

2.2 Analytical methods

One bulk organic material for AMS ^{14}C dating were picked from the sediment profile D4 of DaQaidam Salt Lake, and the pretreatment followed by acid–alkali–acid processes [9]. Before AMS ^{14}C dating, the sample was gently crushed and dispersed in deionized water. Then, it washed with 2 mol/L hot HCl acid to eliminate carbonates, followed by an alkali wash (0.5 mol/L NaOH) to remove secondary organic acids, a final acid rinse to neutralize the solution before drying. All samples were chemically pretreated, combusted and cryogenically purified in Beta Analytic Inc of Miami in the United States of America.

All samples for XRD analysis were air-dried at room temperature (25 °C), ground in a mortar and pestle, and passed through a 63 μm sieve. Phillips X-pert Pro X-ray diffraction with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) at a scanning rate of 2° min $^{-1}$ for 2 θ ranging from 10° to 80°. Mineral identification and concentration were estimated from the bulk mineral diffractograms, using the intensity of the strongest peak for each mineral with an automated searchmatch computer program X-Pert HighScore Plus. Duplicate analyses of mineralogy for 20 samples in

Table 1. AMS ^{14}C age, the reservoir-effect calibrated age and the calibrated calendar age from sediment profile D4 in DaQaidam Salt Lake.

Laboratory ID	Depth (cm)	Material dated	^{14}C age (yr BP)	Calibrated age (yr BP)	Calendar age (cal yr BP)
Beta-467195	533–540	TOC	10370 \pm 30	8570 \pm 30	9498 (9529) 9554

3.2 Mineralogical and lithostratigraphic records

The sediment profile D4 is located in the south central of DaQaidam Salt Lake (figure 1), pinnoite deposits ranged from 549 to 735 cm, and the sediments above 549 cm represented a series of successive sedimentary sequence in perennial water-body since early Holocene. More 70 samples from profile D4 were determined by XRD analysis, The main saline minerals are composed of, on average, 29.1% carbonate (calcite, aragonite, dolomite and hydromagnesite), 16.0% gypsum, and 15.4% halite. The detrital components include, on average, 15.6% quartz, 6.6% chlorite, 4.4% muscovite and 3.8% albite. Within the detecting limit of XRD analysis, pinnoite ore is the only borate mineral detected from sediment profile D4 of DaQaidam Salt Lake.

3.2.1. Evaporite minerals

Evaporite minerals can be used as effective proxy records to interpret the paleoclimatic and paleoenvironmental changes. The compositions of authigenic evaporite

different lithostratigraphic units, indicated that the error of mineralogical data is approximately $\pm 5\%$. The experiment was conducted at Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, China.

3 Results and discussion

3.1 AMS ^{14}C chronology

The sediments of DaQaidam Salt Lake are mainly evaporitic minerals, so no suitable samples with sufficient amount of organic matter for radiocarbon measurement. Fortunately, only one bulk organic material for AMS ^{14}C dating were picked from the sediment profile D4 of DaQaidam Salt Lake. In addition, the sediment profiles D2 and D4 are in the same deposition system of DaQaidam Salt Lake, we obtained the ^{14}C reservoir-effect value of profile D2 in previous study [6]. Therefore, As shown in Table 1, the AMS ^{14}C age, the reservoir-effect calibrated age and the calibrated calendar age of sediment profile D4 was obtained from DaQaidam Salt Lake in Qaidam Basin. The calendar age was transformed by IntCal13 calibration curve procedure [10].

minerals in the lacustrine sediments are closely related to the hydrochemistry of lake water. With the evaporation and concentration effect and the increase of salinity, in general, the crystallization sequence of evaporite minerals as follows: carbonate (calcite, aragonite, dolomite and hydromagnesite) \rightarrow sulfate (gypsum and mirabilite, etc.) \rightarrow halite (sodium chloride, etc.).

The evaporite minerals in the sediment profile D4 are mainly composed of gypsum and halite (figure 2). Both halite and gypsum contents fluctuated frequently, with the average content reached 15.4% and 16.0%, respectively. The gypsum content were lowest ranged from 186 to 258 cm and 331 to 735 cm in the profile, which reflected relatively higher inflow and lower brine salinity, and vice versa. Therefore, according to the characteristics of sedimentary facies reflected by profile D4, We believed that the change of sedimentary facies was the main cause of evaporite compositions from sediment profile D4 in DaQaidam Salt Lake, and the salinity change of lake water was a secondary factor. Among evaporite minerals, when the gypsum and halite dominated in the lake sediment, the sedimentary environment is in a relatively shallower lacustrine facies.

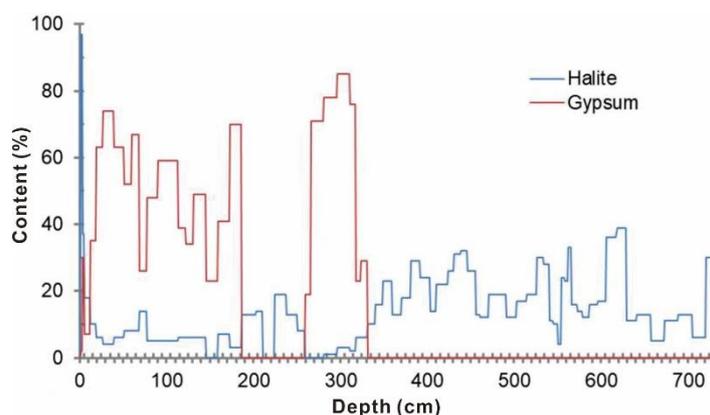


Figure 2. The gypsum and halite compositions from sediment profile D4 in DaQaidam Salt Lake.

3.2.2. Carbonate minerals

The crystalline precipitation of carbonate in the water-body is mainly controlled by the Mg/Ca ratio. The calcite began to precipitation when the water contained a small amount of Mg²⁺, and the aragonite precipitated when the concentration of Mg²⁺ increased. When the Mg/Ca ratio is relatively higher, the high-magnesium calcite can be crystallized. Only under the condition of higher Mg/Ca ratio, higher temperature and slower crystallization rate, the dolomite with standardized compositions and high

degree of order was formed. Finally, with the evolution of lake water, when the Mg/Ca ratio reached 20–30 with the pH value increasing to 9.1, the hydromagnesite precipitated [11].

XRD results showed that the carbonate minerals in the sediment profile D4 are mainly composed of calcite, aragonite, dolomite and hydromagnesite (figure 3). Except calcite, other three carbonate minerals such as aragonite, dolomite and hydromagnesite fluctuated frequently and abruptly.

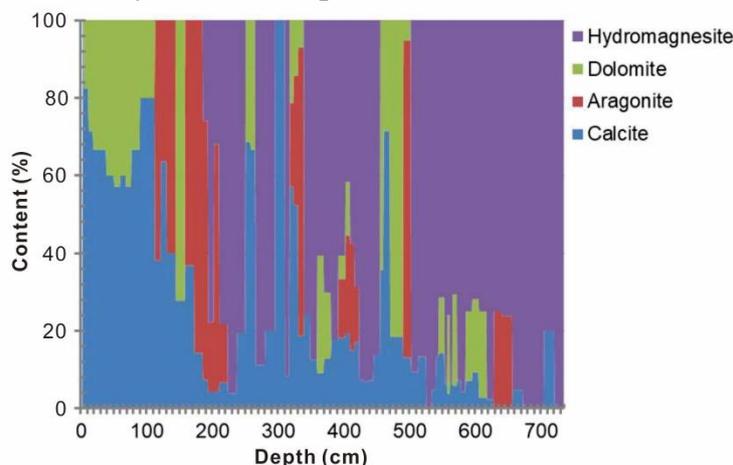


Figure 3. The carbonate compositions from sediment profile D4 in DaQaidam Salt Lake.

3.2.3. Detrital minerals

The detrital mineral content in lacustrine sediment indicated the change of lake water inflow and hydrodynamic conditions. In general, the relatively higher detrital content indicated that more lake water

inflow with higher water level, and the lake was in the desalination phase, and vice versa.

The quartz and clay mineral content reached 42% and 22% ranged from 251 to 258 cm in the profile, respectively, which reflected the period of higher lake water inflow and lower brine salinity. In addition, the quartz and clay mineral content displayed the similar variation trend (figure 4).

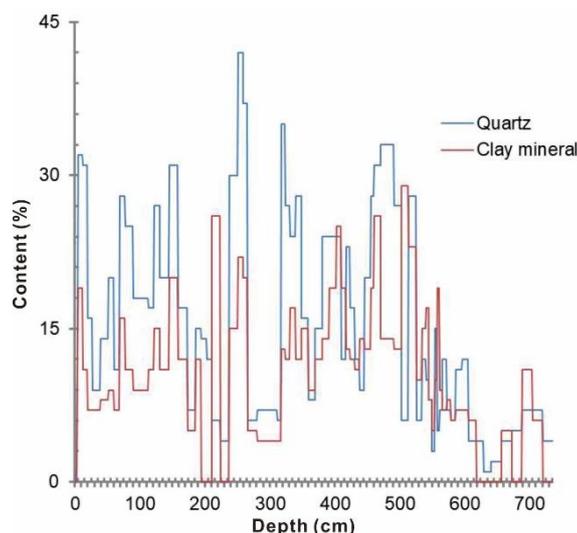


Figure 4. The detrital compositions from sediment profile D4 in DaQaidam Salt Lake.

3.2.4. Pinnoite mineral

XRD results showed that the main components of pinnoite deposit from sediment profile D4 are pinnoite, hydromagnesite, halite and detrital

minerals (figure 5). The characteristics of laminated pinnoite ore layer enriched in 29.1% hydromagnesite, suggesting that the paleo-lake level went down seasonally to near-dry conditions due to the intense evaporation and concentration effect [7].

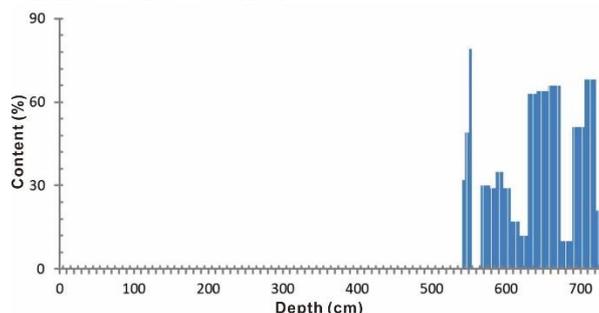


Figure 5. The pinnoite content variation from sediment profile D4 in DaQaidam Salt Lake.

According to the sediment characteristics and mineral compositions of profile D4 from DaQaidam Salt Lake, the lithostratigraphic sequence can be divided into four sedimentation units from bottom to top, as follows:

Unit I (735–541 cm) is the basal sediment, which is characterized by massive pinnoite deposit, with an average value of 38.3% pinnoite and no more than 16% B₂O₃ content.

Unit II (541–331 cm) is characterized by interbedded layer of black grey salt-bearing silty mud and black nodule with the lithology and mineral compositions changed. The gypsum mineral disappeared abruptly, hydromagnesite, calcite and halite contents were relatively stable, and clay mineral and quartz contents increased abruptly.

Unit III (331–186 cm) is characterized by grey salt-bearing silty mud. The gypsum and hydromagnesite content fluctuated frequently, the halite and calcite contents decreased, but clay mineral and quartz contents reached up to the maximum.

Unit IV (186–0 cm) is characterized by interbedded layer of earth yellow evaporite and black grey salt-bearing mud. Compared to unit III, the gypsum content increased obviously, and the halite and calcite contents were relatively stable, but clay mineral and quartz

contents decreased to some extent. Especially, hydromagnesite mineral disappeared abruptly.

3.3 Brine evolution and hydro-climate change

AMS ¹⁴C chronological results demonstrated that the pinnoite deposit in unit I of sediment profile D4 formed in the early Holocene period. It is estimated that boron content in brine when pinnoite deposit formed was at least equivalent to the modern brine, what is more, the pinnoite deposit would reduce the boron content in original brine. Thus, we concluded that the boron content reached up to 600 mg/L in modern brine just due to the no considerable amount of boron minerals been formed, and the boron content in brine enriched and concentrated steadily including accumulation in original brine.

Compared to unit I, the mineral compositions as well as sedimentary structure illustrated that the lake water flowed into DaQaidam Salt Lake decreased in unit II after borate deposit formed, and lake level was relatively shallower with higher salinity.

In addition, increasing clay mineral and obviously decreasing saline nodule as the main characteristics in unit III, with the gypsum content fluctuated frequently, suggesting the water depth and inflow increased to some

extent. With the increasing clay mineral content, TOC content obviously increased with a small quantity of dolomite. Dolomite is generally related with enhanced reducibility in lakebed environment [12], and the carbonate content maybe controlled by Mg/Ca ratio in brine. Compared with the II phase, lithostratigraphic characteristics and mineralogical evidence mentioned above illustrated that the lake brine area expanded a lot in the III phase.

The sedimentary structure of unit IV is completely different from units III and II, reflecting more frequent dilution–salinization fluctuation and water level higher–lower alternation on decadal to centennial scales in lake region. In general, the lake region had been moving towards aridification with relative higher brine salinity and lower lake level since late Holocene period.

4 Conclusions

After pinnoite deposit formed in the lakebed since Holocene period, the hydrochemical type of surface brine unchanged, and the hydrochemistry on seasonal, decadal, centennial and millennial scales were controlled by the precipitation in mountainous area. Especially, the considerable amount of boron minerals had not been formed, boron content in brine enriched and concentrated.

Since Holocene period, the lake sediment displayed three different sedimentary environment, as follows: pinnoite deposit dominated in the early phase with relatively shallower paleo-lake water level and higher brine salinity; the salt-bearing mud deposit as the main characteristics in the middle phase with relatively deeper water level and stronger reducibility; the interbedded layer of evaporite and salt-bearing mud as the sedimentary characteristics showed that intensive fluctuation of lake water inflow on decadal scales for the past several thousand years in late Holocene period.

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