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Thermal origin of continental red beds in SE China: An experiment study

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ABSTRACT

The origin of continental red beds in SE China is the result of high diagenetic temperatures, rather than an arid climate during their deposition. Here we present results from an experimental study where black mud was heated to demonstrate the formation of red beds. Diffuse reflectance spectroscopy (DRS) of heated samples enables determination of the relative proportion of goethite and hematite. Iron in black mud is predominantly in the form of goethite that has an initial dehydration temperature of ca.150 °C. Increasing temperature or prolonged heating time is accompanied by decreasing goethite and organic content, increasing hematite and red colouration. Heat provided to subsiding red bed basins is supplied by cooling of an intracrustal granitic magma layer. The thermal model can explain vertical colour, temperature, redox and mineral zonation in red bed sequences, from red (hematite-bearing), through green-yellow (Cu, Zn, V sulphide mineralization) to grey-black (hydrocarbon, halite-bearing) sediments. The model can also be used to help prospect for hydrocarbon and halite deposits in the SE China red bed basins.

1. Introduction

The origin of continental red beds is not only of petrological and sedimentological interest, but is also economically important in that they host Cu, U, V mineralization, halite deposits and contain hydrocarbon reservoirs. Goethite and hematite are the main iron-bearing minerals in red beds, with fine-grained hematite giving red beds their characteristic colour. The formation of red beds is often considered to be related with an arid climate (e.g. Schmalz, 1968; Van Houten, 1961; Deng and Qian, 1987), and their distribution has been used to reconstruct paleo-latitude and paleo-continents (e.g. Wegener, 1924; Frakes, 1979; Seyfert and Sirkin, 1979). However, over the last few decades several studies have suggested that the formation of red beds are not necessarily related to arid climate because the presence of hematite is commonly automorphic (Van Houten, 1973; Walker, 1976; Turner, 1980). Recently, Chen and Grapes (2007) have proposed a model for a thermal origin of red beds related to in-situ crustal melting where the transformation of goethite to hematite occurs under conditions of elevated diagenetic temperatures. Although this model can reasonably explain various geological, geophysical and geochemical phenomena related to red beds, experimental verification from heating experiments on sediments are crucial to verify the process. In this paper, we report the results of an experimental study on the formation of red beds. Our results support a thermal origin of continental red beds in SE China during diagenesis.

2. Heating experiments

2.1. Starting material and preparation

As red beds mostly occur in pluvial, alluvial, deltaic and lacustrine facies, Holocene black mud (2 kg) with about 5% sand from the Pearl River Delta sediments with a composition similar to that of Mesozoic red beds, was used as the starting material for thermal experiments. X-ray diffraction (XRD) analysis shows that the mud is essentially composed of quartz, muscovite, illite, chlorite, kaolinite, and a very small amount of indeterminate Fe-oxide, possibly goethite and/or ferrihydrite, adsorbed onto clay minerals.

Following natural air-drying, the black mud was a 10 × 10 × 5 cm^3 light brown- coloured block, and was divided into 4 subsamples. Subsamples 1, 2 and 3 were separately powdered to 200-mesh in an agate mortar. Some powder of subsample 1 was examined using diffuse reflectance spectroscopy (DRS); others

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were soaked in 5% acetic acid and 10% hydrogen peroxide solution, then rinsed with distilled water, separated by centrifuge and dried at 55 °C for XRD analysis. Powders of subsamples 2 and 3 were respectively heated in Experiments 1 and 2. Subsample 4 was retained as a 5 × 5 × 5 cm^3 block for Experiment 3.

2.2. Experimental procedure

2.2.1. Experiment 1

Powders of subsample 2 (~50 g) were heated at a constant temperature of 450 °C in a muffle furnace at heating times of 1, 2, 5, 8, 12, 24, and 64 h. Seven samples were then analysed by DRS.

2.2.2. Experiment 2

Powders of subsample 3 (~50 g) were divided into seven equal parts. The seven samples were then heated for 24 h in a muffle furnace at 150, 200, 250, 300, 350, 400, and 450 °C, and then analysed by DRS.

2.2.3. Experiment 3

Subsample 4 was heated on an electric hot plate at 450 °C. After ~3 h, the temperature gradient across the block reached a constant ~300 °C at the base and ~70 °C at the top. After heating at 450 °C for 7 days, the lower part of the mud block had undergone a significant colour change as shown in Fig. 1. Four samples were taken from the heated block at 0–1, 1–2, 2–3 and 3–5 cm intervals upward from the base, and these were designated **a**, **b**, **c** and **d** respectively (Fig. 1). The four samples were powdered to 200-mesh in an agate mortar and analysed by DRS.

2.3. Diffuse reflectance spectroscopy (DRS) analysis

Traditionally, the transformation of goethite or other ferric oxyhydroxides to hematite has been measured by paleomagnetic analysis (e.g. McCabe and Voo, 1983; Charusiri et al., 2006). In this study, DRS analysis was used because of the advantage of high test speed and accuracy. The results are comparable with those of paleomagnetic analysis.

DRS analysis of the experimental samples was made using a Perkin-Elmer Lamdba 950 ultraviolet/visible/near-infrared spectrophotometer, where the measuring range is 190–2500 nm and scan interval is 1 nm. Data from the 400–700 nm interval (i.e. the visible spectral band) was utilized, and first derivation values were calculated at 10 nm intervals, each of which was then plotted at the midpoint of each 10 nm interval (i.e. the 400–410 nm value is plotted at 405 nm, etc.) and expressed as %/nm (Baslsam and Damuth, 2000; Ji et al., 2007).

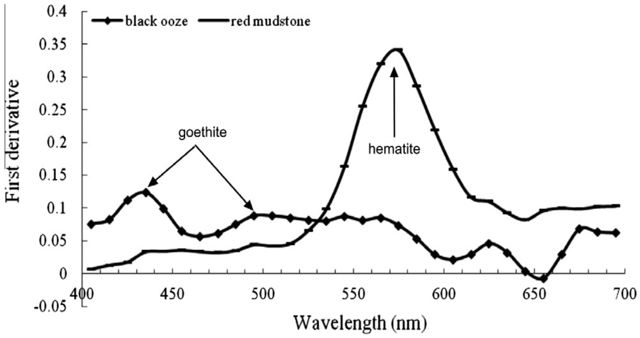

Fig. 2. DRS first derivative curves of black mud sediment from the Pearl River Delta and Early Cretaceous red mudstone from the Sanshui Basin, Guangdong Province, China.

2.4. Experimental results

2.4.1. Air-dried black mud

For comparison with heated samples, unheated, air-dried starting black mud was analysed by DRS. As shown in Fig. 2, the DRS first derivative curve shows characteristic peaks of goethite, with the main and secondary peaks occurring at 435 nm and 495 nm, similar to the curve of goethite in Yangtze River sediments (Li and Yang, 2012).

2.4.2. Red mudstone

For comparison with the heated black mud samples, red mudstone from the Early Cretaceous red bed sequence of the Sanshui Basin, Guangdong Province, SE China, was analysed by DRS. Fig. 2 shows the DRS first derivative curve with a clear characteristic peak of hematite at 575 nm, without characteristic peaks of goethite.

2.4.3. Experiment 1 samples

Fig. 3A shows DRS first derivative curves of samples from experiment 1, where seven samples were heated at 450 °C for different times in a muffle furnace. The sample heated for 1 h shows a goethite peak (435 nm) that significantly declines (the peak occurring at 445 nm should be the characteristic clay peak, e.g., illite and chlorite (Ji et al., 2006)), and a weak hematite peak (565 nm), implying dehydration of goethite and formation of hematite begins at ~450 °C. With longer heating time, the hematite peak gradually increases. Comparison of the hematite peaks of the red mudstone (575 nm) and heated black mud samples (565 nm) indicates that, the peak-height of the heated samples is lower due to their low

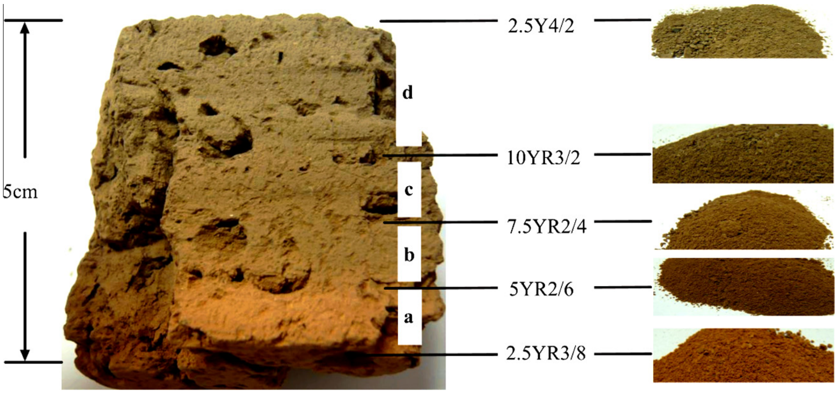

Fig. 1. Colour variation of an air-dried black mud block heated on a hot-plate at 450 °C for 7 days together with Munsell-colour values of the powders (right) from each interface of the vertical intervals from which 4 powdered samples (**a**, **b**, **c**, **d**) were taken.