Evidence for Element Mobility in Some Metavolcanic Rocks in the Vicinity of Mineralized Areas in the Arabian Shield

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ABSTRACT. Forty-three samples of volcanic rocks were selected from 5 widely spaced mineralized areas within the Hulayfah Group in the Arabian Shield. These samples were analysed for major and minor oxides as well as Nb, Zr, Y, Ti and P. The analyses were plotted on some of the commonly used petrochemical discrimination and variation diagrams in a trial to test the mobility of elements, but not to deduce tectonic setting or magma type. Nb and Y showed the highest mobility, Ti and Zr showed relatively moderate mobility with Ti being somewhat more mobile, but P showed the least mobility. It is suggested that the partial pressure of carbon dioxide, and whether it is buffered by an external source or not, have a considerable effect on the mobility of these elements during metamorphism and alteration.

Introduction

Discrimination diagrams based on major and minor oxides as well as trace elements are frequently used to identify magma types and geotectonic settings (Barker and Arth 1976, Pearce and Cann 1973, Pearce 1975, Pearce and Gale 1976, Winchester and Floyd 1976, Pearce *et al.* 1977, Garcia 1978, Beccaluva *et al.* 1979, Fox 1979, Mullen 1983, Pharaoh and Pearce 1984, and Soliman 1988). Some of these diagrams are designed for unaltered rocks and others are designed for rocks of a certain range of composition (e.g. Pearce and Cann 1973, Beccaluva *et al.* 1979, Mullen 1983, Pharaoh and Pearce 1984 and Soliman 1988). On the other hand, Floyd and Winchester (1975) and Winchester and Floyd (1976 and 1977) have devised other diagrams based on immobile elements for use with altered and metamorphosed rocks. In addition, Harker and other triangular variation diagrams have also been utilized to

identify magma series and to assign petrographic names to volcanic rocks. In the Arabian Shield, several workers applied some of these diagrams for various purposes in their study of the volcanic rocks; from these we mention Shanti (1982), Roobol *et al.* (1983 and 1984), Qadhi and Hussein (1984), Tofig and Al Shanti (1984), Duyverman (1984) and Tayib and Al Shanti (1984). In the present work, it was found that basaltic rocks around five mineralized areas in the Arabian Shield do not plot within the expected fields on some discrimination diagrams. This was interpreted as due to mobility of some trace elements, which probably took place during alteration associated with mineralization. So, forty-three samples, ranging from basaltic to rhyolitic in composition, were selected from the five mineralized areas to investigate the mobility of some trace elements by using variation and discrimination diagrams. Thus, it should be emphatically stated at the outset that: it is not intended here to use the variation and discrimination diagrams to determine the tectonic setring or the magma type of the studied rocks, but the aim of this contribution is to indicate that these diagrams could be very helpful in disclosing element mobility.

Samples of the Present Study

Five volcanogenic sulphide occurrences within the Hulayfah Group volcanics and its equivalents in the Arabian Shield (Fig. 1) were selected for the present study. The five areas are Ash Shizm, Um Ad Dammar, As Safra, Al Musayna'ah and Um Ash Shalahib. They differ in their detailed geologic setting and nature of mineralization. Forty-three samples of volcanic rocks from these areas were analysed for major oxides and the trace elements Zr, Nb and Y (Table 1). The petrographic identification of these samples is given in Table 2. In the present routine identification of the studied samples, dacite, rhyodacite and rhyolite were grouped together as acidic rocks and collectively given one symbol on some of the diagrams. Previous workers (e.g. Delfour 1983, Tayib and Al Shanti 1983, and Qadhi and Hussein 1984) indicated that the Hulayfah volcanics are dominantly calc-alkaline. All the investigated samples are affected by low grade regional metamorphism with the development of greenschist facies minerals, mostly epidote, chlorite, albite, calcite and to a lesser extent actinolite. Epidote is the most abundant metamorphic mineral and occurs in all the rocks, even in the most fresh rhyolite. Chlorite is specially abundant in the basaltic rocks, which occur only in Ash Shizm. Sericite and kaolinite also occur as minor alteration products in some samples. In spite of this, the original textures and relics of the parent volcanic minerals are preserved in many cases. The analyses were recalculated on a water free basis before plotting on the diagrams. The chemical analyses were carried out at the Laboratories of the Faculty of Earth Sciences, King Abdulaziz University. Zr, Nb, Y, Ti, P, Si, Al, Ca and K were determined by XRF technique. Mg, Mn, Na and total Fe were determined by atomic absorption technique. Water and FeO were determined by wet chemical techniques. Precision and accuracy are estimated to be 3% or better.



FIG. 1. Location of the studied sulphide occurrences.

Sample	1	2	3	4	5	6	7	8
Weight Percent								
SiO,	49.40	49.86	47.72	44.47	51.06	47.49	55.20	74.17
TiO,	0.88	0.75	1.29	1.29	0.96	0.76	1.24	0.27
Al ₂ Õ ₃	13.99	14.45	14.42	14.99	13.54	14.75	14.08	11.51
Fe ₂ O ₃	2.92	3.83	3.55	4.50	5.02	5.11	3.59	1.90
FeO	7.61	6.10	8.26	7.40	5.40	4.74	8.44	2.30
MnO	0.21	0.22	0.20	0.20	0.14	0.20	0.26	0.11
MgO	7.93	6.57	6.51	5.05	6.66	7.38	4.27	0.71
CaO	8.81	12.53	6.00	10.52	7.52	14.57	7.01	2.52
Na ₂ O	2.70	2.64	3.40	2.66	2.95	0.82	2.98	4.41
K ₂ O	0.76	0.03	0.93	0.15	0.20	0.09	0.70	0.15
P_2O_5	0.13	0.16	0.11	0.15	0.12	0.19	0.13	0.08
sum	95.34	97.14	92.39	91.38	93.57	96.10	97.90	98.13
PPM								
Nb	12	12	23	21	10	15	15	25
Zr	31	31	17	29	7	55	50	48
Y	5	5	5	5	5	5	5	11

TABLE 1. Chemical analyses of the studied samples.

TABLE 1. (Contd)

Sample	9	10	11	12	13	14	15	16	
Weight Percent									
SiO,	73.15	74.65	68.28	74.15	25.80	78.60	74.66	66.14	
TiO,	0.20	0.21	0.35	0.24	1.08	0.11	0.16	0.60	
Al ₂ Ó,	11.35	11.69	13.03	11.82	16.76	6.77	11.46	15.08	
Fe ₂ O ₃	1.93	1.53	2.04	1.84	4.15	1.80	1.04	1.70	
FeO	1.36	1.44	2.59	1.94	21.73	5.82	2.62	3.16	
MnO	0.11	0.10	0.10	0.05	0.66	0.16	0.10	0.11	
MgO	0.96	1.09	1.63	1.02	13.11	2.96	4.46	2.58	
CaO	4.09	3.80	3.83	3.40	1.40	0.23	0.21	5.74	
Na ₂ O	3.37	1.85	5.78	3.99	0.91	0.56	0.67	2.91	
K,Õ	0.34	2.02	0.19	0.26	0.02	0.41	1.80	0.87	
P ₂ O ₅	0.09	0.09	0.09	0.08	0.05	0.06	0.06	0.11	
sum	96.95	98.47	97.91	98.79	85.67	97.48	97.24	99.00	
РРМ									
Nb	30	31	23	24	12	5	16	16	
Zr	91	63	79	52	38	7	7	29	
Y	12	14	16	10	10	5	5	5	

TABLE I. (Contd)

Sample	18	19	20	21	22	23	24	25
Weight Percent								
SiO,	65,78	54.14	70.82	77.70	65.50	76.10	73.82	76.54
TiO ₂	0.28	0.26	0.51	0.11	0.36	0.08	0.09	0.12
Al,Ô,	11.07	15.88	13.68	11.52	12.06	11.80	11.82	11.87
Fe,O,	3.16	4.03	1.06	0.28	2.72	1.36	1.17	1.43
FeO	2.08	5.35	2.87	0.32	1.44	0.29	0.22	0.29
MnO	0.07	0.23	0.08	0.02	0.10	0.03	0.03	0.01
MgO	8.38	5.76	1.34	0.10	7.78	0.20	0.22	0.16
CaO	0.27	8.89	1.67	0.64	0.58	0.48	1.10	0.26
Na ₂ O	0.56	3.81	7.06	7.29	0.58	3.78	3.87	3.54
K,Õ	0.42	0.30	0.42	0.50	2.89	4.24	4.18	4.80
P_2O_5	0.08	0.14	0.08	0.06	0.06	0.06	0.06	0.06
sum	92.15	98.79	99.59	98.54	94.07	98.42	96.58	99.08
РРМ								
Nb	14	15	12	15	5	78	105	66
Zr	8	7	7	5	25	39	72	73
Y	5	5	5	8	5	22	27	20

TABLE 1. (Contd)

Sample	26	27	28	29	30	31	32	33
Weight Percent								
SiO,	76.59	74,98	61.35	55.73	53.07	57.18	53.47	49.70
TiO,	0.15	0.16	1.38	1.18	1.12	1.12	1.08	0.82
Al ₂ Õ ₂	11.83	11.81	12.50	15.36	16.46	13.89	15.42	12.53
Fe,O,	1.02	1.12	3.05	3.04	1.62	8.66	5.51	2.13
FeO	0.72	0.65	3.48	4.85	6.82	4.31	3.52	14.90
MnO	0.01	0.01	0.08	0.13	0.16	0.02	0.03	0.04
MgO	0.20	0.23	2.17	5.54	4.95	3.28	3.30	5.25
CaO	0.60	0.74	3.70	7.91	8.51	0.47	1.91	0.34
Na ₂ O	2.99	3.23	4.36	3.84	3.49	2.00	2.10	0.64
K ₂ Õ	5.18	5.15	2.51	0.69	1.30	6.84	8.11	5.95
P_2O_5	0.06	0.06	0.12	0.15	0.15	0.07	0.07	0.06
sum	99.35	98.14	94.70	98.42	97.65	97.84	94.52	92.36
РРМ								
Nb	66	63	33	5	5	5	15	18
Zr	138	71	92	62	103	12	43	42
Y	24	17	13	5	5	5	12	31

Тавн-	1. (C	`ontd)
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Sample	.34	35	36	.37	38	39	40	41
Weight Per	cent							
SiO	59.55	49.43	53.78	64.37	55.76	78.82	72.84	76,98
TiO	0.73	1.08	1.40	1.35	1.07	0.31	0.53	0.35
ALO,	11.95	14.17	15.40	11.74	13,97	11.12	11.13	10.87
Fe.O ₂	2.72	2.68	2.38	10.69	5.31	0.30	4.22	0.26
FeO	9.73	8.51	5.31	1.29	4.63	0.72	0.36	0.72
MnO	0,03	0.03	0.13	0.01	0.02	0.02	0.00	0.02
MgO	5.19	7.65	4.18	0.39	3.86	1.78	0.12	0.72
CaO	0.39	3.50	7.39	0.86	4.52	2.20	0.36	2.03
NasO	1.05	2.34	3.06	4.76	3.65	4.48	3.40	7.25
K ₂ O	5.75	6.18	0.87	0.57	3.00	0.36	3.45	0.30
P ₂ O ₈	0.06	0.10	0.13	0.06	0.01	0.08	0.06	0.07
sum	97.15	95.67	94.03	96,89	95.80	100.19	96.47	99.57
PPM								
Nb	10	12	5	5	10	12	5	10
Zr	198	22	28	17	64	27	27	22
Y	5	8	8	5	11	5	5	5

TABLE 1. (Contd)

Sample	43	4.4	45					
Weight Percent								
SiO,	55.82	72.62	65.90					
TiO,	0.71	0.28	0.36					
ALO,	16.27	10.56	9.23					
Fe ₂ O,	1.72	0.84	6,06					
Fe ₂ O	3.30	1.11	4,49					
MnO	$\begin{array}{c} 0.11 \\ 5.60 \\ 8.42 \\ 1.55 \\ 1.46 \end{array}$	0.21	1.49					
MgO		1.98	4.01					
CaO		6.04	4.84					
Na ₂ O		3.61	1.50					
K ₂ O		1.78	0.64					
P.O. sum PPM	0.15 98-11	0.06 99.09	0.11 98.63					
Nb	10	16	12					
Zr	37	30	109					
Y	5	5	16					

		Chemical Identification					
	Petrographic Identification	TAS diagram (Fig. 2)	Zr/TiO ₂ -SiO ₂ (Fig. 3)	Nb/Y-Zr/TiO ₂ (Fig. 4)			
1 2 3 4 5 6 7 8 9 10 11 12 13 14	altered basalt altered basalt altered basalt altered basalt basalt metabasalt altered basalt altered rhyolite altered rhyolite altered rhyolite altered rhyolite altered rhyolite metarbyolite	basalt basalt basalt basalt basaltic andes. basaltic andes. basaltic andes. rhyolite rhyolite rhyolite dacite rhyolite	subałk. basalt subałk. basalt subalk. basalt subałk. basalt andesite subałk. basalt andesite rhyolite rhyolite rhyolite rhyolite rhyolite	ałkali basalt alkali basalt alkali basalt basanite nephelinite basanite nephelinite basanite nephelinite basanite nephelinite basanite nephelinite basanite nephelinite basanite nephelinite alkali basalt			
14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31	metarhyolite metarhyolite deleted* metarhyolite andesite metarhyolite	rhyolite dacite dacite basaltic andes. rhyolite	rhyolite dacite dacite? andesite dacite? rhyolite dacite rhyolite rhyolite rhyolite rhyolite rhyolite rhyolite rhyolite andesite andesite	basanite nephelinite basanite nephelinite basanite nephelinite basanite nephelinite alkali basalt alkali basalt alkali basalt trachyte trachyte trachyte trachyte trachyte trachyte trachyte trachyte trachyte trachyte			
31 32 33 34 35 36 37 38 39 40 41 42 43 44 45	andesite andesite andesite andesite andesite andesite andesite altered rhyol. rhyol. tuff rhyol. tuff rhyol. tuff rhyol. tuff rhyolite rhyolite rhyolite	rachyandesite trachyandesite trachyandesite andesite phonotephrite andesite daeite andesite rhyolite rhyolite rhyolite trachyandesite rhyolite dacite	andesite andesite andesite basalt andesite dacite? andesite rhyolite rhyolite rhyolite andesite dacite dacite dacite	alkali basalt subalk. basalt subalk. basalt subalk. basalt subalk. basalt alkali basalt alkali basalt alkali basalt alkali basalt alkali basalt alkali basalt alkali basalt alkali basalt			

TABLE 2. Comparison of petrographic and chemical identification of the studied rocks.

Sample Locations

1 to 13: Ash Shizm

14 to 21: Umm Ad Damar

22 to 30: As Safra

31 to 38: Al Musayna'ah

39 to 45: Umm Ash Shalaheeb

Encluding dacite and thyodacite.

* Deleted for extreme silicification.

Diagrams for Chemical Classification of Volcanic Rocks

Three diagrams used for the chemical classification of volcanic rocks were selected for plotting the present analysis.

1. TAS diagram (Fig. 2, after Le Bas et al. 1986)

The studied samples were plotted on this diagram, which was proposed by the IUGS for the chemical classification of the volcanic rocks to see how the major chemistry of these rocks conform with the petrographic identification. From this diagram, we note the following :

1.1) The SiO₂ content of the majority of the samples lies within the range specified by the petrographic identification, except few basalt and andesite samples, which show slight enrichment in silica.

1.2) Several samples show a clear enrichment in alkalis and are thus separated from the calc-alkaline field and moved to the alkaline field or even to the feldspathoidal field, while the rest of the samples lie in the calc-alkaline field. Although there is no dividing line between the rhyolite and alkali rhyolite field, the samples from As Safra (encircled) show moderate enrichment in alkalis with respect to other rhyolites. So, various degrees of alkali metasomatism is indicated in, at least, some of the studied samples.

2. SiO₂ vs Zr/TiO₂ diagram (Fig. 3, after Winchester and Floyd 1977)

The shift of some samples from the calc-alkaline field would be expected to be towards the alkaline field, if there were a mutual consistency among the chemical parameters of these rocks in indicating their nature. But here, the shift is further away from the alkaline field, bringing some samples outside the realm of the diagram. This is clearly due to the decrease of the Zr/TiO_2 ratio in, at least, some of the studied rocks, indicating the mobility of one or both elements.

3. Zr/TiO, vs Nb/Y diagram (Fig. 4, after Winchester and Floyd 1977)

The effect of decreased Zr/TiO_2 ratio is quite clear in shifting the samples downwards in the diagram. At the same time, the effect of increased Nb/Y ratio is also very clear in shifting most of the samples to the alkaline and feldspathoidal fields.

Thus, from these three simple diagrams we demonstrate the mobility of, at least, two of the four "thought immobile" trace elements, namely Zr and Ti. We will now use some other diagrams to investigate the mobility of these elements.

Discrimination Diagrams

1. P₂O₅ vs Zr diagram (Fig. 5, after Winchester and Floyd 1976)

This diagram was proposed to discriminate between tholeiitic and alkalic basalts. The studied basalts plot where they would be expected from petrographic identifica-







FIG. 3. SiO₂ against Zr/FiO₂ diagram for the studied rocks, after Winchester and Floyd, 1977. (Sample identification as in Fig. 2).





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tion and from previous works. This result indicates that phosphorous was not mobilized to the extent to alter the signature of the rocks. This diagram was first used here because any mobilization of Zr would not affect the position of samples at the level of P_2O_5 content. Furthermore, nonbasaltic rocks were also plotted here as well as in diagrams to follow, merely to show their relative position within the different fields. This diagram also shows the variation of Zr content in the studied samples.



FIG. 5. P₂O₈ against Zr diagram for the studied rocks, after Winchester and Floyd, 1976.
Dot = Basalt
Square = Andesite
Triangle = Rhyolite

TiO₂ vs Zr/P₂O₅ (Fig. 6) and Nb/Y vs P₂O₅ (Fig. 7) diagrams (after Winchester and Floyd 1976)

In Fig. 6, about half the basalts and andesites are shifted from the subalkalic field to the alkalic field, which suggests that either Ti had increased or Zr had decreased in the studied rocks. Three samples plot beyond the right limit of the diagram due to their higher value of $Zr/P_2 O_5$ ratio. Fig. 7 shows the effect of the increase of Nb/Y ratio in most of the studied rocks.



FIG 6. TiO₂ against Zr/P₂O₅ diagram for the studied rocks, after Winchester and Floyd 1976 (symbols as in Fig. 5).



FIG. 7. Nb/Y against Zr/P₂O₅ diagram for the studied rocks, after Winchester and Floyd 1976 (symbols as in Fig. 5).

3. Ti vs Zr diagram (Fig. 8, after Pearce and Cann 1973)

This diagram was proposed to identify several magma types of basaltic rocks. In the light of field and petrographic data, this diagram would suggest a LKT magma type for basalts of Ash Shizm (1 to 7) and a CAB magma type for the andesites (33, 38, 30). However, eight samples of both the basalts and andesites fall outside the realm of the diagram towards the increase of Ti coupled to a lesser extent with a decrease of Zr. The distribution of the points representing rhyolites also shows a wide dispersion of both elements independent of each other. So, Ti and Zr were both mobilized in the studied rocks to various degrees, and this, we believe, is the cause of the inconsistency observed in Fig. 2 and 3.



FIG. 8. Ti against Zr diagram for the studied rocks, after Pearce and Cann 1973 (Sample identification as in Fig. 2).

4. Relation between Nb and Y

The relation between these two elements may be illustrated by plotting each of them against silica as shown in Fig. 9 and Fig. 10, respectively, as well as plotting them against each other in Fig. 11. Figure 9 was proposed by Pearce and Gale (1976) to discriminate between volcanic and within plate magma types for basaltic rocks.



FIG. 9. Nb against SiO₂diagram for the studied rocks, after Pearce and Gale 1976 (Symbols as in Fig. 5).

Most of the studied basalts and andesites fall in the area of overlap between the fields of volcanic arc basalt and within plate basalt due to increased Nb content so that there is an ambiguity in identifying the magma type. It also shows the wide variation of Nb content in the rhyolitic samples, particularly in most of As Safra samples (23 to 27, note also that these samples showed effects of alkali metasomatism in Fig. 2). Figure 10 shows that Y was coherent with Nb during mobilization, but to a lesser degree. In other words, both the two elements increase in at least some of the studied rocks, but with different rates so as the net result is a decrease of Nb/Y ratios. The precision of analyses decreases towards lower values and in case of Y, 22 samples have Y content below detection limit (10 ppm) and were plotted as having 5 ppm Y. The coherence between Nb and Y in the range of their high values is further illustrated in Fig. 11, where they show positive correlation.



SiO, wt. %

FIG. 10. Variation of Y against SiO_2 in the studied rocks.



FIG. 11. Variation of Nb against Y in the studied rocks.

Conclusion

Applying the discrimination diagrams to the studied rocks revealed some chemical characteristics which may be summarized in the following points :

1. Alkali metasomatism is well displayed in the samples of Al Musayna'ah (andesites), As Safra (rhyolites) and to a lesser degree in the remaining areas.

2. Nb and Y showed the highest mobility, Ti and Zr showed relatively moderate mobility with Ti being somewhat more mobile, while P showed the least mobility.

3. The discrimination diagrams used here are very effective in revealing some of the chemical variations induced upon the studied rocks since their formation; both basaltic and rhyolitic rocks may be treated in the same way. We propose and encourage this trend with the application of as many diagrams as possible in a trial to establish some specific procedures for testing element mobility. In this respect, it should be noted that the mobility of a certain element is only noticed when the respective sample plots outside its expected field. If the sample moved within its field, the mobility of the causing element would pass unnoticed. This effect can be largely overcome by plotting each element or oxide against several other parameters in independent diagrams.

4. Searching for a reason of mobility of elements which are supposed to be immobile, Hynes (1980) and Murphy and Hynes (1986) found that the partial pressure of carbon dioxide and whether it is buffered by an external source or not, have a considerable effect on the mobility of these elements during alteration and metamorphism.

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and _____ (1977) Geochemical discrimination of different magma series and their differentiation products using immobile elements, *Chemical Geol.* **20**: 325-343. أدلــة تحرك بعض العنــاصــر في بعض الصخــور الـبركـانيـــة المتحـولــة بجــوار مناطــق تمعــدن في الــدرع العــربي

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مستخلص . تم اختيار أربعة وثلاثين عينة من صخور بركانية من خمس مناطق تمعدن متباعدة من صخور مجموعة الحُلَيْفَة في الدرع العربي . وتم تحليل هذه العينات للأكاسيد الرئيسة والقليلة بالإضافة إلى عناصر النيوبيوم والزركونيوم والتيتريوم والفوسفور ، ثم وُقَعت هذه التحاليل على بعض الأشكال المستخدمة عادة في التمييز والتغاير البنيوي أو النوعية الصهارية . وقد أظهر كل من النيوبيوم واليتريوم أقصى درجة تحرك ، بينها أظهر كل من التيتانيوم والزركونيوم تحركا مدن النيوبيوم واليتريوم أقصى درجة تحرك ، ما من الزركونيوم . أما الفوسفور ، فقد أظهر أقل درجة تحرك من بقية العناصر . ويرى الباحثون أن الضغط الجزئي لثاني أكسيد الكربون ، وإذا كان هذا الضغط الجزئي مثبتًا بمصدر خارجي ، هما من الأسباب التي لها تأثير مباشر على تحرك هذه العناصر أثناء عمليتي التحوُّل والتغير .