Chemical and isotopic evidence for secondary alteration of natural gases in the Hetianhe Field, Bachu Uplift of the Tarim Basin

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Abstract

H₂S and CO₂ are found in elevated concentrations in the reservoirs near the Carboniferous–Ordovician unconformity in the Hetianhe Field of the Tarim Basin, NW China. Chemical and isotopic analyses have been performed on produced gases, formation waters and reservoir rocks to determine the origin of CO₂ and H₂S and to explain the heterogeneous distribution of isotopic and geochemical characteristics of petroleum fluids. It is unlikely that H₂S and CO₂ had a mantle component since associated helium has an isotope ratio totally uncharacteristic of this source. Instead, H₂S and CO₂ are probably the result of sulphate reduction of the light hydrocarbon gases (LHG). Increasing H₂S concentrations and CO₂/(CO₂ + C₆C₄/C₃O₂) values to the west of the Hetianhe Field occur commensurately with increasingly heavy hydrocarbon gas δ¹³C values. However, thermochemical sulphate reduction is unlikely because the temperatures of the reservoirs are too low, no H₂S or rare pyrite was detected in deeper reservoirs (where more TSR should have occurred) and inferred δ³⁴S values of H₂S (from late-stage pyrite in the Carboniferous and Ordovician reservoirs) are as low as −24.9‰. Such low δ³⁴S values discount the decomposition of organic matter as a major source of H₂S and CO₂. Bacterial sulphate reduction of the light hydrocarbon gases in the reservoir, possibly coupled indirectly with the consumption of organic acids and anions is most likely. The result is the preferential oxidation of δ¹²C-rich alkanes (due to the kinetic isotope effect) and decreasing concentration of organic acids and anions. Modern formation water stable isotope data reveal that it is possible that sulphate-reducing bacteria were introduced into the reservoir by an influx of meteoric water from the west by way of an inversion-related unconformity. This may account for the apparently stronger influence of bacterial sulphate reduction to the west of the Hetianhe Field, and the consequent greatest decrease of the δ¹³C-CO₂ values and the greatest increase in δ¹³C values of the alkane gases.

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1. Introduction

Light hydrocarbon gases are considered generally to be stable under conditions of petroleum reservoirs in sedimentary basins. δ¹³C values of methane and ethane have thus been used to determine maturity of source rocks based on empirical δ¹³C–Rₗ relationships (e.g. Stahl and Carey, 1975; Schoell, 1983; Faber, 1987; Huang et al., 1999). This approach can thus be used to identify the areal distribution of source rocks. However, post-generation effects have been suggested to be significant (Krooss and Leythaeuser, 1988), and may blur genetically distinct isotopic fractionations in reservoirs (Prinzhofer and Huc, 1995). In H₂S-bearing pools, δ¹³C values of gaseous hydrocarbons have been shown to become heavy as a result of thermochemical sulphate reduction (TSR; Krouse et al., 1988; Connan et al., 1996; Worden and Smalley, 1996).

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Gas pools in the Hetianhe Field, Bachu Uplift of the Tarim Basin, NW China (Fig. 1), occur near the Carboniferous–Ordovician unconformity. The low-temperature sandstone and carbonate reservoirs in this field (40–80 °C) are characterized by high H2S concentrations and the presence of sulphate minerals.

It is interesting to note that the geochemistry of natural gas in this field shows several parallel trends from the east to west, with increased CO2 and H2S concentrations and heavier δ13C values for methane, ethane and propane towards the west. This manuscript presents new data from gases, formation waters and authigenic minerals, and attempts to evaluate the mechanism of secondary alteration of the natural gases and $R_o$–δ13C relationship in this field.

2. Geological settings

The Hetianhe Field, located in the south of the Bachu Uplift (Fig. 1), is the second largest gas field discovered in the Tarim Basin. The Bachu Uplift is bordered to the east by the Central Tarim Uplift. The gas and condensate pools are mainly found in the Hetianhe horst structure near the Carboniferous–Ordovician unconformity.

The Hetianhe area was uplifted by two reverse faults in the north and south (Fig. 1b) during the late Caledonian (late Silurian) to early Hercynian Orogeny (early Carboniferous). As shown by the W–E cross section (Fig. 2), thrusting in the west of Hetianhe was significantly greater than in the east as the result of different structural stresses (Jia, 1997; Wang, Z. et al., 1999).

Petroleum system analysis reveals that there are two potential source rocks, several reservoirs and caprocks in the Bachu Uplift (Fig. 3, Sun et al., 1999; Wang, Q., 1999; Zhang, S., et al., 1999; Wang, T. et al., 1999; Zhang, G. et al., 2000). One possible source rock is a Cambrian marl and argillaceous dolomite located to the north of the Hetianhe Field. The Cambrian source rock, an algal dominated type I source rock, encountered in Well He4 in the Bachu Uplift has $R_o$ values from 1.65 to 2.05% (i.e. post mature), total organic carbon (TOC) values ranging from 0.21 to 2.14% (with an average of 0.81%, $n = 40$), a hydrogen index up to 40.52, and δ13C values from −29.4 to −31.8% (Zhang, S. et al., 1999; Wang, Z. et al., 1999). The source rock interval with TOC > 1.0% in the Well He4 is 108.5m thick (Zhang, S. et al., 1999). The other possible source rock is a type III, Carboniferous carbonaceous mudstone with $R_o$ from 0.65 to 0.86%, δ13C from −24.6 to −27.5% (Wang, Z. et al., 1999).

The burial and geothermal history of the Well He4 shows that rapid sedimentation took place during the Cambrian, Carboniferous through to the Permian, and finally in the Neogene. Significant uplift occurred during the late Silurian, the end of the Devonian to early Carboniferous and the period from the late Permian to the Eocene (Fig. 4). The strata experienced maximum burial and heating at the end of early Permian. The maturation of sedimentary organic matter in the Hetianhe Field was influenced by various events. The Cambrian source rock first became mature as the result of subsidence prior to middle Ordovician, and oil generation was considered to

Fig. 1. Location map showing (a) Tectonic units of the Tarim basin and location of the Hetianhe Field; (b) major faults and the location of major gas or oil exploration wells in the Hetianhe Field.
Fig. 2. A west–east cross section (AB) showing greater erosion in the west than in the east, variation of total dissolved solids and $\delta^{18}$O of formation water and methane $\delta^{13}$C$_{1}$ along the Carboniferous and Ordovician unconformity in the Hetianhe Field. See Fig. 1(b) for the map location of the cross section.

Fig. 3. Generalised stratigraphic column for the Bachu Uplift showing complex petroleum systems. Data from the Quaternary to Lower Ordovician are derived from the Hetianhe Field, and the Cambrian from wells He 4 and Fang 1.
reach a peak during the Devonian (Zhang, S. et al., 1999; Zhang, G., et al., 2000). The oil migrated to the Ordovician during the Silurian and Devonian but became biodegraded and oxidized to bitumen as the result of uplift during the late Caledonian (late Silurian) to early Hercynian orogeny (early Carboniferous) (Fig. 4, Wang, T. et al., 1999; Zhang, G. et al., 2000). Carboniferous and Permian sedimentation resulted in natural gas generation from the Cambrian through to the end of Permian. The generated gases were trapped within the Cambrian strata below the anhydrite and salt beds, and then re-migrated upward and accumulated in Carboniferous and Ordovician reservoirs (Zhang, S. et al., 1999; Zhang, G., et al., 2000). Organic matter maturation of the Carboniferous source rock occurred due to Neogene and, locally, Eocene sedimentation and the resulting condensate accumulated in Carboniferous and Ordovician reservoirs during the Himalayan Orogeny (Neogene) (Zhang, S. et al., 1999; Wang, Z. et al., 1999; Zhang, G., et al., 2000).

3. Analysis methods

Gas and water samples were obtained through drill-stem testing (DST) or repeat formation testing (RFT) from gas or water intervals. Chemical compositions of natural gases were measured using gas chromatography in the Tarim Oilfield Laboratory. H$_2$S contents were measured using an MX2000 gas detector equipped with an electric pumping system and a gas-injection cap with a detection limit of 10 ppm. These data were collected from daily published exploration reports from the Tarim Basin, and only those data measured before acidification are reported in this paper (since acidification artificially leads to increased H$_2$S in the produced fluids). Gases with intense H$_2$S smell must have H$_2$S less than the analytical detection limit (since the human nose is insensitive to H$_2$S > 5 ppm), but are assumed to have a H$_2$S concentration of 5 ppm for comparison reason. Gas carbon isotopic compositions of CO$_2$ and light hydrocarbon gases were measured on MAT251 or MAT 252 mass spectrometers. Some data were collated from Wang, Z. et al. (1999) and Wang, T. et al. (1999). Isotopic data are here reported relative to the Pee Dee Formation Belemnite standard (PDB) with a precision of about ±0.1‰. Anhydrite and elemental sulphur samples for S isotopic analyses were extracted from hand-specimens, and pyrite was extracted by disaggregation of limestone. The analyses of anhydrite and elemental sulphur were carried out at the Institute of Geology and Geophysics, CAS, China, and formation water sulphate δ$^{34}$S in Leeds University, UK. The methods have been published elsewhere (e.g. Cai et al., 2001b; Jassim et al., 1999), and results were reported in the standard delta ($\delta$) notation relative to Canyon Diablo Troilite (CDT).

Formation water samples were filtered through a 0.45 μm filter. Water samples for analysis of organic acids and anions were preserved by adding 0.5 mg HgCl$_2$, and measured by means of isotachophoresis within one month with a precision of ±2 to 8% (Liu et al., 1993). The analytic methods for water chemistry and δD and $\delta^{18}$O can be found in Cai et al. (2001a).

4. Reservoir fluid geochemistry

4.1. Gas chemistry

In the Hetianhe Field, natural gases contain significant amounts of H$_2$S (up to 2000 ppm). No H$_2$S has been found in the Cambrian reservoirs. The vertical distance between H$_2$S-bearing pockets or compartments and the unconformity is mostly less than 220m, except in Well 4 where the gas pool is 450 m above the unconformity. Laterally, the H$_2$S concentration and CO$_2$ molar percentage [CO$_2$/(CO$_2$+ΣC$_{1-4}$)] or $X_{CO_2}$ increase. The H$_2$S concentrations tend to increase with increasing $X_{CO_2}$ as outlined in Fig. 5.

All the natural gases in the Hetianhe Field have a dryness coefficient ($C_1/ΣC_{1-4}$) > 0.9. In the Ordovician pools, light hydrocarbon gas (LHG) accounts for up to 95.5% of the natural gas by volume (LHG% = 100–N$_2$%–CO$_2$%, Table 1) in the eastern part of the field (e.g. from Well 7). The LHG percentage is significantly lower in the western part of the field (e.g. only 72.7% from Well 3). A trend of decreasing proven LHG reserves westward was observed. The reserves in the Well 3 compartment are about one twelfth of that in the Well 8 pool. The Lower Carboniferous pools show a

![Fig. 4. Burial history of well He4. Isotherms are constrained by fission track data and vitrinite reflectance measurements (modified after Zhang, S. et al., 1999).](image-url)
similar trend, and the proven reserves in the Well 3, 5 and 8 compartments are in a proportion of 0.32: 1.17: 1.33, respectively (Wang, Z. et al., 1999).

4.2. Isotopic compositions of the natural gases

The Hetianhe Field gases have similar $^{3}$He/$^{4}$He ratio from 1.07 to 1.17×10$^{-7}$ ($n = 4$). The $\delta^{13}$C ranges for methane ($\delta^{13}$C$_{1}$) are $-38.2$ to $-35.6\%$; for ethane ($\delta^{13}$C$_{2}$) they are $-37.8$ to $-34.9\%$; for propane ($\delta^{13}$C$_{3}$) they are $-33.5$ to $-31.1\%$; and finally for butane ($\delta^{13}$C$_{4}$) they are $-30.3$ to $-27.6\%$ (Table 1). The lightest $\delta^{13}$C$_{1}$ value of $-39.6\%$ in the area was reported by Zhang, G. (2000). From the east to west, the $\delta^{13}$C values of these light hydrocarbon gases become heavier with increasing CO$_{2}$ molar percentages. Positive relationships were observed between the CO$_{2}$ molar percentage and

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**Table 1** Chemistry and isotopic compositions of natural gases

| Well | Age | Depth | H$_{2}$S | CH$_{4}$ | C$_{2}$H$_{6}$ | C$_{3}$H$_{8}$ | C$_{4}$H$_{10}$ | CO$_{2}$ | N$_{2}$ | $\delta^{13}$C$_{1}$ | $\delta^{13}$C$_{2}$ | $\delta^{13}$C$_{3}$ | $\delta^{13}$C$_{4}$ | $\delta^{13}$C$_{CO2}$ | $^{3}$He/$^{4}$He |
|------|-----|-------|---------|--------|--------------|---------------|---------------|-------|------|----------------|----------------|----------------|----------------|----------------|------------------|---------|
| 5    | C$_{2}$ | 1050 | 79.4 | 1.29 | 0.17 | 0.04 | 0.4 | 18.7 | – | – | – | – | – | – | 1.17 |
| 4    | C$_{2}$ | 1048 | 1073 | 78.6 | 0.67 | 0 | 0 | 10.1 | 10.6 | $-35.6$ | $-35.1$ | $-31.1$ | $-27.6$ | $-13.6$ | – |
| 8    | C$_{1}$ | 1663 | 5 | 78.9 | 1.81 | 0.72 | 0.37 | 0.6 | 17.6 | $-38.2$ | $-37$ | $-32.7$ | $-29.8$ | – | – |
| 8    | C$_{1}$ | 1885 | 5 | 78.9 | 1.84 | 1.01 | 0.39 | 0.5 | 17.3 | $-38.1$ | $-37.8$ | $-33.3$ | $-29$ | – | – |
| 7    | C$_{1}$ | 1779 | – | 81.7 | 0.05 | 0.09 | 0.28 | 0.8 | 17 | – | – | – | – | – | – |
| 7    | C$_{1}$ | 2146 | 1275 | 79.5 | 1.86 | 1.96 | 0.34 | 2.7 | 13.3 | $-37.6$ | $-37$ | $-32.9$ | $-29.9$ | $-12.1$ | – |
| 6    | C$_{1}$ | 1718 | – | 79.3 | 0.13 | 0.79 | 0.37 | 3.3 | 14 | – | – | – | – | – | – |
| 6    | C$_{1}$ | 2089 | 81 | 80.8 | 1.47 | 0.71 | 0.21 | 3.1 | 13.7 | $-37.0$ | $-36.7$ | $-32.2$ | $-29.5$ | $-15.3$ | – |
| 5    | C$_{1}$ | 1482 | – | 82.6 | 0.68 | 0.24 | 0.08 | 3.1 | 13.3 | $-36.2$ | $-35.7$ | $-33.3$ | $-29.9$ | $-8.2$ | 1.07 |
| 4    | C$_{1}$ | 1170 | 1067 | 78.2 | 0.67 | 0 | 0 | 10.6 | 10.6 | – | – | – | – | – | – |
| 4    | C$_{1}$ | 1202 | 1056 | 80 | 0.34 | 0 | 0 | 9.1 | 10.7 | $-35.8$ | $-36.6$ | $-32.2$ | $-29.3$ | – | – |
| 3    | C$_{1}$ | 1509 | 1623 | 77.2 | 0.27 | 0.07 | 0.1 | 11.9 | 11.9 | – | – | – | – | – | – |
| 7    | O$_{2,3}$ | 2206 | – | 80.4 | 1.99 | 0.71 | 0.34 | 3.1 | 13.4 | – | – | – | – | – | – |
| 7    | O$_{2,3}$ | 2220 | 87 | 88.5 | 3.31 | 0.84 | 0.42 | 3.9 | 2.9 | – | – | – | – | – | – |
| 7    | O$_{2,3}$ | 2280 | 1080 | 80.9 | 0.97 | 0.33 | 0.19 | 1.6 | 16.0 | $-37.8$ | $-37.3$ | $-33.5$ | $-30.2$ | $-5.7$ | 1.16 |
| 7    | O$_{2,3}$ | 2352 | 26 | 90 | 3.37 | 1.09 | 0.42 | 1.4 | 3.5 | $-37.6$ | $-37.2$ | $-33.1$ | $-29.9$ | – | – |
| 6    | O$_{2,3}$ | 2153 | 2000 | 76 | 2.48 | 2.13 | 0.15 | 7.4 | 11.8 | – | – | – | – | – | $-18.4$ |
| 6    | O$_{2,3}$ | 2335 | 1998 | 73.4 | 1.42 | 0.43 | 0.18 | 10.0 | 14.6 | – | – | – | – | – | $-18.2$ |
| 5    | O$_{2,3}$ | 1606 | – | 82.2 | 0.83 | 0.28 | 0.1 | 3.0 | 13.6 | – | – | – | – | – | $-19.3$ |
| 8    | O$_{1}$ | 2345 | 155 | 82.6 | 1.4 | 0.52 | 0.28 | 1.0 | 13.7 | $-37.9$ | $-35.5$ | $-33.2$ | $-30.3$ | $-8.6$ | – |
| 8    | O$_{1}$ | 2388 | – | 83.4 | 1.18 | 0.45 | 0.25 | 1.3 | 13.3 | $-37.8$ | $-37.2$ | $-33.1$ | $-29.8$ | $-8.3$ | 1.08 |
| 4    | O$_{1}$ | 1513 | 1080 | 78.3 | 0.41 | 0.08 | 0 | 10.6 | 10.7 | $-35.6$ | $-36.7$ | $-31.8$ | $-28.8$ | – | – |
| 4    | O$_{1}$ | 1638 | 5 | – | – | – | – | – | – | – | – | – | – | – | – |
| 3    | O$_{1}$ | 1754 | 1162 | 72.2 | 0.48 | 0.02 | 0 | 14.8 | 12.5 | – | – | – | – | – | – |
| 3    | O$_{1}$ | 1795 | 1109 | 81.1 | 0 | 0 | 0 | 13.5 | 5.4 | – | – | – | – | – | – |
| 2    | O$_{1}$ | 2573 | 742 | 80.1 | 2.34 | 0.16 | 0 | 8.0 | 9.4 | $-35.6$ | $-34.9$ | – | – | – | – |
| 1    | O$_{1}$ | 2306 | 1100 | – | – | – | – | – | – | – | – | – | – | – | – |

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*H$_{2}$S is in ppm, and other gas chemistry in vol%; $\delta^{13}$C$_{1}$ (CH$_{4}$), $\delta^{13}$C$_{2}$ (C$_{2}$H$_{6}$), $\delta^{13}$C$_{3}$ (C$_{3}$H$_{8}$), $\delta^{13}$C$_{4}$ (C$_{4}$H$_{10}$) and $\delta^{13}$C$_{CO2}$ are in $\%$PDB, $^{3}$He/$^{4}$He in $\times 10^{-7}$.

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*a* Age based upon the strata that the gas sample was collected from.

*b* Depth is set as the medium point between perforation, in m.

*c* – represents no measurement or not available.
(1) $\delta^{13}C_1$, (2) $\delta^{13}C_3$, (3) $\delta^{13}C_4$ with correlation coefficient values of 0.92, 0.83 and 0.72, respectively (Fig. 6). Excluding an anomalous data point ($\delta^{13}C_2 = -35.5\%$, Well 8 2345m), a positive correlative relationship also exists between the $\delta^{13}C_2$ and the CO$_2$ molar percentage with a coefficient of 0.66. Measurement error and other possibilities cannot be excluded for the datum.

The $\delta^{13}C$ values of the gas samples taken from the western part of the Hetianhe Field are much heavier than those of the gases from similar stratigraphic intervals (Carboniferous and Ordovician) with deeper burial depth (3600–4800 m) in the Central Tarim Uplift. For example, analyses of eight gas samples produced from the Tz 4 field show an average $\delta^{13}C_1$, $\delta^{13}C_2$ and $\delta^{13}C_3$ values of −42.8, −40.4 and −33.9\%o respectively (Chen et al., 1997; Cai et al., 2001b). These values are 7.2, 5.5 and 2.8\%o lighter than those of the corresponding LHG produced from the western part of the Hetianhe Field. When only gases in the Hetianhe Field are considered, the largest differences of $\delta^{13}C_1$ and $\delta^{13}C_2$ have been shown to be 4.0 and 2.9\%, respectively (Zhang, G., 2000). Of the two gas samples, the $\delta^{13}C_1$ values (−35.8 and −36.7\%o, respectively) are heavier than $\delta^{13}C_2$ (−36.6 and −36.7\%o, respectively), showing a partial reversal in the carbon isotope values.

When data from the Hetianhe gases are plotted on the ln(C$_1$/C$_2$) vs ( $\delta^{13}C_1$− $\delta^{13}C_2$) diagrams (Prinzhofer and Huc, 1995), the dots show a trend of increase in ($\delta^{13}C_1$− $\delta^{13}C_2$) with rise in ln(C$_1$/C$_2$) (Fig. 7), and a small variation in ln(C$_2$/C$_3$) relative to ($\delta^{13}C_2$, $\delta^{13}C_3$) (Fig. 8).

The $\delta^{13}C$ values of CO$_2$ in the Hetianhe gases range from −5.7 to −19.3\%o (Table 1). A $\delta^{13}C$CO$_2$ value of −24.6\%o was reported in the west of this area (Sun et al., 1999). In general, the CO$_2$ with lighter isotopic values and higher CO$_2$ contents occur in the western part of the field while heavier values and relatively high contents occur in the east as shown in Table 1 and Fig. 6.

5. Formation water chemistry, $\delta$D, $\delta^{18}$O, and organic acids and anions

Formation water chemistry (Table 2) shows that pH values range from 6.3 to 8.0. The waters contain relatively abundant SO$_4^{2−}$. The SO$_4^{2−}$ concentrations, mostly greater than 1000 mg/l, do not appear to vary with reservoir depth or age. The HCO$_3$ concentrations vary widely (298–3000 mg/l), and are higher in the west than in the east. The opposite was seen for the total dissolved solids (TDS), which decrease from 37 g/l in Well 6, 29 g/l in Well 5 in the east, to 26 g/l in Well 4 in the west.

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**Fig. 6.** $\delta^{13}C$ values of CO$_2$ and light hydrocarbon gases vs. CO$_2$ molar percentages. $\delta^{13}C$ values are abnormally heavy in comparison with those of Central Tarim gases shown schematically in the right box.

**Fig. 7.** Variation of $\delta^{13}C_1$−$\delta^{13}C_2$ versus ln(C$_1$/C$_2$) showing possible origins for the evolution trends. The symbol (□) represents the sample with abnormal heavy $\delta^{13}C_2$.

**Fig. 8.** Variation of $\delta^{13}C_2$−$\delta^{13}C_3$ versus ln(C$_2$/C$_3$) showing a small variation of ln(C$_2$/C$_3$) relative to the isotopic difference.
(Fig. 2). Significantly, in a vertical sense, the lowest TDS values were observed in formation waters near the Carboniferous–Ordovician unconformity (Fig. 2, Mei et al., 1998).

The δD and δ18O data for all seven water samples plot below the Global Meteoric Water Line (MWL) \[δD = 8 \times δ^{18}O + 10\] (Fig. 9), and are thus considered to be typical formation waters. A least-squares fit to all data intersects the meteoric water line (MWL) at δD = −79.6‰ and δ18O = −11.4‰, close to the present-day isotopic compositions of waters from the Kongque River in the Tarim Basin (δD = −73‰, δ18O = −11.5‰).

The formation waters have more negative δ18O values in the west than in the east. From the west to east, the δ18O values are −2.1‰ in Well 4, −1.9‰ in Well 6 and −1.0‰ in Well 7 in the Lower Carboniferous waters (Fig. 2). A similar trend occurs in the Ordovician.

The bottom-hole temperatures of the reservoirs in the Hetianhe Field are below 80 °C, and the concentrations of organic acids and anions (OAA) in the formation waters are below 42 mg/l (Fig. 10). These are in sharp contrast with the oil and gas reservoirs in the Tabei and Central Tarim Uplifts, where the reservoir temperatures range from 80 to 142 °C, with much higher OAA concentrations (Cai et al., 1996; Fig. 10).

6. Occurrence and isotopic compositions of sulphur-bearing mineral species

Pyrite, anhydrite and celestite were observed in the Carboniferous and Ordovician reservoir rocks of the Hetianhe Field. Authigenic pyrite occurs in various forms, either as anhedral agglomerates or along bedding planes or fractures. Among the 360 thin sections examined, nearly 140 contain pyrite with the relative percentage ranging from less than 1% to 5%. Pyrite occurs in subhedral crystals and partially replaces early calcite cement and carbonate grains.

Anhydrite is widespread and exists in the Middle Cambrian, Ordovician and Carboniferous reservoir rocks examined. Celestite was encountered in Carboniferous limestones from the 1900–1934 m interval of Well 8. Native sulphur has not been uniquely identified in core samples, but a small mine (Keping Sulphur Mine) has exploited native sulphur in the Tianshan Mountains.

![Fig. 9. Stable isotopic composition of Hetianhe Carboniferous and Ordovician formation water, with the Meteoric Water Line (MWL), standard mean ocean water (SMOW) and present-day Kongque River water plotted for reference. All water samples plot sloping towards the MWL with an intersection at δD = −79.6‰ and δ18O = −11.4‰, close to that of Kongque River water (δD = −73‰, δ18O = −11.5‰).](image)

![Fig. 10. Variation of the concentrations of organic acids and anions (OAA) vs. temperature showing less than 42 mg/l OAA in the Bachu formation waters whilst high OAA in other parts of the Tarim Basin.](image)
in the northwest of Bachu Uplift, close to the Keping Fault (Fig. 1b).

It can be seen from many thin sections from core that calcite occurs as pseudomorphs after anhydrite in the habit of columns or plates. Low-relief anhydrite was often replaced by high-relief calcite. Fibrous, acicular anhydrite clearly coexists with yellow elemental sulphur in the Keping Sulphur Mine.

The $\delta^{34}S$ values measured for anhydrite in Ordovician rocks is around $+26.0\%$, within the $+25$ to $+30\%$ range expected for Ordovician marine sulphates (Claypool et al., 1980). In contrast, the $\delta^{34}S$ value of anhydrite isolated from a Cambrian sample (Well Fang1, at 4606 m) is around $+33.7\%$. Analyses of four authigenic pyrite samples gave $\delta^{34}S$ values from $-24.9$ to $+11.6\%$ (Table 3). The maximum $\delta^{34}S$ difference between pyrite and Ordovician anhydrite is $51.0\%$, whereas a difference of up to $58.6\%$ was observed between pyrite and Cambrian anhydrite.

Analyses of two elemental sulphur samples from the Keping Sulphur Mine gave an average $\delta^{34}S$ value of $+2.3 \pm 4.1\%$. The dissolved sulphates in formation waters in the Ordovician and Carboniferous have very similar $\delta^{34}S$ values from $+13.5$ to $+16.6\%$ ($n = 6$) (unpublished data). These values are slightly less positive than the lower limit of $\delta^{34}S$ values of Carboniferous seawater sulphates, and are significantly less positive than Ordovician seawater $\delta^{34}S$ (Claypool et al., 1980). The differences between pyrite with the least positive $\delta^{34}S$ value and formation water sulphates range from 38.4 to 41.5\%.

7. Discussion

7.1. Origin of CO$_2$ gas

CO$_2$ can be derived from a variety of sources: bacterial and thermal degradation of organic matter, decomposition of carbonates, and degassing of the mantle and atmosphere (e.g. Dai et al., 1996; Wycherley et al., 1999; Cai et al., 2001b). $\delta^{13}C$ values of CO$_2$ and the stable isotope ratio of helium ($^{3}$He/$^{4}$He ratio) have been widely used to distinguish the source of the CO$_2$.

The $^{3}$He/$^{4}$He ratios show no significant difference among the samples from the east and the west in the field, suggesting the He has a similar source. The ratio is 2–3 times higher than that from the Central Tarim (Cai et al., 2001b), but much lower than that of mantle-derived He ($1.1 \times 10^{-5}$) and atmospheric He ($1.4 \times 10^{-6}$) (Mamyrin and Tostikhin, 1984). So the He is mainly derived from the crust, not from the mantle (Wang, T. et al., 1999). Thus, it is reasonable that mantle-derived and atmospheric CO$_2$ are not significant in the field.

The origins of CO$_2$ can be distinguished in terms of $\delta^{13}C$ values (e.g. Dai et al., 1996; Wycherley et al., 1999). Inorganically derived CO$_2$ has $\delta^{13}C$ values close to $0\%$ while organic CO$_2$ is usually lower than $-7$ to $-10\%$ (Dai et al., 1996; Wycherley et al., 1999).

In the Hetianhe Field, the $\delta^{13}C$ values of the CO$_2$ have a wide range from $-5.7$ to $-19.3\%$. Since no significant CO$_2$ has originated from the mantle or the atmosphere, the highest $\delta^{13}C$ value indicates the CO$_2$ is a mixture of inorganically and organically derived CO$_2$. The lowest value of $-19.3\%$ in the study may reflect the mixing of methane-derived and inorganically derived carbon (e.g. Machel et al., 1995), hence the derivation of the CO$_2$ from LHG oxidation cannot be excluded. The positive correlative relationship between the H$_2$S and molar CO$_2$ concentrations suggests both may have a similar origin, whilst the weak correlation might be related to pyrite and calcite precipitation or an inorganically derived pre-existing CO$_2$ contribution. However, the western gases in the area have lower $\delta^{13}C$ values and higher CO$_2$ contents, suggesting that increase in CO$_2$ contents might have originated mainly from organic matter, perhaps from light hydrocarbon gases.

7.2. Origin of H$_2$S gas and pyrite cement

H$_2$S gas may be derived from four different sources (Orr, 1977; Krouse et al., 1988; Worden and Smalley, 1996): bacterial sulphate reduction (BSR), thermochemical

<table>
<thead>
<tr>
<th>Sampling location</th>
<th>Strata</th>
<th>Depth (m)</th>
<th>Mineral</th>
<th>$\delta^{34}S$ ($%$, CDT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well 7</td>
<td>O$_{2+3}$</td>
<td>2186</td>
<td>Pyrite</td>
<td>$+11.2^*$, $+11.6$</td>
</tr>
<tr>
<td>Well 8</td>
<td>O$_{2+3}$</td>
<td>2023</td>
<td>Pyrite</td>
<td>$-24.9$</td>
</tr>
<tr>
<td>Well 8</td>
<td>O$_{2+3}$</td>
<td>2021</td>
<td>Pyrite</td>
<td>$+0.5$</td>
</tr>
<tr>
<td>Well 8</td>
<td>O$_{1}$</td>
<td>2362</td>
<td>Pyrite</td>
<td>$-18.5$</td>
</tr>
<tr>
<td>Keping Sulphur Mine</td>
<td>O$_{2+3}$</td>
<td>0.8</td>
<td>Native sulphur</td>
<td>$+5.2$</td>
</tr>
<tr>
<td>Keping Sulphur Mine</td>
<td>O$_{2+3}$</td>
<td>0.6</td>
<td>Native sulphur</td>
<td>$-0.6$</td>
</tr>
<tr>
<td>Well 8</td>
<td>O$_{1}$</td>
<td>2362</td>
<td>Anhydrite</td>
<td>$+26.0$</td>
</tr>
<tr>
<td>Well Fang 1</td>
<td>Cambrian</td>
<td>4602</td>
<td>Anhydrite</td>
<td>$+33.7$</td>
</tr>
</tbody>
</table>

* Measured in Leeds University, UK, others measured in the Institute of Geology and Geophysics, CAS, China.
sulphate reduction (TSR), thermal degradation of sulphur-enriched crude oils and kerogen, and juvenile H2S.

Juvenile origin of the H2S in the Hetianhe Field is unlikely since no mantle-derived He was detected as discussed previously. The other three potential sources will be discussed in the following in detail.

7.2.1. Decomposition of organic matter

In general, organically derived H2S is thought to have a δ34S value very close to the parent S-enriched kerogen and oil (Orr, 1977). Marine kerogen contains sulphur that has a δ34S value that is typically about 15% lower than the contemporary seawater. Thus, Ordovician and Cambrian kerogen (and resulting organically-derived H2S) should have a δ34S of about +11% and +19%, respectively (Claypool et al., 1980). Unfortunately, no δ34S data were measured directly on H2S gas.

However, H2S tends to precipitate as pyrite when Fe is available. The iron may be expelled from mudstone interbedded with limestone, or derived from Fe-bearing detrital minerals in limestones (Cai et al., 2001b). The early calcite cements and carbonate grains that were partially replaced by pyrite and the fact that pyrite may occur in fractures suggest the pyrite was precipitated during late diagenesis. Late-stage pyrite is often considered to be a TSR product (Machel et al., 1995; Cai et al., 2001b), but non-cubic pyrite (framboidal or anhedral agglomerations) suggests fast crystalline growth under a relatively low temperature condition. In other words, the pyrite was likely formed in a low-temperature, late-diagenesis setting, and is expected to have a similar δ34S value to the H2S gas. Since the δ34S values (−24.9%, −18.5%) of the pyrite in the Hetianhe Field are lower than those of both Cambrian and Ordovician kerogens, and also the values are lower than the assumed minimum δ34S value (−17%) of the H2S from thermal degradation of organic sulphur (Aplin and Coleman, 1995), the H2S was unlikely to have been derived from an organic source.

7.2.2. Thermochemical sulphate reduction (TSR)

TSR is generally considered to take place at a temperature greater than 125 °C in deep carbonates that contain anhydrite (Worden et al., 1995; Cai et al., 2001b) and results in elevated concentrations of H2S and CO2 in the reservoirs. The H2S has δ34S values close to its precursor sulphates (Orr, 1977; Krouse et al., 1988).

That sulphate reduction occurred in Bachu Uplift is suggested by the positive correlation between the H2S concentration values and XCO2. The latter has been used to indicate the extent of sulphate reduction (Krouse et al., 1988). If the H2S originated due to TSR in the Cambrian, a small or negligible sulphur isotopic fractionation would be expected during the transformation of SO4−2 to S2− (Orr, 1977). However, the maximum H2S difference between pyrite and Cambrian anhydrite or seawater (up to 58.6‰) is much too large for the H2S to have been the result of TSR.

It is very important to note that natural gases with high H2S content in the Hetianhe Field occur almost exclusively near the Carboniferous–Ordovician unconformity. No H2S and negligible pyrite were observed in reservoirs near and within the Cambrian strata indicating that H2S was unlikely to have migrated from Cambrian strata.

7.2.3. Bacterial sulphate reduction (BSR)

Since we have argued against the sulphur being derived from organic matter, thermochemical sulphate reduction and juvenile H2S, the H2S in the Hetianhe Field most probably originated from BSR.

Sulphate reducing bacteria (SRB) are generally considered to be active under restricted conditions: temperatures less than 60–80 °C, low to moderate salinities, strictly anoxic conditions and no more than about 5% H2S (e.g. Machel et al., 1995; Peters and Fowler, 2002).

Low temperature (40–80 °C) and sulphate-enrichment in the Hetianhe Field appear to have provided favourable conditions for most SRB to grow on. This could explain the large sulphur isotope fractionation (up to 51‰) between the Ordovician pyrite and anhydrite in the eastern part of the field, or about 40‰ between the pyrite and the formation water sulphates. The large δ34S fractionation suggests BSR took place under a relatively open diagenetic system with a plentiful sulphate supply. If microbial sulphate reduction takes place in a closed system, residual sulphate is enriched in 34S relative to the seawater as reduction proceeds (e.g. Aharon and Fu, 2000). In the case of the Hetianhe Field, the formation sulphate δ34S values are lighter than those of Carboniferous and Ordovician seawater. It is possible that the values represent the mixing of isotopically light sulphates from sulphide re-oxidation with isotopically heavy sulphates from anhydrite dissolution as a result of meteoric water influx.

Low sulphate reduction rates could be indicated by the fact that large volumes of LHG can still coexist with high SO42− in the eastern part of the field. This is consistent with the result of anaerobic oxidation of methane under laboratory conditions (Davis and Yarbrough, 1966). It is likely that the variable δ34S values of pyrite (Table 3) resulted from locally different sulphate reduction rates.

In the areas away from the Hetianhe Field in the eastern Keping County, H2S may have reacted with oxides within ground water to generate native sulphur. Anaerobic microbial oxidation of H2S could also lead to formation of native sulphur (Sassen et al., 1988). The elemental sulphur sampled from the Keping Sulphur Mine has δ34S values within the range for the pyrite in the Hetianhe Field (Table 2), supporting the preceding mechanisms.
7.3. Substrates for sulphate reduction bacteria (SRB)

It is generally thought that sulphate reducing bacteria mainly deplete organic acids and anions (OAA) (e.g. Jobson et al., 1979).

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

(1)

In the formation waters of the Hetianhe Field, OAA are absent or extremely low (< 42 mg/l), suggest that OAA might have been depleted by the micro-organisms. However, some recent observations and experiments have shown that methane might be depleted directly or indirectly coupled to OAA (e.g. Davis and Yarbrough, 1966; Kirkland and Evans, 1976; Panganiban et al., 1979; Aharon and Fu, 2000; Boetius et al., 2000). The reaction of sulphates with methane may be written as follows:

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

(2)

The above reaction could explain isotopically-enriched residual gaseous hydrocarbons in the area. Because micro-organisms responsible for methane oxidation have not been isolated and OAA are present in low concentrations in the Hetianhe Field waters, it is reasonable to conclude that SRB might have utilized both OAA and LHG as substrates. A similar case was reported for the natural microbial populations of Lake Mendota surface sediments (Panganiban et al., 1979), where sulphate, acetate and methane were required for SRB growth. LHG and OAA oxidation is expected to result in an increase in HCO$_3^-$ concentration, thus favouring CaCO$_3$ precipitation. Note that late calcite cement and calcite replacement of pre-existing anhydrite are observed in the area.

7.4. Relationship between $\delta^{13}C$ and $R_o$

The Hetianhe gases show that most of the gases have similar $\ln(C_2/C_3)$ relative to $\delta^{13}C_2-\delta^{13}C_3$ differences, and that $\delta^{13}C_1$ becomes closer to $\delta^{13}C_2$ as $\ln(C_1/C_2)$ values increase. These relationships are explained to result mainly from kerogen thermal cracking but not significantly from crude oil cracking according to experimental results and the case-study of Angola gases (e.g. Prinzhofer and Huc, 1995).

In the study area, the $\delta^{13}C$ values of methane are as high as $-35.6\%$ (Table 1). The thermal maturity level of the source rock that generated the methane is estimated to have reached 2.5–2.7% $R_o$ (vitrinite reflectance equivalent), using the empirical $\delta^{13}C_1- R_o$ relationships compiled for China (Chen et al., 1993; Huang et al., 1999). For all the gases from the Hetianhe Field, using the model of Huang et al. (1999), inferred $R_o$ values for the gas source rock are 2.3 to 2.7% and 1.5 to 2.1% based on the $\delta^{13}C_1- R_o$ and the $\delta^{13}C_2- R_o$ relationships, respectively. Using the models of Berner et al. (1995) and Berner and Faber (1996), the inferred $R_o$ values are 0.6 to 0.8% based on the relationship between $\delta^{13}C_2$ and $\delta^{13}C_3$ and are about 1.3–1.6% based upon $\delta^{13}C_1$ measurement alone. These values are expected to be slightly larger when $-31\%$ for the Cambrian organic matter rather than $-30\%$ is used as the gas precursor $\delta^{13}C$ in the model of Berner and Faber (1996). Because the sapropelic type of gas-cracking with a gas dryness coefficient $>0.9$ in the Hetianhe Field can not be a product of the “oil-window” stage (Huang et al., 1999), the equations of Huang et al. (1999) established on the Tarim Basin may be more reasonable. As a line of supporting evidence, the inferred $R_o$ value for the Hetianhe gases is $>2.0\%$ based on the $\delta^{13}C_1- R_o$ model of Faber (1987). Other factors such as heating rate, extent of gas generation and kerogen-dependent gas generation rate may influence the $\delta^{13}C_1- R_o$ relationship (Tang et al., 2000). We can conclude that models developed for one basin do not necessarily work for another (Jenden et al., 1988; Lorant et al., 1998).

However, the estimates based upon the $\delta^{13}C_1- R_o$ equations of Huang et al. (1999) and Chen et al. (1993) are much higher than the maximum $R_o$ values of the potential source rocks in the Bachu Uplift area (e.g. 1.65–2.06% in Well He4, 1.63–1.81% in Well Fang 1—Zhang, S. et al., 1999). There exist large differences between the two results based on the models of $\delta^{13}C_1$ alone and the $\delta^{13}C_2$ and $\delta^{13}C_3$ relationship of Berner and Faber (1996) and Huang et al. (1999). All these suggest that the $\delta^{13}C$ values of the methane have been positively shifted by post gas generation effects.

7.5. Isotope effects associated with LHG anaerobic oxidation

The light hydrocarbon gases involved in thermal anaerobic oxidation (such as TSR) have been shown to have increasingly less negative $\delta^{13}C$ values. For example, as a result of TSR, ethane and propane $\delta^{13}C$ values were reported to shift by up to $+10\%$ for $\text{C}_2\text{O}_2 = 0.15$ (Krouse et al., 1988) or by $+2$ and $+10\%$, respectively (Connan et al., 1996). However, we argue against TSR as the origin of the $\text{H}_2\text{S}$, thus TSR is not the mechanism for the $\delta^{13}C$ shift of the light hydrocarbon gas in the Hetianhe.

It has been shown that bacterial anaerobic oxidation results in a positive shift in $\delta^{13}C$ values for light hydrocarbon gases. At the base of the sulphate reduction zone, $\text{C}_2\text{H}_4$ is preferentially oxidised yielding CO$_2$ depleted by approximately $9\%$ in the heavy isotope relative to the methane (Alperin et al., 1988). The heavier $\delta^{13}C$ values for the light hydrocarbon gases associated with higher $\text{XCO}_2$ and $\text{H}_2\text{S}$ contents in the Hetianhe Field (Fig. 6) indicate that the higher $\delta^{13}C$
values of residual gases could have resulted from the relatively greater extent of C\textsuperscript{12} preferential depletion by SRB in the western part of the Hetianhe Field. The greater carbon isotope fractionation of methane than ethane and propane during BSR and the inversion of \( \delta^{13}C \) values for methane and ethane (i.e. \( \delta^{13}C_1 > \delta^{13}C_2 \)) imply that methane was depleted to a greater degree in this case. Although the \( \delta^{13}C \) inversion may occur during low and high pyrolysis temperature stages of gas generation in laboratory experiments (Berner et al., 1995; Tang et al., 2000; Cramer et al., 2001), the yield of no more than 1% of the total gas generated during the low-temperature stage (Tang et al., 2000) and likely leaking of the early-stage gas from the system in reservoirs suggest that the \( \delta^{13}C \) reversal is unlikely to have been inherited from the low-temperature decomposition of organic matter.

It has been proposed previously that SRB prefer methane to higher molecular weight hydrocarbon gases (Whiticar, 1999) or liquid phase petroleum as methane is a simpler and smaller molecule (Aharon and Fu, 2000). Similarly, one might expect that SRB would deplete preferentially more methane than ethane, propane and other larger hydrocarbons with slightly more complicated structures, based on the \( \delta^{13}C \) values observed above. This result is clearly different from that reported for TSR by Krouse et al. (1988).

The model of residual methane (Whiticar and Faber, 1986; Whiticar, 1999) can be used to describe the relationship among the proportion of methane oxidation, isotopic shift and fraction factor according to:

\[
\delta^{13}C_{1,i} = \delta^{13}C_{1,i} + \epsilon_C(1 - F)
\]

where \( \delta^{13}C_{1,i} \) and \( \delta^{13}C_{1,i} \) are the methane \( \delta^{13}C \) prior to oxidation and at time \( t \), respectively. \( F \) represents the fraction of depleted methane at time \( t \). The fraction factor \( \epsilon_C \) ranges from about 4 up to about 30 based upon aerobic culture experiments and model calculation using field data (Whiticar, 1999 and references therein). If we assume \( \epsilon_C \) as 17, the median value of the \( \epsilon_C \) data range (4 to 30), and the largest \( \delta^{13}C_1 \) difference for the Hetianhe gases of 4.0\% according to the data of Zhang, G. (2000) as indicated in the previous text, i.e., \( (\delta^{13}C_{1,\text{r}} - \delta^{13}C_{1,i}) = 4.0\% \) and \( \epsilon_C = 17 \), then about 25\% methane was utilized by SRB in the area using the above equation. If we assume \( \epsilon_C \) as 9 (Alperin et al., 1988) and the largest \( \delta^{13}C_1 \) difference for the gases \( (\delta^{13}C_{1,\text{r}} - \delta^{13}C_{1,i}) \) as 2.6\% in the study (Table 1), then about 30% methane was depleted in the area.

7.6. The origin of SRB

The precise origin of SRB is difficult to constrain, but the majority of SRB in the Ordovician and Carboniferous reservoirs of the Hetianhe Field were unlikely to have survived since the Ordovician or Carboniferous, owing to the deep burial, uplift and meteoric influx these reservoirs have experienced. Tectonic history analysis shows that the Bachu area was uplifted during the Himalayan Orogeny, resulting in the erosion of Permian strata and upper part of Carboniferous in the western part of the study area (Jia, 1997; Wang, Q., 1999). It is possible that the western part of the area became an area for meteoric water recharge. The \( \delta\text{-}\delta^{18}O \) relationship in the study area is similar to that in the Central Tarim Uplift (Cai et al. 2001a), possibly indicating a similar origin. Thus, the formation waters in Hetianhe Field were subsequently infiltrated by meteoric water. The meteoric water could have flowed eastward along the unconformity. The suggestion is supported by the trends of decreasing TDS in vertical proximity to the unconformity, and decreasing \( \delta^{18}O \) data and TDS from east to west laterally. Microbes including SRB could have been carried by the freshwater into the reservoirs near the unconformity. As the western side was closer to meteoric water recharge area, the number of active SRB might have been greater and BSR was more effective. Similar cases have been reported previously in the Tabei Uplift of the Tarim Basin (Cai et al., 1996) and in North Iraq (Jassim et al., 1999).

8. Conclusions

An integrated approach involving gas chromatographic analysis, gas and mineral stable isotope analysis, petrography, and formation water chemistry and isotope analysis was employed to try to account for light hydrocarbon gas alteration in the Hetianhe Field, Tarim Basin. We have proposed that preferential oxidation is the most likely cause of \( ^{13}C \)-enriched light hydrocarbon gases in the west of the Hetianhe Field. The preferential \( ^{12}C \) oxidation of light hydrocarbon gases to generate CO\textsubscript{2}, accompanied by partial reduction of sulphates to \( \text{H}_2\text{~S} \) and pyrite, was most likely the result of sulphate reducing bacteria coupled to oxidation of organic acids and anions as well as petroleum fluids. The sulphate reducing bacteria might have been carried into the reservoirs near the Carboniferous/Ordovician unconformity in the west where there is a modern meteoric water recharge zone. Empirical \( ^{13}C\text{-}R\text{\_~}} \) relationships cannot be used here because the gas carbon stable isotope has been affected strongly by processes within the reservoir.

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