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Geochemistry of the Karkheh River Sediments, Khuzestan Province, Iran: Evidences for Natural Contamination

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Abstract: Sediment samples were taken along a 60 km segment of the Karkheh River in Khuzestan province, southwest of Iran. The Karkheh River with a catchment area of about 50.000 km^2 carries sediments very different from those of neighboring areas. This river drains through metamorphic, igneous and sedimentary rocks from north to south. In order to determine trace elements concentrations, geochemical behavior of these elements and mineralogy in the Karkheh river sediment, seven samples from north to south of the Shoosh city were analyzed using INAA and XRD. Mineralogical studies indicate that heavy minerals such an ilmenite, magnetite, garnet and zircon are major fractions of the Karkheh river sediments. Geochemical data show relatively high concentrations of Fe, Ti, Cu, Ni, Cd, Co, Pb, Zn and As in the sediments when compared to same River sediments in Khuzestan Province. Concentrations and distribution of trace element and REE in the sediments have been influenced by erosion of the distal catchment areas. The results suggest a natural source for sediment pollution (e.g., Pb and As). The results show that in many cases as the Karkheh River, contaminated rock and soil in the catchment area can be a major source for sediment contamination.

Key words: Geochemistry, sediments, Khuzestan, Karkheh, Iran

INTRODUCTION

A reconnaissance study of stream sediment heavy minerals, geochemistry, source and distribution of trace elements including heavy metals was carried out in a 60 km segment of the Karkheh River, southwest Iran. The Karkheh River is one of the major rivers in the Khuzestan province and western of Iran and one of the country's longest (>400 km). It travels from the northern parts of Zagros Mountains to the south and southwest. This river cuts through a variety of rock environments. Many cities and industries are located along its course and the Karkheh.

River provides freshwater and drinking water for these cities, as well as sand and gravel for construction. The concern that anthropogenic pollution may be affecting the safety of the water resources has led to this study along 60 km length of the Karkheh River. Although, there have been a few sedimentological and mineralogical studies of river sediments in the Khuzestan region, the distribution, concentration and source of trace elements and heavy metals in these sediments have received little attention. This study attempts to gain insights into the concentrations, distribution patterns and an assessment of whether, the source of the geochemical signatures are of local derivation or imported from the upper reaches of the river. In addition, the economic potential of river sediments would be considered.

GEOLOGICAL AND HYDROGRAPHIC SETTING

The Karkheh river catchment area includes several large rivers in the west and southwest of Iran. The river system starts in a relatively cool, abrupt ridge and valley area in the north and flows to the warm and flat regions in the south traversing the Zagros oragenic/metallogenic belt. This belt is the product of three major geotectonic events during subduction between the Arabian and Iranian plates (Alavi, 2004). The belt consists of there parallel tectonic zones from NE to SW: The volcanic-plutonic zone (Urumieh-Dokhar belt); The Sanandaj-Sirjan metamorphic zone; The Zagros fold belt (Alavi, 2004). The rocks in the volcanic-plutonic belts vary from basalt to trachy-andesite lavas and pyroclastics to plutonic bodies of gabbro, diorite and granodiorite.

In its upper reaches, the Karkheh River cuts the Sanandaj-Sirjan metamorphic belt, which consists of schists, slates, phyllites and high-grade metamorphic

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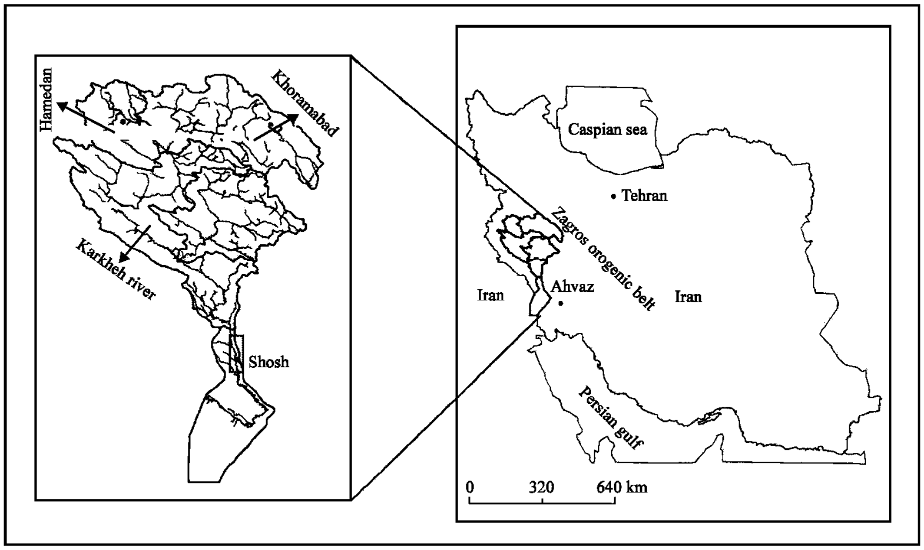

Fig. 1: Geographical situation of the Karkheh River catchment and the study area

rocks. In the southern parts, the river and tributaries dissect Zagros sedimentary rocks, mainly shale, limestone, sandstone and conglomerates. In the norther part of the study area, the river runs over conglomerates and sandstones.

The drainage basin of the Karkheh river system has an area of 50.000 km^2 (Fig. 1). Rapid erosion in its rugged Zagros area headwater is combined with high water flow resulting results in a large sediment load. The rock fragments and minerals derived from erosion of the banks of the river and its tributaries are transported south and accumulate after the break in slope where, the river reaches the flat plain. The surficial distribution of sediments shows miscellaneous layers and mixture of sands, silts and hard muds, clearly delineating varying hydraulic conditions of the river. The sand and much of the coarse silt are typically composed of quartz. The fine silt and clay fractions are dominated by clay minerals. The sediments and its minerals were subjected to sorting by size and specific gravity, as well as some chemical dissolution during transportation. The concentration of heavy and insoluble minerals plays an important role in the geochemistry of the sediments.

SAMPLING METHODOLOGY

A sampling program was performed covering the area from north to south near Shosh city (Fig. 1) about 60 km along the river system. Samples, spacing 500-700 m, were collected from recent and relatively old sediments. Studies of satellite images, geology and topographic maps help to select the location of systematic sampling. About 1 kg of sediments was taken from main channel near the bank under a water depth of 50-100 cm. The samples were sealed in thick plastic bags and quickly sent to geochemistry laboratory of Shahid Chamran University, Ahvaz, Iran.

The samples are washed carefully to remove contamination from organics. Also, the organic matter was removed by addition of few cc of concentrated hydrogen peroxide with hot water. They were dried half and hour in an oven at about 60°C. Then clean samples were divided into several parts for the microscopic, XRD and geochemistry study. The samples were divided into gravel to sand fraction (>0.1 mm) and silt to clay fraction (<0.1 mm) by sieving in order to investigate mineralogy and geochemistry. The mineralogy of the sediments was examined by XRD and the petrographic microscope. Based on these studies >20 heavy mineral are distinguished in the Karkheh river sediments. Of all selected samples, 7 sediment bulk samples were chosen for trace element geochemistry using Instrumental Neutron Activation Analysis (INAA) in Esfahan laboratory.

MINERALOGY OF SEDIMENTS

Mineralogical study of these sediments shows considerable proportions of minerals such as pyroxene, biotite and a number of heavy minerals. The variation and local concentration of heavy minerals is high. Most of the heavy minerals originate in mafic, ultramafic and metamorphic rocks, which outcrop about 250-400 km to the north, beyond the study area. The transportation,

Table 1: Major heavy minerals (g t^{-1}) in the Karkheh River sediments

Heavy minerals sample no	Zircon	Rutile	Ilmenite	Garnet	Epidote	Hematite	Magnetite
KH-1229	9.20	0.80	388.5	547.0	612.0	1285	150
KH-1237	4.00	3.50	7.5	61.5	906.0	248	81
KH-1252	5.50	2.35	113.0	547.0	245.0	489	270
KH-1258	0.45	0.40	86.0	210.0	439.0	658	-
KH-1279	6.00	6.50	54.5	179.0	315.0	414	1305
KH-1294	11.00	9.00	90.0	217.0	391.5	-	216
KH-1300	1.00	2.00	52.5	170.0	228.0	-	-

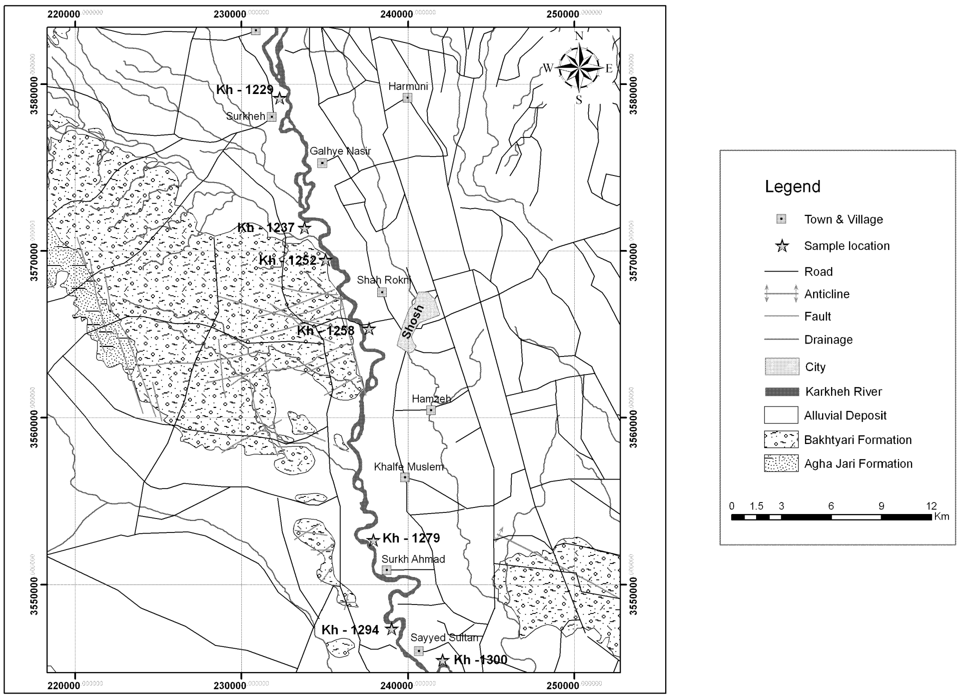

Fig. 2: Geological map of the Karkheh River area

deposition and redeposition of the heavy minerals have led to dispersed anomalous accumulations along the river. The distribution of heavy minerals was studied using statistics indicating a restricted number of populations in terms of geochemistry.

The texture, mineralogy and economic importance of sediments in the study area were described by Zarasvandi and Liaghat (2004). There are three anomalous areas, where the heavy minerals are relatively concentrated. The first area in the north, which coincides with outcrops of conglomerate, is the area rich in zircon, ilmenite and garnet. The second area characterized by the highest concentration of garnet and is in the middle of study area. The third area, which is in the south, shows high content of ilmenite and rutile. In general, these 3 areas contain traces of pyrite, cinnabar, galena, carbonate minerals and gold. The microscopic examination showed that heavy mineral grains are mostly irregular to rounded shapes. Most important heavy minerals in the selected samples are given in Table 1.

GEOCHEMISTRY

The geochemistry of river sediments has been receiving much attention as it reflects the source, natural processes and human activities in the watershed and studies of the major and trace element distribution in these sediments contribute to a better understanding of these processes (Zhang and Wang, 2001). Although, heavy metals have been extensively studied, other elements including REE have received little attention. Sediment samples were collected along the main channel of the Karkheh River and intersection of this channel with small channels from the locations shows in Fig. 2. Concentrations of major, trace and rare earth elements, which were analyzed by INAA, are shown in Table 2.

Table 2: Major (wt%) and trace elements(ppm) from the Karkheh River sediments

Sample no/ elements	KH-1229	KH-1237	KH-1252	KH-1258	KH-1279	KH-1294	KH-1300
Ag	<0.7	<0.73	<0.75	<0.72	<0.71	<0.70	<0.73
Al	6.45*	6.92*	6.60*	7.22*	7.12*	6.59*	7.86*
As	27.2	20.4	22.8	15.1	18.8	17.1	10.2
Au	<6.8	<4.4	<7.5	<7.7	<6.5	53.2	8.05
Ba	0.44*	<215	0.93*	0.23*	0.35*	0.37*	0.31*
Br	129	126	213	212	21.8	23.5	18.4
Ca	3.67*	6.87*	4.28*	4.91*	4.54*	4.44*	5.44*
Cl	<33	67.8	<357	<308	<281	<279	<307
Co	139	40.1	102	98.8	115	129	85
Cr	7.56*	0.51*	4.86*	4.97*	6.34*	7.08*	4.39*
Cs	<0.63	0.3	<0.66	0.32	1.42	0.28	<0.64
Cu	<389	<394	863	<442	<421	<419	<446
Fe	25.5*	23.3*	24.1*	24.2*	22.3*	27.3*	22.3*
Ga	25.8	26.7	20	29.5	28.5	23.6	29.4
Hf	68.5	40.6	58	70.3	69.3	77.7	57.6
Hg	<1.1	<0.76	<1.1	<1.1	<1.1	<1.13	<1.0
In	<0.22	0.16	<1.24	<0.98	<0.89	<0.87	<1.05
Ir	<51	<20	<49	<38	0.11	<0.05	<0.05
K	0.16*	0.23*	0.12*	0.15*	0.15*	0.14*	0.17*
Mg	2.41*	1.48*	2.45*	1.80*	2.52*	2.20*	1.81*
Mn	0.65*	0.51*	1.20*	0.82*	0.76*	0.87*	1.02*
Mo	47.3	9.8	29.3	11	<7.0	<7.1	22.8
Na	0.16*	0.28*	0.18*	0.17*	0.18*	0.13*	0.18*
Ni	336	<95	228	175	259	263	210
Rb	<14	8.83	<13	6.48	<12	<13	<12
Sb	5.54	5.04	4.24	37.9	4.16	5.51	4.04
Sc	39.5	52	47.9	40.6	43.5	40.8	47.5
Sn	<138	<131	<141	<138	<136	<136	<133
Sr	160	410	338	0.11*	281	67.4	142
Ta	5.06	9.28	4.1	5.15	4.12	4.61	3.98
Th	40.7	46.5	51.7	33	35.4	34.6	26.7
Ti	5.45*	5.28*	4.99*	6*	5.41*	6.25*	4.62*
U	9.88	7.38	8.83	8.52	8.02	9.18	5.55
V	871	599	670	809	790	905	679
W	<15	<3.5	<15	<16	<16	<15	<13
Zn	492	100	401	314	363	472	323
Zr	0.24*	0.17*	0.19*	0.42*	0.17*	0.27*	0.22*
Se	0.35	<48	0.28	<0.07	0.14	0.25	<0.07
La	183	151	203	202	151	162	146
Ce	378	324	441	452	366	401	324
Nd	114	76.3	184	162	96.7	117	116
Sm	28.6	27.3	29.9	32	23.9	24.8	21.7
EU	4.15	5.9	4.22	7.18	6.56	6.85	6.1
Gd	1.4	1.2	8.71	1.6	1.7	7.15	5.56
Tb	4.07	4.37	6.08	4.12	3.74	4.16	4.26
Dy	25	21.7	42	23.8	27	24	31.2
Tm	5.36	2.57	4.86	4.91	5.59	5.94	4.22
Yb	18.6	16.4	37	18.4	19.3	18	23.1
Lu	3.04	2.29	6.06	3.21	3.36	3.76	4.5

*In Percent and Au in ppb

TRACE ELEMENTS

Trace element concentrations in sediments are mainly driven by the weathering of bedrock and catchments area (Yang and Rose, 2005). Concentration of major and trace elements in Table 2 show that concentration increased in the sediments during the weathering and transportation. Peaks in the Al, Si, Ca, K, Na, Mg, Rb, Sr and Ba concentration as indicators of erosion indicate that a high amount of catchment area with conglomerate, sandstone, shale and carbonate from the northern source areas washed into the river and sediments. Rapid change in climate could increase concentration of these elements in the study area (Norton *et al*., 1992). In general, concentration of most of the immobile trace elements, especially the transition elements including Ti, V, Cr, Fe, Co, Ni, Cu and U are very high in the Karkheh River sediments in comparison with similar areas such as Karoon River (Diagomanolin *et al*., 2004) and some UK lake sediments (Yang and Rose, 2005). The peaks of concentrations of these elements correlate with mentioned areas with heavy-mineral bearing sediments. Concentration of immobile and heavy metal elements increase with increasing of heavy minerals such as ilmenite, magnetite, rutile, zircon and garnet along the river. High concentrations of Pb in the sediments could be the result of affinity of Pb for minerals containing Ti or human activity. Good correlation of areas with high concentrations of Pb with industrial areas indicates that in addition of natural processes, human activity are caused Pb pollution in the Karkheh River sediments. The As concentration shows some peaks in some parts of the Karkheh River. Arsenic is sensitive to changes in redox conditions. When reducing conditions prevail, As is released from sediments. As concentrates easily in oxic sediments by absorption on and/or co-precipitation with hydrous Iron and Mn oxides (Yang and Rose, 2005). Therefore, association of As with Fe and Mn-bearing minerals in the Karkheh river sediments can make As contamination in the drinking water.

RARE EARTH ELEMENTS

Rare Earth Elements (REE) are considered as useful indicators of various surface geological processes in the surficial environment of river systems. REE are generally contained in small accessory minerals, such as zircon, titanite, etc. Therefore, to have some control on variability in grain size, samples were taken from both middle of the main channel and near the margins. In order to estimate distribution pattern and geochemical behavior of REE, the proportion of these elements were analyzed in 7 bulk sediment samples using INAA. Mineralogy, chemical composition and grain size of samples was considered before analysis. Plots of UCC and NASC-normalized REE (Taylor and McLennan, 1985). Figure 3 and 4 data show almost uniform REE patterns. This pattern caused by river transportation process and high level of terrigenous mixing from different lithological units (McLennan, 1989). The REE pattern also, shows a minor enrichment of the Heavy Rare Earth Elements (HREE) compare to the Light Rare Earth Elements (LREE), with a major depletion of Gd. Other elements such as Ce and Eu show no significant anomalies. The result of mineralogy and sedimentology in samples show that the ratio of the heavy minerals compares to light minerals is 2:1. These heavy minerals in the Karkheh River sediments and some of ferromagnesian minerals (e.g., pyroxene and biotite) are show low content of Gd in their chemical compositions. This factor with low mobility of Gd creates high depletion of Gd in samples.

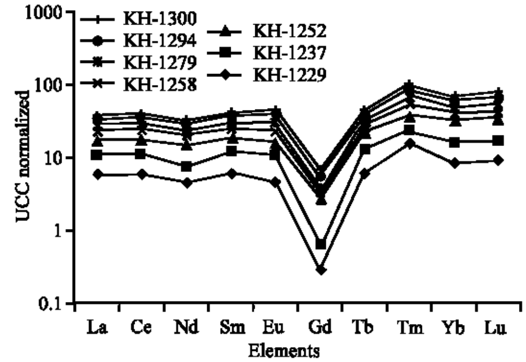

Fig. 3: REE diagram normalized to upper crust composite for the Karkheh River sediments. Normalization based on data from McLennan (1989)

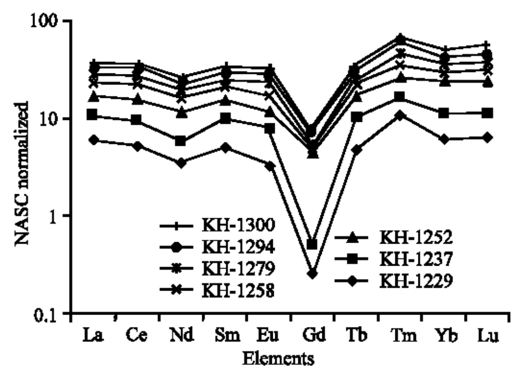

Fig. 4: REE diagram normalized to north american shale composite for the Karkheh River sediments. Normalization based on data from McLennan (1989)

In general, physical weathering and abundance of REE bearing minerals with terrigenous mixing seem to be major controlling factors for distribution of REE in sediments of the Karkheh River. The lack of any significant anomalies for Ce and Eu indicate that clay minerals and redox processes have not played a major role in modifying the distribution of the REEs (Szefer *et al*., 1998).

DISCUSSION

The Karkheh River sediments in the Khuzestan province was chosen for this study because, this is one of the most important flooding river with high thickness of sediments and very large catchments area. Also, many cities and industrial area are located along this river. Field observations and mineralogy of the Karkheh sediments indicate that these sediments derived predominantly from igneous and metamorphic rocks form the Sanandaj-Sirjan zone. Geochemical characteristics of sediments were controlled by mineralogy of these sediments especially heavy minerals such as ilmenite, magnetite, zircon, rutile, pyroxene and biotite, which are formed in mafic rocks. Catchment erosion affects elemental concentration in the Karkheh River sediments.

These concentrations depend on the composition of the rocks and trace element concentration of the soil in the catchment area. Geochemical data show that concentration of heavy metals and REE usually is high in the Karkheh River sediments and correlated with heavy mineral-bearing areas. Geochemical distribution of many of trace elements in the Karkheh River sediments was caused by natural processes such as weathering and transportation of sediments. But these processes were very intense and therefore concentration of these elements is higher than the background levels. Contaminated sediments in the study area can turn into pollution sources for the Karkheh River. For Pb and As, in addition of natural processes, human activity and industrials along the river are probable sources. Also, based on field observations war equipment from the war between Iran and Iraq were buried in the Karkheh sediments and may be it can be sources for Pb and As pollutions especially is north parts.

REE concentration in the Karkheh River sediments is similar to the sediments in other rivers, which cut this type of catchment areas (Borrego *et al*., 2005). NASC and UCC normalized patterns show, for all samples a minor depletion in LREE relative to MREE and HREE with a negative Gd anomaly. These patterns can be caused by mixing of different sediments in the catchment area with similar mineralogy. REE patterns of bulk sediments are very similar to heavy mineral samples of the Karkheh River sediments. Garnet and Fe-Ti bearing minerals are dominant minerals in the Karkheh sediments and ever controlled REE pattern in the sediments. No significant Ce and Eu anomalies the sediments indicate that clay minerals are not a major fraction in the sediments and with reducing processes not played a significant role in distribution of the REEs.

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