# *Trace elements in pyroxenes and amphiboles from ultramafic rocks of the Urals*

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*Summary.* The minor elements Li, Sc, V, Cr, Co, Ni, Ga, Rb, and Sr have been determined in a number of diopsides and horneblendes from ultramafic rocks of the Gussevogorsk, Baranchinsk, and Nizhne-Tagilsk massifs in the Urals. Actinolite and anthophyllite are rare contact metamorphic products; they too were analysed. The diopside and hornblende from the earlier-formed rocks, richer in olivine, contain more Cr and less V and Ti than those from the later-formed rocks.

THE compositional particularities of the pyroxenes and amphiboles of some ultrabasic gabbro–pyroxenite–dunite massifs of the Urals were studied. The ultrabasic rocks of the Gussevogorsk, Baranchinsk, and Nizhne-Tagilsk massifs were investigated in greater detail. The first two massifs are composed mainly of pyroxenites; the Nizhne-Tagilsk massif has a concentric-zoned structure: the central part ($\sim$50 %) is formed by dunites and the marginal zone by pyroxenites. The area of each massif is about 30 $Km^2$. The chief rock-forming minerals of the ultrabasic rocks are diopside, hornblende, and magnesian olivine ($Fa_{10}$). The ore minerals are titanomagnetite, ilmenite, and chromite; the secondary ones are serpentine, chlorite, anthophyllite, actinolite, uralite, etc.; 2 to 3 Kg samples were taken at points 100 to 250 m apart in each massif.

At Gussevogorsk (Kachkanar region) the main rock-forming mineral is diopside. In the diallage pyroxenite of this massif it averages 74·4 % (51·1–92·6); in olivine-pyroxenite, 74·2 % (63·8–87·0); in hornblende-pyroxenite, 61·1 % (26·9–81·0). Wehrlites, having 49·4 % (30·5–64·2) diopside content and olivinites with 12·3 % (6·4–30) are distributed in subordinate quantity in this massif.

Diopside is the main rock-forming mineral of olivine-, diallage-, and hornblende-pyroxenites and wehrlites; it is also present in olivinites and occurs rarely in dunites of gabbro–pyroxenite–dunite formations of the Urals. It is usually fresh, but is sometimes exposed to uralization and serpentinization. Its optical constants ($2V_\gamma$ 51–59°; $\gamma$:[001] 36–46°)

and specific gravity (3·24–3·28) do not vary significantly. Debyeograms are identical.

The chemical composition of diopside from different types of ultrabasic rocks varies slightly (table I). That from hornblende and diallage

TABLE I. Chemical composition of diopside*

| | 140 | 1740 | 1741–II | 101 | 640 | 1854–II |
|---|---|---|---|---|---|---|
| $SiO_2$ | 49·26 % | 50·80 | 51·50 | 50·67 | 52·13 | 52·60 |
| $TiO_2$ | 0·55 | 0·41 | 0·30 | 0·31 | 0·32 | 0·21 |
| $Al_2O_3$ | 4·05 | 2·04 | 2·70 | 2·56 | 2·00 | 1·69 |
| $Fe_2O_3$ | 4·04 | 3·50 | 1·24 | 2·35 | 1·48 | 1·59 |
| FeO | 3·64 | 4·21 | 3·67 | 3·02 | 3·25 | 2·72 |
| MnO | 0·17 | 0·11 | 0·05 | 0·13 | 0·11 | 0·08 |
| MgO | 14·13 | 15·29 | 16·41 | 16·51 | 16·71 | 16·80 |
| CaO | 23·69 | 23·31 | 23·70 | 23·46 | 23·90 | 24·00 |
| $Na_2O$ | 0·10 | 0·09 | 0·11 | 0·16 | 0·12 | trace |
| $K_2O$ | 0·07 | 0·06 | | 0·02 | | |
| $H_2O-$ | n.d.† | n.d. | 0·16 | n.d. | 0·15 | 0·30 |
| $H_2O+$ | 0·51 | 0·70 | 0·35 | 0·55 | 0·40 | 0·25 |
| Total | 100·21 | 100·52 | 100·19 | 99·74 | 100·57 | 100·24 |
| Sp. gr. | — | 3·24 | 3·27 | 3·26 | 3·28 | 3·28 |
| $f$ (%) | 17·8 | 17·4 | 12·6 | 11·5 | 11·3 | 10·3 |
| Li | $<$ 0·0005 | $<$ 0·0005 | — | 0·0003 | 0·0003 | — |
| $Sc_2O_3$ | 0·013 | 0·015 | 0·015 | 0·015 | 0·014 | — |
| $V_2O_5$ | 0·022 | 0·033 | 0·025 | 0·027 | 0·020 | — |
| $Cr_2O_3$ | — | 0·017 | 0·088 | 0·32 | 0·050 | — |
| Co | — | n.d. | — | 0·002 | 0·004 | 0·006 |
| Ni | 0·0045 | 0·012 | 0·010 | 0·008 | 0·010 | — |
| Ga | 0·0006 | 0·0007 | 0·0004 | 0·0006 | 0·0003 | 0·0003 |
| Rb | — | 0·003 | — | — | n.d. | n.d. |
| Sr | 0·016 | 0·019 | 0·020 | 0·010 | 0·010 | — |
| $ZrO_2$ | 0·003 | 0·002 | 0·002 | 0·003 | 0·003 | — |

140, hornblende-pyroxenite; 101, olivine-pyroxenite (Baranchinsk massif); 1740, diallage-pyroxenite; 1741–II, pyroxenite olivinite; 1854–II, wehrlite (Gussevogorsk massif); 640, olivine-pyroxenite (Nizhne-Tagilsk massif).

* All results were obtained in the analytical laboratories of IMGRE by gravimetric and spectrographic analysis and by means of flame photometry. Analysts: V. N. Arkhangelskaya, L. I. Serdobova, N. A. Korovina, L. A. Sneg, L. N. Baum, and others.

† n.d. not detected; — not determined.

pyroxenite is characterized by a higher ratio[1] ($f$ = 15·1–20·3 %, results of six analyses); its ferrosilite content is higher (9·37–13·70 mol. %) than in the diopside of olivine-pyroxenites and olivinites. According to Hess (1941) the pyroxenes of olivine-pyroxenites and of wehrlites fall in the diopside field, but the pyroxenes of hornblende- and diallage-pyroxenites are sahlites near the field of diopside (fig. 1). M. M. Veselovskaya (1950)

[1] $f = 100(FeO+Fe_2O_3)/(MgO+FeO+Fe_2O_3)$.

and E. Ya. Ploshkina and V. G. Fominykh (1963) also place the monoclinic pyroxenes of ultrabasic and basic rocks in the fields of diopside and sahlite.

Some pyroxenes show up to 4 % $Al_2O_3$, but in most cases there is 2 to 3 %, in agreement with the data of Deer, Howie, and Zussman (1963). The highest contents of $Al_2O_3$ are recorded in diopside from a hornblende-pyroxenite in contact with gabbro and in pyroxene from schlieren-like assemblages of coarse (up to 10 cm) diopside crystals. However, the larger pyroxene grains do not always have the higher content of $Al_2O_3$.

The *f* of diopside from olivine pyroxenites, wehrlites, and olivinites (usually barren) ranges from 7·5 to 12·6 % (results of six analyses). The ferrosilite molecule content is 4·71 to 8·24 %. It is typical that the *f* ratio (11·3 %) and the content of $Al_2O_3$ (2 %) in diopside (sample 640) from pyroxenite of the outer zone surrounding the dunite core of the Nizhne-Tagilsk massif are very near those of the diopside of barren pyroxenites of other large massifs (Gussevogorsk, Baranchinsk massifs and others); nor are there any essential differences in other components (table I).

The trace element content of the diopside is a useful indicator of changes in the conditions of mineral formation. Diopsides from different types of ultrabasic rocks show noticeable variations in the contents of Sc, V, Ti, Cr, Ni, and Sr. Other trace elements present show less variation: $\leqslant$ 0·0007 % Ga, $\leqslant$ 0·003 % $ZrO_2$, $\leqslant$ 0·006 % Co, $\leqslant$ 0·003 % Rb, $\leqslant$ 0·0005 % Li, $\leqslant$ 0·001 % Ln, $\leqslant$ 0·0003 % Ge, $\leqslant$ 0·0004 % In.

The determinative methods used are described by Borisenko, Zhuravlev, and Sosnovskaya, 1961 (spectrographical determination of $Sc_2O_3$), Borisenko and Serdobova, 1965 ($V_2O_5$, $TiO_2$, $Cr_2O_3$, and Ni), Fabrikova, 1961, Fabrikova and Isaeva, 1963 (flamephotometric estimation of Li, Rb, and Sr), and Saltykova and Fabrikova, 1958 (chemical determination of Ga). The precision of the determinations is from 5 to 20 %.

Diopsides from hornblende- and diallage-pyroxenite are characterized by higher content of $Sc_2O_3$, $TiO_2$, $V_2O_5$, Ga, and Sr and by lower content of $Cr_2O_3$ and Ni. In diopside from olivine-pyroxenites and olivinites (usually barren) a contrary pattern is observed (table II, diopside from rocks of Gussevogorsk massif). Cr is distributed in a more contrasty manner; the content of $Cr_2O_3$ in the diopside of olivine-pyroxenites, wehrlites, and olivinites is approximately 100 times higher than that in hornblende- and diallage-pyroxenites.

Hornblende occurs mainly in the pyroxenites. The average hornblende content in hornblende-pyroxenite of the Gussevogorsk massif is 22·2 %

(10·2–58·2), in diallage-pyroxenite 3·8 % (1·2–10·0), and in olivine-pyroxenite 1·7 % (0·5–4·8). It amounts to 95 % in some areas of the Baranchinsk and Gussevogorsk massifs composed of hornblendite. The hornblende is formed later than diopside and usually is allotriomorphic in regard to it. There are also some small intergrowths of hornblende in

TABLE II. Trace elements in diopside (ppm)

| Rock | $Sc_2O_3$ | | | $TiO_2$ | | | $V_2O_5$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| Hornblende-pyroxenite | 9 | 110–200 | 170 | 9 | 3400–5400 | 4600 | 9 | 390–490 | 440 |
| Diallage-pyroxenite | 9 | 100–220 | 170 | 9 | 2600–6500 | 4200 | 10 | 240–460 | 350 |
| Olivine-pyroxenite | 8 | 90–160 | 130 | 10 | 2000–4600 | 2500 | 9 | 220–340 | 250 |
| Wehrlite | 1 | — | 150 | 2 | 1700–1900 | 1800 | 2 | 220–240 | 230 |
| Olivinite | 5 | 90–150 | 120 | 4 | 1500–3600 | 2500 | 5 | 220–310 | 250 |

| Rock | $Cr_2O_3$ | | | Ni | | | Ga | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| Hornblende-pyroxenite | 8 | 15–18 | 15·4 | 8 | 50–100 | 80 | 4 | 6–10 | 8 |
| Diallage-pyroxenite | 8 | 15–170 | 38 | 9 | 50–120 | 80 | 3 | 4–7 | 6 |
| Olivine-pyroxenite | 9 | 340–2300 | 1200 | 6 | 85–110 | 100 | 5 | 5–6 | 5·2 |
| Wehrlite | 1 | — | 1000 | 1 | — | 100 | — | — | — |
| Olivinite | 5 | 900–1700 | 1400 | 4 | 100–120 | 110 | 4 | 4–6 | 5 |

1, number of samples; 2, limits; 3, mean.

pyroxene grains. It is pale green in transmitted light, and pleochroic in green tones; $2V_\gamma$ 80–82°, $\gamma$:[001] 18 to 22°, $\gamma-\alpha$ 0·024–0·025, sp. gr. 3·10–3·17.

The chemical composition of hornblende from different types of rocks is not the same; a lower $f$ (23·6–24·9 %) and higher content of Mg (16·40–15·90 %) are characteristic for hornblende from olivine- and diallage-pyroxenites. The hornblendes from hornblendite and pegmatoid gabbro are characterized by higher $f$ (28·3–25·0 %) and a lower content of MgO (14·35–14·92 %) and $Cr_2O_3$, but by higher contents of $TiO_2$ and $V_2O_5$ (table III).

Table IV shows average trace-element contents in hornblende from olivine- and hornblende-pyroxenites. The variations in content of $TiO_2$, $V_2O_5$, and $Cr_2O_3$ are most significant. It should be noted that hornblende, being deposited later than diopside, is characterized by a higher content of $TiO_2$, $V_2O_5$, and Ga. Titanomagnetite, also later than diopside, is enriched in the same elements.

The main part of the rare and minor elements in ultrabasites occurs in the dispersed state as an isomorphic component in host minerals.

TABLE III. Chemical composition of hornblende

| | R-100 | 1892-A | 1718-A | 1702 | 1889-A | 1857-A | 909 | 819 |
|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 40·41 | 40·20 | 41·35 | 40·73 | 41·25 | 42·23 | 53·19 | 57·21 |
| $TiO_2$ | 1·83 | 2·01 | 1·93 | 1·99 | 1·57 | 1·33 | 0·14 | 0·09 |
| $Al_2O_3$ | 14·18 | 13·84 | 12·91 | 13·79 | 14·12 | 12·11 | 2·50 | 2·53 |
| $Fe_2O_3$ | 4·99 | 5·13 | 6·64 | 5·10 | 4·72 | 5·07 | 1·93 | 0·80 |
| FeO | 7·84 | 7·87 | 5·86 | 6·77 | 6·83 | 6·67 | 6·43 | 5·53 |
| MnO | 0·16 | 0·10 | 0·09 | 0·10 | 0·12 | 0·04 | 0·13 | 0·02 |
| MgO | 14·35 | 14·61 | 14·92 | 15·68 | 15·90 | 16·40 | 20·57 | 30·51 |
| CaO | 13·20 | 12·22 | 12·91 | 12·60 | 12·30 | 12·35 | 13·80 | 1·12 |
| $Na_2O$ | 2·15 | 0·84 | 1·59 | 1·64 | 1·38 | 1·25 | 0·44 | 0·08 |
| $K_2O$ | 0·37 | 0·76 | 0·42 | 0·51 | 0·44 | 0·61 | 0·13 | 0·11 |
| $H_2O-$ | n.d. | 0·15 | 0·34 | 0·11 | 0·12 | 0·12 | 0·60 | — |
| $H_2O+$ | 0·55 | 1·60 | 0·85 | 0·80 | 1·32 | 1·70 | 0·11 | 1·50 |
| Total | 100·03 | 99·33 | 99·81 | 99·82 | 100·07 | 99·88 | 99·97 | 99·65* |
| Sp. gr. | 3·15 | 3·15 | 3·17 | 3·17 | 3·12 | 3·10 | 3·03 | 3·01 |
| $f$ (%) | 28·3 | 28·2 | 25·0 | 24·4 | 24·0 | 23·6 | 16·6 | 9·8 |
| Li | n.d. | 0·0002 | 0·0002 | 0·0004 | n.d. | 0·0002 | — | — |
| $Sc_2O_3$ | 0·018 | 0·020 | 0·020 | 0·013 | 0·016 | 0·016 | 0·0034 | 0·0025 |
| $V_2O_5$ | 0·15 | 0·15 | 0·15 | 0·16 | 0·106 | 0·053 | 0·025 | 0·005 |
| $Cr_2O_3$ | n.d. | n.d. | n.d. | 0·0044 | 0·0068 | 0·035 | 0·45 | 0·22 |
| Co | — | 0·004 | 0·0037 | 0·003 | — | 0·003 | 0·0019 | — |
| Ni | 0·004 | 0·01 | 0·01 | 0·01 | 0·007 | 0·013 | 0·054 | 0·070 |
| Ga | 0·0011 | 0·0012 | 0·0013 | 0·0015 | 0·0013 | 0·0014 | 0·0005 | 0·0002 |
| Rb | — | — | 0·004 | 0·005 | — | — | — | 0·001 |
| Sr | — | 0·044 | 0·043 | 0·03 | 0·036 | 0·05 | 0·008 | 0·011 |
| $ZrO_2$ | — | 0·006 | 0·003 | 0·005 | — | 0·002 | — | — |

Hornblende from: 1892-A hornblendite; 1718-A pegmatoid gabbro, contact with pyroxenite; 1702 hornblende-pyroxenite; 1889-A diallage pyroxenite; 1857-A olivine pyroxenite (Gussevogorsk massif); R-100 gabbro-pegmatite (Baranchinsk massif). Actinolite from: 909 peridotite. Anthophyllite from: 819 peridotite (Baranchinsk massif).

* Includes 0·15 F.

This mode of occurrence of minor elements is defined by their low concentration in the melt and by the similarity of their crystallochemical constants to those of rock-forming elements (Green, 1959). The most important is the role of Fe, Mg, and Al. For diopside and hornblende the following schemes of substitution are possible:

$$Mg^{2+}, Fe^{2+} \leftarrow Zr^{4+}, Ti^{4+}, Ti^{3+}, Cr^{3+}, V^{3+}, Sc^{3+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Ge^{2+}, Li^{+};$$
$$Ca^{2+} \leftarrow Ln^{3+}, Sr^{2+};$$

$$Fe^{3+}, Al^{3+} \leftarrow Ti^{4+}, Ti^{3+}, V^{3+}, Cr^{3+}, In^{3+}, Ga^{3+};$$
$$Si^{4+} \leftarrow Ti^{4+}, Ge^{4+}, Al^{3+}, Ga^{3+}.$$

The substitution of $Mg^{2+}$ by $V^{3+}$, $Cr^{3+}$, $Ti^{3+}$, and $Ti^{4+}$ and of $Si^{4+}$ by $Ti^{4+}$ in diopside was proved in experiments of A. I. Tsvetkov (1951).

Details of the composition and structure of the host mineral may also promote the dispersion of minor elements. If the mineral has a more complex composition (hornblende) with easier compensation of charge in heterovalent isomorphism, it is able to accommodate more trace

TABLE IV. Trace elements in hornblende (ppm)

| | $Sc_2O_3$ | | | $TiO_2$ | | | $V_2O_5$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| Hornblende-pyroxenite | 5 | 130–200 | 180 | 7 | 17 000–24 000 | 19 700 | 7 | 850–1600 | 1200 |
| Olivine-pyroxenite | 4 | 120–160 | 140 | 4 | 13 300–16 000 | 15 000 | 4 | 530–680 | 660 |

| | $Cr_2O_3$ | | | Ni | | | Ga | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 |
| Hornblende-pyroxenite | 5 | 15–78 | 27 | 5 | 100–130 | 110 | 4 | 12–24 | 16 |
| Olivine-pyroxenite | 4 | 240–650 | 430 | 4 | 85–140 | 110 | 3 | 14–19 | 16 |

1, number of samples; 2, limits; 3, mean.

elements in its structure. While $Sc^{3+}$, $V^{3+}$, $Cr^{3+}$, $Ga^{3+}$, and $Ti^{4+}$ have rather similar crystallochemical constants, their content in pyroxenes and amphiboles apparently differs: the content of $V_2O_5$, $TiO_2$, and Ga is usually higher in hornblende and that of $Cr_2O_3$ is higher in diopside. The hornblende contains also more Sr (0·04–0·05 %), Rb (0·004–0·005 %), and 0·01 % $Ln_2O_3$; in diopside there is $\leqslant$ 0·002 % $Ln_2O_3$. The important reason influencing the distribution of trace elements in the crystallization process is the ability of some trace elements to be retained longer than others in the residual melt. These elements are: Fe, Al, and Ga, also V and Ti (Borisenko and Serdobova, 1965), Sr, Rb, and Ln. On the contrary, Cr, Ni, and Co are removed from the melt into the solid phase in the early stages of crystallization. Thus, V, Ga, and Ti together with Fe and Al are retained in the melt and then enter into the composition of hornblende and titanomagnetite.

It is notable that the succession of formation of the rocks exerts an influence on the content of some minor elements in the same mineral. As was shown in tables II and IV, diopside and hornblende from the rocks rich in olivine (i.e. earlier rocks) contain less V and Ti and more Cr than the same minerals from diallage- and hornblende-pyroxenites. Thus the trace-element content in diopside and hornblende together with the *f* ratio are features of the time of formation of the minerals.

Actinolite and anthophyllite result from contact metamorphism, and occur rarely. They are found in peridotites at contacts with gabbro (Baranchinsk massif) as anchimonomineralic concentrations. The width of zones composed of anthophyllite and actinolite is about 1 metre. The actinolite has $2V_\alpha$ 75°, $\gamma$:[001] 16°, and the anthophyllite $2V_\alpha$ 77°, $\gamma-\alpha$ 0·022. These minerals are characterized by a lower *f* (16·6, 9·8 %) and moderate content of Sc, V, Ga, Sr, and Rb, but they have higher contents of Cr and Ni (table III). Most of the trace elements were inherited from primary minerals: *olivine* and *pyroxene*. Anthophyllite was formed in rocks rich in olivine (Borisenko *et al.*, 1965) while actinolite developed in rocks rich in pyroxene. The average contents of trace elements in peridotites of this massif are very close to the contents of the same elements in the anthophyllite and actinolite: $Sc_2O_3$ 0·003 %, $TiO_2$ 0·14, $V_2O_5$ 0·04, $Cr_2O_3$ 0·32, Co 0·007, Ni 0·095, Ga $\leqslant$ 0·0005, Sr 0·009 (from 10 to 15 determinations for each element).

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