Sm [17].

The diagenesis of clay minerals in lacustrine sediments is a disputed topic. The clays in Core SG-1 in the Qaidam Basin probably underwent early diagenesis based on their curves and relationship between them (**Figures 4 and 5**) [18]. Climate changes, to some extent, control on the degree of alteration of the primary minerals and the composition of the secondary products. In the clay minerals, the exchange between the interlayer water and the ambient water recorded the diagenetic information. For instance, the $\delta^{18}\text{O}$ and δD of the different clays and interlayer water record temperatures that range from surface temperatures to hydrothermal temperatures of about 150–200°C [19]. In situ precipitation of I/Sm minerals may take place in chemical and isotopic equilibrium with the reacting solution [20, 21]. However, in high saline conditions, the reaction or the above exchange may be extremely slowly.

2.2.2 The $\delta^{18}\text{O}$ and δD of the interlayer water

The $\delta^{18}\text{O}$ of the interlayer water ranged from –11.8 to 82.95‰ with the average of 20.8‰, and the δD ranged from –114.3 to 165.5‰ with the average of –35.6‰

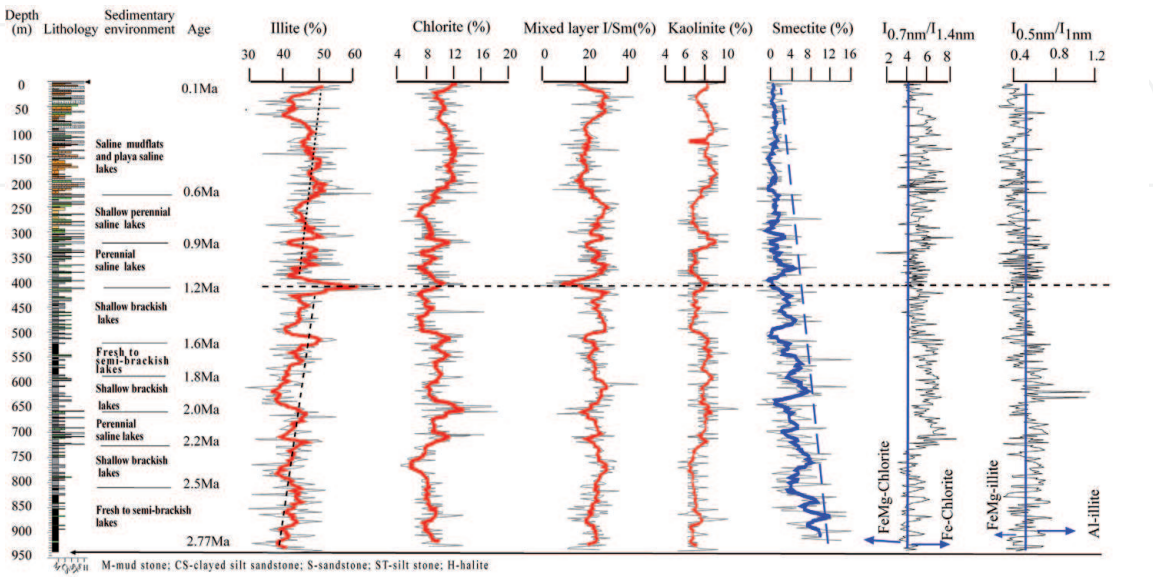


Figure 3. Variations in the amount of illite, chlorite, kaolinite, smectite, and illite/smectite (I/Sm) and in the chemistry of illite (15Å/110Å ratios) and chlorite (17Å/114Å ratios). Colored lines represent a five-point running average. Sedimentary environments are from Wang et al. [10]; ages are from Zhang et al. [9].

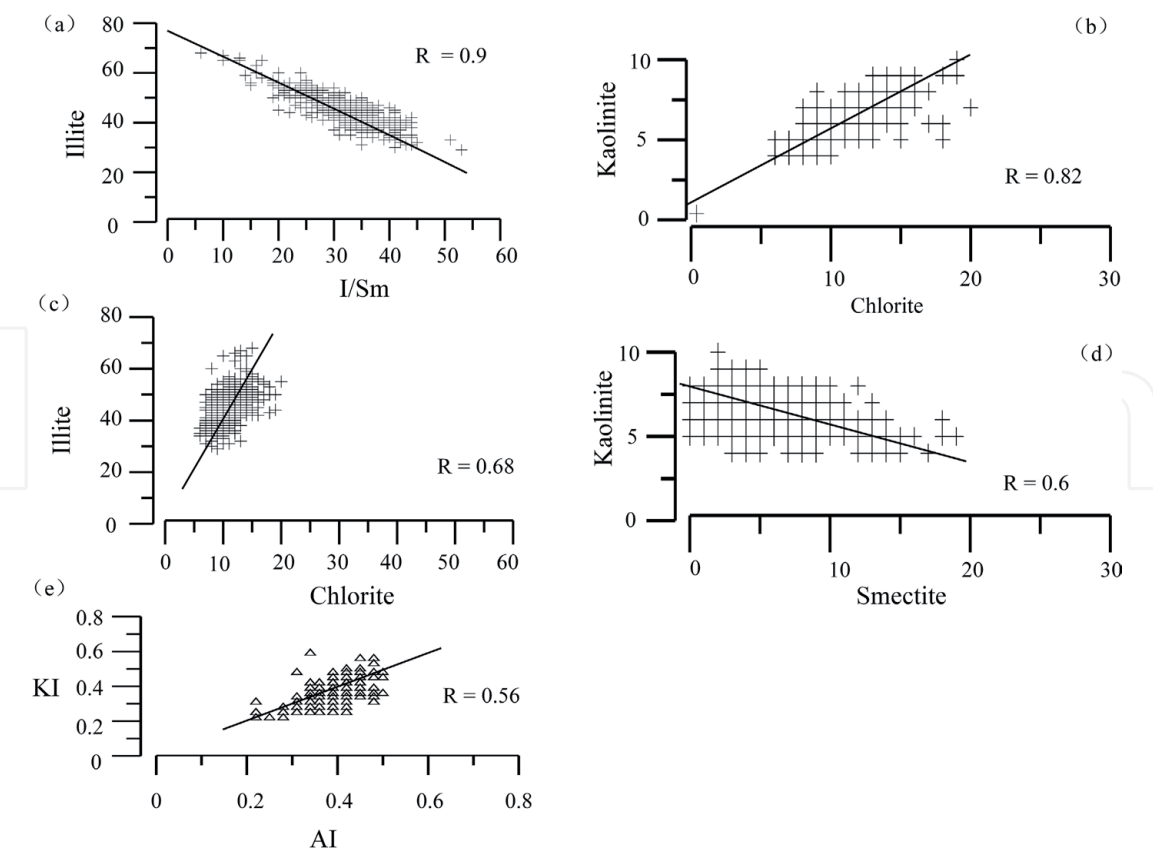


Figure 4.
Correlations between the abundances (%) of (a) illite and I/Sm, (b) chlorite and kaolinite, (c) illite and chlorite, (d) smectite and kaolinite, (e) KI (Kübler index), and AI (Árkai index).

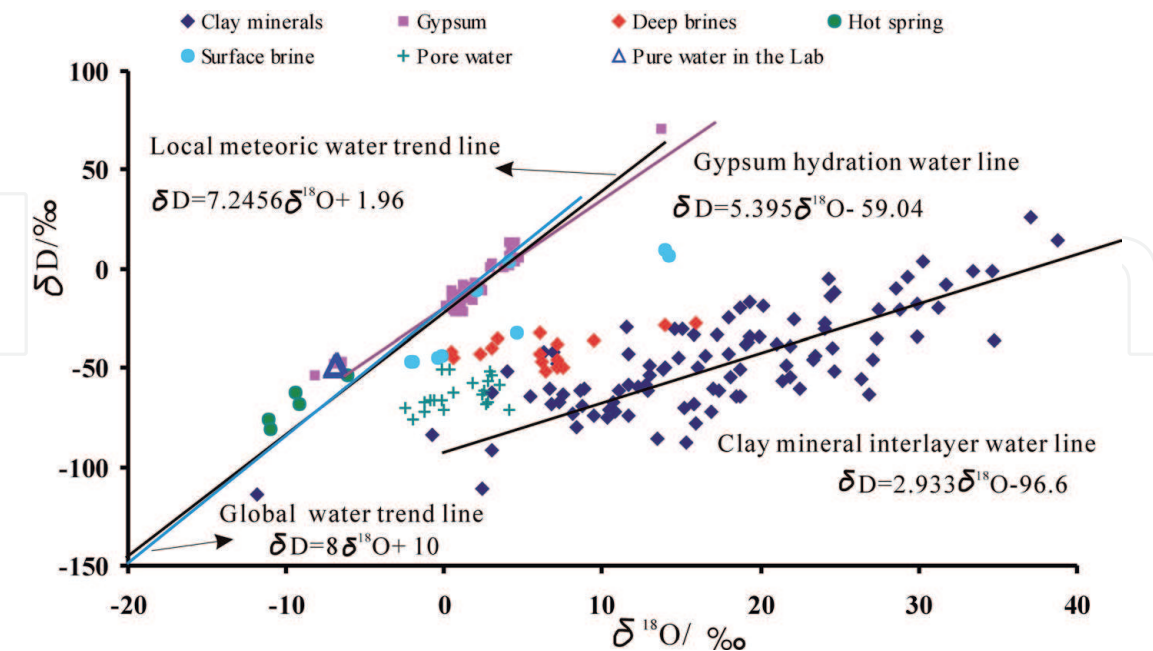


Figure 5.
Relationship between the $\delta^{18}\text{O}$ and δD of the interlayer water of the clay minerals and different types of water from the Qaidam Basin. The global and modern local meteoric water lines are from Craig [22] and Li et al. [23], respectively. The present-day precipitation and hot spring data are from Zhang [24]. Gypsum hydration water data are from Li et al. [14], deep brine water data are from Fan et al. [25], and surface water and pore water data are from Xiao [26] and Fan et al. [25]. The large differences in the $\delta^{18}\text{O}$ and δD of the pure water and the interlayer water of the clay minerals suggest that the interlayer water did not exchange with the pure water and other water used during the processing and pretreatment.

(**Figure 5**). They exhibit a roughly linear relationship and are significantly correlated ($R = 0.96$), indicating that these isotopes share the same sources. The isotopes of the interlayer water possibly recorded the brine composition which contained interstitial water or pore water derived from lake water and underwent strong evaporation. This could be understood as the following. (a) Some of the $\delta^{18}\text{O}$ and δD of the interlayer water are close to those of surface water, deep brine, and pore water. (b) The rates of isotopic exchange between the interlayer water and the ambient water are very fast and, sometimes, are less than a few days. Therefore, the exchange rate between the structural oxygen of the clay minerals and that of the ambient water could be insignificant over a 2.8 Ma time span at a temperature of $\leq 100^\circ\text{C}$ [27, 28]. (c) The slopes of the $\delta^{18}\text{O}$ and δD of the interlayer water are smaller than that of the gypsum hydrated water that recorded the evolution of lake water or subsurface water (**Figure 5**), suggesting the interlayer water underwent more stronger evaporation than gypsum hydrated water. (d) The $\delta^{18}\text{O}$ and δD of the interlayer water of clay minerals are very different with those of pure water (**Figure 5**), which was used to treat the clay minerals.

Independent of the oxygen isotopic exchange, the hydrogen isotopic exchange occurs by a proton exchange mechanism [28, 29]. The hydrogen isotopic exchange between smectite and its ambient water is very fast and significantly relative to that between illite and kaolinite with their ambient water [28].

2.3 Gypsum and the $\delta^{18}\text{O}$ and δD of hydrated water

2.3.1 Gypsum

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), one of the most abundant evaporite minerals occurring as a syndepositional evaporite, carries information about brines from which they precipitate. There are several shapes of gypsum crystals (**Figure 6**). These prismatic and tabular gypsum layers were vertically aligned, indicating primary subaqueous precipitates and with bottom nucleation [31, 32]. Some euhedral gypsum crystals were scattered in the mudstone-siltstone layers, which are possibly formed by evaporation of pore water or interstitial brine and regarded as diagenetic gypsum. Based solely on their morphology, it is not easy to confirm gypsum to be synsedimentary or diagenetic, because there is no diagnostic relationship between crystal morphology and depositional environment [33]. Besides the aligned gypsum, scattered euhedral crystals may be significant for understanding the evolution of lake water, because pore water or interstitial brine may have originated from infiltration of lake water. The Core SG-1 showed an increase of evaporite mineral contents upward, and the strata were mainly horizontal and not affected by tectonic deformation [10]. Therefore, these selected gypsums may have been primary in origin in arid, or aqueous, young lacustrine. These environments contain deposits that have never been exposed or deeply buried and may also retain their original isotopic compositions [34–36].

Minor cations such as Sr^{2+} , K^+ , and Mg^{2+} may be incorporated into gypsum lattice via substitution for Ca^{2+} during the coprecipitation process because they have similar ionic radii. Different cations are selectively attracted to particular faces [37, 38]. For example, the (1 1 1) face is covered by either calcium ions or sulfate clusters and the (1 1 0) and (0 1 0) faces by both calcium and sulfate clusters [39]. Na^+ is preferentially adsorbed on (1 1 1) surface of sulfate salts that is dominantly occupied by Ca^{2+} [39, 40]. However, the presence of Na^+ also impedes the (1 1 1) face growth and, as a result, minimizes parallel to its c axis [36, 39]. K^+ has a similar inhibitory effect [40]. Because of the difference in coordination number between Ca^{2+} (eight in gypsum) and Mg^{2+} (six in most minerals), Mg^{2+} will disturb gypsum

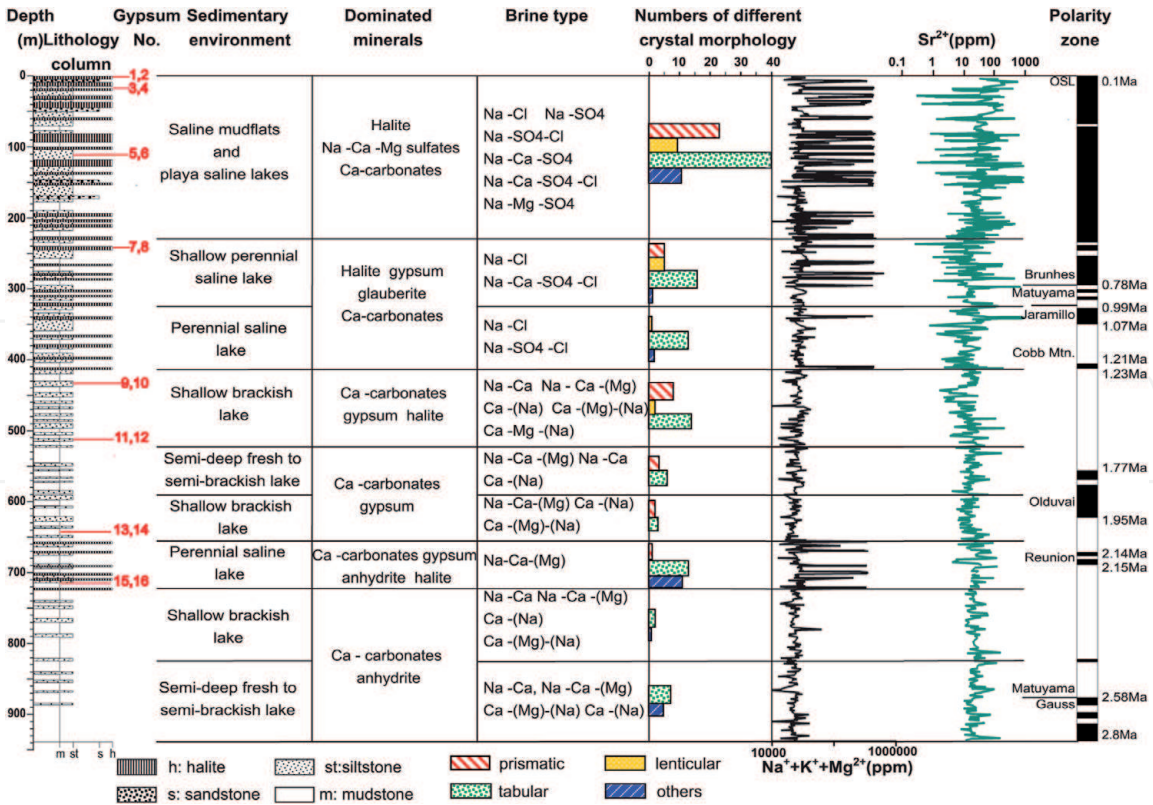


Figure 6. The monoclinic gypsum exhibits four principal forms in the Core SG-1 [30]: prismatic crystals, lenticular crystals, and tabular crystals. The tabular and prismatic crystals tend to increase with decreasing depth. The red numbers mean that the same kind of crystal morphology can appear in different environments and different crystal morphologies can also occur in the same depositional environment.

growth along c axis [41]. Preferentially adsorbed on the (1 1 0) face, Sr²⁺ forms epitaxial deposits of strontium sulfate [39]. Therefore, K⁺, Na⁺, and Mg²⁺ make the c value smaller, while Sr²⁺ reduces a and b values. As a result, there have different gypsum morphologies.

2.3.2 The $\delta^{18}\text{O}$ and δD of hydrated water

The $\delta^{18}\text{O}$ of gypsum hydrated water ranged from -4.21 to 8.69% , with average of 5.74% ; and the δD was from -72.77 to 49.73% , with average of -28.09% . They exhibit a roughly linear relationship with the slope of 5.39 , and its mother water-line has a slope of 5.52 (Figure 7). The $\delta^{18}\text{O}$ and δD appear to be much lower than those of today's mean precipitation ($\delta^{18}\text{O} = -9.25\%$ and $\delta\text{D} = -41.3\%$) [14]. This indicated a slightly weaker evaporation and/or colder climate than today [36, 43]. On the other hand, the $\delta^{18}\text{O}$ and δD are close to those of the Altyn Tagh Mountain groundwater that sourced from meteoric water (Figure 7). It is therefore likely that meteoric water was the main source of hydration water during gypsum formation.

In general, gypsum could be formed in the following ways: in situ formation (e.g., resulting from the oxidation of sulfide minerals); hydration of anhydrite; and direct deposition from an evaporating solution saturated with gypsum [44]. If gypsum was formed in situ formation, the $\delta^{18}\text{O}$ and δD of hydrated water would reflect those of meteoric and/or surface waters [44, 45]. If it is formed from the hydration of anhydrite, which is assumed to be a Rayleigh process, both the hydration water and its mother water would be expected to move along a line with a negative $\Delta\delta\text{D}/\Delta\delta^{18}\text{O}$ [46, 47]. In this study, the $\Delta\delta\text{D}/\Delta\delta^{18}\text{O}$ value was 5.39 [14], suggesting evaporation to be the major geochemical process for gypsum deposition, that is, the gypsum in the Core SG-1 was likely to deposit directly from brines. The degree

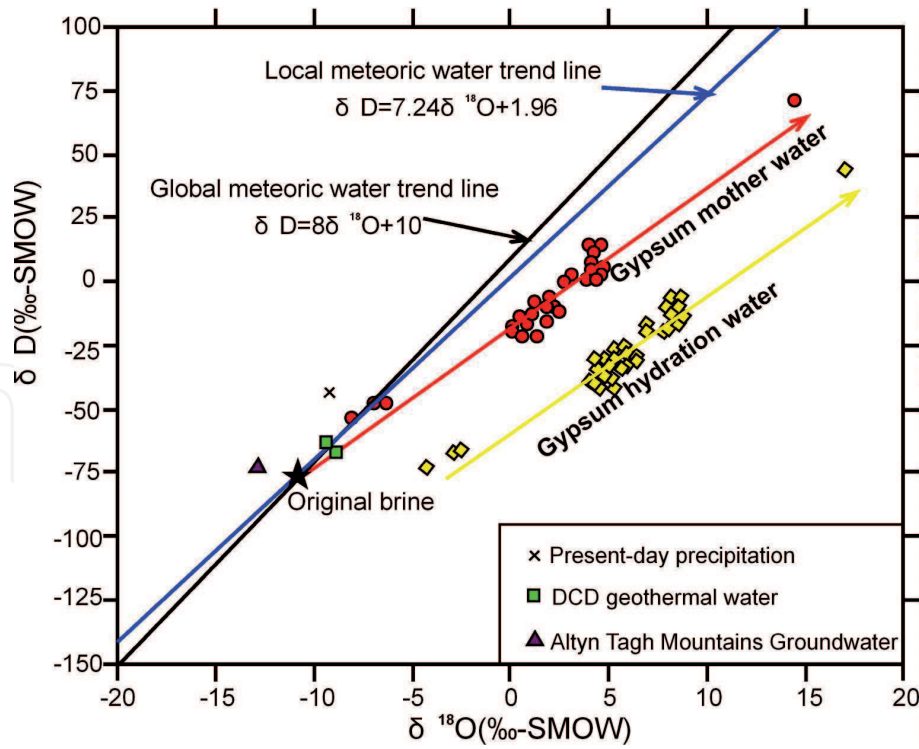


Figure 7.

Relationship between $\delta^{18}\text{O}$ and δD of gypsum hydration water and mother water as compared to meteoric water and different types of water from the Qaidam Basin. The global and modern local meteoric waterlines are from Craig [22] and Li et al. [23], respectively. The present-day precipitation and Dachaidan geothermal water are from Zhang [24]. Altyn Tagh Mountain groundwater data are from Wang et al. [42].

of evaporation depends upon the salinity and atmospheric humidity [22, 48]. In humid conditions, $\Delta\delta\text{D}/\Delta\delta^{18}\text{O}$ gradients are usually between ~ 5 and ~ 6 , whereas the gradient can be low as 2.5–4 in arid regions. The evaporation line gradient for present-day Qaidam Basin meteoric water is lower 4.4 [24], which is less than that of gypsum hydration water in Core SG-1. This suggested that brine in the 2.2–0.1 Ma had lighter isotopes than today's local meteoric water and that evaporation was weaker than today's.

2.4 Paleoclimatic implications

The climate in the area indicates a long-term persistent aridification event in inland Asia, which is supported by several climate proxies [10–15]. The $\delta^{18}\text{O}$ and δD of the clay interlayer water and gypsum hydrated water both reflect the compositional variations of the lake water or pore water and record changes in environment [14, 18]. According to the significant positive relationship between $\delta^{18}\text{O}$ and δD and their low slope (2.933, **Figure 7**), most of the interlayer water could be from pore water and lake water in an evaporative environment. The main factor contributing to the variations in the $\delta^{18}\text{O}$ and δD water was probably E/P value oscillations, which were linked to the climate changes.

Both the lake water and gypsum hydrated water, their curves of the $\delta^{18}\text{O}$ and δD , display a stepwise increasing trend (**Figure 8**), indicating a drying trend from 2.2 to 0.1 Ma. This is consistent with the global cooling trend, which is also recorded by the $\delta^{18}\text{O}$ of marine sediments (**Figure 8**). The lower values of $\delta^{18}\text{O}$ and δD in 1.2–0.1 Ma than in 2.77–1.2 Ma (**Figure 8**) agreed with the sedimentary changes from brackish lakes to saline and playa lakes [10]. Compared with brackish lakes, it is harder for brines in mudflat and playa lakes to lose water. The occurrence of Na_2SO_4 -bearing salt minerals such as glauberite, thenardite, mirabilite, and bloedite [11] and the high $\delta^{18}\text{O}$ of carbonates [13] also suggest the climate to be extremely

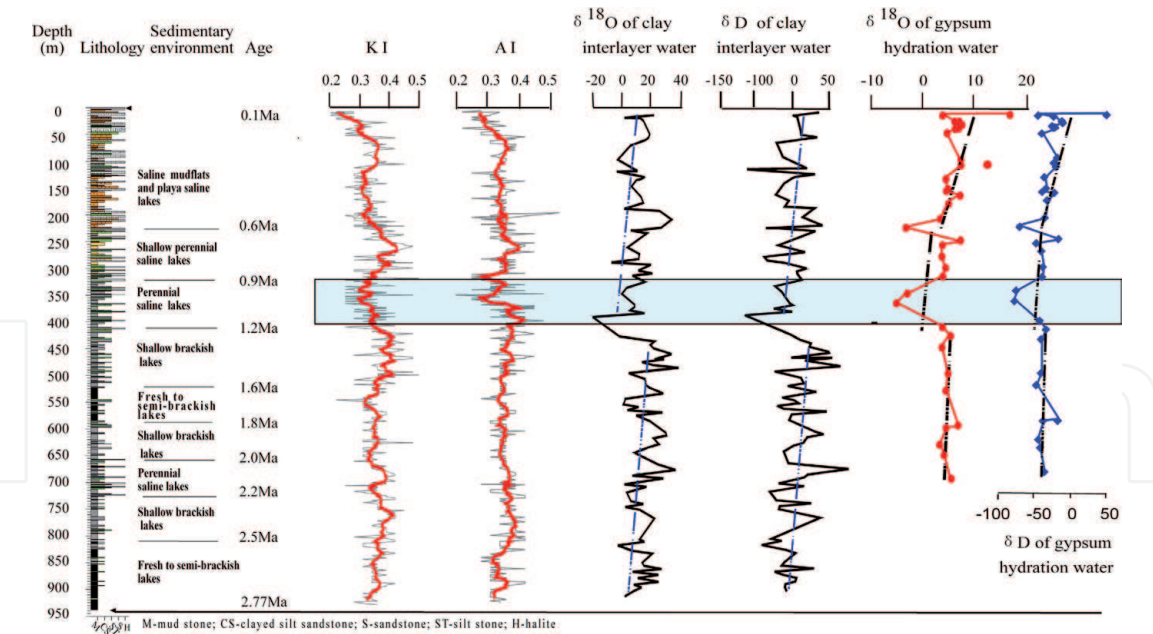


Figure 8.
Hydrogen and oxygen isotopes of gypsum hydrated water and interlayer water of clay minerals vs. depth. The lithologic column and sedimentary environment are from Wang et al. [10]. The ages were based on paleomagnetic results of Zhang et al. [9].

arid in 1.2–0.1 Ma. At about 1.2–1.1 Ma, the low value was likely due to the MPT cold event, which was also recorded in other places in the Qaidam Basin [49]. This is also consistent with other proxies in Central Asia such as lithological and sedimentary records, evaporative minerals, pollen records, grain size, and trace elements [10–13, 49–51].

In summary, δ¹⁸O and δD of the gypsum hydrated water, and interlay water of clay in high saline conditions, both have recorded environmental signals.

3. The isotopes of Sr, S, and B of halite in saline conditions

Halite is common in evaporite deposits. Today, exploited evaporite deposits are most found in the arid and semiarid deserts of the world (the areas between latitudes 15° and 45° both north and south of the equator). Tectonics, climate, and origins of brine are the prime controls on most evaporite deposits. However, the origins of brine were a big topic. Giant evaporite deposits typically originate from brines with a marine or/and land origin(s), along with varying inputs from deeply circulated meteoric, basinal, and hydrothermal fluids [52]. The isotopes of S, Sr, and B of halite could be very useful in determining the origins of brine. We used well-known accepted methods to analyze halite and the isotopes to distinguish origins of brine for the evaporite deposits in Laos and Southern China.

3.1 Geological setting and the Core ZK2893

3.1.1 Geological setting in Laos and Southern China

Southeast Asia is composed of a series of Gondwana-derived continental blocks which experienced heterogeneous collision with the closure of multiple Tethyan Ocean branches (see reviews in Metcalfe [53, 54]). The Khorat Basin (KB) in Thailand and Sakhon Nakhon Basin (SNB) and the Lanping-Simao Basin (LSB) in Southwest China belong to the Indochina Block (**Figure 9**). The central part of the

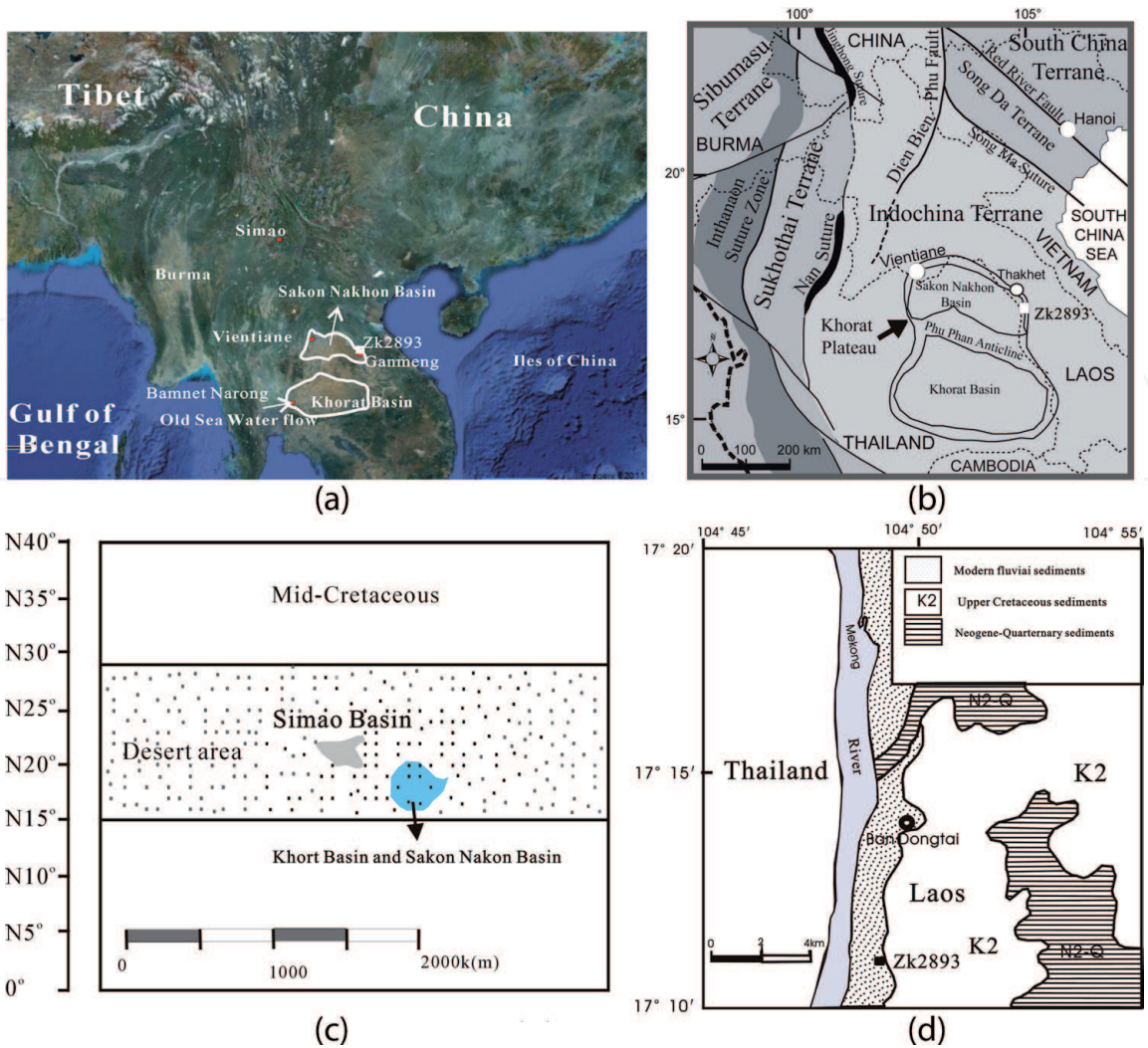


Figure 9. (a) Google Earth map showing the locations of the Sakon Nakhon Basin and the Khorat Basin; (b) tectonic map modified from Sone and Metcalfe [55] and El Tabakh et al. [56]; (c) location of Khorat Basin and Sakon Nakhon Basin, in the Middle and Late Cretaceous (after El Tabakh et al. [56]); (d) geological map showing the general distribution of sediments in the study region (after Zhang et al. [57]).

Indochina Block (the Khorat Plateau) is relatively rigid with respect to the Simao Terrane (including the LSB) and has been experiencing clockwise rotation of about 15° up to the present day [58, 59]. The location of LSB changed from 25.7° N in Cretaceous to 18.6°N in Paleocene and Eocene [60]. This suggested that the LSB was gradually southward approaching the KB and SNB.

During the Middle and Late Cretaceous, salts formed; however, these salt formations lie atop thick nonmarine sediments of the Mesozoic Khorat Group. The nonmarine sediments were more than 5 km thick, which were deposited in the Late Triassic [56, 61, 62]. From the very Late Triassic to the Early Cretaceous, the KB and SNB were filled with fluvial and lacustrine facies [56]. Due to the occurrence of similar salt minerals within the same tectonic belt in KB and the LSB, they have formed in brines from similar sources [63].

In the mid-Cretaceous, the basins (LSB, KB, and SNB) were within the sub-tropical high-pressure belt [64]. However, the scale of the Mengye potash deposit in the LSB is much smaller than those in the KB and SNB of Thailand and Laos [63]. This surprising contrast drove many scientists to explore it in the area for ~50 years. But no consensus has therefore been reached regarding their fluid origins [56, 65, 66].

3.1.2 The Core ZK2893 in Laos

The lithostratigraphy contained three evaporite-clastic cycles, upper member (148.4 m to top), middle member (299.2–148.4 m), and lower member cycles (595.4–299.2 m), which are composed of evaporite unit and red-colored siliciclastic unit (**Figure 10**). The lithostratigraphy of the core could match with a reviewed section by El Tabakh et al. [56]. Blocky halite beds were only present in the lower and middle members (**Figure 11**). Chevron or cumulate crystals were well developed. Some thin salt units are observed (**Figure 10**), suggesting salt dissolution to be happened and their dissolved solutes to be mixed with their adjacent mudstone. Salt dissolution resulted in a lack of salts in many cores and the deposition of anhydrite [56].

3.2 Halite

The evaporite minerals in the halite beds are pure, massive red halite in ZK2893 (**Figure 11**). Some samples have trace or minor anhydrite content [60]. Compared with gypsum, the crystal shapes of halite seldom vary. But halite is much easier to be dissolved and recrystallized than gypsum. The halite crystals in the Core ZK2893 were primary, because (a) the primary fluid inclusions were developed (**Figure 12**), suggesting the halite was not dissolved; (b) the curve of Br in the core changed with depth (**Figure 13C**), consistent with the Br curve of primary halite (**Figure 13A**) and very different with the Br curve of secondary halite (**Figure 13B**); and (c) the Br of basal halite was the lowest in the core, suggesting the primary halite to have been preserved.

Basal halite is defined as the first Cl mineral to be precipitated during the evaporation of seawater/lake water. During syndepositional and early diagenetic processes, Br content of basal halite is stable [69, 71], and the initial compositions of

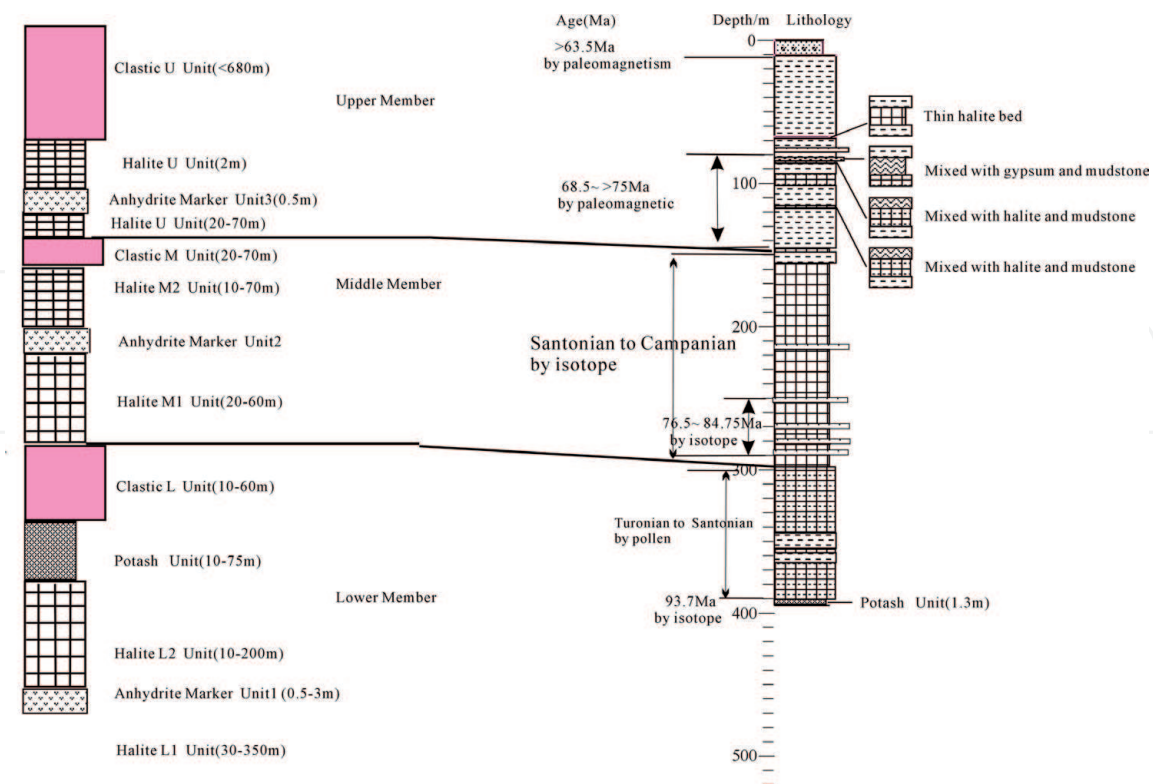


Figure 10. Left: lithostratigraphical review of the evaporite formation of the Khorat basin and Sakhon Nakhon Basins, after El Tabakh et al. [56]. Right: lithostratigraphy of Core ZK2893 (this study). The paleomagnetic ages are from Zhang [67]; the pollen ages are from Zhong et al. [62]; the isotopic ages are from Hansen et al. [68].



Figure 11.
Photos of halite in Core ZK2893 (after Li et al. [60]).

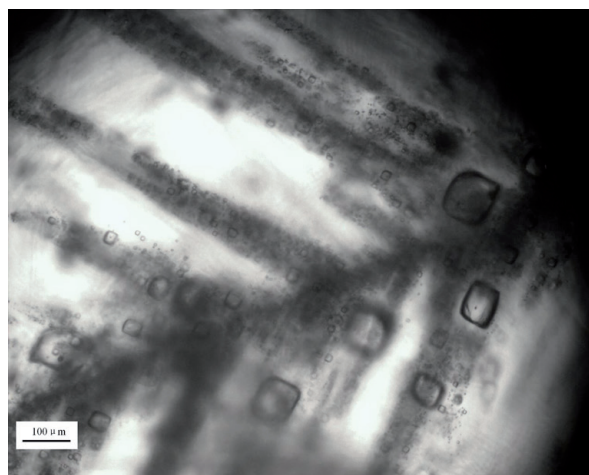


Figure 12.
Photomicrographs showing primary fluid inclusion banding in chevron halite.

brine are well-preserved in basal halite [60, 71]. Therefore, the Br content of basal halite can be used to reconstruct the composition and origins of paleo-water. For example, Siemann [71] used the Br content of primary basal halite to reconstruct the Br variations in seawater over the past 500 Ma.

3.3 The isotopes of sulfur, strontium, and boron

Isotopic compositions of sulfur, boron, and strontium could be more robust indicators of the origins of evaporites (marine vs. continental origins).

3.3.1 Sulfur isotope

Waters from continental sources in general have lower $\delta^{34}\text{S}$ values than those from contemporary seawater. The ^{34}S values of freshwater usually range from -5 to 5% , while that of recent seawater is globally uniform with value being $20 \pm 0.5\%$ [72]. Sulfate minerals (such as gypsum and anhydrite) have stable $\delta^{34}\text{S}$ values and are typically resistant to diagenetic alteration [72–74]. Factors influencing the $\delta^{34}\text{S}$ values of evaporative sulfates are marine and nonmarine contributions, reservoirs, and redox [72, 74]. For example, bacterial-facilitated sulfate reduction is preferentially enriched in lighter ^{32}S isotope, and therefore, the residual sulfate minerals

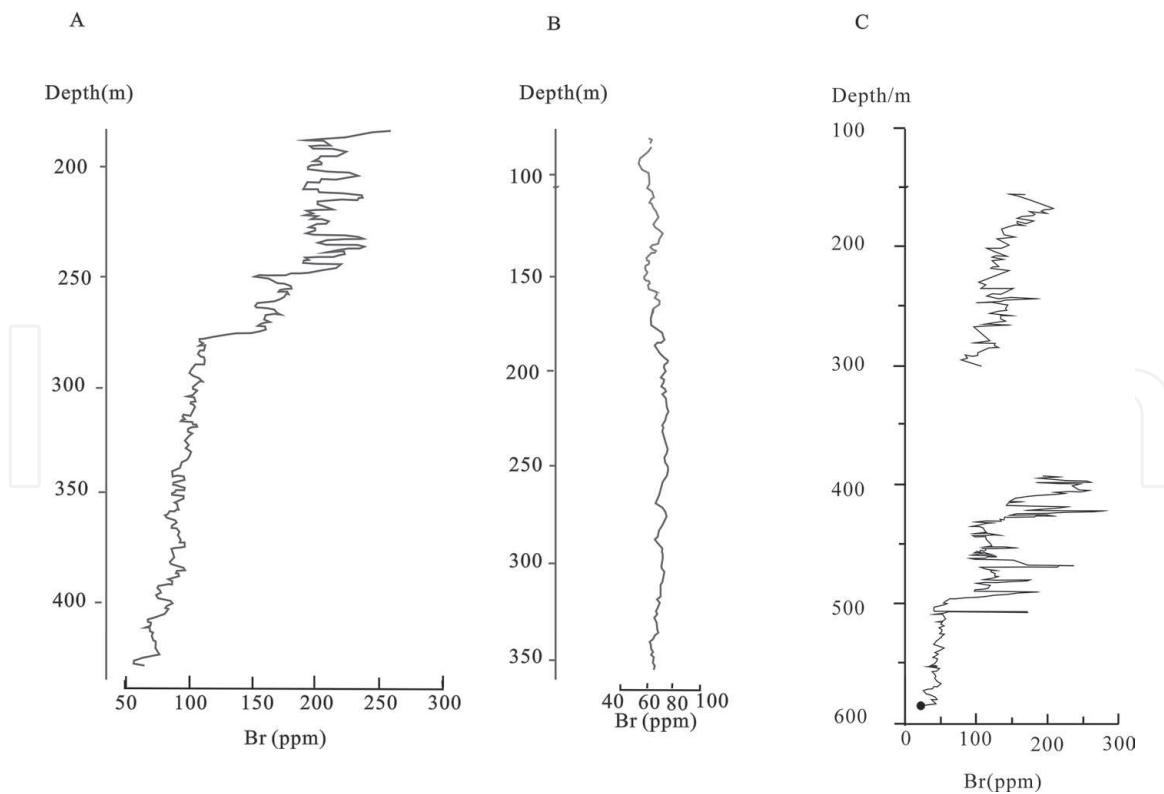


Figure 13.
 (A) Curves of Br in primary halite in KB, after Hite and Japakasetr [69]. (B) Curves of Br in secondary halite, after Hite and Japakasetr [69]. (C) Curves of Br in the Core ZK2893 in SNB, Laos [70], suggesting the halite in the core to be primary.

(such as gypsum) will enrich heavy ^{34}S [72, 73]. In contrast, reservoir effects can decrease $\delta^{34}\text{S}$ values of the subsequently precipitated gypsum. If sulfate evaporites precipitated in a closed system, the $\delta^{34}\text{S}$ values expectedly display a gradual decrease upward in a vertical stratigraphic sequence. The reservoir effect played an active role influencing the $\delta^{34}\text{S}$ values of gypsum, anhydrite, and halite in the abovementioned basins (**Figure 14**).

The average of $\delta^{34}\text{S}$ values increase from the lower to the upper member, which indicates an evaporation effect. Microbial effect on the core's $\delta^{34}\text{S}_{\text{SO}_4}$ values may be insignificant. This could be understood in the following. (a) There is no relationship between sulfate concentrations and the $\delta^{34}\text{S}_{\text{SO}_4}$ values of halite (**Figure 14**). Generally, microbial sulfate reduction can result in an inverse correlation of them [78]. And (b) the $\delta^{34}\text{S}$ values observed in the halite and anhydrite are very similar. Redox recycling of bacterial reduction can result in the enrichment of $\delta^{34}\text{S}$ values and significant difference within evaporites [72, 73]. Therefore, $\delta^{34}\text{S}$ in this study could be used to identify the origins of brine. In the Core ZK2893, all of $\delta^{34}\text{S}$ values are lower than, or similar to, those of contemporary seawater (**Figure 14**), suggesting a possible continental origin. Both the $\delta^{34}\text{S}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values of halite are lower than those of Middle Cretaceous seawater (**Figure 14**) with a short range dispersion, shorter than that between $\delta^{34}\text{S}$ and SO_4 values (**Figure 14**), suggesting that paleo-lake water possible to be mixed with freshwater.

3.3.2 Strontium isotope

Strontium is a divalent alkaline earth element. Its isotope composition is almost homogeneous with modern seawater with $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.709175–0.709235 [79, 80]. Because the Sr composition/isotope ratios for the weathering and erosion of rocks are high [81], the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for river water evince a large range

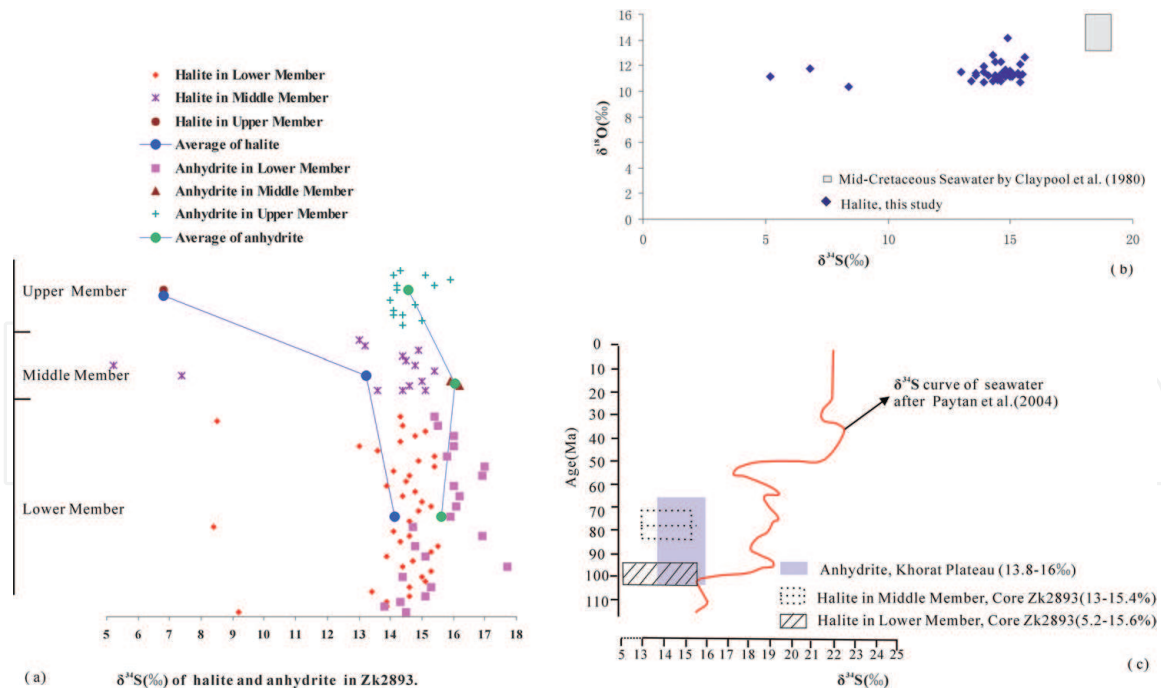


Figure 14.

(a) $\delta^{34}\text{S}$ values of halite for Core ZK2893 and anhydrite. Anhydrite data are from El Tabakh et al. [58] and Xu [75]. (b) Plot of $\delta^{34}\text{S}$ - $\delta^{18}\text{O}_{\text{SO}_4}$ of halite and Mid-Cretaceous seawater. Mid-Cretaceous seawater data are from Claypool et al. [76]. (c) Comparison of $\delta^{34}\text{S}$ values between halite in this study and seawater. The $\delta^{34}\text{S}$ curve of seawater from Paytan et al. [77].

from 0.7074 to 0.803 (**Figure 15**). In a continental setting, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for continental waters is almost always higher than that for marine waters (**Figure 15**). The $^{87}\text{Sr}/^{86}\text{Sr}$ values of Paleocene halite in the Qaidam Basin (a continental basin), for example, were higher than those of Paleocene seawater (**Figure 9**). Thus, the $^{87}\text{Sr}/^{86}\text{Sr}$ values of authigenic minerals are very variable and higher than those of seawater when the minerals are precipitated from a solution.

As no fractionation of Sr isotopes occurs during halite precipitation, the measured halite $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for Core ZK2893 (ranging from 0.707443 to 0.708587) could represent those of the parent solution. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the lower member ranged from 0.707443 to 0.708587, averaging 0.707693, while those for the middle member ranged from 0.70752 to 0.708105, averaging 0.70764. There was only one $^{87}\text{Sr}/^{86}\text{Sr}$ ratio value in the upper member, of 0.708163. In the lower member, the possible reasons for the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the upper part (**Figure 15**) are (a) the permeation of continental waters from the middle clastic unit into the halite layers and (b) an inflow of continental waters into the Sakhon Nakhon Basin during the shrinkage process of the basin. However, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios exhibit no significant variability in the middle member [83], suggesting no, or little, penetration of continental waters into the halite layers. The $^{87}\text{Sr}/^{86}\text{Sr}$ and $1/\text{Sr}$ halite ratios in Core ZK2893 do not show a linear relation but rather a weak positive relation (**Figure 15a**). Some $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are far higher than those of contemporary seawater, indicating the possible input of continental waters into these evaporite basins; these $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the lower member are lower than, or similar to, those of Cretaceous seawater; further, mean Middle Cretaceous $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are similar to those of paleo-seawater (**Figure 15b**), suggesting a marine remnant origin.

3.3.3 Boron isotope

Natural boron, a highly soluble element, has two stable isotopes (^{10}B and ^{11}B) with approximate abundances of 20 and 80%, respectively. Boron isotope

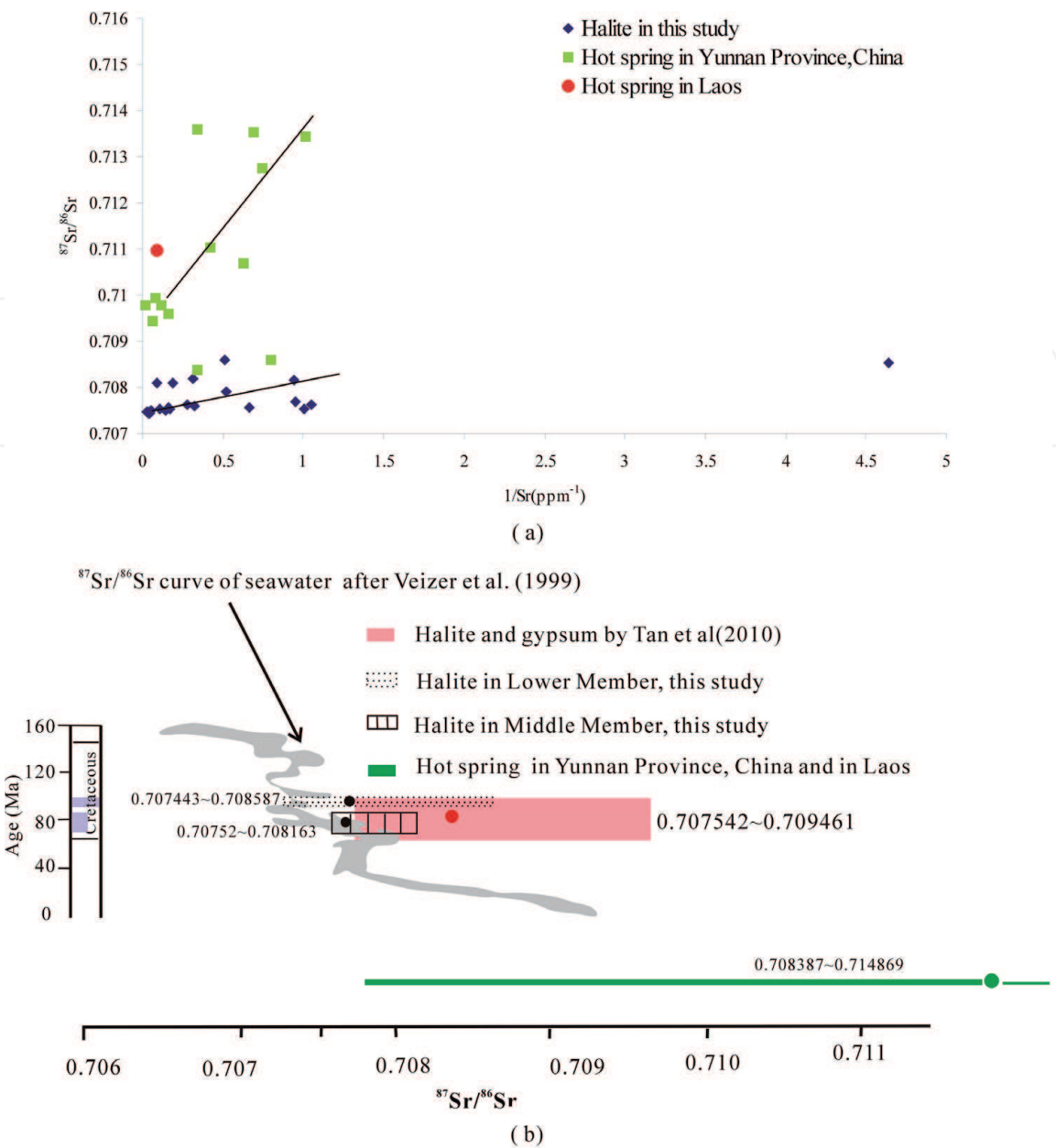


Figure 15.
(a) Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ and $1/\text{Sr}$ of halite and hot spring water; and (b) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in halite, gypsum, hot spring water and saline lake water: A dot indicates a mean value. Gypsum data are from Tan et al. [66], hot spring data for Yunnan Province in China, and for Laos, are from Bo et al. [82].

fractionation is dependent upon the distribution of boron species, temperature, and pH, but pH is the key factor [84–89]. Dissolved boron exists mainly in the form of $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4$, which are dominantly present as $^{11}\text{B}(\text{OH})_3$ at low pH values and as $^{10}\text{B}(\text{OH})_4$ at high pH values [85–88]. Because pH values increased with the increasing extent of evaporation, the minerals precipitated in early stages have higher $\delta^{11}\text{B}$ values than those of minerals precipitated in later stages. Generally, the sequence of $\delta^{11}\text{B}$ values of different minerals is following as: carbonate > gypsum > borate > halite > sylvite. As boron was present in inclusion [90], the $\delta^{11}\text{B}$ values of halite and sylvite are exactly representative of those for contemporary paleo-brines. Therefore, the $\delta^{11}\text{B}$ values of halite and sylvite are higher than those in carbonates and borate minerals, and all of minerals have lower $\delta^{11}\text{B}$ than those of brine. In the Core ZK2893, however, the $\delta^{11}\text{B}$ values of halite and sylvite were lower than those of borate minerals (**Figure 16**). One possible reason is that there have different sources of brines, such as continental, marine residue and groundwater/hydrothermal brine. In the LSB, China, most of $\delta^{11}\text{B}$ values of

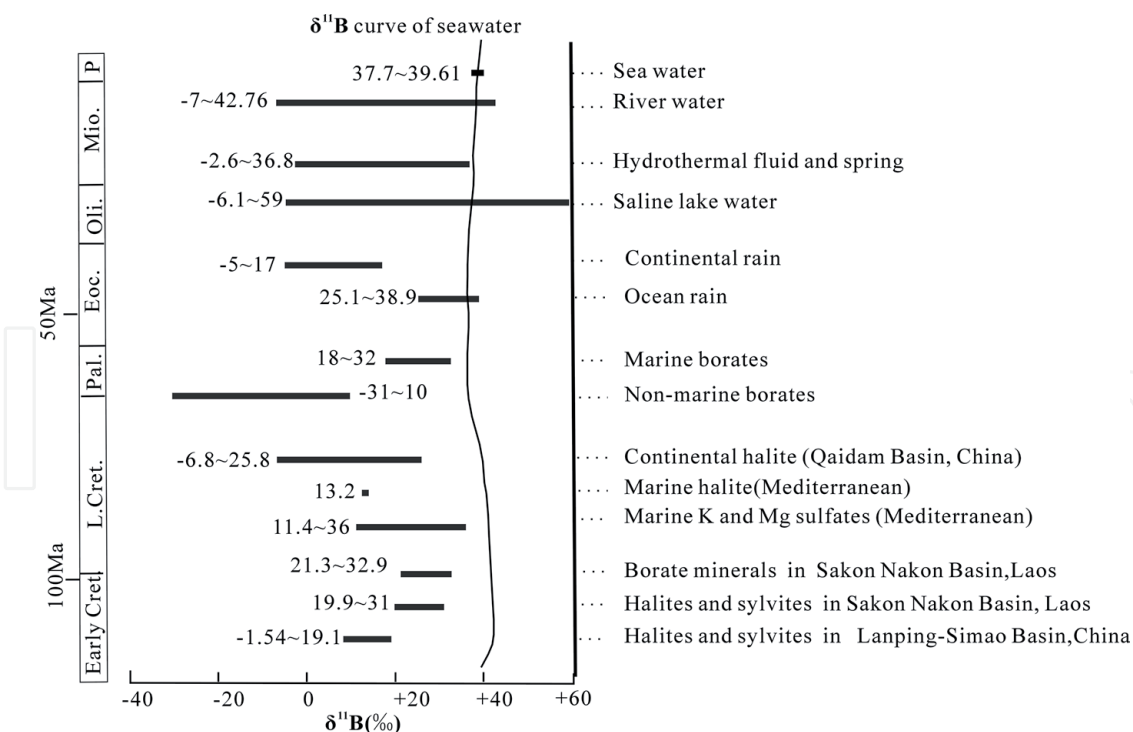


Figure 16.

$\delta^{11}\text{B}$ values from published papers. Marine and nonmarine borates after Swihart et al. [91], Xiao et al. [90], and Palmer and Helvacı [85]. Seawater after Vengosh et al. [86] and Foster et al. [89]. River water after Vengosh et al. [7]; Rose et al. [92]; and Lemarchand et al. [93]. Halite after from Vengosh et al. [86]; Liu et al. [94]; and Kloppmann et al. [95]. Borate minerals in SNB after Zhang et al. [96]. Halite and sylvite in SNB after Tan et al. [66]. Halite and sylvite in LSB after Zhang et al. [97]. Curve of seawater after Lemarchand et al. [98].

halite and sylvite ranged from -1.54 to 19.1% , which are lower than those in Laos ($19.9\text{--}31.1\%$) (**Figure 16**). This suggested the paleo-brines in LSB, China, are from Laos and diluted during the flow process.

Comparison of $\delta^{11}\text{B}$ values between known marine minerals and unknown minerals is a useful way to distinguish marine and continental origin. In nonmarine setting, some $\delta^{11}\text{B}$ values of hydrothermal fluid, saline lake water and river water, are higher than those of seawater (**Figure 16**), that is, lower $\delta^{11}\text{B}$ values of minerals than that of seawater are not indicate continental origin. The comparison of $\delta^{11}\text{B}$ between salt minerals is valid. Although the $\delta^{11}\text{B}$ values of halite in Laos were lower than those of seawater, they were near to those of marine borates (**Figure 16**). This suggested minor or trace marine origin. The $\delta^{11}\text{B}$ values of the evaporite in LSB in China are lower than, but some are near to, those of halite and sylvite in SNB, Laos, also suggesting continental origin with minor residual seawater.

In summary, halite isotopic compositions (in the form of $\delta^{34}\text{S}$ – $\delta^{18}\text{O}_{\text{SO}_4}$ values, $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{11}\text{B}$) appear to represent an original composition associated with brine. These isotopic proxies indicate that continental and hydrothermal origins are likely to be more important sources of evaporite deposits than marine origins for these Laotian evaporite deposits.

4. Summary

The gypsum in the Core SG-1 was deposited directly from brines and was stable after deposition. The $\delta^{18}\text{O}$ and δD curves of hydrated water in gypsum record the evolution of paleo-lake in Qaidam Basin, Western Tibetan Plateau since 2.2 Ma, including the famous cold event, mid-Pleistocene event.

In high saline conditions, the clay minerals from Core SG-1 may have undergone early diagenesis. The primary illite and chlorite contents in Core SG-1 were lower than those observed, while the primary smectite and kaolinite contents were higher than those observed. After early diagenesis, there were no isotopic exchange between the interlayer water and the ambient water. The $\delta^{18}\text{O}$ and δD values indicated the interlayer water of clay minerals to be more concentrated than those of hydrated water. The isotopic composition of the interlayer water reflects variations in the pore water/lake water or in the reacting solutions and also records changes in environment.

Using isotopic compositions of salt minerals to identify origins of brine is a complex topic. It should be careful to use sole isotope to identify the origins. For the evaporite deposits in LSB in China and NSB, in Laos, these isotopic proxies, including $\delta^{34}\text{S}$ - $\delta^{18}\text{O}_{\text{SO}_4}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and $\delta^{11}\text{B}$, indicate that continental and hydrothermal origins are likely to be more important than marine origins.

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