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To cite this article: G D Zheng et al 2010 J. Phys.: Conf. Ser. 217 012048

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Iron speciation in bleached rocks by hydrocarbon leaching in Dushanzi Mud Volcano, NW China

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Abstract. Mud volcano is a typical petroleum leaching system, which normally result in bleaching effect to surrounding rocks. The result of Mössbauer spectroscopy of rock samples collected from the Dushanzi mud volcano system revealed clear variations in iron species. Compared to the unbleached reddish sedimentary rocks, the bleached rocks are dominated by reducing iron species such as paramagnetic ferrous iron (para-Fe²⁺), ferrous iron in siderite (sid-Fe²⁺), sulphide and pyrite (pyr-Fe²⁺) whereas the original reddish rock is enriched in ferric iron including iron in hematite (hem-Fe³⁺) and paramagnetic ferric iron (para-Fe³⁺). A reduction of ferric iron species and hydrolysis of iron along with oxidation of hydrocarbons should be one of the main processes along bleaching by hydrocarbons to rocks.

1. Introduction
The occurrence of oil and gas related mud volcanoes normally result in sharp variations of rocks properties such as surface colours and structures, especially the colour change of rocks from bright reddish to green, deep gray or black known as bleaching effect. Mud volcanoes that produce bleaching effect on rocks in and around the mudflow craters and vents, can serve as a direct indicator of the characteristics of petroleum reservoirs. The changes of rocks mineral composition and chemical transformation of elements, especially the redox sensitive elements such as iron, caused by the migrating hydrocarbons can be utilized in surface exploitation and environmental issues. However, only limited information is available on the chemical speciation of iron-bearing minerals, probably due to limitations of technology. It is not so easy to get information on chemical species of iron either qualitatively or quantitatively in solid materials such as soils, sedimentary rocks by routine or typically chemical techniques. As one of few available methods, Mössbauer Effect offers a potential for obtaining information about the proportion of ferrous and ferric iron species in both crystalline and amorphous materials and has been applied in a wide range of scientific fields, including the iron chemistry of sediments (Manning, and Ash, 1979; Mørup et al., 1985; Hilton et al., 1986; Zheng et al., 2001). In this paper, iron species of bleached rock samples collected from the Dushanzi mud volcano were investigated for their iron speciation in order to understand the bleaching effect on the reddish sedimentary beds by released hydrocarbons in an inland basin under a very arid climate.

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2. Samples and experiment

The Dushanzi mud volcano is located on the northern piedmont of the Tianshan Mountains, which are standing as the southern margin of the Junggar Basin in Xinjiang Uighur Autonomous Region of northwest China. The Junggar Basin is one of the largest Mesozoic-Cenozoic sedimentary basins enriched in fossil fuels including coal, crude oil and natural gas in China. Because of continuous northward thrusting of the Tianshan Mountains, there occurred several zones of tectonic folds in front of the mountains. Dushanzi anticline is one part of the fourth zone lied from west to east. The Dushanzi mud volcano occurs in the northern side of the Dushanzi anticline, which appears as a single yellowish hill with an elevation of about 940 meters above sea level. A normal fault was found along the crest of the Dushanzi anticline, which provides pathways for eruption of fluids and mud. The Tertiary formation of red beds at surface was bleached because of hydrocarbon-induced alteration (Fu et al., 2007).

Seven samples (DSZ-01 to DSZ-07) with various colours were collected from the bleached rocks around the mud craters. A reddish rock sample, as numbered as DSZ-00, was also collected from the original sedimentary sequence far from the hydrocarbon craters for comparison. The sample DSZ-07 with strong gasoline smell was freeze dried whereas other samples are dry. All samples were crushed into powder with an agate mortar and pestle in the laboratory.

For $^{57}$Fe Mössbauer measurement, 250-335 mg of the powdered sample without any chemical pretreatment was gently pressed into a brass sample holder (16 mm in diameter, 1 mm thick). The sample holder was closed at both ends with iron-free plastic tap. The Mössbauer spectra were obtained with an Austin Science S-600 Mössbauer spectrometer using a $\gamma$-ray source of 1.11 GBq $^{57}$Co/Rh at a constant temperature of either 293 K (room temperature) or 78 K (liquid nitrogen temperature). The obtained spectra were fitted to Lorentzian lineshapes using standard line shape fitting routines. Half-width (HW) and peak intensity of each quadruple doublet was constrained to be equal. Isomer shifts (IS) were expressed with respect to the centroid of the spectrum of metallic iron foil.

3. Results and discussion

3.1 Characterization of iron speciation

The $^{57}$Fe Mössbauer spectra of all the samples at room temperature (RT, constant at 293 K) and liquid nitrogen (LN) temperature (78 K) were shown in Fig. 1 and Fig. 2, respectively. Several overlapped doublets and sextets were observed in these spectra. The curve fitting with iron components was robust because the Chi-squared values were sufficiently small. For the spectra obtained at RT (Fig 1), two doublets with a smaller quadruple splitting were ascribed to either paramagnetic high-spin ferric iron ($\text{para-Fe}^{3+}$) or iron in pyrite ($\text{pyr-Fe}^{2+}$). The former, $\text{para-Fe}^{3+}$, probably originated from clay minerals and/or hydrated Fe(III) oxides (Manning and Ash, 1979). The $\text{para-Fe}^{3+}$ in the samples DSZ-01 through DSZ-07 was most likely in the form of hydroxides whereas the $\text{para-Fe}^{3+}$ in the sample DSZ-00 was mainly due to ferric iron in clay minerals such as smectite based on the Mössbauer parameters and the XRD pattern (data are not shown).

The ferrous iron in pyrite was fitted using the following Mössbauer parameters constrained by values of isomer shift (IS) 0.307 mm/s and quadruple splitting (QS) 0.610 mm/s for the Mössbauer spectra at 293 K. Pyrite was considered absent when the calculated peak area of $\text{pyr-Fe}^{2+}$ was lower than the detection limit, and calculated as 3 times larger than the standard deviation of the baseline count (Kuno et al., 1998). The doublets with a larger quadruple splitting were attributable to paramagnetic low-spin and high-spin ferrous iron, $\text{para-Fe}^{2+}$ (inner) and $\text{para-Fe}^{2+}$ (outer), respectively. According to their Mössbauer parameters, the $\text{para-Fe}^{2+}$ (outer) with higher IS, QS, and HW might be the iron in clay minerals and/or oxide whereas the $\text{para-Fe}^{2+}$ (inner) with lower IS, QS and HW might be the ferrous iron in siderite (Ram, et al., 1998; John et al., 2004; Medina et al., 2006).

For the sextets, at least two types of iron minerals could be identified as magnetite and pyrrhotite according to their RT Mössbauer parameters. Compared with the Mössbauer spectra at RT (Fig 1) and LN (Fig 2), there was some variation in the samples DSZ-01, 03 and 05 that displayed as a doublet at RT but a sextet with about 48.3-4 Tesla at LN temperature, indicating a special iron species other than...
very fine particles of hematite. This iron species may be the super-paramagnetic ferric iron, because the magnetic field of the sextet in these three samples appeared to be small. Existence of an admixture of ferric hydroxides or ferric oxides with various degree of hydration was estimated based on the difference of the parameters between RT and LN Mössbauer spectra.

Figure 1. Mössbauer spectra of samples from Dushanzi mud volcano, measured at room temperature (298 K)

Figure 2. Mössbauer spectra of samples from Dushanzi mud volcano measured at liquid nitrogen temperature (78 K)

With the presence of various iron species among the bleached and unbleached rocks, reduction of ferric iron species into ferrous ones appeared to be the major geochemical process of iron in the rocks with petroleum bleaching. In addition, iron reduction processes appeared to follow certain sequences; probably the reduction of hematite was the earliest reaction, and then goethite and magnetite followed. At the same time, the reduction of ferric iron in smectite to ferrous iron in chlorite would be the main mechanism in the conversion of clay minerals from smectite to chlorite and illite. In addition, the hydrolysis of ferric iron compounds could be also one important step of geochemical reactions during the bleaching processes.

3.2 Significance to reservoirs properties

The inorganic-organic interactions have been considered to be important geochemical reactions for the change of petroleum reservoirs (Spiro, 1984; Mayer, 1994; Larter and Aplin, 1995) because the mineralogical and geochemical changes may give strong impact on the properties of reservoir rocks, including porosity and permeability. Reservoir properties such as the porosity and permeability may change with the formation of secondary minerals as well as the dissolution of original minerals such as quartz, feldspar and other silicate minerals. These interactions could lead to the enlargement of fractures and pores of the oil-gas reservoirs along with the depletion of minerals, especially the dissolution of felsic minerals such as quartz and feldspar. On the other hand, the decreasing of the porosity and permeability of reservoir rocks could be caused by the precipitation of secondary minerals and newly formed cements. Siderite, pyrite and other ferrous iron-bearing compounds as revealed in this study may contribute much to the properties change of petroleum reservoirs, and also the cover layers as the same.
The newly formed minerals during the bleaching process, including clay, silicate and various carbonate minerals, could change the porosity and permeability of rocks. Bleaching process could significantly affect the reservoir and capping layers with low porosity and low permeability, such as the Triassic rocks in the Erdos Basin in northwest China. In some cases, the porosity of a reservoir might be reduced until their fractures and holes were closed, and the reservoir layer became a cap layer under some specific conditions. On the other hand, increase in the porosity and permeability might occur in some reservoirs by the dissolution of minerals due to the hydrocarbons-mineral interactions during oil and gas migration and accumulation. In such cases, the petrologic features of the reservoir could be changed and even converted to different types of formations such as the dolomitized carbonate reservoirs for sour gas deposits in the Sichuan Basin, SW China (Ma et al., 2008). All those changes could be investigated by Mössbauer Effect as ME is effective to almost all iron species in solid materials and iron speciation is one of the major process along with hydrocarbons bleaching.

4. Conclusions
Chemical speciation of iron was greatly influenced by the releasing of hydrocarbons in the Dushanzi mud volcano system. Along with bleaching, a reduction of iron was the primary process in oil-gas bleaching to the rocks. Almost all ferric iron species in the original reddish rocks were reduced into ferrous species such as the iron in siderite, chlorite, even sulphide and pyrite associated with reduced sulphur species.

Acknowledgements
G.Z. gratefully acknowledged the support of K.C. Wong Education Foundation, Hong Kong to attend the ICAME2009 in Vienna. This study was financially supported as the “100-Talent” program from Chinese Academy of Sciences in 2006-2009.

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