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RELATIVE ABUNDANCES OF MINOR AND TRACE ELEMENTS IN MAFIC PHASES FROM THE SOUTHERN PART OF THE KOHISTAN ARC

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ABSTRACT

Many pyroxenes, granet, hornblende, epidote, biotite, and one each of olivine and chromite from amphibolites, gabbronorites and ultramafic rocks were analysed for up to 21 minor and trace elements. Like major elements, many of these also are systematically distributed between the coexisting mineral pairs and trios. Orthopyroxene contains higher amounts of MnO, Co, Ni, Zn, and lower TiO_2*,* Na_2O*, Li, Pb, Cr, V, Zr, Sr, Ba, Y, Nd and La as compared to clinopyroxene. Biotite Contains more Cr, Cu, Li, Pb, and Ni than pyroxenes and hornblende. The amounts of* TiO_2*,* Na_2O*,* K_2O Fe_2O_3 *and Ni are higher in hornblende than in pyroxenes and garnet. Garnet is impoverished in Li, Ni, V and Zn as compared to clinopyroxene and hornblende.*

INTRODUCTION

The Creto-Tertiary Kohistan magmatic arc covers about 24000 km² area in northern Pakistan. The southern half of the arc is occupied by the Kamila amphibolites, the Chilas mafic-ultramafic complex (gabbronorites and related rocks), the Jijal complex (mafic-ultramafic granulite facies rocks) and quartz diorites-tonalites (see maps in Tahirkheli and Jan, 1979; Butt et al., 1980; Bard, 1983a; Coward et al., 1986). These rocks have been the subject of extensive petrological investigations during recent years (Jan an Kempe, 1973; Shams, 1975; Jan, 1977, 1988; Jan and Asif, 1983; Bard, 1983b; Khan, 1988; Khan et al., 1989). Details of mineral chemistry have been presented by Jan and Howie (1980, 1981, 1982, 1987), Bard (1983b), and Khan et al. (1989).

This paper presents an integrated account of the relative abundances of up to 21 minor and trace elements in coexisting mafic phases, mostly pairs but some trios and a few quartets. It is based on 130 mineral analyses presented in the publications of Jan and Howie (op. cit) and Jan (1977). The coexisting phases in a particular group of rocks seem to have been formed mostly under physico-chemical equilibrium, as revealed by textural relations, systematic distribution of major elements, and fairly consistent PT estimates based on their chemical composition. The systematic partitioning of minor and trace elements (Figs. 1 and 2) is in general agreement with reliable published data (cf. Henderson, 1984, 1986).

In recent years, several workers have used minor and trace elements in minerals for various purposes, such as thermobarometry, tectonic environments, mineral-melt equilibria and petrogenesis. It then becomes imperative that the minor and trace elements should be determined accurately and precisely. Like the major elements, these should also display systematic distribution between coexisting phases. Therefore, the relative abundances of elements between coexisting minerals may be used as a measure of the accuracy of the analyses. Application of this criterion to the recently published literature reveals possible flaws in certain analyses determined by rapid methods. The Kohistan minerals were carefully analysed under similar conditions and it is hoped that they may serve as a quick guide for comparison and assessment.

Analytical Techniques. The analyses were performed on mineral concentrate from samples showing equilibrium textures. Many of the samples were also analysed by electron microprobe to confirm that the mineral phases of interest were either unzoned or only marginally zoned. The specimens were ground to < 150 BSM. Magnetite was removed by hand magnet and the remaining material was split into mafic and felsic concentrates by disc magnetic separator. The mafic concentrates were ground further to < 200 BSM (but garnets dowm to 300 BSM) before further splitting and concentration by Frantz isodynamic magnetic separator. Final purification was obtained by the use of heavy liquids through centrifuge. Only those mineral concentrates were analysed which showed a purity of more than 98.5% under microscope.

Chemical analyses were performed by atomic absorption (Unicam SP 1990), using emission mode for alkalis. TiO_2 and P_2O_5 were determined colorimetrically, Unicam SP 600 Series 2 spectrophotometer. FeO was determined by titration, using Wilson's (1955) method. Each element was determined twice, using the same bulk solution. Closely spaced standard solutions were used for control and international standards for comparison. Fifteen mineral analyses were duplicated by automatic XRF. In these Zr, Sr, Ba, La, Ce, Nd and Y were also determined. Ferric iron, manganese, phosphorous, potassium and sodium were analysed in oxide form and are presented as such; others are in elemental form. Mineral symbols used are: Bt = biotite, Chr = chromite, Cpx = clinopyroxene, Ep = epidote, Grt = garnet, Hbl = hornblende, Ol = olivine, and Opx = orthopyroxene (Kretz, 1983).

RELATIVE ABUNDANCES OF ELEMENTS

The analysed mineral phases can be grouped into three assemblages: A) forsterite-enstatite (En 75–91)-diopside-chromite based on the study of the four minerals in a harzburgite and of the two pyroxenes in websterites of the Jijal complex that has undergone garnet granulite grade metamorphism, B) orthopyroxene (En 64-51)-Ca-rich clinopyroxene-hornblende-biotite based on the analyses of two to three, but in one rock all four, of the phases in the granulite facies gabbornorites of the Chilas complex and a few quartz diorites and amphibolites, and C) garnet-Ca-rich clinopyroxene-hornblende-epidote based on the analyses of two to three of these minerals in the high-pressure garnet granulites of the Jijal complex and some amphibolites. It must be pointed out that it is not being suggested that a hypothetical rock composed of all the eight phases must have the same pattern of element distribution as those displayed by the four-phase assemblages. The relative distribution of the elements in the coexisting pyroxenes is statistically more meaningful because of a higher number of analyses (22 pairs), all from mafic to ultramafic granulites. This paper does not deal with the theoretical aspects of element partitioning in coexisting minerals. It only draws attention to relative preference (i.e. concentration) of elements between the associated minerals which are considered to have reached physico-chemical equilibrium. For general information on theoretical aspects of element partitioning, the reader is referred to Deer et al. (1978, 1982) and Henderson (1986).

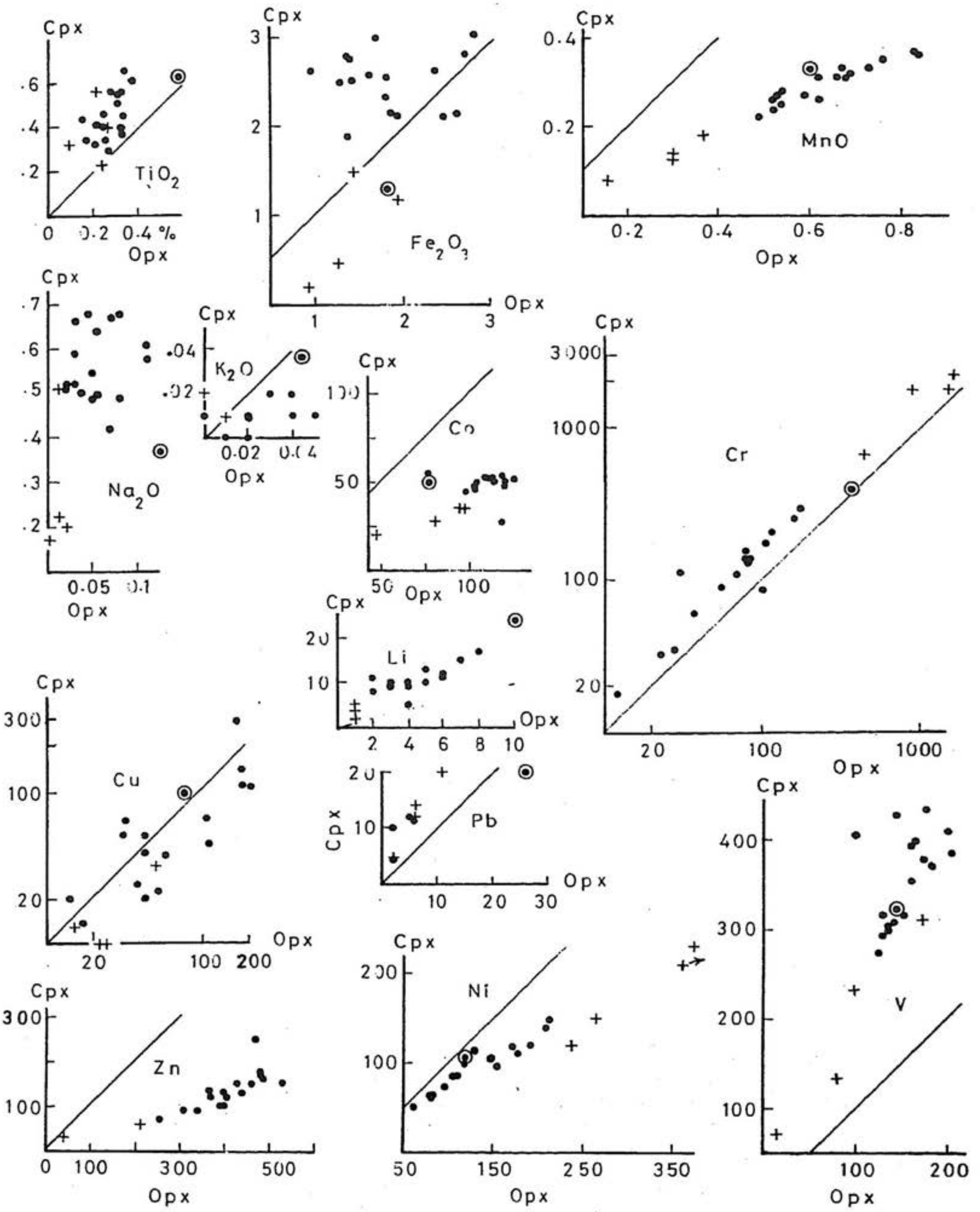

Fig. 1. Distribution of minor and trace elements between the pyroxene pairs. Diagonal line has a slope of 1. Crosses: ultramafic rocks; dots: mafic rocks; circled dot: quartz diorite. TiO_2, Fe_2O_3, MnO, Na_2O and K_2O in weight percentages, others in parts per million.

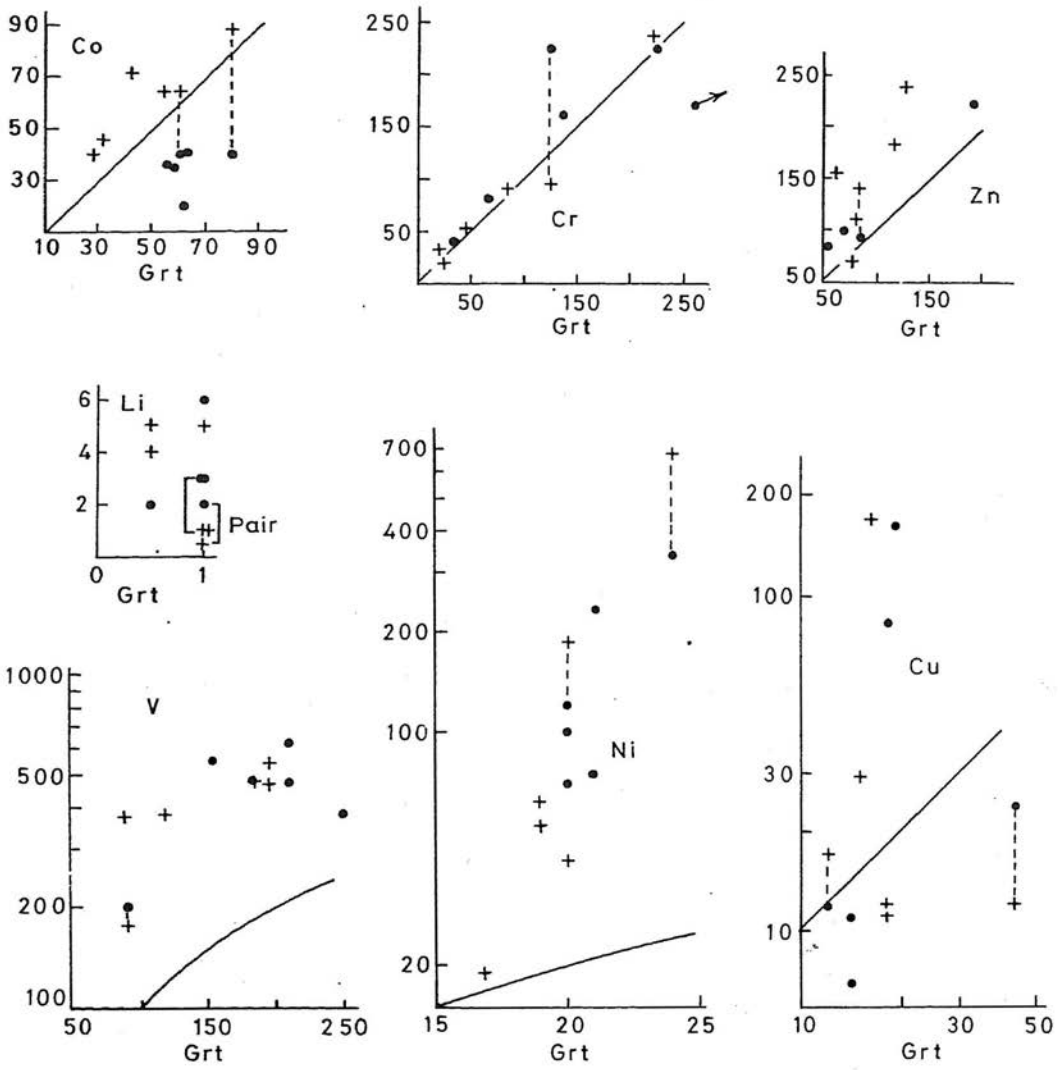

Fig. 2. Distribution of trace elements between garnet-clinopyroxene pairs (dots) and garnet-hornblende pairs (crosses). Coexisting hornblende and clinopyroxene are joined by tie-lines. Values are in parts per million. Diagonal line has a slope of 1.

1. Cobalt (Co)

A) Chr > Ol > Opx > Cpx

B) Bt > Opx > Hbl > Cpx

C) Hbl > Grt > Cpx > Ep

The partitioning of Co in the coexisting mineral phases is very systematic. The amount of Co in orthopyroxene is 1.7 to 2.9 (but mostly 2.2 to 2.4) times that in the associated clinopyroxene (Fig. 1). The Co ratio in Opx: Cpx pairs in the Bushveld complex ranges from 1.4 to 1.5 (Atkins, 1969), in the mafic granulites of Central Australia from 2.8 to 3.8 (Woodford and Wilson, 1976), in peridotites from western Alps from 2.1 to 3.1 (Ottonello et al., 1984) and in the gabbronorites of the Paninsular Ranges batholith, Southern California, from 1.5 to 4.4 with one value of 0.9 (Smith et al., 1983). The partitioning of Co in Hbl: Grt and Cpx: Grt pairs can be seen in Fig. 2, whilst biotite contains 1.4 to 2.0 times more Co than hornblende.

2. Chromium (Cr)

A) Chr > Cpx > Opx > Ol

B) Bt > Hbl > Cpx > Opx

In the garnet granulites and garnetiferous amphibolites the distribution of Cr in the mafic phases is erratic; however, it is mostly higher in clinopyroxene than in garnet. In the garnet-free amphibolites it prefers hornblende over epidote. Compared to orthopyrexene, clinopyroxene is 1.1 to 1.9 (mostly 1.2 to 1.7) times more enriched in Cr (Fig. 1). The Bushveld, Central Australian, and western Alps clinopyroxenes contain, respectively, 1.9 to 2.8, 1.3 to 2.2, and 1.9 to 3.3 times more Cr than their coexisting orthopyrexenes (Atkins, 1969; Woodford and Wilson, 1976; Ottonello et al., 1984).

3. Copper (Cu)

A) Chr > Opx > Cpx > Ol

B) Bt > Opx generally > Cpx generally > Hbl

Cu does not display a consistent pattern of distribution in the mineral phases analysed from the garnet granulites and amphibolites. The data of Atkins (1969) and Woodford and Wilson (1976) also do not show a consistent distribution of Cu between pyroxene pairs, but the Central Australian clinopyroxene contains more Cu than in the associated hornblende (Woodford and Wilson, 1976).

4. Ferric Iron (Fe_2O_3)

B) Hbl > Cpx generally > Opx

C) Ep > Hbl > Cpx > Grt

The Fe_2O_3 wt% content of biotite does not show a systematic pattern of distribution with those of the pyroxenes, but it is generally lower than that of hornblende. DeVore's (1957) data show that biotite contains more Fe^{3+} than does orthopyroxene. In Kohistan only five orthopyroxenes, including the three most magnesian (Mg no > 75), contain more and the remainder contain less Fe_2O_3 than their associated clinopyroxenes. A survey of "wet" chemically analysed samples from different areas (Howie, 1955; Binns, 1965; Davidson, 1968; Wilkinson, 1971; Sen and Manna, 1976; Murthy, 1976; Woodford and Wilson, 1976) also shows that Fe_2O_3 is preferentially accommodated in most clinopyroxenes than in orthopyroxenes. The Opx in these areas is predominantly less magnesian than "bronzite". The data of Atkins (1969) and Rao et al. (1979), however, suggest the reverse Orthopyroxenes analysed by these workers, incidentally, are also highly magnesian except three compositions reported by Atkins (1969).

Whether "enstatite-bronzite" generally contain more Fe^{3+} than their associated Ca-rich clinopyroxenes needs to be explored further despite that DeVore's (1957) data do not support this.

5. Lead (Pb)

A) Chr > Cpx > Opx > Ol

Pb distribution is not clear in the remaining assemblages because of its low levels of concentration (generally below the 5 ppm detection limit). When detected, however, it is higher in biotite than in the associated pyroxenes and hornblende. Garnet may have higher or lower Pb content than the clinopyroxene, but hornblende does not contain more Pb than clinopyroxene. Woodford and Wilson (1976) reported more Pb in hornblende than in clinopyroxene.

6. Lithium (Li)

A) Cpx > Opx > Ol > Chr

B) Bt > Cpx > Opx > Hbl

C) Cpx > Hbl generally > Grt > Ep

Li content in the analysed phases is generally < 13 ppm, but it is much higher in biotite (12 to 155 ppm) an only up to 1 ppm in garnet and 3 ppm in epidote. The ratio of Li in Cpx : Opx commonly ranges from 2 to 3, but reaches up to 5.5. In one rock, hornblende contains more Li than orthopyroxene.

7. Manganese (MnO)

A) Chr > Opx > Ol > Cpx

B) Opx > Cpx > Hbl > Bt

C) Grt > Cpx > Hbl > Ep

Like Li and Co, the distribution of MnO also is consistently systematic between the coexisting mineral phases, except in one rock in which it prefers hornblende over clinopyroxene. The lowest intake of it in the epidote as compared to the other minerals may explain the scarcity of piemontite in high-grade metamorphic rocks not rich in manganese. The MnO wt% values of orthopyroxenes are 1.8 to 2.3 (mostly 2.0 to 2.2) times higher than those of the associated clinopyroxenes. Such relations are also shown by pyroxenes from other areas (Carstens, 1958; Binns, 1965; Davidson, 1968; Atkins, 1969; Jayawardena and Carswell, 1976; Sen and Manna, 1976; Woodford and Wilson, 1976; Smith et al., 1983), including volcanic prageneses (Wilkinson, 1971). Lindh (1974) noted that Mn (in terms of mole fraction Mn/ (Mn + Mg + Fe)) is equally distributed between pyroxene pairs if mole fraction Mn in orthopyroxene is less than 0.008, whilst more manganiferous pyroxenes show a weak enrichment of Mn in orthopyroxene. This difference depends "on Mn having an attraction for the clinopyroxene M2 position. Ionic radius is concluded to be more important in determining the ionic distribution in pyroxenes than crystal-field energies" (Lindh, 1974). The mole fraction Mn levels in the Kohistan pyroxenes conform to Lindh's observations.

8. Nickle (Ni)

A) Ol > Chr > Opx > Cpx

B) Bt > Hbl > Opx > Cpx

C) Hbl > Cpx > Ep generally > Grt

In one sample, hornblende is poorer than epidote in Ni content. The Hbl: Opx Ni ratios range from 1.5 to 1.8 and are similar to those (1.5 to 2.1) of Central Australia (Woodford and Wilson, 1976). In the Peninsular Ranges, hornblende may contain more or less Ni than orthopyroxene. Orthopyroxene in Kohistan generally contains 1.2 to 1.8 times more Ni than its associated clinopyroxene. For the Bushveld pairs the ratios range from 1.3 to 1.4 (Atkins, 1969), for the Central Australian pairs from 1.1 to 1.6 (Woodford and Wilson, 1976), for the Peninsular Ranges pairs from 0.7 to 25.0 (Smith et al., 1983), and for those of Western Alps from 1.3 to 2.3 (Ottonello et al., 1984).

9. Phosphorous (P_2O_5)

P_2O_5 was not detected in most of the minerals. In the measured samples, the determined values may be suspected because of its very low levels. It was detected in 14 pyroxenes and, in the case of pairs, it is higher in most clinopyroxenes than in orthopyroxenes. The present data agree well with those of Jayawardena and Carswell (1976). This rather systematic partitioning may suggest that P is accommodated in the structure of the pyroxenes rather than being due to apatite impurities (cf. Koritnig, 1964).

Phosphorous was not detected in garnet and biotite, but half of the hornblende and epidote samples contain trace amounts (up to 0.06 wt%) of P_2O_5. Divakara Rao and Satyanarayana (1971) reported much higher amounts of P_2O_5 in garnet (0.06 – 0.40%) and hornblende (0.10 – 0.22%) form Mysore, India. Such high values are apparently erroneous. In the 162 garnet analyses compiled by Deer et al. (1982), only a few contain P_2O_5 in the range of 0.1 to 0.2 wt%.

10. Potassium (K_2O)

Measurement of the low levels of K_2O in most of the Kohistan minerals, like P_2O_5, may not be accurate. No systematic distribution of K_2O is noted between garnet, clinopyroxene and epidote. The quantity of K_2O in the orthopyroxenes ranges from nil to 0.08% (average 0.02) and that in clinopyroxenes from nil to 0.05% (average 0.01). In those cases where both the pyroxenes contain measurable amounts, K_2O is mostly enriched in orthopyroxene over clinopyroxene (Fig. 1), but both are impoverished as compared to hornblende. Jayawardena and Carswell (1976) report higher amounts of K_2O in clinopyroxene (0.00 – 0.04%) than in orthopyroxene (0.00 – 0.01%).

11. Sodium (Na_2O)

A) Cpx > Opx > Ol > Chr

B) Hbl > Cpx > Bt > Opx

C) Hbl > Cpx > Ep > Grt

In clinopyroxene and, especially, hornblende, the amount of Na_2O may be many times higher than the rest of the minerals. With rare exception, the Na_2O content of orthopyroxene does not exceed 0.10 wt%. Average Na_2O in garnet is 0.03% and in epidote 0.20%. There is a possibility that the high Na_2O of the epidote is a consequence of plagioclase impurities (compare with the list of analyses in Deer et al., 1984).

12. Titanium (TiO_2)

A) Cpx > Opx > Ol

B) Bt > Hbl > Cpx > Opx

C) Hbl > Cpx > Grt

TiO_2 values in epidote are erratic due, probably, to rutile and/ or ilmenite impurities. Although some orthopyroxene analyses with higher Tio_2 contents than those of the coexisting clinopyroxene have been reported, DeVore's (1956), Carstens' (1958), and Woodford and Wilson's (1976) data show that clinopyroxene is invariably enriched in TiO_2 as compared to orthopyrexene (see also Dear et al., 1978). In Kohistan, the ratio of TiO_2 in clinopyroxene/ orthopyroxene ranges from 1.1 to 3.2 (average 1.7) but in most cases it falls between 1.3 and 2.0 (Fig.1).

13. Vanadium (V)

A) Chr > Cpx > Opx > Ol

B) Bt > Cpx > Opx

C) Cpx > Ep > Grt

The V content of hornblende is 2 to 5 times (ignoring one pair) higher than orthopyroxene but it may be more or less than those in biotite and clinopyroxene. The Cpx : Opx V ratio ranges from 1.6 to 4.0 but mostly is 2.0 to 2.5. In the Bushveld pairs it ranges from 2.9 to 3.5 (Atkins, 1969), in Central Australian pairs from 2.5 to 3.0 (Woodford and Wilson, 1974), and in the Peninsular Ranges from 1.9 to 2.3 (Smith et al., 1983). In Central Australia and Peninsular Ranges, the V ratio in the hornblende: clinopyroxene pairs is fairly consistent (2.1 to 2.6, and 1.8 to 2.2, respectively).

14. Zinc (Zn)

A) Chr > Opx > Ol > Cpx

B) Opx generally > Bt > Hbl > Cpx

C) Hbl > Cpx > Grt > Epi

The ratios of Zn contents of different mineral pairs in Kohistan are: Bt/Hbl = 1.6 – 2.3, Opx/Cpx = 1.2 – 3.9 (mostly 2.7 – 3.7), and Hbl/Cpx = 1.2 – 1.50 Woodford and Wilson's (1974) ratios for Opx/Cpx pairs (2.3 to 3.6 with one 5.6) and Hbl/Cpx pairs (1.3 to 1.5) are very close to those of Kohistan.

15. Zr, Sr, Ba, La, Ce, Nd, Y

These elements were determined by automatic XRF in a garnet-clinopyroxene pair from a garnet granulite, a hornblende-epidote pair in an amphibolite, and three pairs of pyroxenes from the Chilas complex. Compared to garnet the clinopyroxene contains higher amounts of Zr, Ce, Nd, and lower of Ba and Y. Nd and Sr were not detected in the garnet and La in either of the two minerals. Compared to epidote, the hornblende contains lower amounts of Zr, Ce, Y and particularly, Sr (326 : 12 ppm) and higher of Ba. Nd was not detected in the hornblende and La in both hornblende and epidote.

The ratios of the elements in Cpx/Opx are: Zr = 8-14, Sr = 8-13 (ignoring one pair with high values: 15 ppm in Opx and 39 ppm in Cpx), Ba = 2.2 – 2.4, Y = 7-10. Nd, Ce and La are below the 3 ppm detection limit in orthopyroxene, but two of the clinopyroxene also have < 3 ppm La whereas the third one contains only 4 ppm. Ce (31–45 ppm) and Nd (19–31 ppm) are substantially higher in the clinopyroxenes, as also suggested by the work of Ottonello et al. (1984). The ratios of some of these elements in the Cpx/Opx pairs are: Zr = 0.8 – 1.1, Sr = 1.4 – 1.6, and Ba = 0.6 – 1.3 in the Bushveld complex (Atkins, 1969), Zr = 6–19 and Ba = 0.5 – 1.4 (with one value of 5.5) in the Central Australian granulites (Woodford and Wilson, 1976), and Sr = 1.5 – 8.1, Ba = 2.0 – 4.5 (with one value of 0.8) and Y = 1.4 – 11.0 in the Peninsular Ranges (Smith et al., 1983).

CONCLUSIONS

Orthopyroxene, clinopyroxene, hornblende, garnet, biotite, epidote, olivine and chromite in the ultramafic rocks, garnet granulites, gabbronorites and amphibolites of southern Kohistan are considered to have formed mostly under physico-chemical equilibrium. Like the major elements, the minor and trace element are also partitioned systematically between pairs and trios of these minerals. The systematic partitioning is a reflection of crystallo-chemical aspects/ requirements of the concerned minerals under the conditions of their formation. Some elements in certain mineral pairs display erratic distribution, the causes of which have not been studied in sufficient detail to arrive at any conclusions.

The distribution patterns conform to reliable literature data pertaining to plutonic and high-grade metamorphic rocks. Therefore, the relative abundances of elements described in this paper may serve in assessing the quality of analyses in rocks of comparable nature. It would be interesting to compare these data with those obtained on minerals which have formed under disequilibrium conditions, but the distribution of Ti, Fe^{3+}, Mn, and Na in pyroxene pairs of calc-alkaline volcanics from New South Wales (Wilkinson, 1971) is in harmony with those of the Kohistan pairs.

The present study is particularly relevant to pyroxene pairs because of a higher number of analyses (19 pairs analysed for 14 elements and three pairs for 21 elements). In the gabbronorites of the Chilas complex, 16 orthopyroxenes (Mg no. 64 to 51) contain higher Co (mostly 2.2 to 2.4 times), MnO (2 to 2.2 times), Zn (2.7 to 3.7 times), Ni (1.2 to 1.8 times), and lower TiO_2 (1.1 to 3.2 times), Zr, Sr (both 8 to 14 times), Ba (2.2 to 2.4 times), Y (7 to 10 times), Cr (1.2 to 1.7 times), Li (2 to 3 times), V (2 to 2.5 times), Na, Pb, Ce, and Nd than their coexisting clinopyroxenes. Excluding a few analyses, orthopyroxene also contains higher amounts of K and Cu, and lower Fe^{3+} and P.

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