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INVESTIGATION ON TRACE ELEMENTS IN CRUDE OILS AND ORGANIC MATERIALS EXTRACTED FROM OIL– FORMING SOURCE ROCKS IN CHINA WITH INAA

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ABSTRACT

A combination of Soxhlet extraction, column chromatography and INAA with GC and GC– MS was used in this work for the study of the abundance patterns of 36 trace elements and their correlation in nearly 100 samples of crude oil and organic materials extracted from oil– forming source rocks from 10 main Chinese oilfields. The low V/Ni ratios of 0.01 to 0.3 state the oil– forming continent environment. The geochemical significance hinted from other trace element abundances is also briefly discussed.

Keywords: Neutron activation analysis Crude oil Trace element pattern

Ⅰ. INTRODUCTION

The abundances, distributions and chemical species of trace elements in crude oils and organic materials extracted from oil– forming source rocks can provide valuable geochemical information about origin, migration and evolution of petroleum[1 2]. In addition, they are essential to refining processing and environmental pollution control as well. However, the concentrations of trace elements in crude oil and organic extracted material are quite low, in most cases at μ g/g or lower. The conventional chemical analysis often has the danger of contamination caused by reagent blank or of volatile loss during ashing and preparation process of organic samples. Thus, some authors applied NAA to determine trace elements in crude oils in the world[3,4]. In this work we systematically studied trace elements in crude oil and organic materials extracted from oil– forming source rocks in China with INAA, mainly because the related data are scarce in literature.

Ⅱ. EXPERIMENTAL

1. Crude oil samples

Collaborated with institutes of petroleum in China, we collected various crude oil samples from 10 main Chinese oilfields: Jianghan, Zhongyuan, Shengli, Liaohe, Kalamayi, Biyang, Dongfeng, Renqiou, Dagang and Songhuajiang. Crude oil samples of about 100 mg each were taken and rinsed with 9:1 (volume) benzene– methanol solution for 24h, then filtered in a funnel containing anhydrous sodium sulphate. The treated oil samples were concentrated to dryness. Aliquot of 20 to 40 mg samples was used for column chromatography separation, gas- chromatography (GC) and GC- mass spectroscopy (MS). The rest was for INAA.

2. Organic materials extracted from rocks

Each 50- 100g of 80- 100 mesh oil- forming source rock samples was extracted in a Soxhlet extractor with 200- 250 ml of 9:1 benzene- methanol or chloroform at 80°C or 65°C, respectively. The extracted organic solution was filtered to remove the fine rock powder in it, then concentrated to dryness for column chromatography separation and analysis.

3. Group fraction separation

The above oil and organic material samples were fractionated as follows:

1) Precipitation and filtration of asphaltene 10 to 30 mg of the oil or organic material samples were dissolved in 30- 40 ml *n*- hexane, then stood for overnight to make asphaltene precipitated. The asphaltene fraction was filtered and repeatedly washed by *n*- hexane until the solvent became colourless. Again, the asphaltene in the container and filter was washed off by 2- chloromethane or chloroform. After concentrated to dryness, it is subject to NAA and column chromatography.

2) Column chromatography separation The organic samples after filtered and separated from asphaltene were subject to column chromatography fractionation, which were divided into 3 group fractions: saturated hydrocarbon, aromatic hydrocarbon and nonhydrocarbon. The first fraction was eluted with *n*- hexane, followed by the aromatic hydrocarbon and non- hydrocarbon with 2- chloromethane and anhydrous alcohol, respectively. The 7:3 (volume) silica gel (60- 80 mesh) and

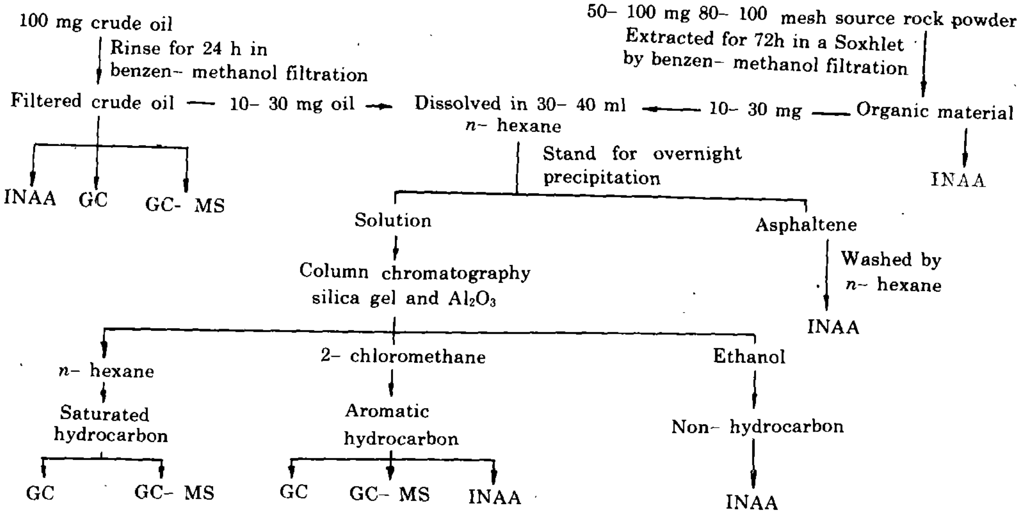

Fig.1 Schematic experimental procedure for group fraction separation

neutral Al_2O_3 (100- 120 mesh) were used as absorbent, beforehand activated for 4h at 180°C and 400°C, respectively.

The fraction of saturated hydrocarbon is only for GC and GC- MS, not subject to INAA, since the concentrations of trace elements in it are too low. The aromatic hydrocarbon was analyzed by GC, GC- MS and INAA. The asphaltene and non- hydrocarbon were only for INAA. Fig.1 shows the experimental procedure of the crude oil and organic material extracted from oil- forming source rock used in this work[5].

4. INAA

Weigh a certain amount of organic samples (several μ g to mg) and transfer them on filter paper disc, then packed by polyethelene foil and heat- sealed. The samples were first irradiated at a neutron flux of 5×10^{11} n · $cm^{-2}.s^{-1}$ in a miniature nuclear reactor at Institute of Atomic Energy (IAE) for short- lived nuclide analysis. After that, the samples were repacked by high- purity aluminium foil and irradiated at 8×10^{13} $n.cm^{-2}.s^{-1}$ in a heavy water cooled reactor at IAE for medium and long lived nuclide analysis. The irradiation conditions of INAA are listed in Table 1.

Table 1

Irradiation conditions for INAA of crude oil and organic materials from source rocks

Nuclide	Irradiation time (s)	Cooling time	Counting time (s)	Neutron flux ($n.cm^{-2}.s^{-1}$)
^{28}Al ^{27}Mg ^{56}Mn ^{24}Na ^{38}Cl ^{51}Tl ^{82}Br ^{66}Cu ^{52}V	300s	60- 90s	300	5×10^{11}
^{198}Au ^{76}As ^{140}La ^{99}Mo ^{153}Sm ^{177}Lu ^{147}Nd ^{166}Ho ^{186}Re ^{24}Na ^{42}K	34h	73- 115h	3000	8×10^{13}
^{192}Ir ^{103}Ru ^{152}Eu ^{159}Gd ^{169}Yb ^{141}Ce ^{160}Tb ^{75}Se ^{65}Zn ^{58}Co	34h	594- 660h	6000	8×10^{13}
^{59}Fe ^{60}Co ^{124}Sb ^{233}Pa ^{86}Rb ^{85}Sr ^{46}Sc ^{131}Ba ^{51}Cr ^{182}Hf ^{134}Cs ^{95}Zr				

All chemical reagents used in this work were repeatedly purified. The filter paper and defatted cotton were treated by benzene or chloroform for 24h. Tridistilled water was used. The replicate blank experiments indicate no significant contribution to gamma spectra from the chemical reagents and materials, but slight peaks of ^{28}Al, ^{59}Fe, ^{60}Co, ^{51}Cr, ^{38}Cl and ^{75}Se, which were corrected in the sample analysis.

Ⅲ. RESULTS AND DISCUSSION

1. Trace element concentrations of Chinese crude oils

The average concentrations of 36 trace elements in the crude oils from 10 main Chinese oilfields determined in this work by INAA are listed in Table 2. Most of them are the transition elements, especially those in the first long period, e.g.Sc, V, Cr, Mn, Fe, Co, Ni, Zn, etc., which exist in almost all the crude oils. It is because they can be complexed or chelated in σ or π bonding form with organic molecules[6].

As well known, the V/Ni ratio can be used as indicator of the deposit environment. Table 3 lists the V/Ni ratios of over 70 crude oils from 10 Chinese oilfields, where also included are the data of other regions for comparison. It is evident that the V/Ni ratios of the Chinese crude oils range from 0.01 to 0.3, far less than those of the crude oils formed in marine sediment environment. The low V/Ni ratio indicates the continental origin of the Chinese crude oils.

Table 2

Average concentrations of trace elements in crude oils of 10 main Chinese oilfields (unit:ppm)

Element	Jianghan	Zhongyuan	Shengli	Liaohe	Kalamayi	Miyang	Dongfeng	Renqiou	Dagang	Songhuajiang
Al	4.44	3.29	4.76	23.8	46.4	2.68	2.22	12.2	2.15	7.03
As	0.07	–	26.2	0.49	0.31	0.04	0.17	0.06	–	0.63
Au	0.003	0.006	0.979	0.003	0.006	0.003	0.005	0.002	–	0.001
Ba	15.5	43.9	1085	124	92.7	3.46	–	8.44	11.0	9.13
Br	16.8	3.31	–	860	19.6	–	–	–	44.0	–
Ce	–	6.21	67.2	–	–	–	–	–	0.11	0.61
Cl	861	25.6	65.8	14000	1000	381	33.3	54.5	4.46	22.5
Co	0.63	2.55	8.87	1.52	0.65	0.81	–	0.14	0.46	0.78
Cr	0.91	1.86	34.4	29.4	2.17	0.82	1.49	0.57	1.68	1.34
Cs	0.03	0.04	–	0.12	0.04	0.017	0.34	0.018	0.100	0.051
Cu	–	–	–	–	7.18	–	–	5.89	–	0.57
Eu	0.01	0.02	0.31	0.01	0.07	0.01	–	0.07	0.01	0.03
Fe	33.5	344	321	1.52	194	9.43	52.9	13.5	16.8	53.5
Hf	0.03	0.03	17.4	–	–	–	–	0.02	–	0.03
Ho	0.07	0.16	5.73	–	0.44	–	0.12	–	–	0.14
I	0.82	–	–	–	22.1	–	–	–	6.19	0.77
Ir	0.01	0.001	0.04	0.002	0.008	0.0004	–	–	–	–
La	0.54	–	30.7	0.09	0.26	–	–	–	–	0.08
Lu	0.01	0.04	0.55	0.009	0.05	0.01	3.32	0.009	0.006	0.01
Mn	0.31	0.93	0.67	16.3	5.89	0.33	0.46	3.21	0.79	1.12
Mg	–	15.3	–	–	–	–	–	–	–	–
Mo	–	0.78	221	–	–	–	–	–	–	–
Na	79.4	17.2	113	29.1	891	148	–	25.3	91.8	25.9
Ni	27.6	36.5	62.9	107	63.6	25.6	58.9	19.7	10.0	6.31
Rb	0.38	1.02	7.27	–	–	–	–	–	–	–
S	19700	4082	–	–	–	–	–	–	–	–
Sb	0.036	0.119	11.4	0.385	0.061	0.03	8.40	0.06	0.096	0.112
Sc	0.004	0.004	3.69	0.005	0.012	0.004	–	0.005	0.002	0.004
Se	3.78	0.45	–	–	143	3.38	8.76	0.12	–	–
Sm	0.22	1.68	30.1	–	1.98	–	–	–	–	–
Sr	140	979	1560	–	1828	–	–	–	–	–
Tb	0.16	0.04	2.75	–	0.13	–	–	–	–	–
Th	0.013	–	9.35	–	–	0.008	–	0.014	0.009	0.03
V	1.23	3.68	1.28	1.50	10.4	0.57	16.6	0.66	0.09	0.06
Yb	0.18	0.66	5.02	–	0.73	0.19	–	–	–	0.15
Zn	1.76	6.98	46.1	62.8	5.83	–	–	–	–	–

Note: The data are the average values of 10 determinations with the SD of 10– 40% for most elements.

In some Chinese oils we found high S content, especially in the Jianghan oilfield (1.97%) and Zhongyuan oilfield (0.4%), which has been confirmed by the discovery of organic S– containing compound there. The high S content is reasonable from the view of geological settings of high salinity anoxic environment.

The crude oil sample in the Shengli oilfield contains 0.979ppm Au and 0.04ppm Ir. The high Au and Ir concentrations imply that during the process of oil formation and evolution the organic geochemical enrichment of the noble metals occured. Thus, it is probably an important ore- forming mechanism of the noble metals.

Table 3

Average V/Ni ratio of crude oil from 10 main Chinese oilfields

Oilfield name	V (ppm)	Ni (ppm)	V/Ni	Ref.
China				
Jianghan	1.23	27.6	0.045	
Zhongyuan	3.68	36.5	0.101	
Shengli	1.28	62.9	0.020	
Liaohe	1.50	107	0.014	
Kalamayi	10.4	63.6	0.164	
Miyang	0.57	25.6	0.022	
Dongfeng	16.6	58.9	0.282	
Renqiou	0.66	19.7	0.034	
Dagang	0.09	10.0	0.009	
Songhuajiang	0.06	6.31	0.010	
Canada Alberta	13.6	9.38	1.45	7
USA California	82.4	193.8	0.425	8,9
USA Wyoming	198.5	112.9	2.65	8,9
Australian	10.20	1.90	5.37	10
Kuweit	31.0	9.50	3.25	11
Libya	20.90	76.80	0.27	8
Venezuela	1318	121.6	10.8	12
Nigeria	9.30	50.0	0.186	3
USSR Romashkin	57.3	21.5	2.67	11

We only determined two halogen elements: Cl and Br. Their correlation coefficients show the negative relationship (- 0.47), which states the competence in the combination of Br and Cl with organic molecules.

The data of rare earth elements (REE) in crude oil are rare in literature, mainly because of their low abundances. In this work a few of REE concentrations in the Chinese crude oils were analyzed. The REE patterns exhibit a Eu negative anomaly, implying that the Chinese oils were formed in an anoxic environment.

2. Trace element distributions in the group fractions of Chinese crude oils

As an example, Table 4 lists the concentrations of trace elements of the crude oil and organic material in the Jianghan oilfield. From Table 4 it can be seen that the concentrations of most trace elements determined in the group fraction (asphaltene, nonhydrocarbon) and organic materials extracted from the source rock are higher than those in the crude oil. The enrichment factors roughly range from 2 to 10, which depend on the electron configulation of element and organic structure of the corresponding group fraction.

The comparison of the trace element abundance patterns in the group fractions with the organic marker obtained by GC and GC- MS indicates the geochemical significance of trace elements as an indicator to judge the oil- to- source correlation. The detailed discussion will be published elsewhere.

Table 4

Trace element distributions in the group fractions of the crude oils and organic material in the Jianghan T26 oil well (unit: ppm, unless otherwise stated)

Element	T26C	T26- 10E	T26- 10AS	T26- 10NC	T26- 10AR
Al	1.87	0.24	4.20	37.9	-
As	-	0.07	-	-	-
Ba	8.37	9.05	14.4	16.9	-
Br	12.2	9.15	44.2	58.0	-
Ce	-	0.24	-	-	-
Cl	34.8	88.4	22.0	24.8	-
Co	0.23	4.64	13.0	18.0	8.56
Cr	1.62	6.18	23.6	30.0	5.92
Cs	0.05	0.03	0.49	-	-
Eu	-	0.02	0.01	-	-
Fe	64.5	88.7	95.3	71.8	-
Hf	0.04	0.15	-	-	-
La	0.76	0.11	1.23	1.01	-
Mn	0.57	-	-	30.6	1.49
Na	322	303	234	633	-
Ni	43.0	98.8	24.3	27.5	22.8
S(%)	2.57	5.26	1.58	3.31	-
Sb	0.19	1.09	0.33	0.49	-
Sc	0.01	0.01	0.04	0.07	0.03
Se	14.5	67.7	-	6.78	-
Th	0.02	0.02	-	-	-
V	1.03	1.52	3.65	1.91	1.13
Yb	0.09	-	-	-	-
Zn	5.03	23.5	99.5	-	22.5

Note: C- crude oil E- organic extrascted material AS- asphaltene NC- nonhydrocarbon
AR- aromatic hydrocarbon - means not detected

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