Stable isotopic and mineralogical investigations of an arid Quaternary lacustrine palaeoenvironment, Western Qaidam, China

Ana-Voica BOJAR, Andrea RIESER, Franz NEUBAUER, Hans-Peter BOJAR, Johann GENESER, Yongjiang LIU and Xiao-Hong GE

Stable isotope analyses on carbonates from lake evaporites collected from the non-marine western Qaidam basin yield a positive excursion from Pliocene to Quaternary times. At Dafeng Shan, the Quaternary sequences are composed of alternating layers of celestine/dolomite and aragonite/calcite/barite with distinct isotopic compositions. The sequence described at Dafeng Shan formed in a low energy, hypersaline lacustrine environment as indicated by the microstructures and evaporitic minerals as well as by the absence of lithoclasts. The peloids, ooids and oncoids described are related to microbial activities in saline lake. The oxygen isotopic composition of the carbonates vary between +34.4 and +39.8‰ (SMOW), representing the heaviest values measured until now. The δ¹⁸O and the δ³⁴S isotopic composition of the celestine range between 20.1 to 22.3‰ (SMOW) and +19 to +22‰ (CDT) respectively, suggesting sulfur recycling via sulfide oxidation. The carbon isotopic compositions of the carbonates show a large negative excursion of up to ~30‰. The microstructures, mineralogy and isotopic compositions as well as the geological context suggest oxidation of methane from a deep source.

Key words: Qaidam, Quaternary, stable isotopes, celestine, carbonates, hypersaline lacustrine environment.

INTRODUCTION

The Himalayas, the Tibetan plateau and the adjacent mountains to the north, are the largest present-day topographic features resulting from continent–continent collision (e.g., Molnar and Tapponnier, 1975; Allègre et al., 1984; Yin and Nie, 1996; Hodges, 2000). The average elevation of the region reaches 4000–5000 metres. The progressive north-south shortening, due to collision, achieves ca. 1400 km (e.g., Zhou and Graham, 1996; Replumaz and Tapponnier, 2003). The Neohimalayan tectonic phase started during the early Miocene (e.g., Hodges, 2000) and has been followed by accelerated denudation during the past few million years. Accelerated denudation may have been triggered by either tectonic activity, as suggested by recent seismic movements within the Himalayan Metamorphic Belt, or by enhanced erosion, possibly related to global climate changes (An et al., 2001; Kayal, 2001; Peizhen et al., 2001; Bojar et al., 2005).

The onset of the Indian and East Asian monsoon, as well as enhanced aridity in the Central Asia, occurred about 8 Ma ago, concomitant with a period of significant increase in the altitude of the Tibetan plateau and with Northern Hemisphere glaciation (Harrison et al., 1992; Prell and Kutzbach, 1992; Molnar et al., 1993; Ramstein et al., 1997; Lehmkuhl and Haselein, 2000; Peizhen et al., 2001; Zhisheng et al., 2001; Guo et al., 2002). Later intensifications of the East Asian monsoon at 3.6 and 2.6 Ma are also related to periods of rapid uplift of the northwestern part of the Tibetan plateau (Qiang et al., 2001; Spicer et al., 2003).

The Qaidam basin is located at the northern edge of the Tibetan plateau. The thick Pliocene-Quaternary deposits were influenced by tectonic processes related to uplift of the Tibetan plateau, as well as by climatic changes related to plateau growth (Harrison et al., 1992; Murphy et al., 1997; Meyer et
The Qaidam basin has been characterized by endorheic drainage through most of its existence (Paleogene to recent), which resulted in the formation of a large continental lake (Chen and Bowler, 1986; Liu et al., 1998; Shi et al., 2001). The Pliocene and Quaternary fill of the Qaidam is exclusively terrestrial and comprises alluvial fan deposits, such as conglomerate and breccia disposed along basin margins. In contrast, the central sectors of the basin can be divided into:

- near-shore with mainly sand and siltstone,
- deep-water deposits, with many thin carbonate intercalations.

Various evaporitic minerals, for examples, sulphates and chlorides, formed during Pliocene to Quaternary regressive phases of lake development (Chen and Bowler, 1986; Lowenstein et al., 1989).

During the Pliocene to Quaternary, there has been a strong tectonic as well as climatic control of sedimentation. Generally the Pliocene to Quaternary are characterized by the driest climate of the Qaidam basin during Cenozoic time. The climatic shift towards arid condition has been related to uplift of the Tibetan Plateau which led to to strengthening of the monsoonal circulation (Wang et al., 1999 and reference therein). We will briefly discuss the main stages of basin history during these periods.

During the late Miocene to early Pliocene, the lake expanded to 200 km from north-west toward south-east. Towards the late Pliocene some of the lakes evolved to an evaporite formation stage. The 1000 m salt-bearing layers contain sulphate and chloride sequences around 200 m thick (Chen and Bowler, 1986), the total thickness of the Pliocene deposits reaching up to 6000 m. The enhanced aridity was due to uplift of the basin in the western region, associated with subsidence in the east, as well as regional cooling (Zhisheng et al., 2001).

From the late Pliocene to the Quaternary, during periods of tectonic deformation, anticlinal and synclinal structures were formed, resulting in segmentation of depositional environments (Song and Wang, 1993; Meyer et al., 1998). Within the synclines, sedimentation continued and produced thick lacustrine sequences 3000 to 4000 m (Liu et al., 1998; Shi et al., 2001; Yan et al., 2002). During the Quaternary, the Qaidam basin evolved as an intramontane basin controlled by western and northern winds, away from the influence of the monsoon. The arid periods alternated with short semi-arid conditions resulting in the formation of large shallow lakes and evaporites (Lowenstein et al., 1989; Phillips et al., 1993; Liu et al., 1998; Duan and Hu, 2001; Shi et al., 2001).

Between the beginning of the Quaternary and ca. 300 ka, there is no detailed information about the climatic evolution of the basin. In contrast much work has been done on deposits younger than 300 ka. At 302±56, 138±6 and 16.3±2.2 ka, U/Th ages indicate transitions from high to low lake level at the end of continental glacial maxima, the ages being mea-

---

**Fig. 1. Simplified map of the western part of the Qaidam basin and location of investigated samples**

---

**GEOLOGICAL FRAMEWORK AND PLIOCENETO QUATERNARY CLIMATE CHANGES IN THE QAIDAM BASIN**

The ca. 120 000 km² large, rhomb-shaped Qaidam basin, containing unusually thick (3–17 km) Mesozoic to Cenozoic sedimentary sequences, is surrounded by the Kunlun/Qimantagh, Qilian and Altyn mountain ranges. The mean surface elevation of the basin floor is ~2700 m, whereas the surrounding mountains reach elevations of over 5000 m. The latest interpretations consider the formation of the Qaidam basin as a response to oblique compression between the left lateral Altyn and Central Kunlun faults (Métivier et al., 1998; Meyer et al., 1998). The basin stratigraphy is well constrained by ostracods, spores, pollen, magnetostratigraphy and seismic stratigraphy (Sun et al., 1999; Wang et al., 1999; Xia et al., 2001 and references therein).
sured on salt layers deposited in the western Qaidam basin. (Phillips et al., 1993). Stable isotope data on fluid inclusions trapped in evaporites from the central part of the basin indicate cold and wet periods at between 50 to 45, 42 to 34 and 28 to 19 ka. Lake level lowering and evaporite formation continued between 19 and 11 ka during a generally dry period. Lake levels rose again during late-glacial and post-glacial times, between 19 and 14 ka, but the age of this event may differ from site to site (Phillips et al., 1993; Yang et al., 1995). Generally, the Holocene is characterised by arid relatively warm climatic conditions.

Sulfate-rich brines occur in the western region of the basin, in contrast with those from the central part which are transitional between sulfate and chloride, with chloride brines predominating in the eastern sector (Chen and Bowler, 1986; Lowenstein et al., 1986). The thickness of the Pliocene to Quaternary evaporite-bearing strata decreases from west to east, because the evaporites started forming earlier in the western part.

The present climate represents the driest period during the last 40 ka, with mean annual precipitation of 25 mm in the centre of the basin and 100 mm along the border. Mean annual evaporation is ~3000 mm, while average temperature variations are from –10 to 20°C. The landscape is characterised by salt lakes, playas and aeolian landforms. Playas and salt lakes, as for example Yiliping and Quarhan, cover about one quarter of the total basin area.

METHODS

Mineralogical compositions were determined using a Siemens D500 powder diffractometer at the Department of Mineralogy at the Landesmuseum Joanneum, Graz, Austria. The samples were prepared with a dental micro-drill and mounted on a glass plate. Microbeam analyses were performed at the Institute of Earth Sciences, using a Jeol JSM-6310 scanning electron microscope equipped with ED- and WD-spectrometers.

Organic carbon content (TOC) was analysed by LECO CS 300 combustion instrumentation and infrared detection at the Institute of Earth Science, University of Graz, Austria. The samples were weighed, treated with 2N HCL solution in order to dissolve carbonates, weighed again and then analysed for TOC.

Carbonate isotopic analyses were performed on whole-rock samples using an automatic Kiel II preparation line and a Finnigan MAT Delta Plus Mass Spectrometer at the Institute of Earth Sciences at the University of Graz, Austria. Reaction of calcite and dolomite with H2PO4 was done at 70EC. NBS-19 and an internal laboratory standard were analysed continuously for accuracy control (Bojar et al., 2001). Analytical precision is 0.1% for δ18O and 0.06% for δ13C. All isotopic results are reported in permil units relative to SMOW and PDB, respectively.

Sulphate isotopic analyses were done at the Institute of Geological Sciences, University of Wroclaw. Sulphates were dissolved in an 18% HCl solution. The solution was filtered and BaSO4 was precipitated, due to addition of 10% BaCl2 solution. The precipitated BaSO4 was rinsed with redistilled water, dried, weighed, powdered in an agate mortar, preheated at 550°C (2 minutes) and weighed again in order to calculate the concentration of sulphate (see Jędrzejek, 2000).

For sulphur isotope analysis, 10 mg of BaSO4 were mixed with 100 mg of V2O5 and 100 mg of pure quartz (Yanagisawa and Sakai, 1983). The mixture was placed at the bottom of quartz glass tubes together with preheated pure copper wire. The tube was attached to the vacuum preparation line and heated at 450°C for approx. 10 minutes to remove any volatile contaminants. Afterwards, the temperature was raised to 950°C and maintained for 25 minutes to complete the reaction. The obtained was frozen in a liquid nitrogen trap and then cryogenically cleaned using dry ice-ethanol mixture (Jędrzejek et al., 2002). Alternatively, the SO2 was obtained using NaPO3 reagent (V2O5 yields the same results and both techniques have been used alternatively for calibration) as described by Halas and Wołczęwicz (1981). The sulphate was reacted under vacuum at 850°C with dry NaPO3 and SO2 were the gaseous products of this reaction. SO2 was reduced to by passing the SO2 over hot (approx. 700°C) pure copper.

For oxygen isotope analysis, it was necessary to obtain oxygen quantitatively from BaSO4. The CO2 was prepared according to Mizutani and Raifer's (1973) technique; the sulphate was reacted with pure graphite at 1400°C under vacuum.

Sulphur and oxygen isotope analyses were carried out using a Varian MAT CH7 mass spectrometer with a modified detection system. The δ18O and δ34S values are given in permil units with reference to SMOW and CDT international standards, respectively. The precision (1σ), obtained for complete analysis of replicate aliquots of standards and samples, was generally better than 0.1‰ for both sulphur and oxygen isotope analysis.

MICROFACIES, MINERALOGY AND STABLE ISOTOPIC COMPOSITION

Carbonate samples for stable isotope analysis from Quaternary strata are generally scarce and have mainly been collected from outcrops of the over Youshashan Anticline, Dafeng Shan, and Xiaoliangshan (Fig. 1). All stable isotope data from late Pliocene and Quaternary deposits are summarised in Table 1.

The Pliocene samples were collected from the southwestern side of the Youshashan Mountains and Ahati. Individual marl layers are 0.1 to 0.5 m thick. Their mineralogy consists of quartz, feldspar, calcite, ± muscovite, ± chlorite, ± dolomite. The main carbonate is calcite. The δ18O composition of carbonates vary between 22 to 26.1‰, the δ13C between –3.8 to –1.1‰.

Generally the Quaternary samples show much higher values of the oxygen isotopic composition. Samples QA 297A-03, QA 298A-03 and QA 297A-01 were collected from shoreline deposits, near the basin border. The mineralogy consists of quartz, calcite, aragonite, ± muscovite, ± chlorite, plagioclase. They show δ18O values between 26.5 and 33.6‰ and δ13C values between 0.1 and 4.6‰.
<table>
<thead>
<tr>
<th>Sample</th>
<th>13C (carbonate PDB)</th>
<th>18O (SMOW)</th>
<th>34S (sulphate, CDT)</th>
<th>18O (sulphate, SMOW)</th>
<th>Formation</th>
<th>Total organic carbon content [TOC %]</th>
<th>Age</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dafeng Shan</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>QA 260 A-03/1</td>
<td>–0.5</td>
<td>38.4</td>
<td>21.9</td>
<td>22.2</td>
<td>Qigequan</td>
<td>Quaternary</td>
<td>0.06</td>
<td>white crust, dolomite</td>
</tr>
<tr>
<td>2</td>
<td>–1.0</td>
<td>38.4</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>white crust, dolomite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>–1.1</td>
<td>39.8</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>matrix, dolomite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>–1.0</td>
<td>38.4</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>matrix, dolomite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>QA 141C</td>
<td>–3.6</td>
<td>39.2</td>
<td>19.4</td>
<td>20.1</td>
<td>Qigequan</td>
<td>Quaternary</td>
<td>0.05</td>
<td>white oncoid, dolomite</td>
</tr>
<tr>
<td>2</td>
<td>–4.4</td>
<td>39.3</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>white oncoid, dolomite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>–3.7</td>
<td>39.3</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>white oncoid, dolomite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>–2.0</td>
<td>38.6</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>matrix, dolomite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>–0.9</td>
<td>38.2</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>matrix, dolomite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>–1.6</td>
<td>38.5</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>matrix, dolomite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>–1.1</td>
<td>38.5</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>matrix, dolomite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>–1.0</td>
<td>38.4</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>matrix, dolomite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>QA 260B-03</td>
<td>–21.0</td>
<td>38.4</td>
<td>21.7</td>
<td>21.5</td>
<td>Qigequan</td>
<td>Quaternary</td>
<td>0.04</td>
<td>matrix/calcite/ aragonite</td>
</tr>
<tr>
<td>QA 260C-03/1</td>
<td>–29.2</td>
<td>34.4</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>Quaternary</td>
<td>0.03</td>
<td>matrix/calcite/ aragonite</td>
</tr>
<tr>
<td></td>
<td>–30.3</td>
<td>35.7</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>matrix/calcite/ aragonite</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>–26.3</td>
<td>35.6</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>matrix/calcite/ aragonite</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>–26.3</td>
<td>35.6</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>matrix/calcite/ aragonite</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>–25.9</td>
<td>35.4</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>matrix/calcite/ aragonite</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>–30.5</td>
<td>35.5</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>matrix/calcite/ aragonite</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>–20.6</td>
<td>36.1</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>matrix/calcite/ aragonite</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>–23.9</td>
<td>36.0</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>matrix/calcite/ aragonite</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>–20.7</td>
<td>36.1</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>matrix/calcite/ aragonite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>QA 261B-03</td>
<td>–2.3</td>
<td>38.2</td>
<td>22.0</td>
<td>22.3</td>
<td>Qigequan</td>
<td>Quaternary</td>
<td>0.04</td>
<td>matrix, dolomite</td>
</tr>
<tr>
<td></td>
<td>–2.4</td>
<td>38.3</td>
<td></td>
<td></td>
<td>Qigequan</td>
<td>matrix, dolomite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The approx. 25 m high exposure at Dafeng Shan contains, from the base to top, a succession of dolomite/celestine and calcite/aragonite layers, alternating with siltstones and fine sandstones (Fig. 2 A, B, C). The lower section is partly cut by meter-thick, discordant, NE-trending celestine veins. In Table 1 the samples are in stratigraphical order, from the bottom to the top. We described the microfacies according to Flügel (2004). For describing the carbonate rocks the classification of Folk (1959, 1962) modified after Strohmenger and Wirsing (1991) has been used.

Sample QA261B-03 contains dolomite, celestine, a few percent of halite and detrital quartz. The cement is composed of micritic dolomite and dolomitic ooids tens of microns across (Fig. 3A, B). The dolomite contains ~0.8 wt% iron. The celestine crystals are dispersed into the dolomitic matrix. The sample can be classified as a packed oomicrite (>50% ooids). The $\delta^{18}O$ and $\delta^{13}C$ of the dolomite is 38.2‰ and –2.3‰, respectively. For sample QA260C-03 (Fig. 4 A) the mineralogy consists of calcite, aragonite, ±barite, ±halite, and detrital quartz. The micritic cement consists of calcite, aragonite and barite (Fig. 4 B, C).

![Fig. 2. Lithological section at Dafeng Shan mine showing the position of the Quaternary samples](image)
barite locally contains up to 20% Sr (Fig. 4 D). Pyrite is concentrated within some layers. Characteristic of these layers is the presence of peloids tens of microns across, with a clotted structure. The peloids consist of calcite, aragonite, barite and pyrite (Fig. 4E–G). The sample can be characterized as a peloid-bearing micrite (between 1 to 10% peloids). An isotopic profile across the stratification of a hand specimen 15 cm across shows $\delta^{18}$O values between 34.4 and 36.1‰ and a large variation in $\delta^{13}$C values of between −20.7 and −30.5‰. Sample QA260B-03 contains dolomite and celestine, voids with celestine crystals being occasionally present (Fig. 5A, B). The dolomite shows $\delta^{18}$O values of around +38.4‰ (SMOW), and $\delta^{13}$C values around −21‰. Sample QA141C-01 contains mainly celestine and dolomite, subordinately halite and detrital quartz (a few percent). The sample contains also white, concentrically grown, ellipsoidal micrite oncoids filled with celestine, and dolomitic peloids showing a clotted structure (Fig. 6A–C). The sample can be classified as an oncomicrite. Voids filled with celestine crystals up to 2 mm across are also present. The micritic dolomite show $\delta^{18}$O values around 38.4‰, and $\delta^{13}$C values around −1.1‰. The oncoids have higher $\delta^{18}$O values of +39.3‰ and lower $\delta^{13}$C values of around −4‰. Sample QA260A-03 is characterised by a micritic matrix surrounding white crusts ca. 2 cm thick (Fig. 7 A). The cement is composed of dolomite, celestine and ±gypsum and clotted dolomitic peloids, the sample can be described as a sparse pelmicrite (Fig. 7 B, C). Thin halite layers are associated with the
white crusts. Celestine crystals grow also in small voids. Both crusts and matrix show similar isotopic compositions, with δ18O values ranging from 38.4‰ to 39.8 and δ13C around –1‰.

For the sequence described at Dafeng Shan there is evidence that most of the observed microstructures are syn-sedimentary; for example, the preservation of in situ formed grains such as ooids, peloids and oncoids, the presence of celestine-halite crusts, the presence of open space pore showing local crystal growth, and the presence of aragonite. There is no evidence of deformation, re-crystallisation, pressure solution or secondary vein-fill within the thin sections.

For the Dafeng Shan exposure (Table 1), the δ18O and δ34S isotopic composition of celestine varies between –20.1 to 22.3‰ (SMOW) respectively from 19.4 to 22‰ (CDT). For all the samples from Dafeng Shan, TOC measurements have been made. The TOC shows little variation, with low values for all samples (Table 1).

The δ18O values of Quaternary carbonates from the Dafeng Shan section vary between 34.4 and +39.8‰ (SMOW). These values are even higher than the ones reported for the calcites and dolomites associated with the saline deposits of the Pripyat Trough, Belarus (Maknach et al., 1994). In these the reported δ18O values are up to +36.6‰, and have been considered the highest measured in continental carbonates. For marine carbonates developed under normal salinity conditions, the highest values reported until now are for siderites from Black Outer Ridge, for which values up to 39‰ (SMOW) are reported (Matsumoto, 1989). The δ13C values show a large negative excursion from values of –2.3‰ in the lower part of the section (QA 261B-03) to values between –21 to –30‰ for QA 260C-03. In the upper part of the section, the matrix dolomite show values from –2 to –1‰ (QA 141C, QA 260A-03/1).

**DISCUSSION AND CONCLUSIONS**

The δ18O values of lacustrine calcite cements that formed in near-surface meteoric phreatic conditions are dependent on water temperature and the δ18O of the lake water. Since the late Pliocene as the lakes evolved as a closed system, with evaporation exceeding precipitation rates, we can consider the allogetic carbonate input negligible. For large shallow closed lakes it is usually assumed that water temperature reflects air temperature (Benson et al., 2002; Leng and Marshall, 2004). In contrast to

Fig. 5. QA 260B-03: A — BSE images: dolomite-celestine micrite, B — voids with celestine crystals

Fig. 6. QA 141C-03: A — white celestine-rich oolites, circles indicate the sampling points, B — BSE images: oolites filled with celestine, C — dolomitic peloid
the regions situated within a monsoon influence, the Qaidam basin during the Quaternary has shown low local air temperatures associated with high values of oxygen isotopic compositions of carbonates (Tian et al., 2003; He et al., 2004).

Isotopic data from the micritic carbonatic matrix indicate two different trends over the Pliocene and Quaternary (Table 1 and Fig. 8): a — a large positive δ¹⁸O and a slight positive δ¹³C shift between the Pliocene and Quaternary; b — during the Quaternary, for the Dafeng Shan outcrop, a large negative shift in the δ¹³C values.

The large positive shift in δ¹⁸O values between the Pliocene and Quaternary is interpreted as a climatic change from relatively humid conditions to cool, arid conditions. Such high aridity conditions and a closed lake environment were deduced for Quaternary strata of this region from other proxies such as, for instance the widespread salt-deposits and the pollen distribution (Chen and Bowler, 1986; Lowenstein et al., 1989; Xingzhen and Hongshun, 1993; Liu et al., 1998; Wang et al., 1999; Lehnhühl and Haselein, 2000).

The presence of celestine and barite also indicates hypersaline conditions. Ba is less soluble than Sr by three and a half order of magnitude and, additionally, during precipitation from aqueous solution Ba is preferentially incorporated into the solid phase (Hanor, 2004). In order to leach Sr and precipitate celestine, highly saline fluids, with a significant concentration of dissolved sulfate and a high Sr/Ba ratio of the leached material should be available (Hanor, 2000). These fluids could penetrate into underlying sediments, leaching pre-existent carbonates or evaporites. Sr solubility decreases with temperature, therefore low-temperature fluids were required for transport. The extremely high δ¹⁸O compositions of dolomite also support a strongly evaporative, closed lake, where such high salinity fluids could develop. Microstructures, the presence of evaporitic minerals as well as the absence of lithoclasts support a low energy, hypersaline lacustrine environment for the formation of the sequence described at Dafeng Shan. There is increasing evidence about the in situ formation of particles as peloids, ooids and oncoids due to microbial activities in saline lakes (Flügel, 2004). The clotted structure of the peloids described points also towards a microbial origin for these grains.

In the Qaidam basin, the average monthly temperatures vary between −10 and +20°C (Tian et al., 2003). As the lake was shallow, we can assume that the water temperature reflects the average monthly temperature, and that carbonates precipitated at temperatures between 0 and 20°C. For the assumed temperature range we can test if the measured isotopic composition of dolomites and aragonite/calcite indicate precipitation from a fluid with similar oxygen isotopic composition or not. We used for the calculations the fractionation factors of O’Neil et al. (1969) for calcite-water, Grossman and Ku (1986) for aragonite-water, and Matthews and Kaltz (1977) for dolomite-water. The calculations show that for the assumed temperature range, the oxygen isotopic composition of dolomite is enriched by 3.2 to 4% with respect to pure calcite and enriched by 2.8 to 3.6‰ with respect to a mixture composed of 70% calcite and 30% aragonite. This mixture represents the mineralogy determined for sample QA260C-03. The mean value of the measured oxygen isotopic compositions for dolomite is 38.5‰ and that of calcite-aragonite mixture is 35.6‰. The difference between these values is 2.9‰, and in the range of calculated isotopic enrichment of dolomite with respect to a calcite-aragonite mixture. The measured isotopic compositions of matrix dolomite is quite constant and vary with 0.6‰ from 38.2 to 38.6‰ (see Table 1) and the isotopic compositions of calcite-aragonite vary with 0.7‰ from 35.4 to 36.1 (except one value). The isotopic enrichment of dolomite with respect to the calcite-aragonite-
ite varies between 2.1 to 3.8‰ and it is in the range of calculated values. This fact suggests that the dolomite and calcite-aragonite precipitated from a fluid with similar oxygen isotopic composition. Thus the change in mineralogy from the Dafeng Shan, from dolomite- celestite to calcite-aragonite-barite, is more likely related to a change in water chemistry, for example, a drop in the sulphate concentration and increase in the carbonate concentration and/or change in redox condition as indicated by the presence of pyrite in the calcite-aragonite-barite sample QA260C-03.

The δ13C isotopic composition of authigenic calcite is usually similar to that of ambient dissolved inorganic carbon (DIC). For a pH of between 6.4 and 10.3, HCO₃⁻ is the main DIC species (Clark and Fritz, 1997). We can expect, for such a hypersaline environment, rather alkaline conditions and the contribution of CO₃²⁻ species to the DIC. In this case the authigenic carbonates will reflect the δ13C composition of dissolved HCO₃⁻ and CO₃²⁻ species. The calcite-bicarbonate fractionation is not temperature-dependent for carbon (Romanek et al., 1992), with the δ13C isotopic value of calcite around 1‰ more positive. The fractionation factor between HCO₃⁻ and HCO₃⁻ can be obtained by combining the equations of Mook et al. (1974) and Deines et al. (1974). The fractionation factor between these species is 0.4‰ and shows practically no variation with the temperature. By changing the distribution of the CO₃²⁻ and HCO₃⁻ species, the carbon isotopic composition of the carbonates will show a small variation of up to 0.4‰.

Usually the isotopic composition of DIC is controlled by: the isotopic composition of waters feeding the lake, photosynthesis/respiration of the aquatic plants and CO₂ exchange between atmosphere and lake water, oxidation of large amounts of organic material. The Quaternary matrix carbonates show δ¹³C values between –2 and 4.6‰, values which are higher than those of the Pliocene carbonates. As the lake evolved as a hydrologically closed lake system during the Quaternary, the δ¹³C values are interpreted to indicate different degrees of equilibration of the DIC with the atmospheric CO₂ (Talbot, 1990). For example, for atmospheric CO₂ which normally has values of –8‰, the δ¹³C isotopic composition of DIC would have values around 2‰, similar to those measured for the Quaternary carbonates.

The large negative carbon isotope excursion from the Dafeng Shan cannot be explained by the variation of one of the factors which usually control the DIC. Usually light groundwater in equilibrium with CO₂ gas at 20°C with δ¹³C CO₂ gas of –23‰, have a δ¹³C DIC of –15‰, which is further in isotopic equilibrium with a calcite characterized by a δ¹³C calcite value of around –14.5‰ (Fritz and Fontes, 1997). Moreover as the TOC contents of the samples from Dafeng Shan are very low the presence of light CO₂ derived from oxidation of large amount of organic matter can be excluded. Only in highly organic shallow lakes, organic matter oxidation can lead to very low δ¹³C calcite dropping to –19‰ (Eastwood et al., in press). Using the fractionation factor for carbon between: CaCO₃-CO₂ gas (Bottinga, 1968) and HCO₃⁻-CO₂ gas (Mook et al., 1974), we can calculate, from the lightest δ¹³C calcite we measured, the δ¹³C CO₂ gas and the δ¹³C DIC in isotopic equilibrium with this calcite. For temperatures between 0 and 20°C the calculated δ¹³C CO₂ gas values are between –45‰ and –41‰ and the δ¹³C DIC are between –36 and –31‰, so far below the typical δ¹³C DIC values of groundwaters.

There are also other mechanisms which may control the composition of lacustrine inorganic carbon DIC, such as the presence of CO₂ resulting from microbial, aerobic or anaerobic oxidation of methane. Bacterial oxidation of methane takes place either in the anoxic environment by sulfate-reducing bacteria when sulfate is available, or in anoxic environment through the activities of methane-oxidizing bacteria (Barker and Fritz, 1981; Sweeney, 1988; Whiticar, 1999). An excess of methane from deeper sources may reach the sediment-water interface, so in this case a combination of both oxidation processes may be possible. Bacteriologically produced methane is strongly depleted in ¹³C, and shows δ¹³C values in the range of –50 to –110‰ (Whiticar, 1999). Thermogenically produced methane has a heavier compositions in the range of –20 to –50‰ (Sackett, 1978; Whiticar, 1999). In the region from where the samples come, the δ¹³C of known methane deposits range between –35 to –45‰ (Zhang et al., 2003), indicating a thermogenic origin. The isotopic composition of the carbonates with a methane-derived carbon source will be generally heavier than those of the methane itself because: a) during methane oxidation processes, the fractionation factor for carbon between CO₂ and CH₄ is positive and according to Whiticar (1999) between 30 and 5‰; b) carbon sources, other than methane, contain relatively more ¹³C (Campbell et al., 2002; Peckmann and Thiel, 2004). For example, for a δ¹³C methan of –45‰ there will result a CO₂ gas with δ¹³C of between –40‰ and –15‰. The calculated carbon isotopic compositions of DIC and calcite in

![Graph](image)
equilibrium with this CO₂ gas at 20°C are: a δ34S_{DMS} between –31‰ and –6‰ and a δ34S_{calcite} between –30.5 and –5.5‰. At Dafeng Shan, the large negative shift in the carbon isotopic composition of carbonates, with variable values between –20 and –30‰, may be explained by participation of a light CO₂ resulting from methane oxidation. The isotopic composition of carbon from Dafeng Shan carbonates matches the isotopic composition of methane measured in the region, indicating rather bacterial oxidation of the thermogenically derived methane. According to our calculations, the oxidation of a methane with lighter compositions than these measured until now, and the presence of bacterial methane cannot be excluded, although no published data on the isotopic composition of such a methane are available. Pyrite, a common mineral in methane carbonates (Peckmann and Thiel, 2004) is also present in sample QA260A-03. It occurs as small pyritiferous carbonate nodules or as films within cavities with secondary carbonates. The presence of pyrite suggests anaerobic methane oxidation and sulfate reduction. If methane reached the sediment-water interface, we can also not exclude aerobic oxidation and liberation of a light CO₂ into the pool. The light CO₂ will also shift the carbon isotopic signature of primary carbonates to lower values. The microfabrics of QA260-03 show primary carbonates with upwardly-directed aggregation and secondary carbonates grown below carbonate crusts and within cavities. This fabric may be interpreted as supporting the presence of both aerobic and anaerobic methane oxidation. In this case, aggregation is associated with precipitation of carbonates from the lake water and the secondary carbonates formed during anaerobic oxidation of methane (Fig. 4C).

In non-marine evaporites, the stable isotopic composition of sulphates reflects local sources and processes. As the basin is situated in the continental interior, in the rain shadow of the Himalayas, we can exclude the presence of marine aerosols as a potential source for sulphates. The basin has also a thick (averaging 8 km) continental sequence, so dissolution of pre-existing marine evaporites is not probable. Therefore we considered that for the Qaidam basin, the sulphates could be derived from dissolution of pre-existing continental evaporites and/or oxidation of sulphides from area surrounding the basin. The temperature dependence of sulfur isotope fractionation is low and similar among sulphate minerals. At low temperatures, isotopic exchange between dissolved sulphate and water has slow exchange rates (Chiba and Sakai, 1985). Accordingly, the sulfur and oxygen isotopic composition of celestine should reflect the composition of the dissolved sulphates, and not that of water.

The sulfur fractionation between sulfate minerals and aqueous sulphates is small (Holser and Kaplan, 1966; Sakai, 1968), therefore the sulfur isotopic composition will approximate to the isotopic composition of the parent fluid. The δ34S of the seawater sulfate is 1.65 less than that of the mineral (Thode and Monster, 1965), seawater sulfate having approx. 21‰ (CDT) (Rees et al., 1978; Longinelli, 1983). The δ34S isotopic composition of celestine from the Dafeng Shan varies between 19.4 to 21.9‰ (CDT) and it is by 3.3 to 0.7‰ lighter than the composition of the sulfates precipitated from seawater. The oxygen isotopic composition of celestine from Dafeng Shan varies between 20.1 to 22.3‰ (SMOW). The δ18O of the associated dissolved sulfate is 3.5‰ less than that of the mineral (Gonfiantini and Fontes, 1963; Lloyd, 1968), thus the isotopic composition of water sulfate varied between 16.6 and 18.8‰ (SMOW). These values are heavier than the present-day dissolved marine sulfate, which is approx. –9.5‰ (Longinelli and Craig, 1967; Rafter and Mizutani, 1967; Longinelli, 1983) but they are in the range of isotopic compositions of sulfate ions from continental saline lakes and brines (Longinelli and Craig, 1967). The oxygen isotopic composition of sulfates measured at Dafeng Shan approach the value of dissolved atmospheric O₂ which is 24.2‰ (Dole et al., 1954; Kroopnick and Craig, 1972) and suggests sulfur recycling via sulfide oxidation. One possible explanation for the stable isotopic composition of sulfates from Dafeng Shan, characterized by slightly depleted sulphur and enriched oxygen isotopic composition in comparison to marine sulphate, would be oxidation of marine sulphides. It is known that sulfide oxidation mechanisms involve small sulfur isotope fractionations, while oxygen isotope fractionations range from 0 to –8.7‰ (Van Stempvoort and Krouse, 1994; Machel et al., 1995).

In conclusion, both δ13C and δ18O data, as well as the presence of evaporitic minerals, show a clear trend towards a dry climate during Quaternary times. In accordance with previous lithological and other environmental data, the oxygen isotopic compositions and mineralogy indicate that the coolest and driest conditions of the whole lifetime of the Qaidam basin occurred during the Quaternary. This may be correlated with a strong phase of surface uplift of both Himalayan and northern Tibet, and synchronously folding-induced segmentation of the basin. The lithological sequence from Dafeng Shan is interpreted to represent deposition of carbonate and evaporitic minerals during a dryer period alternating with wetter periods when fine silicilastic minerals, as found at the bottom and top of the sequence, were deposited. A plausible explanation for the large negative shift of carbon isotopic composition found at Dafeng Shan is methane leakage from underlying natural gas and oil deposits. The oxygen isotopic composition of celestine minerals is heavier than that of the marine-derived sulfates, while the sulfur isotopic composition is slightly lighter than the composition of marine sulfates suggesting sulfur recycling via sulfide oxidation. The sulfides could be, for example, eroded from areas surrounding the basin.

Acknowledgements. We acknowledge support for field work in the Qaidam basin by both NSF of China and Qinghai Oil Company. M.-O. Jędrzejek, (Laboratory of Isotope Geology and Geoeoclogy, Wroclaw) is thanked for aid with the sulphate isotopic analyses. S. Halas, (Lublin University) and K. Žak (Prague) are thanked for a helpful review. J. P. Smoot is thanked as well. For laboratory work financial support was provided by FWF Project 16258-N06.


