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Evaluating rare earth elements as a proxy for oil–source correlation. A case study from Aer Sag, Erlian Basin, northern China

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ABSTRACT

The use of rare earth elements (REE) for oil–source correlation has not yet been established. In order to evaluate the potential of REE as proxies for oil–source correlation, we used traditional correlation approaches, including biomarkers and trace elemental ratios (V/Ni and Ni/Co), to identify the source rock of oil sands using isolated organic extracts of mudstones and oil sands, and by analyzing the organic extracts and their corresponding whole rock material for REE compositions by inductively coupled plasma-mass spectrometry (ICP-MS). Oil–source correlations using REE were not consistent with conclusions based on biomarker data and trace element ratios. Only one pair of oil–source rock relationship was successfully established using REE. REE concentrations of crude oils could possibly be controlled by the quantities of metal complexes and functional groups that provide complexing sites for V and REE as well as secondary alteration processes (e.g., thermal alteration and biodegradation). REE patterns might be linked to the organic matter types of source rocks. Although an accurate oil–source relationship failed to be established using REE in this study, REE could potentially be a novel complementary proxy for oil–oil and/or oil–source correlations when supplemented by traditional correlation approaches, including biomarkers.

1. Introduction

Traditional geochemical tools for oil–source correlation such as biomarkers and carbon isotopes can be hampered by thermal maturation and secondary alteration (including biodegradation and water washing) and can lose their original significance (Peters et al., 2005). Although these alterations might change the concentration of trace elements in crude oils, some elemental ratios remain constant in many instances, such as the V/Ni ratio (Al-Shahristani and Al-Atyia, 1972; Lewan, 1984; Tissot and Welte, 1984; López et al., 1995). Numerous studies (Hodgson and Baker, 1959; Al-Shahristani and Al-Atyia, 1972; Lewan and Maynard, 1982; Lewan, 1984; Hitchon and Filby, 1984; Ellrich et al., 1985; Hirner, 1987; Curiale, 1987; Barwise, 1990; Oluwole et al., 1993; Filby, 1994; Frankenberger, 1994; López et al., 1995, 1998; Akinlua et al., 2007, 2015; Finlay et al., 2012) have indicated that the concentration and distribution of trace elements in crude oils provide not only vital information for the origin and maturation of petroleum as well as depositional environment of its source rocks, but also a potential tool for oil–oil and/or oil–source correlation. For a long time, due to discovery of organometallic carriers (porphyrin complexes) and relatively high abundance of V and Ni in crude oil (Lewan and Maynard, 1982; Tissot and Welte, 1984; Barwise, 1990; Filby, 1994), V and Ni in crude oil have received more attention than other trace elements and have been used widely in petroleum exploration. Other trace elements have also been studied and applied, including Co, Mo, Pt, Pd, Re and Os (Hirner, 1987; Odermatt and Curiale, 1991; Greibrokk et al., 1994; Selby et al., 2007; Akinlua et al., 2007; Finlay et al., 2012).

Rare earth elements (REE) refer to the lanthanide elements, from La to Lu, which generally exhibit similar chemical properties (Henderson, 1984; Rollison, 1993). Their chemical similarities induce systematic partitioning in a variety of systems. Therefore,

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REE and their concentration patterns have been widely used in studies of the origin of materials, and the physical and chemical environmental variables of various geological processes (Henderson, 1984; Murray et al., 1990; Jiang et al., 2007). Less attention has been paid to the application of REE to petroleum systems.

Related studies have focused on two aspects. One is the depositional environment reconstruction of source rocks (Murray et al., 1990; Pi et al., 2013). In particular, REE compositions of kerogens (petroleum precursors) could place better constraints on oceanic redox conditions (Pi et al., 2013). The other is the classification of crude oils or solid bitumens. For example, Parnell (1988) found that the contents of dysprosium (Dy) may be of value in discriminating between solid bitumens from different sources. Akinlua et al. (2008) classified Niger Delta oils of different sources using the contents and patterns of light rare earth elements (LREE). Jiao et al. (2010) analyzed REE compositions of two end-member oils of the Cambrian–Ordovician in the Tarim Basin, and determined whether oils derived from mixed sources.

Most recently, Dr. M. Totten and his colleagues from Kansas State University have done extensive work on REE compositions of crude oils from Kansas and Oklahoma in order to distinguish the source and origin of oils (Ramirez-Caro, 2013; McIntire, 2014; Kwasny, 2015). Ramirez-Caro (2013) compared REE patterns of Mississippian oils and Devonian Woodford shale oils from Anadarko Basin, and demonstrated that Mississippian oils were generated from the Woodford shales. McIntire (2014) and Kwasny (2015) found that distinct REE patterns occurred in crude oils from different zones of the Lansing-Kansas City formations in central-south Kansas, and determined, together with the use of K/Rb ratios, whether oil was derived locally or remotely. In addition, Clauer et al. (2006) studied REE behavior of organic-rich shales during hydrous pyrolysis, and found a significant change in the heavy REE in the HCl-leachate after pyrolysis.

Unfortunately, since the early work of Manning et al. (1991) who evaluated Nd isotope values ($^{143}Nd/^{144}Nd$) and Sm/Nd ratios as potential tools for oil–source correlation by comparing both ratios in source rocks, hydrous pyrolysates from source rocks and crude oils, oil–source correlation studies using REE have been reported only rarely. The main purpose of the present study is to analyze REE compositions of organic extracts of mudstones and oil sands, identify the source rocks of oil sands using traditional correlation approaches, including biomarkers and trace elemental ratios, and evaluate the potential of REE as a correlation proxy.

2. Sample location and geological setting

Twenty-one samples were collected from the Lower Cretaceous of the Aer Sag, Erlian Basin, northern China (Figs. 1 and 2), including 14 mudstone samples and 7 oil sand samples (Fig. 1 and Table 1). The newly found Aer Sag, located on the northeast margin of the Erlian Basin, first produced commercial oil in 2006. It is a NE

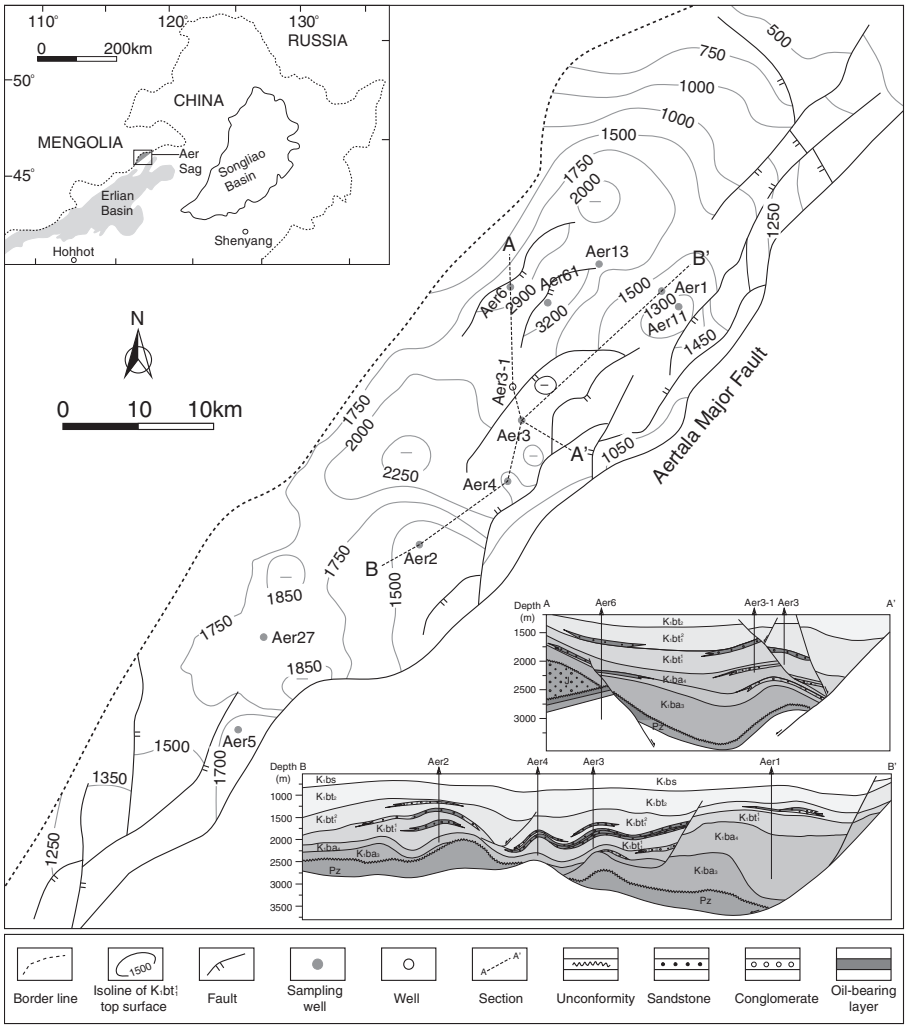

Fig. 1. Outline map of geological structural units in Aer Sag, Erlian Basin (modified after Zhao et al., 2012).