Delta J. Sci. 2008, 32: 77- 90

GEOLOGY

GEOCHEMISTRY OF SOME RECENT SURFACE SEDIMENTS NORTH AL WAJH, NW SAUDI ARABIA

A.M.B. Moufti* and I.H. Arafa**

* Department of Mineral Resources and Rocks, Faculty of Earth Sciences, King Abdulaziz University, B.O.Box 80206, Jeddah 21589, Saudi Arabia, and ** Former Head of the Geological Museum, Geology Department, Faculty of Science, Cairo University ,Giza. Egypt

(Received: 15 October 2008)

Absract: The present paper discusses the geochemical characterization of some recent surface sediments collected from Al Wajh, N W Saudi Arabia. The interpretations are based on geochemical, and mineralogical data on both the heavy and the light fractions. The heavy minerals fraction belonging to the grain size intervals; 40-63, 63-125 and 125-250 µm were separated by bromoform (specific gravity of 2.87). About 30 samples were collected from the three surveyed wadis, 9-10 for each. The chemical analysis was conducted on 16 trace elements, including most heavy metals using atomic absorption spectrometry (AAS) and inductively coupled plasma (ICP) procedures.

The obtained data of Cr, Cu Pb, V, Zn and As are heterogeneous and have high standard deviation (δ) while Ni has limited variability. Geographically, the samples of Wadi Thalabah display higher Cr, Zn and Co concentrations, especially at the flux of the wadi where the black beach sand sediments contain 529, 302 and 50 ppm of Cr, Zn and Co, respectively. These black sand sediments are also enriched in most other trace elements (except for As, Ba, and Pb). In spite of the fact that the alluvium sediments display high concentration of As,u, Ba and Sr, they are markedly depleted in rest of the analyzed elements. Beach and dune sediments have nearly similar average values. The absence of close relation between heavy metals content and grain size indicates immaturity of the investigated sediments at the southern sector of Al Wajh Duba region.

Keywords: Geochemistry, stream sediments, sand dunes, beach sediments, heavy metals

INTRODUCTION:

Northwestern Saudi Arabia is mostly occupied by Neoproterozoic basement crystalline rocks. The studied stream samples were collected from dry wadis dissecting these shield rocks between Al Wajh and Duba (Fig. 1). The generalized geological map of Al Wajh quadrangle that includes the three studied wadis at the present work is given in figure 2. The Precambrian rocks at the three studied wadis (Wadi Al Miyah, Wadi Haramil & Wadi Thalbah) are represented by wide varieties of rocks. Metavolcanics dominate as massive basalt to basaltic andesite. They are covered by Holocene to Recent terraces especially in the small tributaries. Pleistocene terraces like those characterizing Wadi Al Hamd are completely missed. At the western extremity of Wadi al Miyah, there are several exposures of pink-colored granites that range in composition from syeno- to monzo-granite. The Phanerozoic sedimentary rocks are situated at both the Azlam basin and the coastal plain. They range in age from Cretaceous to Recent. Much older sedimentary successions are found at Al Wajh quadrangle in its northeastern extremity, being represented by Paleozoic clastics, mainly sandstones. The coastal sediments are represented by clastics of the Miocene Raghama Formation that non-conformably overlies the Precambrian Za'am group. The wadi filling shows lamination and different kinds of pebbles. The rippled black sand is directly recorded on the beach where the black sheets of Fe-Ti oxides cap light-colored beach sediments rich in heavy minerals (mainly zircon and monazite).

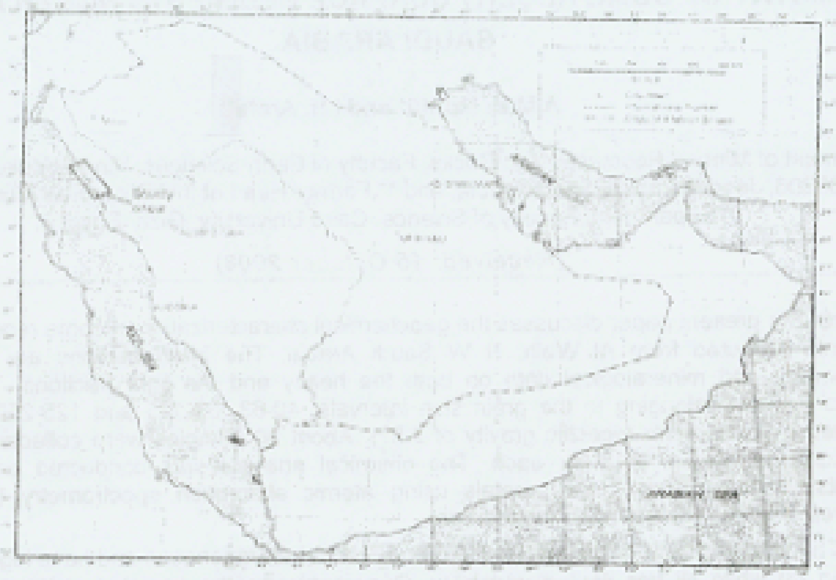


Fig.1:Location map of the study area

Aim of study, sampling and methodologies:

The objective of the present work is to study the geochemical behavior of the trace elements in the surface sediments of Al Wajh area in NW Saudi Arabia. These elements are believed to be transported exclusively as terrigenous components and, therefore, reflect the chemistry of their sources (McLennan, *et al.*, 1980). The trace elements concentration in these sediments is a result of competing influences of provenance, weathering, diagenesis, sediment sorting and the aqueous geochemistry of the individual elements (Rollinson, 1993). Geochemical studies of sediment are used as a good tool for mineral exploration, and gives information on weathering and transport processes.

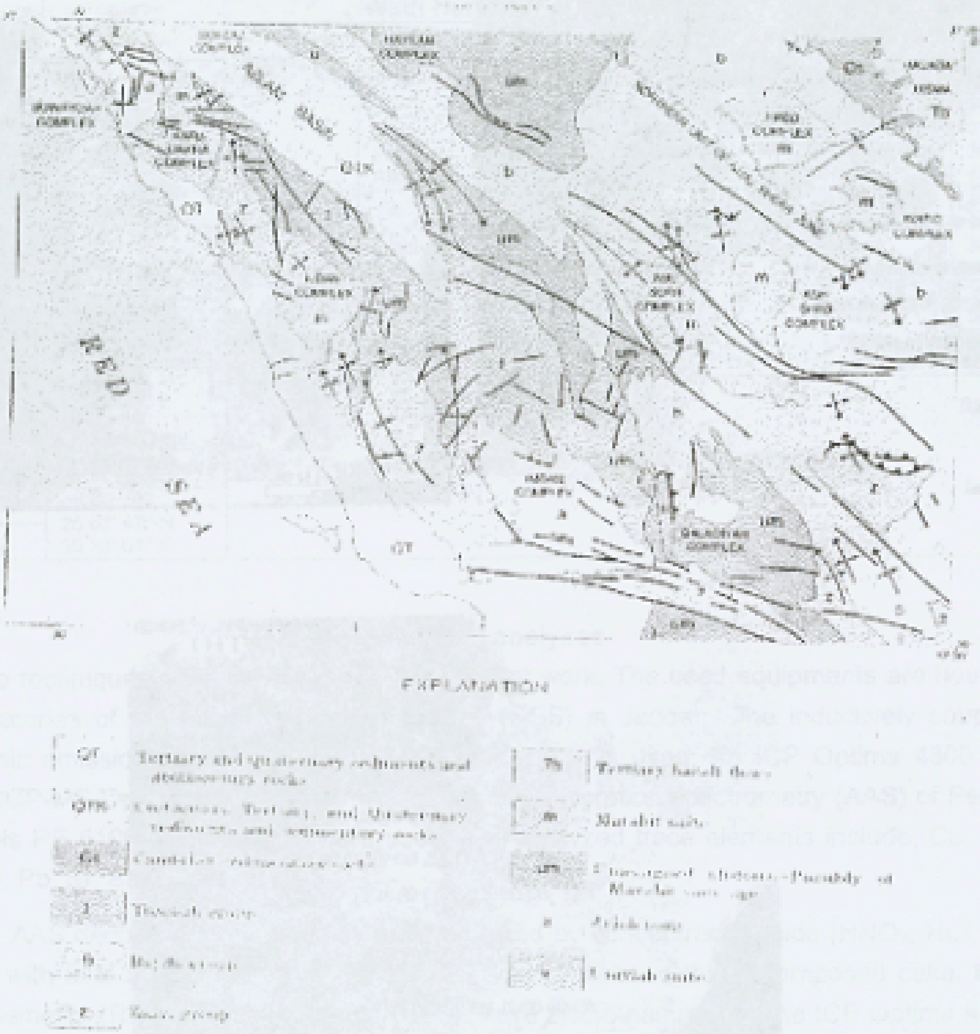


Fig.2: Generalized geological map of Al Wajh quadrangle (from Davies and Grainger, 1985)

Samples were collected to represent the uppermost 30cm of the wadi alluvium sediments, beach sediments, dune sediments and beach black sand in the study area. Twenty-seven samples were collected from the three surveyed wadis (Figs. 3, 4 & 5), nine samples from each. The geographic location of the collected samples and their description are given in table 1. About 2-4 kg of each sample was quartered and subjected to screening on a phi set of standard sieves attached to a rotating shaker for about 20 minutes. Fractions of heavy minerals in the grain size ranges of 40-63 µm, 63-125 µm and 125-250 µm were separated using bromoform (specific gravity of 2.87). The index figure which is a measure of the heavy minerals abundance relative to the light fraction components is calculated.

The concentration levels of the heavy metals; Cr, Cu, Pb, V, Zn and As differ from one sample to another, except for Ni. Geographically Cr, Co and Zn are high in the black beach sand sediments of Wadi Thalabah with averages of 529, 50 and 302 ppm, respectively (Table 5). The relationship between the heavy metals content and grain size is inferred. The fine grain size (40-63µm) is not always the richest in heavy metals (MH20B). Some sand sized samples (125-63 µm, Table 2) show tendency to accumulate more heavy metals than the finer size. As to awareness of present workers, the aridity of the study area is the main cause of the heavy metals poverty in the <63µm fine particles. (Krumgalz 1989) reported high concentrations of metals in the >0.250 mm fractions, due to the formation of agglomerations, although this was probably an unusual finding.

Chromium: Cr dominants over other heavy metals with maximum of 588 ppm and average of 336 ppm. The highest value is recorded for sample number TH14C, black sand sediment. While the least concentration for light fraction of sample number MH14 C (Table 2). Such high concentration of Cr is apparently of lithogenic origin, as suggested by their high degree of association with silicates. Ni–Cr enriched hydrothermal veins originated at late deformation events related to the shearing of the area or mafic dykes found in association with ophiolitic serpentinites may be the possible sources. Ohta, *et al.*, (2005) reported that the enrichment of Cr and Ni in the stream sediments of Hokkaido in Japan is explained by the dominance of ultramafic rocks in the source region which is the case of NW Saudi Arabia (Qadi, *et al.*, 2007).

The correlation between Cr and both Zn and Ni are the strongest among the analyzed heavy metals (Fig.6). This is due to the different type of sediments and frequencies of minerals bearing these heavy metals.

Craw (2001) and Bose and Sharma (2002) reported that the absence of linear correlation between As, Cu, Pub, Zn may be caused by different dissolution and transport characteristics of these metals in secondary environment as well as their emplacement into the host rock at different levels and phases.

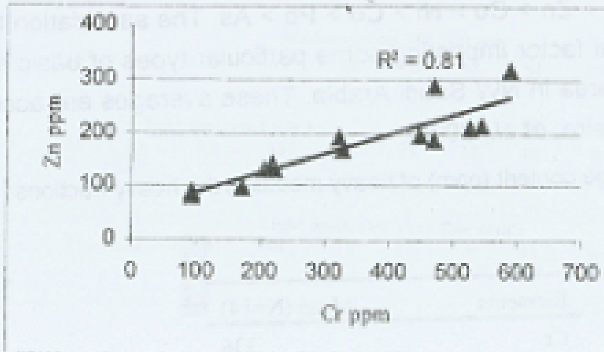


Fig.6: Binary strong geochemical relation between Zn and Cr

Intimate coherence between Cr and the high field strength elements (HFSE) such as Nb and Zr besides Y and La (Figs. 7 and 8) may indicate that Cr is accumulated along with the detrital heavy minerals enriched in the incompatible and rare earth elements such as biotite, amphibole, tourmaline and zircon.

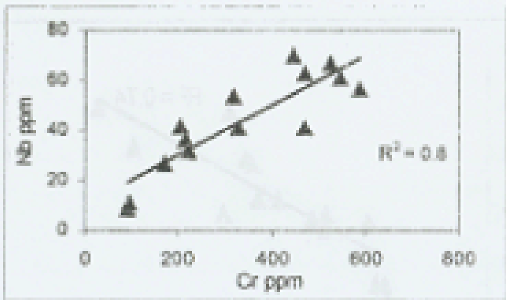


Fig. 7: Binary geochemical relation between Cr and Nb

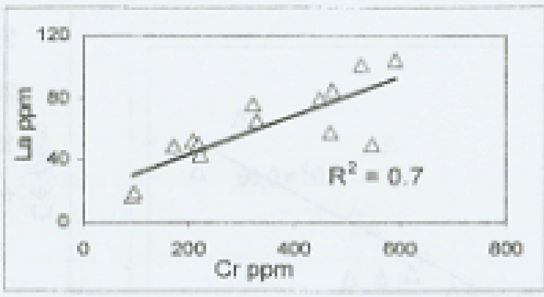
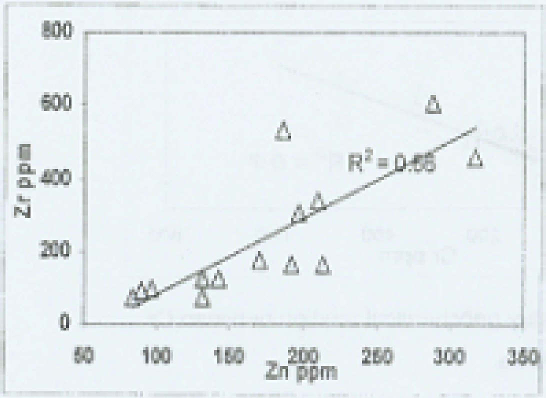


Fig. 8: Binary geochemical relation between Cr and La

Vanadium: It is one of the lightest members of the first row transition elements. It has three main oxidation states (+3, +4 and +5). It is incompatible in most silicate minerals, although it may be moderately compatible in some pyroxenes. It is present as a trace element in pyroxene, amphibole, mica, and apatite. Mafic rocks are typically enriched in V relative to most intermediate and felsic rocks. Primitive magma types including calc-alkaline, alkaline and tholeiitic rocks have broadly similar V concentrations (Wedepohl, 1978).

In the present study, vanadium is the second highest heavy metal in abundance among the analyzed ones (up to 354 ppm, averaging about 256 ppm). The highest values are recorded for the sediments of Wadi Al Miyah (Sample MH17C). Iron oxy-hydroxides seem to be main accumulator for vanadium.

Zinc: It ranges between 84 and 316 ppm with highest values in most of Wadi Haramil and Wadi Thalabah sediments. In contrary, the samples of Wadi Al Mayiah are depleted in Zn. Hochella, *et al.*, (2005) reported that Zn, As and Pb are present in secondary sulfides. The most Zn-enriched ilmenite that contain up to 43 wt % ZnO has been recorded in schist from the Black Mountains, California (Whitney *et al.*, 1993). Zn shows a tendency to be incorporated in silicates and oxides replacing Fe^{+2} and Mg^{+2} positions (Wedepohl, 1978) so that ilmenite, sulfides, garnet, biotite and pyroxene are the acceptable examples of minerals that accommodate Zn ions. Zinc concentrations correlate significantly with Cr, Co and some of the analyzed incompatible elements (Nb, Y, Zr), and also with Ce and La (Figs. 9& 10). These strong correlations are no doubt controlled by lithological factors in the original provenance.



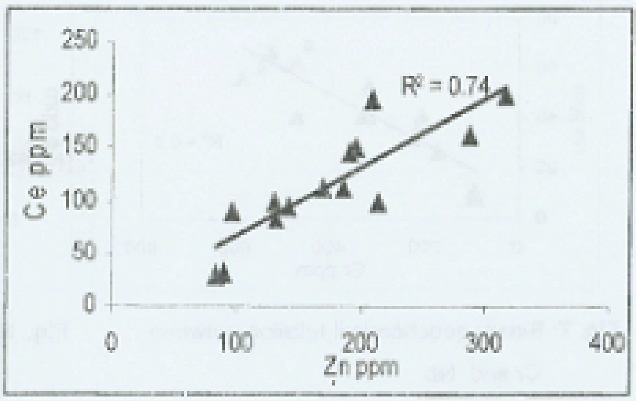


Fig.9 Binary geochemical relation between Zn and Ce

Fig.10 Binary geochemical relation between Zn and Zr

The variation in Zn with respect to grain-size is insignificant (with few exceptions). Zn contents in the coarse grain size fraction can be either higher or lower than that in the fine grain size heavy fractions.

Nickel: It is recorded in all of the studied samples at a range from 37 to 82 ppm with its distinct higher concentration in W. Haramil sediments (station HR5D Table 2). Turekian (1978) stated that Ni is abundant in deep marine sediments (up to 300 ppm) but much less so in coastal sediments (39 ppm).

Arsenic: It is widely present as an accessory element in sulphide minerals such as galena, pyrite and sphalerite. It is also concentrated in phosphate minerals such as apatite due to the similarity of the PO^{4-} and AsO^{4-} groups. Arsenic is used as a pathfinder element for Au, Ag and other precious metals which are well documented in several literatures (e.g. Plant, *et al.*, 1988). As content in the studied sediments is relatively low (from detection limit, i.e., 5.5 up to 33 ppm). Its higher concentration was observed in three stations (two from W. Haramil and one from W. Al Miyah with averages of 33, 24 and 21 ppm, respectively.

Cupper: It is a chalcophile element forming several minerals, including chalcopyrite covellite, and malachite but is more widely dispersed at trace levels in mica (biotite), pyroxene and amphibole. Thus, it shows a greater affinity for mafic than for felsic igneous rocks. In common with other chalcophile elements, Cu is strongly concentrated in sulphide minerals either in the form of disseminations in the igneous rocks or formed during hydrothermal mineralization. Copper contents in the heavy fractions extracted from the studied surface sediments range from 33 ppm to 400 ppm.

There are some strong similarities, but some major differences, between the Cu distribution in the studied samples and the much higher value found in some samples from W. Al Miyah, e.g. sample MH17C (400 ppm). Higher value has also been recorded in W. Haramil (sample HR5D, 104 ppm).This may be attributed to higher frequencies of sulfide minerals.

Cobalt: It is present as an accessory element in pyroxene, amphibole, mica, garnet and it also associates iron sulphides (pyrite, arsenopyrite and pyrrhotite), in addition to oxide accessory minerals, such as magnetite. Cobalt, together with Cr and Ni, is indicative of mafic rocks

(Wedepohl, 1978). In the studied surface sediments, Co shows even distribution in the majority of samples ranging from 21 to 53 ppm with an average of 40 ppm (Table3).

Distribution of heavy metals and trace elements:

The distribution of average heavy metals and trace elements contents shows that the black sand sediments are enriched in most elements (except for As, Ba, and Pb). Although alluvium sediments record high As, Ba and Sr values, they are depleted in most other elements. Nearly similar average values throughout beach and dune sediments can be noticed (Table 5).

Table 5: Average trace element content (ppm) for alluvium, black sand, beach and dune sediments

Average	As	Ba	Ce	Co	Cr	Cu	La	Li	Nb	Ni	Pb	Sr	V	Y	Zn	Zr
Alluvium	14.9	191.3	110.3	40.7	317.0	120.6	58.7	9.7	43.7	57.6	21.4	599.9	302.1	76.9	156.3	156.3
beach sediments	5	75	112	38	469	61	58	8	63	54	24	539	330	85	186	531
Black sand	5	58.5	182	50	529	49	95	6.5	49	55	7	336	206	113	302	533
Dune sediments	6	125	152	48	447	57	80	10	70	63	8	379	245	112	196	307

High field strength elements (HFSE): The high field strength elements (HFSE) such as Zr, Hf, Nb, Ta, and their related elements such as Y are incompatible and usually concentrate in t at the late stages of the magma crystallization. Consequently, they are accommodated in the crystal structure of the detrital minerals of interest, namely ilmenite, rutile, cassiterite, zircon, monazite and apatite (Dill, *et al.*, 2008). *Zr*, Y and Nb are relatively insoluble in natural waters and hence they have the greatest potential for being carried by the solid load during erosion and sedimentation, thus preserving an imprint of the silicate composition of the provenance (Taylor and McLennan, 1985). The studied sediments are enriched in the high field strength elements; Zr, Nb and Y, besides the analyzed two rare-earth elements (La and Ce). The enrichment order can be summarized as follows: Zr > Ce > Y > Nb, with mean contents of 238, 115, 79 and 60 ppm, respectively (Table 4). Cerium is the most abundant so-called rare-earth element where the studied heavy minerals are enriched in Ce contents covering a wide range in the studied heavy minerals fraction (83-201 ppm). Black sand sediments exhibit high Ce values all over the study area and this can be attributed to sorting and high monazite concentration in the black sand. Ce gives very strong correlation with La (Fig. 11) and similar good correlation with Nb although with lesser magnitude (Fig. 12).

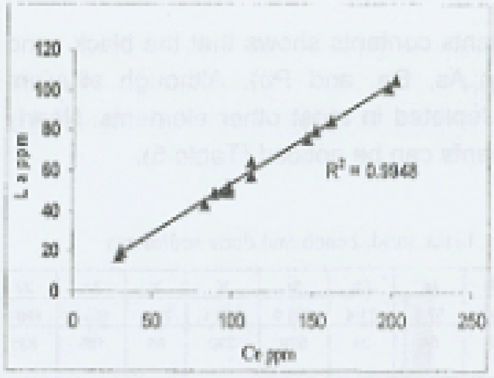


Fig.11: Binary geochemical relations between Ce and La

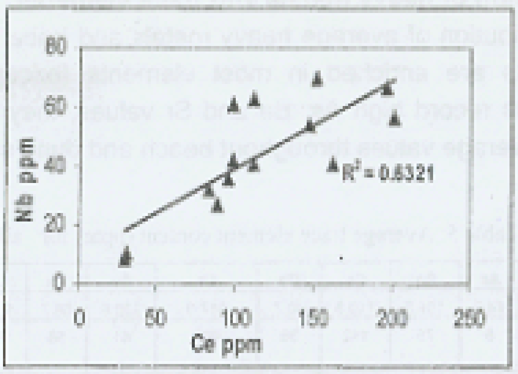


Fig.12Binary geochemical relations between Ce and Nb

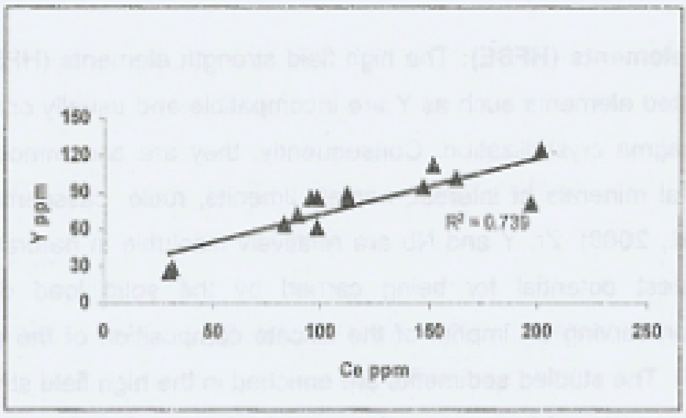


Fig.13: Binary geochemical relations between Ce and Y

Zirconium displays very low mobility under most environmental conditions, mainly due to the stability of the principal host mineral zircon. The Zr content of sedimentary rocks is very much related to the presence of detrital heavy minerals, such as zircon and to much lesser extent titanite (sphene).

In the studied sediments, zirconium has nearly the same strong correlation with Y, La and Ce and Nb. However, Nb occurs in accessory minerals different than zircon such as iron titanium oxides. Hence, it is evident that the geochemical trends of HFSE are essentially controlled by the composition of the accessory minerals in the studied sediments. Most of the studied heavy fractions show an enrichment of Y. Its highest value is recorded in Wadi Thalbah sediments. Apatite is possible main host for Y in the studied sediments. Y shows positive correlation with Ce, La and Nb (Fig.13).

Conclusions

1. The heavy metals; Cr, Cu, Pb, V, Zn and As vary in concentration from one type of surface sediments to another. In contrary, Ni does not show significant variation.

2. The geographical distribution of the samples showed higher Cr, Co and Zn concentrations mainly in the black sand sediments of Wadi Thalabah with an average of 529, 50 and 302 ppm for the three elements, respectively.

3. There is no clear relationship between heavy metals and trace element contents with the grain size. The finest grain size is not necessarily the most enriched in trace elements.

4. As far as the present investigators are aware, aridity of the study area is the main cause of the heavy metals poverty in the <63 µm fine particles. The distribution of average heavy metals and other trace elements content clearly shows that the black sand sediments are enriched in most elements (except for As, Ba and Pb).

5. Although alluvium sediments host high As, Ba and Sr, they are depleted in most of other analyzed elements. In contrary, the beach sediments and black sands are better accumulator of trace elements. Nearly similar average values among the beach and dune sediments are identified.

6. The studied sediments are enriched in the high field strength elements; Zr and Nb, besides the analyzed rare-earth elements (La, Ce and Y).

7. The heavy metals are not intimately correlated with each other. It is evident that the geochemical trends of heavy metals and other trace elements are essentially controlled by the composition of the accessory minerals in the studied sediments, particularly the heavy ones.

References

Anderson, D. (2003): Introduction to Heavy Metal Monitoring. Natural environment Research Council. CEH, 1p.

Beeson, R (1984): The use of fine fraction of stream sediment in geochemical exploration in arid and semi arid terrain. J Geochem Exploration 22, 119–132

BOSE, P. & SHARMA, A. 2002: Role of iron in controlling speciation and mobilization of arsenic in subsurface environment. Water Researches 36, 4916Ð4926.

CRAW, D. (2001): Tectonic controls on gold deposits and their environmental impact, New Zealand. Journal of Geochemical Exploration 73, 43-56.

Davies, F.B. and Grainger, D.J. (1985): Explanatory notes on the geologic map of Al Muwaylih quadrangle, Sheet 27A, Ministry of Petroleum and Mineral Resources, Deputy Ministry for Mineral Resources, Jeddah, Saudi Arabia, 31 p.

Dill H.G., A. Techmer, B. Weber and M. Füßl (2008): Mineralogical and chemical distribution patterns of placers and ferricretes in Quaternary sediments in SE Germany: The impact of nature and man on the unroofing of pegmatites Journal of Geochemical Exploration, Volume 96, Issue 1, January 2008, Pages 1-24

Fletcher WK (1997): Stream sediment geochemistry in today's exploration world. Proceedings of exploration 97' 4th decennial international conference on mineral exploration

Ferreira da Silva E, Cardoso Fonseca E, Matos JX, Patinha C, Reis P, Santos Oliveira JM (2005): The effect of unconfined mine tailings on the geochemistry of soils, sediments and surface waters of the lousal area (Iberian Pyrite Belt, Southern Portugal). Land Degrad Develop 16:213–228.

Hochella F.M., Jr., Moore N.J, Putnis V.C., Putnis A., Kasama T. and Eberl D. Dennis (2005): "Direct observation of heavy metal-mineral association from the Clark Fork River Superfund Complex: Implications for metal transport and bioavailability". Geochimica et Cosmochimica Acta. V.69, pp.1651-1663.

Krumgalz, B. S. (1989): 'Unusual grain size effect on trace metals and organic matter in contaminated sediments', Mar. Pollut. Bull. 20(12), 608–611

McLennan, S.M., Nancy, W.B., Taylor, R., (1980): Rare earth element–thorium correlations in sedimentary rocks, and the composition of the continental crust. Geochim. Cosmochim. Acta 44, 1833–1839.

Ohta, A., Imai, N., Terashima, S., Tachbana, Y., (2005): Influence of surface geology and mineral deposit on the spatial distributions of elemental concentrations in the stream sediments of Hokkaido, Japan. J. Geochem. Explor. 86, 86–103.

Plant JA, Hale M, Ridgway J (1988): Development in regional geochemistry for mineral exploration. Trans Inst Min Metall Sect B: Appl Earth Sci 97, B116–B140

Rollinson, H.R., 1993: Using Geochemical Data: Evaluation, Presentation, Interpretation. Longman, 352 pp

Taylor, S.R. and McLennan, S.M. (1985): The Continental Crust: its composition and evolution. Blackwell Scientific Publishers, Oxford.

Turekian, K.K., (1978): Strontium: abundance in rock forming minerals; strontium minerals. In: Wedepohl, K.H. (Ed.): Hand book of Geochemistry, vol. II/4. Springer-Verlag, pp. 38–D-1-17.

Wedepohl, K.H., (1978): Zinc: abundance in rock forming minerals, phase equilibria, zinc minerals. In: Wedepohl, K.H. (Ed.), Hand book of Geochemistry, vol. II/3. Springer-Verlag, pp. 30–D-1-12.

Whitney DL, Hirshmann M, Miller MG (1993): Zincian ilmenite - ecandrewsite from apelitic schist, Death Valley, California, and the paragenesis of (Zn, Fe)TiO3 solid solution in metamorphic rocks. Can Mineral 31:425-436

جيوكيميائية بعض الرسوبيات السطحية الحديثة بشمال الوجه، شمال غرب المملكة العربية السعودية

أسعد محمد بكر مفتي* و ابتسام حسن محمد عرفه**

* قسم الثروة المعدنية والصخور، كلية علوم الأرض، جامعة الملك عبد العزيز، ص. ب. 80206، الرقم البريدي 21589 جدة، المملكة العربية السعودية.

** المديرة السابقة لمتحف قسم الجيولوجيا، كلية العلوم، جامعة القاهرة، جمهورية مصر العربية

تناقش الورقة الحالية الخصائص الجيوكيميائية لبعض الرسوبيات السطحية التي تم جمعها من منطقة الوجه بشمال غرب المملكة العربية السعودية. واستنتاجات الورقة تمت بناءا علي المعلومات الجيوكيميائية والبتروجرافية والمعدنية لكل من القطفات الخفيفة والثقيلة التي تم فصلها من هذه الرسوبيات. هذا وقد تم فصل أحجام مختلفة من قطفات المعادن الثقيلة وهي 40-63، 63-125، 125-250 ميكروميتر وذلك باستخدام سائل البروموفورم (كثافته النوعية 2.87 جم/سم^3). وقد بلغ عدد العينات حوالي 30 عينة مأخوذة من أودية المياة وحرامل وثلبة بواقع 9-10 محطة بكل وادي. وتم تحليل القطفات لمعرفة تركيزات 17 عنصر شحيح وذلك باستخدام تقنيتي طيف الامتصاص الذري (AAS) والبلازما المستحثة المزدوجة (ICP).

والبيانات المعطاة لعناصر الكروم والنحاس والرصاص والفانديوم والخارصين والزرنيخ غير متجانسة وتتميز بانحراف معياري (δ) كبير، بينما عنصر النيكل يتميز بمحدودية الاختلاف.

والقطفات الثقيلة المفصولة من العينات المأخوذة من وادي ثلبة بها تركيزات عالية من عناصر الكروم والخارصين والكوبالت خصوصا بالمصب عند البحر حيث تحتوي رماله السوداء هناك علي 529 و 302 و 50 جزء من المليون من العناصر الثلاثة علي التوالي. كما تتميز تلك الرمال السوداء بإثراء معظم العناصر الشحيحة الاخري باستثناء عناصر الزرنيخ والباريوم والرصاص. وعلي الرغم من أن الرواسب الوديانية المدروسة بها تركيزات عالية من عناصر الزرنيخ والباريوم والاسترنشيوم فإنها مميزة بالنزع بالنسبة للعناصر الشحيحة المتبقية. وبخصوص رسوبيات الكثبان والرسوبيات الشاطئية فهي تتميز بنسب تكاد أن تكون متشابهة من محتوي العناصر الشحيحة. وقد تم التوصل إلي أن عدم وجود علاقة وثيقة بين محتوي العناصر الشحيحة وحجم الحبيبات يوضح عدم نضج الرسوبيات المدروسة بالقطاع الجنوبي من منطقة ضبا-الوجه.