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Geochemistry of organic matter and elements of black shale during weathering in Northern Guizhou, Southwestern China: Their mobilization and inter-connection

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ABSTRACT

Different from previous studies on effect of weathering upon geochemical variation along a single weathered profile, this paper provides a new methodology validated by comparing a weathered outcrop samples and their stratigraphic counterpart un-weathered core samples in a nearby shallow borehole. This outcrop and borehole penetrated the Ordovician-Silurian Wufeng–Longmaxi shales, located in the same anticline structure in the northern part of Guizhou Province, Southern China. The mineral composition, major, trace and rare earth elements (REEs) composition and Rock-Eval parameters of outcrop and core samples were analyzed and compared. Organic matter (OM) was observed in the microscope and extracted for elements analysis. The results show that short-term weathering still has significant influence on OM, mineral and elemental composition of black shales. The elements composition shows the outcrop profile was moderately weathered. The REEs compositions do not alter much during weathering process and the REEs composition and their relative ratios still are valid for rock origin determination. The OM, mainly composed by graptolite and bitumen, even entering the highly-over thermal maturity, is still sensitive to the weathering with a systematic loss 30–50% of TOC along the outcrop profile, which suggests that the OM consumption is predominantly controlled by weathering duration and the distance from the weathering surface. In turn, OM has significant influence on the trace elements transportation behavior during weathering. Some trace elements associated with the OM such as V, Cr, Th, U, Ni and Co, change significantly in their absolute concentration during weathering, but their relative ratios do not necessarily change too much and might be still reliable proxies for paleo-environmental determination. The mobility of shale minerals during weathering is in the following order: plagioclase > potassium feldspar and dolomite > pyrite and OM. Short-term weathering can also result in considerable transportation of elements and significant variation of minerals content in black shale, which may pose potentially high environmental and engineering risk in the regions rich in black shale.

1. Introduction

Black shale tends to suffer from chemical weathering in nature due to its high content of organic matter (OM) and unstable minerals (e.g. feldspar and pyrite). The weathering of black shale has drawn attention over the past decade for its unique environmental and petrophysical impact (Jaffe et al., 2002; Jin et al., 2013; Petsch et al., 1999; Renock et al., 2016; Fan et al., 2012a, 2012b). Weathering of black shales produces CO2 and releases many redox sensitive trace elements (RST) to rivers, including U, Re and Mo. This weathering process contributes significantly to atmospheric CO_2 budgets in geological time scale as well as RST budgets in the oceans (Dalai et al., 2002; Derry et al., 1992; Li et al., 2015; Wildman et al., 2004). Development of shale oil and gas resources in recent years might further accelerate the process of shale weathering and elements transportation (Jiang et al., 2015; Luo et al., 2016). Besides, studies on the geochemical characteristics of black shale and their variations with weathering are also necessary for better understanding the possible effects on hydrocarbon source rock quality assessment (Littke et al., 1991; Marynowski et al., 2011a; Marynowski et al., 2011b).

A popular research method used in previous weathering studies is based on a single weathered profile which was examined vertical geochemical alteration from its weathered soil surface downward to the protolitho (Jin et al., 2010; Jin et al., 2013; Petsch et al., 1999;

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Wildman et al., 2004). However, this method is valid only if the original property of shale is homogeneous along the whole profile. Actually, shale has very intensive vertical heterogeneity in mineral and elemental composition (Chen et al., 2015a,b; Fathi and Akkutlu, 2009; Fan et al., 2012a). Hence, here we provide a new comparison method between fresh core samples from a shallow borehole (less than 700 m deep) and its nearby stratigraphic counterpart outcrop profiles which was exposed in the air over 30 years. The Longmaxi shale is widely distributed in south China and recent active exploitation and development of shale gas were carried out in these shales (Ling et al., 2015; Liao, 2013; Song et al., 2004). Through comparing a couple of close-distanced Longmaxi shale well and outcrop profile, this paper aims to (1) examine the geochemical variation of Wufeng–Longmaxi black shale due to short-term weathering, (2) understand the collateral variation of mineralogy and elements composition with organic matter (OM) during weathering, and (3) check the validity of OM-related elements indicators for paleo-environment determination after weathering.

2. Geological setting

The study area is located in the northern edge of Guizhou Province, Southwestern China, which tectonically belongs to the southeastern part of Upper Yangtze Plate (Fig. 1). This area is bounded by regional faults and well-developed fractures (Wu et al., 2014; Zeng et al., 2016). Strata developed in this region include Sinian (Z), Cambrian (), Ordovician (O), Silurian strata (S), Permian (P) and Cretaceous (K). Overlaid by Silurian Longmaxi formation, the Ordovician Wufeng formation can be subdivided into two parts. The lower part is organic-rich black shale, composed by laminated carbonaceous and calcareous shale with a high concentration of graptolite and OM. The upper part, termed as Guanyingqiao limestone, is a kind of biogenic limestone with a thickness of less than 0.3m in this region, and can be a good mark for strata identification (Chen et al., 2014; Luo et al., 2016). The Longmaxi formation also consists of two parts. The lower part consists of black to dark argillaceous shale, interbedded with siltstone, deposited in the deep shelf, whereas the upper part is interbedded with siltstone and gray laminated calcareous shale (Chen et al., 2015a,b; Liu et al., 2013; Wang et al., 2016).

3. Samples and methods

3.1. Sampling and correlations between outcrop and well profiles

Sixteen fresh core samples were collected from Wufeng–Longmaxi shale section in a newly drilled shallow Well XY1 and 10 weathered samples were collected from its stratigraphic counterpart section in nearby roadcut outcrop profile (29 km in distance) which were exposed in the air over 30 years (Fig. 2). The well and outcrop profile are located in the opposite flanks of an anticline near the Xishuixian County, northern Guizhou Province (Fig. 1). The Guanyinqiao limestone serves as a mark for confirming the sequence boundary.

Gamma values of the outcrop profile were measured with CIT-3000F/DF portable gamma spectroscopy detector, and Gamma data of well XY1 were collected from gamma logging. The logging TOC calculated from logging and lithological combination was used to correlate with each other and provide stratigraphic framework for samples comparison (Fig. 3 and Table 1). The correlation between fresh and weathered samples can be confirmed further by mineral and elemental composition data.

3.2. Experimental methods and data process

All samples were polished for petrographic observation and partially crushed into millimeter size for mineralogy, elemental composition and Rock-Eval pyrolysis analysis. Petrographic samples preparation method follows Standard GB/T 15588-2013 on a Zeiss Axio Imager in white and blue incident light. Samples were viewed under oil immersion using a 40 objective with a measuring diaphragm with a 3 mm diameter spot size and an interference filter with a passband peak of 546 nm. TOC content was measured by Leco infrared carbon/sulfur

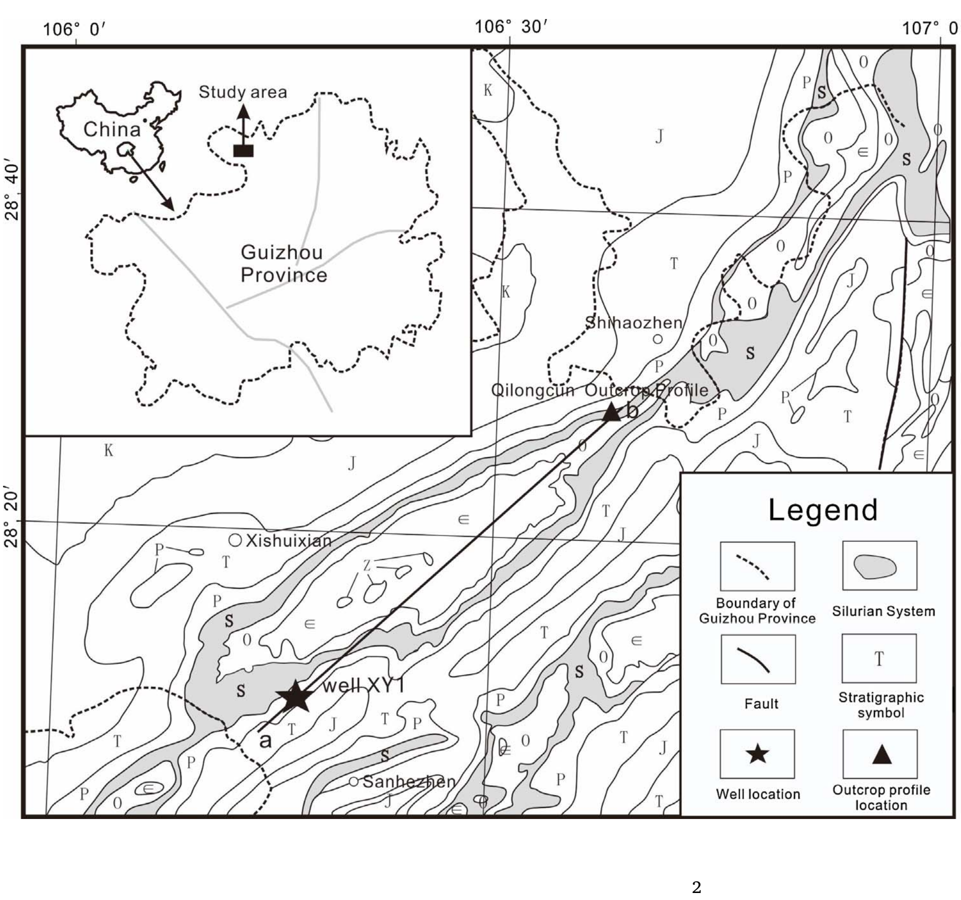

Fig. 1. The geologic map of study area with location of sampling well and outcrop profile. The lines a and b marked the location of cross section in Fig. 2A.