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# Geochemistry of platinum group elements in marine oil shale from the Changshe Mountain area (China): Implications for modes of occurrence and origins

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ABSTRACT

The Shengli River–Changshe Mountain oil shale zone, located in the North Qiangtang depression, northern Tibet plateau, represents a potentially largest marine oil shale resource in China. Eighteen samples, including oil shale and micritic limestone, were collected from the Changshe Mountain oil shale to determine the concentrations, the modes of occurrence, and origins of platinum group elements (PGEs) in marine oil shale. The oil shale samples from the Changshe Mountain area exhibit low total PGE contents ranging from 3.196 to 8.071 ng/g with a weighted mean value of 5.383 ng/g, while the micritic limestone samples from the Changshe Mountain area exhibit a little lower ranging from 0.471 to 5.669 ng/g. PGEs in oil shale samples are characterized by high contents in Pd (3.23 ng/g), Pt (1.60 ng/g), and Os (0.32 ng/g), as compared to Rh (0.083 ng/g), Ru (0.112 ng/g), and Ir (0.043 ng/g).

The individual PGEs of oil shale samples from the Changshe Mountain area exhibit various modes of occurrence. Ru and Ir are mainly controlled by clay minerals and partly present as sulfide. Rh is mainly associated with sulfide and possibly present as clay minerals. Pt is associated with clay minerals and sulfide, and Pd is controlled by organic matter and pyrite, while Os is mainly present in organic matter. Three possible sources of PGEs were identified in oil shale seams in the Changshe Mountain area. Ru and Ir are mainly terrigenous inputs. Rh and Pt are derived from mixed sources (seawater and terrigemnous supply), while Pd and Os are mainly derived from seawater. The terrestrial source of the oil shale seams in the Changshe Mountain oil shale was the Suowa Formation limestone and the Nadi Kangri felsic volcanic rocks.



## 1. Introduction

Oil shale, as an alternative energy resource, has received much attention (Dyni, 2006; Liu et al., 2009). In China, the amount of exploit available resources of oil shale is about 243.2 billion tons (Liu et al., 2009). Most of oil shale deposits were formed in lacustrine environments, such as Tertiary oil shale in the Maoming (Zhang et al., 2007) and Fushun areas (Qian and Wang, 2003), and Cretaceous oil shale in the Songliao basin (Wang et al., 1996).

In May 2006, the Shengli River oil shale deposit was discovered in the Qiangtang basin. Preliminary analyses of organic geochemistry in oil shale samples showed that their deposition occurred in a relatively anoxic marine environment (Fu et al., 2008). In 2007, a feasibility study of the prospect of oil shale was undertaken by Chengdu Institute of Geology and Mineral Resources. A new marine oil shale zone was discovered in the Changshe Mountain area, northern Tibet, China (Fu et al., 2009). This zone, combined with the oil shale zone found in the Shengli River area, represents a largest marine oil shale resource in China. Therefore, studies of these oil shale zones are important for assessing petroleum prospects in the Qiangtang basin and the overall significance of marine oil shale researches in China.

In recent years, platinum group elements (PGEs) in coal and shale have received much attention (Pasava, 1993; Evans and Chai, 1997; Dai et al., 2003, 2004, 2005a,b; Yang, 2006; Křibek et al., 2007; Seredin, 2007; Seredin and Finkelman, 2008; Qi and Gao, 2008; Bratskaya, et al., 2009). Finkelman and Aruscavage (1981) reported that the concentration of Pt in coal is generally less than 5 ng/g, that of Pd generally less than 1 ng/g, and Rh less than 0.5 ng/g. Dai et al. (2003) studied the concentrations of noble metals in Chinese coals and proposed five possible sources of noble metals in coal. A study by Yang (2006) showed that the low-temperature hydrothermal fluids play a dominant role in the enrichment of noble metals in the coal. Oil shale may also contain PGEs due to its similar composition with coal. Understanding the concentrations and occurrences of PGEs in oil shale is significant both practically in the utilization of potentially valuable trace metals in oil shale and theoretically in oil shale formation, because noble metals in oil shale may serve as an indicator of mineralization and can be widely utilized due to their chemical stability. However, up to now very few works have been done on the distribution of PGEs in oil shale, especially in marine oil shale. In this paper, we report the results of PGEs in marine oil shale from the

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Changshe Mountain area, northern Tibet, China, and address the possible modes of occurrence and origins of PGEs in marine oil shale.

## 2. Geological setting

The Qiangtang block, bounded by Hoh Xil–Jinsha River suture zone to the north and Bangong Lake–Nujiang River suture zone to the south, respectively, consists of the North Qiangtang depression, the central uplift and the South Qiangtang depression (Fig. 1a). The Shengli River–Changshe Mountain oil shale zone is located in the southern part of the North Qiangtang depression, northern Tibet plateau, China (Fig. 1a), comprising the Shengli River oil shale and the Changshe Mountain oil shale (Fig. 1b). This zone is exposed for a distance of more than 50 km in an east–west direction and 30 km in a north–south direction (Fig. 1b). The proven reserves of the Shengli River–Changshe Mountain oil shale have been estimated to exceed 1 billion tones (Fu et al., 2009), potentially the largest marine oil shale resources in China.

The Changshe Mountain oil shale is located in the northern part of the Shengli River–Changshe Mountain oil shale zone. Oil shale samples from the Changshe Mountain area have relatively high total organic content (7.02–16.32%) and ash yield (53.22–82.12%) with low total sulfur ($S_{t,d}$) content (0.67–1.52%) and intermediate shale oil content (3.85–11.76%) (Table 1) (Fu et al., 2010a).

## 3. Samples and analytical methods

The studied section is located in the Changshe Mountain area, northern Tibet, China (Fig. 1b). Eighteen samples were collected from this section (Fig. 2). Thirteen of them were collected from oil shale seams with a vertical sampling interval of 30 cm on average, and the other five samples were collected from micritic limestone layers.

The minerals in oil shale and micritic limestone samples were examined by powder using an X-ray diffraction (XRD) of Bruker D8 Advance diffractometer (Bruker, Germany) equipped with a Cu-target tube and a curved graphite monochromator at 35 kV and 40 mA in Tianjin Institute of Geology and Mineral Resources. Samples were step-scanned from 5° to 70° with a step size of 0.02° (2$\theta$). The analytical procedures were followed the method described by Chinese National standard SY/T6210-1996.

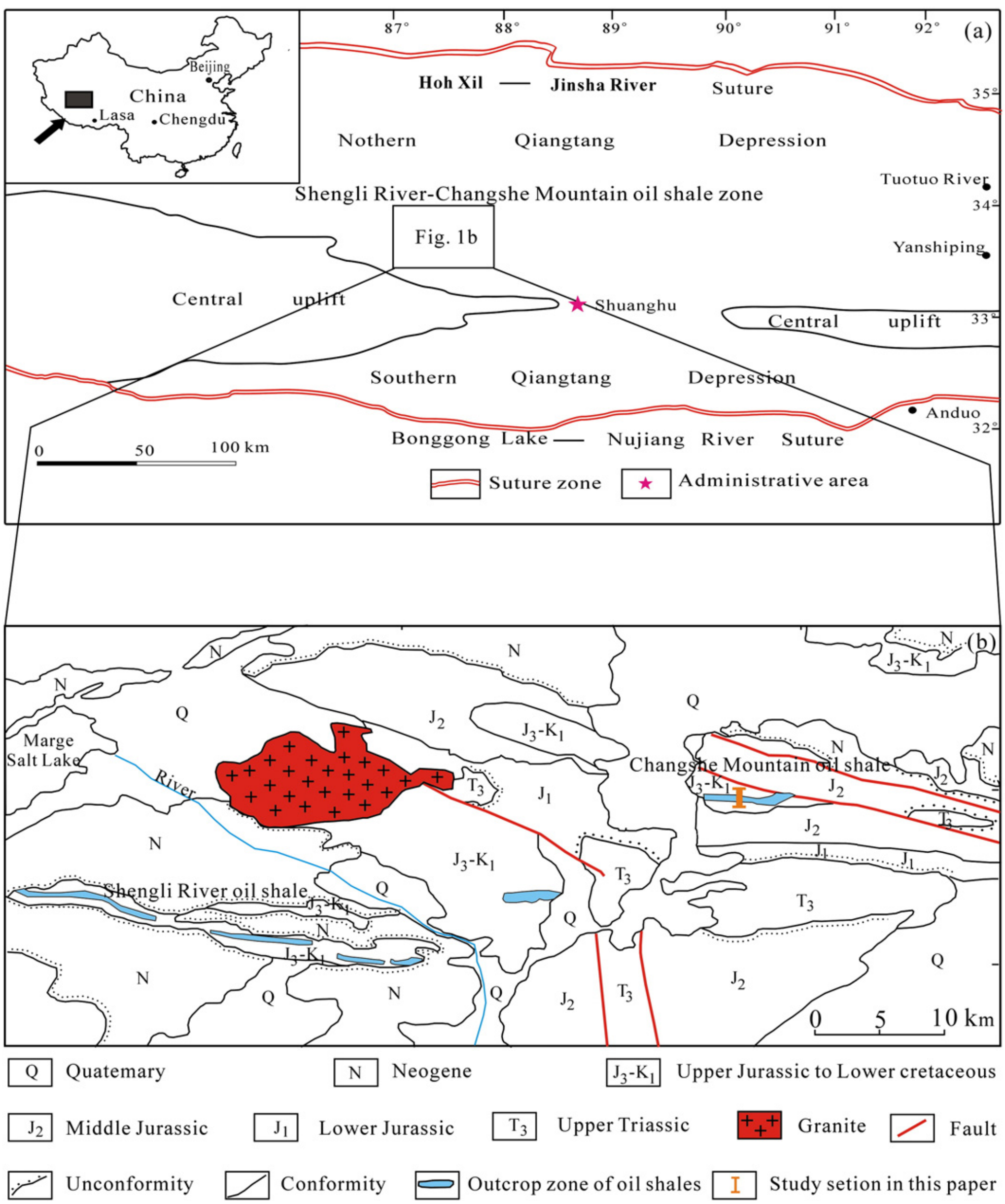


**Fig. 1.** (a) Generalized map, showing location of study area. (b) Simplified geological map of the Shengli River–Changshe Mountain area, showing location of oil shale section.