Pyrite morphology in the first member of the Late Cretaceous Qingshankou Formation, Songliao Basin, Northeast China

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ABSTRACT

The study of sedimentary pyrite morphological characteristics provides useful information on depositional environments and early diagenetic processes and can be used as an indicator of redox conditions in ancient lake bottom waters. The results of this study in the Songliao basin in northeastern China show that euhedral crystals and framboids are the dominant pyrite forms in the mudstones of the first member of the Qingshankou Formation (K2qn1). The framboidal size distribution indicates that during the deposition of K2qn1, redox conditions in the bottom water fluctuated from oxic–dysoxic to euxinic–anoxic to oxic–dysoxic. The presence of euxinic–anoxic bottom water suggests that an anoxic event developed in the Songliao ancient-lake and continued for 196 ka. The development of an anoxic bottom environment was the most important factor in hydrocarbon source rock formation in the Songliao Basin.

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1. Introduction

The Songliao Basin, located in Northeast China, is the largest Mesozoic continental sedimentary basin in China and is also the largest Cretaceous basin in the world. This basin contains a continuous sequence of Cretaceous lacustrine strata and is therefore a significant source of information contributing to the reconstruction of the Cretaceous continental environment in China (Yang et al., 1985; Wang et al., 1994; Gao et al., 1994; Stratigraphy Committee of China, 2002). This basin is a critical region for research into Cretaceous continental strata geological events and global climate change (Wang, 2006). The depositional period of the Late Cretaceous Qingshankou Formation is important because during the period major source rocks were deposited in the Daqing oil field (Yang et al., 1985; Gao et al., 1994; Li et al., 1995). Previous research has shown that large-scale transgressive events and lake anoxic events (LAEs) might have occurred during the deposition of the first member of the Qingshankou Formation (K2qn1) (Hou et al., 2000; Wang et al., 2001; Hou et al., 2003; Li and Pang, 2004; Huang et al., 2007). A characteristic mineral in the organic matter-rich sedimentary pyrites is an important mineral proxy for reconstructing the sedimentary environment (Raiswell and Berner, 1985; Davis et al., 1988). The study of pyrite morphology can provide information on depositional environments and early diagenetic processes. Pyrite framboids are densely packed, generally spherical aggregates of submicron-size pyrite crystals, and their size distribution can be an indicator of the redox conditions in bottom waters (Wilkin et al., 1997; Wignall and Newton, 1998; Wignall et al., 2005; Shen et al., 2007; Zhou and Jiang, 2009). Recognition of the development of redox conditions in bottom water is significant for understanding ancient lake evolution and events and the formation of hydrocarbon source rocks.

Previous studies of the sedimentary environment of the Qingshankou Formation in the Songliao Basin have focused on paleontology, magnetostratigraphy, isotope stratigraphy, cycle stratigraphy, mineral assemblage characteristics and geochemical characteristics. Pyrite-related research has focused on the sulfur isotope composition in pyrite (Wang et al., 1996); studies on pyrite morphology have not been systematically conducted. The size distributions of framboidal pyrite provide an effective and feasible method for the recognition of a redox environment in the bottom water of ancient lakes. Well “SLCORE I” (Cretaceous Continental Scientific Drilling in Songliao Basin) was selected for the study because 100% of the core was recovered from the K2qn1 in the South well. The strata are dominated by dark gray, olive gray and olive-black mudstones, which provide an ideal lithology for sedimentary environment research. Dark mudstone was sampled at 0.5 to 1 m intervals. Reflective microscope (RM), scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) methods were used to investigate the occurrence of forms of pyrite in the mudstone in the K2qn1. Their distribution variation with depth was analyzed, and then pyrites with different forms were studied.
2. Geological setting

The Songliao Basin, located in Northeast China, is a large Mesozoic and Cenozoic continental lacustrine basin. The current basin is an alluvial plain swamp where the Songhua, Nen and Liaohe Rivers meet. Cretaceous sedimentary rocks are widely distributed underneath Cenozoic deposits. Cretaceous, Jurassic and pre-Jurassic outcrops are scattered near the edge of the basin (Chi et al., 2000). The tectonic evolution of the basin included four different events, i.e., Late Jurassic thermal rifting, Early Cretaceous extensional fracturing, mid Early Cretaceous thermal subsidence, and late Cretaceous tectonic inversion (Chen et al., 1996; Liu, 1996). On the basis of regional tectonics, the basin can be subdivided into six tectonic units: the north plunge zone, central sag zone, northeast uplift zone, southeast uplift zone, southwest uplift zone, and western slope zone (Fig. 1) (Gao et al., 1994; Li and Guo, 1998). The basement of the basin is formed by Paleozoic metamorphic, volcanic and magmatic rocks overlain by Jurassic, Cretaceous and Cenozoic sedimentary rocks. From the bottom to the top, the sedimentary sequences of this basin are as follows: Lower Cretaceous Huoshiling, Shahezi and Yingcheng formations; Denglouku and Quantou formations; Upper Cretaceous Qingshankou, Yaqjia, Kenjiang, Sifangtai and Mingshui formations; an Eocene–Oligocene Yi’an Formation; a Miocene Da’an Formation; and a Pliocene Taikang Formation (Liu et al., 1992).

The Qingshankou Formation (K\textsubscript{2qn}) also outcrops near the Songhua River, which is located at the western strip of the Qianguo Band Banner, Denglouku, Binxian Daqing Oilfield Petroleum Geology Writing Group, 1993. The first member of the Qingshankou Formation (K\textsubscript{2qn1}) is widely distributed in the basin and is only disrupted on the western edge of the basin. The K\textsubscript{2qn1} is a deep-lacustrine deposit (Fig. 1), with a dominant lithology of black mudstone, gray-black mudstone, and shale with low oil-bearing potential. The thickness of the strata is 300 to 500 m. The laminated oil shale developed in the K\textsubscript{2qn1} with a partially dark brown color, resulting in thin-layer siderite bands (lens) and dispersed pyrite. The K\textsubscript{2qn1} is one of the most favorable source rocks in the Songliao Basin, with a thickness of 25 to 164 m. It is in conformable contact with the underlying Quantou Formation and the overlying K\textsubscript{2qn2–3} Daqing Oilfield Petroleum Geology Writing Group, 1993.

Previous paleontological (Gao, 1982; Ye and Zhong, 1990; Ye, 1991; Gao et al., 1992, 1994), magnetostratigraphy (Fang et al., 1989), isotope stratigraphy (Wang et al., 1995; Huang et al., 1999), and cyclostratigraphy (Wu et al., 2008) studies have generally regarded the K\textsubscript{2qn} as belonging to the Late Cretaceous. During the K\textsubscript{2qn1} deposition period, the lacustrine basin was rapidly subsiding.

![Fig 1. Tectonic division and paleogeographic reconstruction of the K\textsubscript{2qn1} in the Songliao Basin, and the location of the South well of “SLCORE-I” (modified after Wu et al., 2008).](image-url)

1 — lacustrine facies; 2 — delta fronts; 3 — delta plain; 4 — fluvial facies; 5 — channel; 6 — boundary of tectonic division (I: north plunge zone; II: central sag zone; III: northeast uplift zone; IV: southeast uplift zone; V: southwest uplift zone; VI: western slope zone); 7 — name of location; 8 — location of South well of “SLCORE-I”.
at a rate greater than that of the sediment supply. Lake transgression further enlarged the lake area and increased water depth. The deposition center is parallel to the subsidence center, and both are located in the Qijia, Gulong and Sanzhao regions. The Gulong Sag contains near shore-shallow lacustrine and semi-deep to deep lacustrine facies (Wang et al., 1994).

Well “SLCORE I” is the world’s first scientific drilling of a total core in Cretaceous continental strata. The purpose of implementing this scientific drilling is to obtain a continuous, high-resolution, less-damaged, less-affected geological record of Cretaceous continental strata and then to discuss the effects of the positive/negative feedback mechanisms of Cretaceous geological events and global climate change on continental strata (Wang, 2006). The well “SLCORE I” consists of a South well and a North well. The South well is located at the nose structure zone in the southern part of the Gulong Sag (45°34′41.348″ N, 124°40′15.581″ E). The downward drilling process encountered formations including the Mingshui, Sifangtai, Neijiang, Yaojia, Qingshankou, and the third and forth members of the Quantou Formation, with a core recovery rate of 99.73%. The depth of K2 qn1 is 1701.52 to 1782.93 m. The strata were cored with 100% core recovery. The lithology of the cores is dominated by dark gray and black mudstone, grayish black silty mudstone, yellowish gray marl and brownish black oil shale (Wan et al., this volume).

3. Analysis methods

A total of 68 samples were taken from the South well cores of “SLCORE I” in the K2 qn1. The sampling depth was 1703.77 to 1782.47 m, and the sampling interval was 0.5 to 1 m; the lithology is dominated by dark gray, olive gray, and olive-black shale. Weathering of a rock’s surface can alter the its geochemical characteristics, and the oxidation products of iron can produce false features, or framboids (Lüning et al., 2003). We selected only fresh surfaces from which to make polished sections. First, a total of 68 polished sections were observed under a reflecting microscope (OLYMPUS BX51M). The forms and diameters of the pyrite observed in the microscope field were recorded (an approximate diameter was recorded if the pyrite had a square or an irregular shape). Subsequently, the section was moved ~0.3 mm, and the statistical parameters were again recorded. This operation was repeated until the end of the section was reached. Finally, moving around a 1 mm line space, we again started collecting statistics along this line until the entire section was completed. The apparent diameter, which is measured under the microscope, is often smaller than the true diameter, but the deviation is no more than 10% (Wilkin et al., 1996). Twenty-six samples were chosen to conduct pyrite surface micro-form observation in the Continental Dynamics Key Laboratory of the Ministry of Land and Resources at the China Academy of Geological Science using a JSM-5601LV SEM. Micro-area element composition analysis of pyrite was conducted by using an INCA energy spectrometer (Software version 4.41) produced by UK OXFORD Co. Ltd. The accelerating voltage was 20 kV, and the focusing distance 20 mm.

4. Experimental results

4.1. Pyrite forms

The experimental results indicate that euhedral crystals and framboids are the dominant pyrite forms in the mudstones. Single euhedral crystals occur as cube, pyritohedron, octahedron and spherulitic shapes. Cubes, the main euhedral crystal type, are generally diffusely distributed. The size of the euhedral crystals varies broadly, from 1 to 15 μm, with an average of 2 to 4 μm (Fig. 2). In some sections, euhedral monocrystals compose the aggregates, which can be divided into biomorphic aggregates and abiological aggregates. The biomorphic aggregates are dominated by ostracoda-shaped (Plate I1) and phytoclast-shaped (Plate I2) aggregates: the euhedral crystals of the ostracod-shaped aggregates consist of cubic and octahedron crystals, and the intercrystalline space is filled with spherulitic microcrystalline pyrite (Plate I3). The diameter of the euhedral crystals of the phytoclast-shaped aggregates is relatively larger, approximately 1 to 6 μm. The abiological aggregates have ribbon (Plate I4), bubble-shaped (Plate I5) and irregularly shaped (Plate I6) forms. The banded aggregates are mostly parallel to the bedding in mudstone; they consist of cube-, octahedral- and spherulitic-shaped crystals, whose sizes range from 2 to 6 μm; the bubble-shaped aggregates are composed of small lenticular-shaped aggregates (Plate III1) oriented subvertically within the strata and consist of heterogeneously sized euhedral crystals, whose sizes range from 1 to 6 μm in diameter. The irregularly shaped aggregates also consist of unevenly shaped euhedral crystals, with particle sizes of 1 to 8 μm in diameter.

Pyrite framboids are densely packed, generally spherical aggregates of submicron-size pyrite crystals; they are bright and have a brassy color under a reflective microscope (Plate II2). The crystals have cube (Plate II3, 4), octahedral (Plate II5) and spherulitic (Plate II6) shapes, with a uniform particle size. The single framboid is generally preserved in a thin layer of clay (Plate III1). The size distribution of the framboids in the K2 qn1 under the reflective microscope is listed in Table 1. The diameter of framboids varies broadly, ranging from 3 to 25 μm. In some sections, poly-framboids composed of single framboids with uneven sizes (6 to 12 μm) are found. Lenticular (Plate III2), dumbbell (Plate III3) and irregular (Plate III4) shapes are observed. The lenticular aggregates have long axes that are nearly parallel to the bedding planes, and both framboidal and euhedral crystals occur (Plate III5). The dumbbell-shaped aggregates consist of relatively uniformly sized (average 8 μm) framboids. For irregularly shaped aggregates, a partially linear arrangement and unevenly sized euhedral crystals exist in the gaps of the framboids. In addition, there are a few euhedral crystal aggregates composed of euhedral monocrysts.

Anhedral pyrite crystals rarely occur and are mainly concentrated at a depth of 1735 to 1766 m. They have irregular shapes. In some anhedral (hypidomorphic) pyrite crystal, the phenomenon of dissolved borders and cavities can be observed (Plate III6).

4.2. EDS analysis results

EDS is an analytical technique used for the quantitative determination of mineral micro-area element composition. During SEM observation, a few pyrite samples of different forms (including the cube, octahedron, pyritohedron, spherulitic euhedral crystals, and framboids) were analyzed by EDS (see Table 2). The analysis results show that the different pyrite crystal forms have different S/Fe ratios, which are scattered around the ideal ratio of 2.00 (Fig. 3). Cubic pyrite...
has an S/Fe ratio of 1.72–2.11, 1.93 on average; pyritohedron has an S/Fe ratio of 1.68–2.25, 1.97 on average; octahedral has an S/Fe ratio of 1.74–2.05, 1.88 on average; spherulitic pyrite has an S/Fe ratio of 2.06–2.25, 2.16 on average; and framboids have an S/Fe ratio of 1.89–2.15, 2.01 on average. In many anoxic environments, H₂S is the most abundant sulfur source during the transformation process.
from FeS to FeS\textsubscript{2} \textit{(Schoonen, 2004)}. Thus, the S/Fe ratio of pyrite is controlled by the supply rate of H\textsubscript{2}S. The more adequate the H\textsubscript{2}S, the closer the ratio will be to the standard value and vice versa; if there is a shortage, the S/Fe atomic ratio will show a relative sulfur deficiency. In addition, other elements such as O, Si, Ca, Al, Na, Mg, and As were detected in some samples. The element was mainly in

**Plate II.** Lenticular-shaped pyrite aggregates and the single pyrite frambooids from K\textsubscript{2}qm\textsuperscript{1} mudstone. 1—partial magnification of bubble-shaped aggregates (I5), which are composed of the small lenticular-shaped aggregates oriented oriented subvertically within the strata and consist of heterogeneously sized euhedral crystal (SEM backscattered electron image with a scale bar of 10 \(\mu\)m, 1749.87 m deep); 2—single frambooid under a reflective microscope (reflecting microscope image with a scale bar of 50 \(\mu\)m, 1722.77 m deep); 3, 4—the single frambooid is composed of the cube euhedral crystals (SEM secondary electron image with a scale bar of 2 \(\mu\)m and 1 \(\mu\)m, respectively); 5—the single frambooid is composed of the octahedral euhedral crystals (SEM secondary electron image with a scale bar of 2 \(\mu\)m); and 6—the single frambooid is composed of the spherulitic euhedral crystals (SEM secondary electron image with a scale bar of 1 \(\mu\)m).
a solid solution (isomorphism) in the pyrite and its content was controlled by the partition coefficient of pyrite. The As would replace the sulfur and affect the S/Fe ratio to some degree. However, other elements were in a mechanical mixing state, and their contents were related to the concentration of the elements in the deposition medium during pyrite formation.

Plate III. The single framboid, poly-framboids composed of single framboids and anhedral pyrite from K2qn1 mudstone. 1—the single framboid occurrences in a thin layer of clay (SEM secondary electron image with a scale bar of 2 μm, 1720.77 m deep); 2—lenticular-shaped poly-framboids aggregates (SEM backscattered electron image with a scale bar of 10 μm, 1726.27 m deep); 3—dumbbell-shaped poly-framboids aggregates (SEM backscattered electron image with a scale bar of 10 μm, 1726.27 m deep); 4—irregular shaped poly-framboids aggregates (SEM backscattered electron image with a scale bar of 20 μm, 1749.87 m deep); 5—partial magnification of lenticular-shaped poly-framboids aggregates (SEM backscattered electron image with a scale bar of 5 μm, 1749.87 m deep); and 6—anhedral pyrite (reflecting microscope image with a scale bar of 50 μm, 1755.87 m deep).
Table 1

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5. Discussion

5.1. Pyrite genesis analysis

The reflecting microscope and SEM observations reveal that the K$_{2}$m$_{3}$ mudstone contains two basic pyrite forms (framboids and euhedral crystals), aggregate forms, and anhedral pyrites. Sedimentary pyrite generally forms in anoxic conditions with the organic matter as a reductant and an energy source. Sulfate is reduced to H$_{2}$S by sulfate-reducing bacteria, and then H$_{2}$S further reacts with iron monosulfate, and eventually, crystalline pyrite is formed and preserved in the sediments (Berner, 1984). The pyrite forms are correlated with the reaction types and ways the pyrite was generated (Goldhaber and Kaplan, 1974; Raiswell, 1982).

The genesis of framboidal pyrite has been controversial for some time. The organic origin view suggested that frambooidal pyrites were the product of sulfate-reducing bacteria (Love, 1957); the inorganic origin view suggested that frambooids were recrystallized hydrous Fe-sulfide gels (Rust, 1935; Schouten, 1946) or were formed by aggregation of greigite (Fe$_{3}$S$_{4}$), (3) aggregation of greigite to pyrite phases saturated solutions. While both amorphous FeS and pyrite are in the supersaturated state, the precipitation rate of fine-grained materials. Meanwhile, flocculation is also affected by water salinity (Sherman, 1953). While in euxinic–anoxic bottom water, a single frambooidal pyrite is gathered into dambbell- and irregular-shaped aggregates (Fig. 4A). While in the pore water of the anoxic sediments, influenced by porosity, water media and other factors, and also affected by the surface tension of water and overlying pressure, the frambooids form lenticular aggregates, and occasionally dambbell- and irregular-shaped aggregates, which occur subparallel to the deposit surface (Fig. 4B).

The process of the formation of euhedral pyrite crystal is generally considered to be direct nucleation and growth from solution (Goldhaber and Kaplan, 1974; Giblin and Howarth, 1984). However, Schoonen and Barnes (1991a, 1991b) noted that pyrites are not formed from solution directly but are transformed from the amorphous FeS that is generated from the initial supersaturated solution. While both amorphous FeS and pyrite are in the saturation state, the nucleation rate of the amorphous FeS is higher than that of pyrite, so rapid nucleation of amorphous FeS constrains the nucleation of pyrite; that is, the precipitation of FeS inhibits the supersaturation of pyrites. Therefore, it is possible that pyrites are generated from amorphous FeS or other single-sulfide-phase saturated solutions. Wang and Morse's (1996) experiment showed that supersaturation is a major factor in controlling single crystal growth, while other factors, such as the concentration of active iron, do not exert as much impact. Pyrite crystal features are affected by crystalline habits and media. Because the cube has the smallest surface energy, the initial pyrite form is a simple cube. With the increase in supersaturation, the crystal forms change from cubic to pyritohedron to octahedral to sphenic crystals. These forms were all found in the mudstone of K$_{2}$m$_{3}$, and they indicated the various growing steps.

The biomorphic aggregates composed of euhedral monocrystals consist of those replacing phytoclasts and/or ostracoda shells. For the phytoclast-shaped shells, the sizes are different and include the cube, octahedron, and pyritohedron shapes. Such assemblies originate from organic matter that was replaced by pyrite during the late diagenetic period (Fig. 4B). For ostracod-shaped shells, the size of...
the euhedral crystals filling the ostracods-shaped chambers is very small. They are mainly cube- and octahedron-shaped shells. Their sizes are more homogeneous, while the crystal sizes at the margin are comparatively larger. The homogeneity could be the result of the shell micro-environment, which may differ from the pore water environment, as the pore water environment is unrestricted (i.e., is more favorable for active organism, sulfate, active iron, and sulfate-reducing bacteria). The shell micro-environment is relatively enclosed, so the growth of pyrite framboids is spatially confined, which enables the formation of euhedral pyrite crystals with an even size. The larger euhedral crystals at the shell’s margin are most likely the result of late diagenetic replacement (Fig. 4A).

The abiological aggregates are mainly banded and bubble-shaped. Banded aggregates mostly consist of pyritohedron and spherical crystals. When Allen (2002) simulated an iron-limited environment, he discovered banded sulfides and proposed that they originated from a natural mineral colloid (Liesegang banding) \([\text{FeOOH} (\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O})]\). The upper part of the bubble-shaped aggregates is composed of a series of oval-shaped aggregates; the lower part is composed of irregularly shaped aggregates that extend nearly perpendicularly to the deposition layer. The particle size at the margin of the oval-shaped aggregates is larger than that at the inner part. The bubble-shaped aggregates are likely related to gas escape. The

![Fig. 3. Distribution of the S/Fe ratio of different pyrite forms. Pyrite forms: 1. cube; 2. pyritohedron; 3. octahedron; 4. spherulitic; 5. framboid.](image-url)
euhedral pyrite crystals, which are buried at depths a few centimeters from the top of the sediments, most likely formed by the following reaction in the early sediments (Berner, 1984):

\[
2\text{CH}_2\text{O} + \text{SO}_2^-_4 \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^-.
\]

As the sulfate reduction rate increased, large amounts of \(\text{H}_2\text{S}\) were produced. Partial \(\text{H}_2\text{S}\) further reacted with the active iron to form a series of iron sulfides and finally formed pyrite. Due to the presence of fractures in uncompacted sediments, where fracture water occurred, the remaining \(\text{H}_2\text{S}\) moved upward in bubble form to escape along the fractures of uncompacted sediments, until it reached the redox interface (below the sediment–water interface). There, the gas was oxidized, and the bubbles' shape extended in the same direction as the fractures during the upward process; however, as the gas moved up, the precipitation of even fine-grained materials blocked the top of the sediments' fractures, and the channels of fractures disappeared, so the \(\text{H}_2\text{S}\) bubbles were encapsulated in the fractures of sediments. With the thickening of the overlying sediments, the vertical pressure on the \(\text{H}_2\text{S}\) bubble was significantly stronger than that in the horizontal direction; therefore, the bubble gradually became oval-shaped. The \(\text{H}_2\text{S}\) bubbles reacted with the adjacent active iron and ultimately formed an oval-shaped euhedral crystal aggregate.

In addition, some irregularly shaped anhedral pyrite crystals can also be found in the mudstone of the \(K_q1\). A few dissolved anhedral pyrite crystals have been observed in borders and caves, most likely caused by late diagenetic transformation.

In summary, a correlation exists between the various pyrite shapes in the \(K_q1\) in the mudstone and the lake bottom water environment resulting from deposition (Fig. 4). The euhedral pyrite crystals are directly nucleated and grown from solution or transformed from amorphous \(\text{FeS}\). Therefore, the euhedral pyrite crystals form in a wider environment; that is, they can form both in the pore water of anoxic sediments under oxic–dysoxic bottom waters and in euxinic–anoxic bottom water bodies and most likely undergo secondary growth after being buried. The pyrite framboidal that are formed in euxinic–anoxic bottom water environments generally have smaller average diameters that fall within a narrow range; in contrast, the framboidal that were formed in the pore water of the anoxic sediments under oxic–dysoxic bottom waters have a larger average diameter and wider range.

**Fig. 4.** Relationships between different pyrite forms from the \(K_q1\) mudstone and lake bottom water. 1 — framboidal; 2 — euhedral crystal; 3 — dumbbell-shaped and irregular framboidal aggregate; 4 — lentoid framboidal aggregate; 5 — ostracoda-shaped euhedral crystal aggregate; 6 — bubble-shaped euhedral crystal aggregate; 7 — ribbon euhedral crystal aggregate; 8 — phytoclast-shaped euhedral crystal aggregate.

**Fig. 5.** “Box-and-whisker” plots of pyrite framboids of the \(K_q1\).
5.2. Relationship between pyrite forms and the sedimentary environment

From the discussion in Section 5.1, we know that different lake bottom water environments may lead to the formation of different pyrite forms. In particular, framboidal pyrite varies with changes in the redox conditions of bottom waters. Many studies have confirmed that the framboid size distribution can be an effective indicator of the redox conditions of ancient bottom waters (Wilkin et al., 1997; Wignall and Newton, 1998; Wilkin and Arthur, 2001; Wignall et al., 2005; Shen et al., 2007; Zhou and Jiang, 2009). The diagram (Fig. 5) based on statistics (Table 1) shows the size distribution of framboidal pyrite in the K2qn1 and indicate that the size distribution of framboidal pyrite varies with depth. Based on the size distribution of framboidal pyrite, the K2qn1 can be divided into three depth intervals: 1770.47 to 1782.47 m, 1751.37 to 1769.87 m and 1704.27 to 1749.87 m. The framboid diameter distribution at the three depth intervals (Fig. 6) shows that in the depth range of 1770.47 to 1782.47 m, the framboid diameter has a range of 4 to 16 μm, 8.8 μm on average; in the depth range of 1751.37 to 1769.87 m, it is 3 to 8 μm, 5.1 μm on average; and in the depth range of 1704.27 to 1749.87 m, it is 4 to 25 μm, 10.8 μm on average. Therefore, at the depth range of 1751.37 to 1769.87 m, the framboid diameter is comparatively smaller, and the range of the size distribution is concentrated, whereas at the depths of 1704.27 to 1749.87 m and 1770.47 to 1782.47 m the framboid diameter is comparatively larger and the size distribution is generally wider. The size distribution of framboids represents an effective indicator of the redox conditions of ancient bottom waters. Accordingly, we can speculate that the redox conditions of ancient bottom waters fluctuated during the deposition of the K2qn1, i.e., that they varied from the oxic–dysoxic (1770.47 to 1782.47 m) to the euxinic–anoxic (1751.37 to 1769.87 m) to the oxic–dysoxic state (1704.27 to 1749.87 m). Based on the variation in the range of framboids sizes, it can be speculated further that the bottom waters of the depositional environment at the depth range of 1770.47 to 1782.47 m may be more subjected to oxygen limitations than those at the depth range of 1704.27 to 1749.87 m.

The 1751.37 to 1769.87 m depth range had euxinic–anoxic bottom water conditions, which might have resulted in the development of an anoxic event in the lake. The sliding window spectral analysis results of the Natural Gamma logging curve in the South well of the K2qn1 "SCORE I" (Wu et al., 2008) showed that the average deposition rate is 9.43 cm/ka at the 1690 to 1782.8 m depth range. Therefore, the duration of the lake anoxic events during the deposition period in the K2qn1 was approximately 196 ka. The reason the euxinic–anoxic lake bottom water environment developed is that the early Turonian global
sea-level rise and, as the water surface of the lake rose simultaneously, sea water may have entered the lake, causing salinity stratification in the lake. Due to a lack of water exchange between the top and bottom waters, the oxygen-rich surface water could not reach the bottom, and an extreme anoxic environment conducive to the accumulation and preservation of organic carbon may have developed, resulting in the formation of the main hydrocarbon source rock in the Kq1n1.

6. Conclusions

(1) In the mudstones of the first member of the Qingshankou Formation (Kq1n1), euhedral crystals and framboids are the dominant pyrite forms. The euhedral crystals consist of cubic, pyritohedron, octahedron, and occasionally spherulitic crystals. There are biomorphic and abiological aggregates composed of euhedral monocrystals. The pyrite framboids are densely packed, generally spherical aggregates of submicron-sized pyrite crystals and are composed of cubic, octahedron, and spherulitic microcrystals of uniform particle size. The poly-framboids have lenticular dumbbell and irregular shapes.

(2) The size distribution of framboidal pyrites in the mudstone of the Kq1n1 varies with depth and can be an effective indicator of changes in the redox conditions in the bottom waters. It is concluded that the redox conditions of bottom water during deposition of the Kq1n1 fluctuated from oxic–dysoxic to euxinic–anoxic to oxic–dysoxic. The sediments occurring at the depth of 1751.37 to 1769.87 m were deposited in a euxinic–anoxic bottom water environment, with an anoxic lake event continuing for approximately 196 ka. Such an environment was favorable for the accumulation and preservation of organic carbon and may have been one of the most important factors in the formation of hydrocarbon source rocks in the Songliao Basin.

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