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Re-Os (ICP-MS) DATING OF MARINE OIL SHALE IN THE QIANGTANG BASIN, NORTHERN TIBET, CHINA

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Marine oil shale from the Shenglihe oil shale section in the Qiangtang basin, northern Tibet, China, was dated by the Re-Os technique using Carius Tube digestion, Os distillation, Re extraction by acetone and ICP-MS measurement. An isochron was obtained giving an age of 101±24 Ma with an initial $^{187}Os/^{188}Os$ ratio of 1.84±0.11(n = 11, MSWD = 3.5). The Re-Os age agrees with the geological age derived from biostratigraphic data, indicating the great potential of the Re-Os method for dating the marine oil shale. Our new data (Bilong Co oil shale) also show that the samples must derive from the same layer of oil shales to determine an accurate and precise depositional age for the marine oil shale with the ^{187}Re-^{187}Os radioisotope system.

Introduction

The Re-Os radioactive isotope system in organic-rich sedimentary rocks such as black shale has been shown to be a viable chronometer for dating clastic sedimentary sequences [1–6]. Pioneering work in this field by Ravizza and Turekian [1] on the upper Mississippian Bakken Formation, North Dakota, yielded a Re-Os isochron age of 354±49 Ma ($\lambda = 1.52\times10^{-11}a^{-1}$) which is within uncertainty of the known stratigraphic age of ~350 Ma. Following on their work, Cohen et al. [3] obtained Re-Os isochron ages of 155±4.3 Ma, 181±13 Ma, and 207±12 Ma ($\lambda = 1.666\times10^{-11}a^{-1}$) from

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outcrops of Jurassic organic-rich shale in England. These isochron ages agree within uncertainty to the respective stratigraphic ages of 149±3 Ma, 187±4 Ma, and 198±4 Ma [7]. Although the potential for widespread application of the Re-Os isotope system in organic-rich sedimentary rocks is high, there are few reports on the age of the marine oil shale using the Re-Os chronometer. In this paper we examine the prospect and feasibility of using the decay of ^{187}Re to ^{187}Os to date marine oil shale.

The Shenglihe oil shale is located in the northern part of the central uplift zone of the Qiangtang basin, northern Tibet plateau, China (Fig. 1), where Mesozoic marine deposits are widely spread. Geologic survey and preliminary analysis of the oil shale samples show that the Shenglihe oil shale was deposited in a relatively anoxic marine environment, with ^{87}Sr/^{86}Sr ratios ranging from 0.70787 to 0.70822. Although Fu *et al*. [8] discussed the sedimentary environment of the Shenglihe oil shale in terms of Sr isotopic compositions, and Wang *et al*. [9] briefly presented related organic geochemical data, the geological age of this oil shale remains unclear.

The Bilong Co oil shale lies in the southern part of the central uplift zone of the Qiangtang basin, northern Tibet plateau, China (Fig. 1), where Mesozoic marine deposits are also wide spread. Geologic survey and preliminary analysis of the oil shale samples show that the Bilong Co oil shale was deposited in a relatively anoxic marine environment in terms of its biomarkers [10] and could be correlated with that of the Early Toarcian anoxic event in Europe [11].

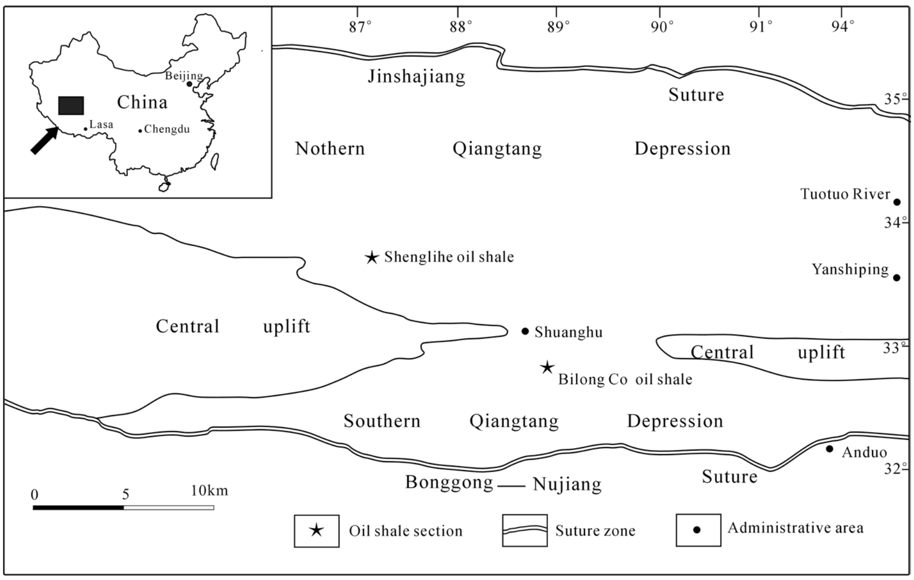

Fig. 1. Generalized map showing location of study area and oil shale deposits.

Samples and analyses

Samples

The Shenglihe oil shale exposed for a distance of more than 2.5 km in an east-west direction and it is 9 m thick. The unit is important for assessing oil and gas resources in the Qiangtang basin. The oil shale sequence consists of two intervals, named XP-11 and XP-13, for the lower and upper units with thicknesses of 3.85 m and 4.82 m, respectively. A total of 13 oil shale samples in this study were collected from the section. Two samples are from the XP-11 unit (XP-11-1-A and XP-11-1-B), and other 11 samples are from the XP-13 unit (Fig. 2). In order to determine accurate and precise depositional ages of the Shenglihe oil shale with the ^{187}Re-^{187}Os radioisotope system and

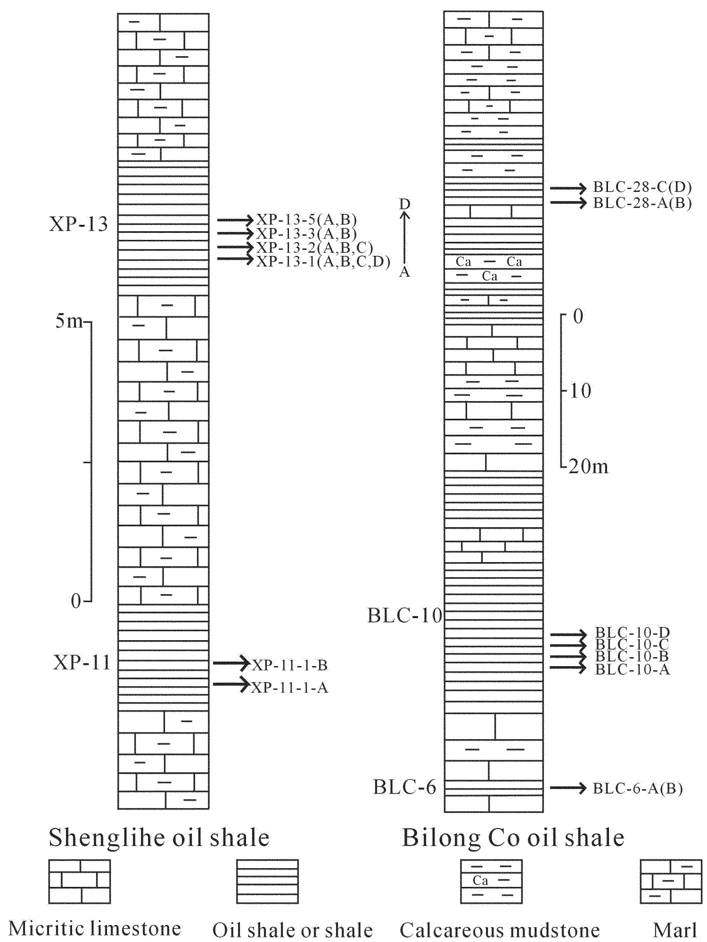

Fig. 2. Shenglihe oil shale and Bilong Co oil shale section showing sample locations.

minimize the influence of detrital Os derived from continental erosion, our samples were collected in a very thin thickness of shale (less than 1 m).

The Bilong Co oil shale is exposed within an area of 3 km by 3 km. The succession is divided into three units characterized by different lithological types. From lower to upper they are gypsum, oil shale interbedded with limestone and mudstone, and marl interbedded with mudstone. Ten oil shale samples were collected from the section. Two samples are from BLC-6 layer (BLC-6-A and BLC-6-B) and four samples are from BLC-10 layer (BLC-10-A, BLC-10-B, BLC-10-C, and BLC-10-D), and four samples are from BLC-28 layer (BLC-28-A, BLC-28-B, BLC-28-C, and BLC-28-D) (Fig. 2).

Analytical methods

Re-Os isotopic analyses were performed in the National Research Center of Geoanalysis, Chinese Academy of Geosciences. The details of the chemical procedure have been described by Shirey and Walker [12], Stein *et al*. [13], Markey *et al*. [14] and Du *et al*. [15]. The procedures are briefly described here.

The Carius tube (a thick-walled borosilicate glass ampoule) digestion technique was used. The samples were crushed and ground no less than 200 mesh using a contamination-free device. During the initial phase of this study some additional experiments were done to test the best ratio of sample to aqua regia used in the Carius tube method by changing the sample size from 0.2 to 0.7 grams. The results showed that Re, Os content did not change significantly for 0.2-g, 0.3-g, 0.4-g and 0.5-g samples, i.e. the dissolution of these samples is the same. However, an explosion occurred during the heating of the Carius tube containing the 0.7-g sample. Considering analytical errors and instrument sensitivity, we concluded that 0.5-g sample was the best ratio for 3 ml of aqua regia.

Approximately 0.5 g sample was precisely weighed and loaded into the Carius tube through a long thin-neck funnel. The mixed ^{190}Os and ^{185}Re spike solution and a 3:5:1 acid mixtures (aqua regia) containing 3 ml of 10 N HCl, 5 ml of 16 N HNO_3 and 1 ml 30% H_2O_2 were added while the bottom part of the tube was frozen at –80 °C to –50 °C in an ethanol-liquid nitrogen slush, and the top was sealed using an oxygen-propane torch. The tube was then placed in a stainless-steel jacket and heated for 24 h at 200 °C. Upon cooling, the bottom part of the tube was kept frozen, the neck of the tube was broken, and the contents of the tube were poured into a distillation flask and the residue was washed out with 40 ml of water.

Separation of osmium by distillation and separation of rhenium by extraction were performed based on the analytical method from Du *et al*. [15]. A TJA X-series ICP-MS was used for the determination of the Re and Os isotope ratio. Blanks during this study were 3.7–11.7 pg for Re and 0.01–0.02 pg for Os.

Results

The Re and Os concentrations and $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ isotopic ratios corrected for total blanks are shown in Table 1. In-run precisions of $^{187}Os/^{188}Os$ ratios determined by ICP-MS and uncertainties in Re and Os concentrations given by isotope dilution, calculation based on the error propagation are also given in Table 1. The $^{187}Re/^{188}Os$ ratios of the XP-11 layer (the lower layer oil shales) from the Shenglihe oil shale section range from 363.1 to 365.9, with an average of 364.5, and $^{187}Os/^{188}Os$ ratios range from 3.262 to 3.289, with an average of 3.2755. Relatively low Re and Os abundances were found in all of the upper layer oil shales (Table). The $^{187}Re/^{188}Os$ ratios of the XP-13 layer (the upper layer oil shales) from the Shenglihe oil shale section range from 212.1 to 292.7, with an average of 272.88, and $^{187}Os/^{188}Os$ ratios range from 2.202 to 2.363, with an average of 2.304. It can be seen that the values from the XP-11 layer are much higher than those from the XP-13 layer. The Re-Os isochron calculated by ISOPLOT [16] is shown in Fig. 3. In ISOPLOT calculation, the input errors in $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ ratios include the uncertainties in weighing the samples and mixed spikes, the spike calibration, the ICP-MS measurement and so on, and are represented by the uncertainty of replicate analyses of the laboratory reference sample and are 1.5% for $^{187}Re/^{188}Os$ and 1% for $^{187}Os/^{188}Os$. The contribution of the uncertainty is relatively small. The decay

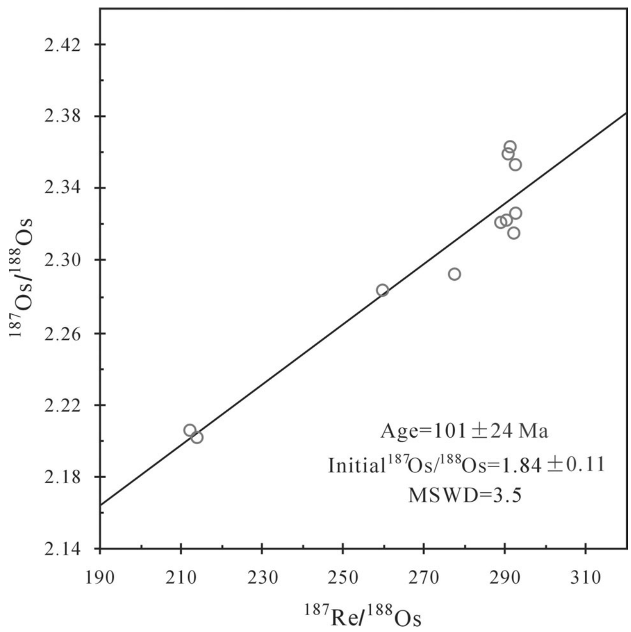

Fig. 3. $^{187}Re/^{188}Os$ versus $^{187}Os/^{188}Os$ plots showing the Re-Os data for whole rock analysis from the Shenglihe oil shale, northern Tibet, China.

Table. **Re-Os isotope data of the marine oil shale from the Shenglihe and Bilong Co oil shale in the Qiangtang basin, northern Tibet, China**

Oil shale	Sample	Re(ng/g)	^{187}Os(ng/g)	^{192}Os(ng/g)	Re/Os	^{187}Re/^{188}Os	^{187}Os/^{188}Os
Shenglihe oil shale	XP-13-1-A	32.29±0.35	0.1623±0.0014	0.5318±0.0043	60.72	290.3±4.0	2.322±0.013
	XP-13-1-B	32.11±0.37	0.1605±0.0016	0.5250±0.0048	61.16	292.4±4.3	2.326±0.020
	XP-13-1-C	32.36±0.28	0.1612±0.0015	0.5298±0.0045	61.08	292.1±3.6	2.316±0.016
	XP-13-1-D	32.14±0.28	0.1622±0.0013	0.5318±0.0039	60.44	289.0±3.3	2.321±0.009
	XP-13-2-A	30.14±0.32	0.1536±0.0015	0.4955±0.0046	60.83	290.9±4.1	2.359±0.021
	XP-13-2-B	30.07±0.28	0.1534±0.0014	0.4938±0.0048	60.9	291.2±3.9	2.363±0.020
	XP-13-2-C	30.86±0.35	0.1560±0.0014	0.5042±0.0046	61.21	292.7±4.2	2.354±0.018
	XP-13-5-A	16.24±0.18	0.1062±0.0010	0.3663±0.0030	44.34	212.1±3.0	2.206±0.015
	XP-13-5-B	16.42±0.18	0.1062±0.0010	0.3668±0.0031	44.77	214.1±2.9	2.202±0.017
	XP-13-3-A	25.50±0.32	0.1410±0.0011	0.4699±0.0037	54.27	259.5±3.9	2.283±0.010
	XP-13-3-B	26.82±0.28	0.1393±0.0013	0.4625±0.0037	57.99	277.4±3.7	2.292±0.016
	XP-11-1-A	41.13±0.39	0.2322±0.0023	0.5416±0.0049	75.94	363.1±4.8	3.262±0.027
	XP-11-1-B	40.14±0.38	0.2268±0.0019	0.5246±0.0039	76.52	365.9±4.4	3.289±0.013
Bilong Co oil shale	BLC-28-A	37.95±0.33	0.1249±0.0014	0.1833±0.0019	207.04	990±13.6	5.182±0.06
	BLC-28-B	37.98±0.34	0.1241±0.001	0.1823±0.0015	208.34	996.4±12.2	5.18±0.025
	BLC-28-C	38.16±0.33	0.1251±0.001	0.1846±0.0017	206.72	988.7±12.6	5.157±0.035
	BLC-28-D	37.99±0.33	0.1284±0.0078	0.1842±0.0015	206.24	986.1±11.7	5.302±0.319
	BLC-10-A	26.41±0.2	0.1045±0.0008	0.1268±0.001	208.28	996.4±11.1	6.275±0.029
	BLC-10-B	26.37±0.22	0.1036±0.001	0.126±0.0012	209.29	1000±12	6.252±0.056
	BLC-10-C	26.73±0.21	0.1048±0.0013	0.1268±0.0015	210.8	1009±15	6.294±0.085
	BLC-10-D	26.37±0.2	0.1044±0.001	0.1328±0.0018	198.57	950±15	5.983±0.081
	BLC-6-A	34.29±0.28	0.0517±0.0007	0.1089±0.0017	314.88	1506±27	3.61±0.064
	BLC-6-B	34.28±0.36	0.0519±0.0006	0.11±0.001	311.64	1490±21	3.591±0.037

constant of ^{187}Re is $1.666\times10^{-11}a^{-1}$ [16]. The marine oil shales (not including XP-11 layer) from the Shenglihe oil shale section give an isochron age of 101±24 Ma with an initial ^{187}Os/^{188}Os ratio of 1.84±0.11(n=11, MSWD = 3.5) (Fig. 3).

The ^{187}Re/^{188}Os ratios of the Bilong Co oil shale range from 950 to 1506, with an average of 1091.26, and ^{187}Os/^{188}Os ratios range from 3.591 to 6.294, with an average of 5.2826. Our data from various layers of Bilong Co oil shale do not define isochrons.

Discussion

Determining accurate and precise depositional ages for black shales with the ^{187}Re-^{187}Os radioisotope system require that several prerequisites be satisfied. These prerequisites are: (1) all samples must be of the same age and have the same initial ^{187}Os/^{188}Os ratio that reflects the composition of seawater at the time of sediment deposition, (2) the Re-Os radiometric dating method assumes that Re and Os in black shales are entirely hydrogenous in origin, (3) the system has remained closed for Re and Os from the time of their deposition until analysis, and (4) the samples must possess a range in Re/Os ratios in order to generate a range in present-day ^{187}Os/^{188}Os ratios. The principles underlying these prerequisites are essentially the same as those for obtaining reliable isotope ages from the marine oil shales. Nevertheless, our data from various layer oil shale do not define isochrons, which is true of the Belong Co oil shale, and also of the Shenglihe oil shale. This indicates one or some of the four conditions given above have been not satisfied perfectly for various layers of oil shale.

However, when only the data points from the same layer oil shale are regressed, the results are indistinguishable from the previous regression. The marine oil shale samples (only from XP-13 layer) from the Shenglihe oil shale section in the Qiangtang basin yield an age of 101±24 Ma with an initial ^{187}Os/^{188}Os ratio of 1.84±0.11 (n = 11, MSWD = 3.5). In order to verify the accuracy and credibility of above age, 19 samples from the Shenglihe oil shale were collected for spore and pollen grain analyses. A number of spores and pollen grains, including *Apiculatisporites*, *Cyathidites minor* Couper, *Cicatricosisporites*, *Jiaohepollis*, *Cerebropollenites*, *Chasmatosporite Ephedripites* cf. *Notensis Cycadopite* and *Classopallis*, were identified in the XP-13 layer oil shale and its overlying formation (marls) from the Shenglihe oil shale section. Although they occur in low abundance, they are stratigraphically useful. Gymnosperm pollens clearly dominate the assemblage (80%); spores are very much subordinate components (20%). The low abundance of *Cicatricosisporites* in this assemblage together with low numbers of *Classopallis* (30%) and *Cyathidites minor* Couper, and two additional taxa, *Ephedripites* and *Jiaohepollis* suggest somewhat younger early Cretaceous [17]. The other major components of this assemblage, such as *Cerebropollenites*, and *Cycadopites*, are common or important elements of the early Cretaceous. Hence we tentatively date this assemblage as early Cretaceous. This agrees with the age derived from Re-Os dating data within the scope of the error, indicating the data from Re-Os dating are credible. Of course, the experimental error is still larger, and the precise isotopic dating for the marine oil shale needs further study. Despite these restrictions, the new examples demonstrate the great potential of the Re-Os method for dating the marine oil shale.

Conclusions

1. Our data from various layers of Bilong Co oil shale do not define isochrons, indicating one or some of the four conditions determining accurate and precise depositional ages for shales with the ^{187}Re-^{187}Os radioisotope system have been not satisfied perfectly for various layer oil shale.
2. The marine oil shale samples (only from XP-13 layer) from the Shenglihe oil shale section in the Qiangtang basin yield an age of 101±24 Ma, which agrees with biostratigraptic data, indicating the great potential of the Re-Os method for dating the marine oil shale.

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