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Gas hydrate stability zone migration occurred in the Qilian mountain permafrost, Qinghai, Northwest China: Evidences from pyrite morphology and pyrite sulfur isotope

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ABSTRACT

Fracture-filling pyrites, which semi-filled or fully filled rock fractures, were commonly found in the cores from all hydrate testing well in the Qilian mountain permafrost. The occurrence of the pyrites is very similar to the "fracture-filling" gas hydrate that occurred in this area, and whose distribution mainly concentrated below the hydrate layer or layer of hydrate associated anomaly. This paper carried out the study in morphology and sulfur isotope for the fracture-filling pyrites. The results show that fracture-filling pyrites consisted of cube form pyrite crystals, directionally spread in a step-like fashion along the fracture surface, and associated with a circular structure; the value of $\delta^{34}S_{CDT}$ ranges from 6.761‰ to 41.846‰, and the most positive excursion exists below the deepest layer of hydrate associated anomaly. The characters in pyrite crystal morphology, sulfur isotopic composition and spatial distribution closely related with the secondary change of metastable gas hydrate reservoir. The permafrost degeneration resulting from climate warming is the most direct cause for gas hydrate stability zone (GHSZ) migration that occurred in the Qilian mountain. The zone between the shallowest and the deepest distribution of the fracture-filling pyrite recorded the possible largest original GHSZ. The top and the bottom of GHSZ have moved downward and upward to a certain extent, respectively, further inferring that the depth of permafrost has decreased about 10 m in the boreholes.

1. Introduction

Gas hydrates are crystalline substances composed of gas and water molecules suspended in a solid structure (Collett et al., 2009; Kvenvolden, 1993); they are also known as metastable minerals, and their formation and/or decomposition depend on the pressure, temperature, composition of gas, salinity of the water and characteristics of the porous medium in which they are formed (Makogon et al., 2007). The pressure and temperature requirements constrain the formation of gas hydrates to permafrost regions and marine sediments in continental margins (Kvenvolden and Lorenson, 2001). The volume of natural gas contained in the world's gas hydrate accumulations far exceeds the volume of known gas reserves (Collett, 2002). The energy contained in natural gas hydrates might be an energy source available for the majority of the 21st century (Makogon et al., 2007).

Permafrost is perennially frozen ground remaining at or below 0 °C for at least two consecutive years (Brown et al., 1998) and covers vast stretches of land at high latitudes and altitudes in both hemispheres (Zhang et al., 1999). It has been shown that gas hydrate accumulated in Arctic regions in association with permafrost in the western Siberia, Russia (Makogon et al., 2007), the Alaska North Slope, USA (Collett et al., 2011), and the Mackenzie Delta, Canada (Dallimore and Collett, 2005; Dallimore et al., 1999). In addition, gas hydrates in recent years have been found in the Qilian mountain permafrost in Qinghai province of China, which belongs to the alpine permafrost at the mid-latitude (Lu et al., 2011a; Zhu et al., 2010, 2011). Thus, gas hydrate in onshore environments is typically closely associated with permafrost. It is generally believed that thermal conditions conducive to the formation of permafrost and gas hydrate have persisted in the Arctic since the end of the Pliocene (about 1.83 Ma) (Collett and Dallimore, 2003), and in the Qinghai–Tibetan Plateau since the late Pleistocene (11–25 kaBP) (Zhou et al., 2000). However, global climate warming is an indisputable fact. According to the Fourth Assessment Report of IPCC (2007), the global surface temperature will increase 1.1–6.4 °C at the end of the 21st century. Empirical evidences have strongly indicated that impacts related to climate warming are well underway in the Polar Regions (Anisimov and Reneva, 2006; Hansen et al., 1998; Morison et al., 2000; Osterkamp, 2005; Serreze et al., 2000; Smith et al., 2002; Walter et al., 2006) and in the Qinghai–Tibetan Plateau (Cheng and Wu, 2007; Li and Cheng, 1999; Nan et al., 2003; Tong and Wu, 1996; Wang, 1993; Wang et al., 2000, 2005; Wu and Liu, 2004; Wu et al., 2006a, 2006b, 2007a, 2007b, 2008; Yang et al., 2010a, 2010b; Zhao

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et al., 2004). Climatic warming can lead to increases in permafrost temperature, thickening of the active layer, and a reduction in the percentage of the terrestrial surface underlain by near-surface permafrost (Akerman and Johansson, 2008; Anisimov and Reneva, 2006; Harris, 1987; Tucker et al., 2004). For example, in the Qinghai–Tibetan Plateau the active layers of permafrost regions are in the trend of getting thicker under the impact of global warming (Wu et al., 2006a). Numerical simulations by Yang et al. (2010a, 2010b) indicated that air temperature on the Qinghai–Tibetan Plateau will continue to increase in the 21st century and significant warming has resulted in extensive degradation of permafrost. Thus, gradual climatic warming also has affected the stability of gas hydrates below the permafrost and caused the gas hydrate stability zone (GHSZ) migration and reduction (Chen et al., 2005). Then, the process of GHSZ migration will be recorded in the form of "footprint" in the gas hydrate reservoir?

Authigenic pyrite has been reported in association with gas-hydrate-bearing sediments both in seafloor and permafrost settings (Chen et al., 2006; Rose et al., 2011; Sassen et al., 2004; Wang et al., 2008) and also documented in nearly all gas hydrate boreholes in the Qilian mountain permafrost, inferring that pyrite formation may be related to the mechanisms controlling the formation and decomposition of gas hydrate (Wang et al., 2011). However, until now there is no real proof for the relationship between the pyrite genesis and the gas hydrate reservoir system in the permafrost. Here we present data from authigenic pyrite termed fracture-filling pyrite that is mainly distributed below the layers of hydrate associated anomaly in the gas hydrate boreholes in the Qilian mountain permafrost. Pyrite morphology and variations in the pyrite sulfur isotopic show that the GHSZ migration occurred in the study area.

2. Geologic settings

Qilian Mountain is located in the northeastern part of the Qinghai–Tibetan Plateau in China. It comprises one of the most important alpine permafrost distribution regions for the Qinghai–Tibet Plateau (Wu et al., 2007a, 2007b). Permafrost area in the Qilian mountain is about 10×10^4 km^2 (Zhou et al., 2000). Its tectonic units are usually divided into the northern Qilian belt (the Hexi Corridor and Zoulangnanshan Mountain), the middle Qilian land (Tuolai Mountain) and the southern Qilian belt. Because Sinian, which is in the Qilian mountains, has endured the continental rift stage (Sinian–Middle Cambrian), ocean floor expansion and the trench–arc–basin system stage (Late Cambrian–Middle Ordovician), and the orogenic stage (after the Middle Ordovician, it experienced subduction orogeny, collision orogeny and intracontinental orogeny), the current tectonic patterns were formed (Feng, 1997).

"Scientific Drilling Project of Gas Hydrate" in the Qilian mountain permafrost is located in Muri coalfield, Tianjun County, Qinghai province of China, where altitude is 4000–4300 m, the mean annual ground temperature is −2.4 °C, and discontinuous permafrost is widely development (Zhu et al., 2006). The data of permafrost thickness from actual measurement and logging estimation showed that the thickness of permafrost ranges from 60 m to 95 m, and in a considerable part of the region the permafrost thickness is greater than 100 m (Pan et al., 2008; Zhou et al., 2000; Zhu et al., 2006). The study area is located in the depression between the tectonic units of mid and southern Qilian and belongs to a graben mode fault depression basin formed in the Yanshan period in the north Qilian deep fault system. Juhugeng orefield is one of the major portions of the Muli coalfield; the middle portion is an anticline composed of Triassic stratum, while the northern and southern flanks are two synclines composed of Jurassic lacustrine coal-bearing strata. Large trust faults were developed on the northern and southern flanks of the anticline and synclines. In the two synclines, trust faults caused a series of further shear fractures to develop in the NE direction, cutting depressions into interrupted blocks. Therefore, the study area is presented with belts running north to south and zones running west to east (Fig. 1) (Lu et al., 2011b, 2013). The exposed strata of the Juhugeng orefield mainly contain Quaternary, Middle Jurassic and Upper Triassic regions. The Upper Triassic basement is widely exposed in the northern and southern areas of the Juhugeng orefield. The anticline axes have lithology that mainly includes black siltstone, mudstone and thin coal seams and are parallel unconformities in contact with the overlying Jurassic. The Middle Jurassic includes the Muri and Jiangcang formations. The Muri formation may be subdivided into upper and lower lithological members. The lower portion of the Muri formation is a braided river alluvial plain environment that deposits a set of coarse clastic rocks; sometimes there is thin carbonaceous mudstone or a thin coal seam, and a basal conglomerate develops at the bottom. The upper constituent of the Muri formation is a lake–marsh environment that deposits dark gray siltstone, fine-grained sandstone, gray fine or medium-grained sandstone and coarse-grained sandstone with two thick coal seams. The Jiangcang formation may also be subdivided into upper and lower lithological members. The lower member of the Jiangcang formation is a delta–lake environment that deposits gray fine- and medium-grained sandstone, as well as dark gray mudstone and siltstone while containing two-six coal layers. The upper member of the Jiangcang formation is a shallow-deep lake environment that deposits a set of fine clastic mudstone, siltstone, gray siltstone, black brown oil shale and lenticular siderite. Quaternary is widely distributed in the drilling area; it contains humus caused by the alleviation and deluvial sand, gravel, angular gravel, ice, etc. (Zhu et al., 2010).

In recent years, geological, geophysical, and geochemical investigations and studies were conducted in the Qinghai–Tibet Plateau permafrost, resulting in the identification of prospective gas hydrate bearing areas within the region (Chen et al., 2005; Huang et al., 2002; Liu and Han, 2004; Lu et al., 2007a, 2007b, 2009; Wu et al., 2006b; Zhang et al., 2001, 2007). Based on the measured gas components of Muri coalfield, combined with the mean annual ground temperature, temperature gradient and thickness of permafrost, Zhu et al. (2006) calculated thermodynamic conditions for the formation of gas hydrate in the Qilian mountain permafrost, results showed that where have the conditions conducive to the gas hydrate formation, and the depth of top of GHSZ and bottom of GHSZ is 171 m and 574 m, respectively, and the thickness of GHSZ is 403 m. According to the past geochemical anomalies, Scientific Drilling Project of Gas Hydrate was conducted in Juhugeng orefield in the Muri coalfield in 2008–2011 by China Geological Survey (CGS). Gas hydrate samples were recovered from several boreholes, and anomalies associated with hydrate were observed in all of the boreholes. The detailed characteristics of gas hydrate and anomalies associated with hydrate will be described in the following section.

3. Geological characteristics of gas hydrate

The combined information from drilling and core experiment studies shows that gas hydrates mainly occur in the Jiangcang Formation of Middle Jurassic in the Muri permafrost. Fracture-filling as the main occurrence type of gas hydrate occurs as the thin-layer-like, flake, block group on the fracture surface of siltstone, mudstone and oil shale (Fig. 2). Pore-filling hydrate disseminated occurs in the porous of sandstone and is difficult to observe by the naked eye, but can be indirectly speculated by continuously emerged bubbles and the water drops, and dispersion-like abnormal low temperature of infrared imaging from the core (Wang et al., 2011; Zhu et al., 2010). The reservoir type was considered by Boswell et al. (2011) and Koh et al. (2012) to be Type R — unique hydrate deposits within rocks. Meanwhile, gas hydrate reservoir has a shallower depth, thinner thickness of permafrost and complex gas composition compared with that in the Arctic hydrate reservoir (Huang et al., 2011; Lu et al., 2011a, 2011b; Zhu et al., 2010). In addition, the gas hydrates are distributed non-continuously in the vertical direction in each boreholes, and the law of hydrate distribution in the lateral areas between drill holes is not apparent due to the rock fracture system that plays an important role in gas hydrate distribution (Wang et al., 2011). Specific geological characteristics of gas hydrate reservoir are summarized in Table 1.