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Geochemistry of ultramafic xenoliths from Kapfenstein, Austria: evidence for a variety of upper mantle processes

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Abstract—Major, minor, and trace element contents have been determined in seven ultramafic xenoliths, the host basanite, and some mineral separates from xenoliths from Kapfenstein, Austria. Most of the xenoliths represent residues after extraction of different amounts of basaltic liquid. Within the sequence lherzolite to harzburgite contents of Al, Ca, Ti, Na, Sc, V, Cr and the HREE decrease systematically with increasing Mg/Fe and decreasing Yb/Sc. Although all samples are depleted in highly incompatible elements, the less depleted end of our suite very closely approaches the chondritic Yb/Sc ratio and consequently the primitive upper mantle composition.

Chromium behaved as a non-refractory element. Consequently it should have higher abundances in basalts than observed, suggesting that most basalts experienced Cr fractionation by chromite separation during ascent.

Several processes have been active in addition to partial melting within the upper mantle beneath Kapfenstein:

- (1) a hornblende has been identified as wet alkali-basaltic mobilisate;
- (2) an amphibole lherzolite is the product of alkali-basalt metasomatism of a common depleted lherzolite;
- (3) two amphibole lherzolites contain evidence for rather pure water metasomatism of normal depleted lherzolites;
- (4) a garnet-spinel websterite was a tholeiitic liquid trapped within the upper mantle and which suffered a subsequent partial melting event (partial remobilization of a mobilisate).
- (5) Abundances of highly incompatible elements are generally very irregular, indicating contamination of upper mantle rocks by percolating liquids (in the mantle).

Weathering is an important source of contamination: e.g. U mobilization by percolating groundwater. Contamination of the xenoliths by the host basanite liquid can only amount to approximately 5.5×10^{-4} parts.

Distributions of minor and trace elements between different minerals apparently reflect equilibrium and vary with equilibration temperature.

INTRODUCTION

THE KAPFENSTEIN locality is part of a volcanic province which extends from Bachern Mountains, Yugoslavia, through S and SE-Styria and S-Burgenland, Austria, into the Balaton area, Hungary ('Styrian volcanic arc'). The volcanic rocks are of late Tertiary age and comprise dacites, andesites, trachyandesites, trachytes, basalts, alkali basalts, basanites and nephelinites (HAUSER, 1954; HERITSCH, 1963, 1965, 1967). Lava compositions have changed in space and time. The older (Miocene) volcanic activity is confined to the southern part of the arc and is characterized by andesitic and trachytic lavas. The younger (Pliocene) volcanics mainly occur from southern Styria eastwards, in Burgenland and in Hungary and are of alkali-basaltic composition (HERITSCH, 1963, 1967; KOLLMANN, 1964). Among these volcanoes there are several tuff cones which contain a wide variety of

xenoliths of crustal and upper mantle origin. Kapfenstein is one of those localities which has early been recognized and subsequently become a classical one (SIMGUND, 1899; HERITSCH, 1908; SCHADLER, 1913; SCHOCKLITSCH, 1935a). Analytical data on xenoliths from Kapfenstein are scarce. A few analyses of minerals from ultramafic xenoliths have been performed by SCHADLER (1913) and ROSS *et al.* (1954). KURAT (1971) described and analyzed a websterite and a lherzolite nodule and ascertained the upper mantle origin of these rocks. Subsequently a petrological and geochemical study of a large suite of ultramafic xenoliths from Kapfenstein was started (KURAT *et al.*, 1976, 1977a, 1979). A few samples of special genetic interest have been selected for an extensive geochemical study (KURAT *et al.*, 1977b) with the objective of characterizing the upper mantle below Kapfenstein and to shed some light on the genesis of these rocks.

SAMPLES AND PROBLEMS

As mentioned before, the volcanic tuff of Kapfenstein contains a variety of xenoliths of upper mantle to shallow depths origin. Extensive descriptions have been given by SCHADLER (1913) and SCHOKLITSCH (1935a). The tuff itself is rather fine grained and very rich in xenoliths mainly of shallow origin. Basaltic scoriae are generally small (up to 1 cm in diameter) and glass-rich (KURAT, 1971). No lava flows have been encountered. Basalt samples suitable for analytical purpose are very rare but occasionally some basaltic 'bombs' are found. Ultramafic xenoliths are generally small-sized (~1 cm) but can reach 30 cm in diameter (HERITSCH, 1908). All shapes from irregular or regular angular fragments to spheroidal 'nodules' are present. Most nodules are friable, whereas angular xenoliths tend to be physically resistant. Most ultramafic xenoliths are medium to coarse grained but grain sizes of up to 1 cm are very rare. All rocks investigated in this study are described in detail in KURAT *et al.* (1979) and SCHULTZ *et al.* (1979).

Short characterizations of the rocks investigated together with the results and open problems of the previous petrological investigations are given below.

Host basanite

Ka 170. Vesicular vitrophyric rock with abundant phenocrysts of augite and plagioclase; common are xenocrysts of olivine, orthopyroxene, clinopyroxene, and spinel which obviously have been derived from peridotite inclusions; interstitial glass is very alkali-rich and bears variable amounts of small plagioclase laths and titanian magnetite (compare KURAT, 1971; SCHULTZ *et al.*, 1979).

Ultramafic xenoliths

Rock samples for this study have been selected from a suite of 36 ultramafic xenoliths after extensive petrological investigation (KURAT *et al.*, 1976, 1977a, 1979). This study showed that the upper mantle below Kapfenstein has a rather monotonous composition. Rocks are almost exclusively members of the spinel-lherzolite-harzburgite-dunite suite with spinel-lherzolite being by far the most abundant rock type. Of that suite characteristic samples from highly residual harzburgite to apparently only slightly depleted lherzolite have been selected for this study. Very few samples document some local inhomogeneities within the upper mantle below Kapfenstein. Four amphibole-spinel-lherzolites and one garnet-spinel websterite (KURAT, 1971) were found in the Kapfenstein locality. Some of these samples have been selected mainly because their genesis cannot fully be understood on the basis of mineral chemical studies alone. A short characterization of ultramafic rocks arranged according to sample number is given below together with their specific genetic problems to be solved in this study.

Ka 103

Garnet-spinel-websterite. This rock has previously been described by KURAT (1971). It consists of clinopyroxene (~60 vol%), orthopyroxene (~30 vol%), 5-10% spinel and minor amounts of garnet and opaques. Texture is granoblastic and clinopyroxenes show extensive exsolution lamellae of orthopyroxene, spinel and garnet. All garnet present has apparently exsolved from clinopyroxene. The petrological study could not resolve the question whether this rock is a cumulate, an igneous rock or a residual rock. KURAT (1971) speculated that it might be a residual rock after partial melting of a previous eclogite rock of picritic or tholeiitic composition.

Ka 105

This sample consists of two parts: an amphibole-spinel-lherzolite with a hornblende attached to it. The hbl-sp-lherzolite is a typical equigranular granoblastic rock with

dispersed greenish-brown titanium pargasites which are integrated into the texture. Close to the hornblende contact there are large sheets of phlogopites and a zone of large clinopyroxenes. The rock is slightly deformed.

The hornblende (a layer of approximately $2 \times 2 \times 6$ cm) consists almost exclusively of coarse-grained (~1 cm) titanium pargasite which has a tendency to form equilibrium triple points. Sulfides (now oxidized) are generally present as droplike inclusions within large hornblende crystals. Olivine (rounded inclusions in hornblende) and phlogopite (intergranular) are rare and irregularly distributed.

The genesis of the hornblende layer (originally probably a vein) is readily understood as a local wet basaltic mobilisate. The open question is whether this mobilisate was locally derived from the amphibole lherzolite or came from a remote site. The presence of phlogopite, the K-rich composition of hornblende, and the high and slightly variable FeO content of olivine (FeO ~10%) in the amphibole lherzolite could be indicative of a primitive composition. Trace element analyses should help to solve the question whether Ka 105 in fact is a primitive sample or a portion of the upper mantle which has been metasomatically altered by a liquid of wet basaltic composition.

Ka 111

Amphibole lherzolite, medium grained; typical equigranular granoblastic; green spinel; clinopyroxenes have sometimes orthopyroxene exsolution lamellae; brown titanium pargasite is located around spinel grains. The overall mineral chemistries are indistinguishable from normal amphibole-free lherzolites. The amphibole has a low K-content (KURAT *et al.*, 1979). This suggests that amphibole was formed late by H₂O-metasomatism. Trace element analysis should show whether this metasomatism was confined to a pure H₂O addition to a normal lherzolite or whether some other mobile elements have been added or not.

Ka 125

Coarse grained lherzolite of the normal dunite-lherzolite series. Spinel is brown and both clino- and orthopyroxenes bear exsolution lamellae. The rock is slightly deformed and some small scale fine-grained recrystallisations have developed at grain boundaries.

Ka 155

Amphibole-lherzolite, medium grained, equigranular granoblastic and slightly sheared. Spinel is brown. Amphibole is very light brown K-poor pargasite, and finely dispersed throughout the rock. There is no apparent textural relationship between spinel, clinopyroxene and amphibole. The low K content of the amphibole suggests a similar genesis as has been mentioned for Ka 111 although the reaction $sp + cpx + H_2O \rightarrow hbl$ is petrographically not apparent. An alternative genetic model could be a partial melting event and extraction of liquid after H₂O-metasomatism has taken place.

Ka 167

Coarse-grained harzburgite of the normal dunite-lherzolite series with dark brownish-red spinels and granoblastic texture. *12th °C. Some negative values on 157*

Ka 168

Coarse-grained lherzolite with brownish green spinels, clinopyroxene exsolution lamellae in orthopyroxene, slightly tectonically distorted. The FeO content of the olivine (9.7 wt%) places the sample at the 'primitive' end of the main dunite-lherzolite series. *slow cooling*

Modal mineral composition

Because most xenolith samples from Kapfenstein are small and coarse-grained, modal mineral compositions

Table 1. Calculated modal compositions of spinel peridotites from Kapfenstein, Austria. Bulk analytical data have been used from Table 2 and mineral data from Table 7 and from KURAT *et al.* (1979)

Sample	Ol	Opx	Cpx	Sp	Amph.
Ka 167	83.4	13.7	2.2	0.6	-
Ka 125	76.4	14.4	7.9	1.4	-
Ka 105	65.4	18.4	8.4	1.2	6.6
Ka 155	56.5	30.2	10.5	2.2	0.6
Ka 111	69.8	17.2	10.6	1.7	0.8
Ka 168	57.2	24.4	14.2	4.2	-

have not been measured by pointcounting thin-sections. Instead, we have used electron microprobe analyses of minerals and bulk analyses of rocks to calculate the modal contents of olivine, orthopyroxene, clinopyroxene, amphibole, and spinel. Such calculations are relevant if all elements used for these calculations are

(a) homogeneously distributed within the minerals

(b) no other minor phase contains significant amounts of these elements.

The calculated modal compositions are given in Table 1.

Since we used major elements in these calculations, trace element analyses of separated minerals and bulk samples provide an independent check on the calculated modal composition. For samples Ka 168 and Ka 167 (see Tables 3 and 7) the abundances of Sc, Yb, Ca, Ni, Co and Na in the bulk samples can be satisfactorily accounted for by the calculated modal mineralogy. Mass balance cannot, however, be achieved for the light REE (LREE). Their abundances must partly be governed by minor phases very rich in LREE.

ANALYTICAL METHODS

For bulk chemical analyses approximately 5-10 g depending on average grain-size of each sample were homogenized and aliquots taken for analyses with different methods. Major elements were determined by instrumental fast neutron (14 MeV) activation analysis (IFNAA, TESCHKE and WÄNKE, 1974) and by X-ray fluorescence

analysis (XRF, PALME and JAGOUTZ, 1977). Instrumental thermal neutron activation analysis (ITNAA) and, in two cases, radiochemical neutron activation analysis (RNAA) has been applied for trace element and Fe determination on 200 mg aliquots. The analytical scheme used is similar to that described by WÄNKE *et al.* (1977a). Mineral separates, prepared by hand-picking under the microscope, have been analysed by ITNAA only.

In Tables 2 and 3 major and trace element contents of the host basanite and 7 ultramafic xenoliths are summarized. Data for Si, Al, and Mg are averages of IFNAA and XRF data. For Ca and Ti the XRF data were used. Iron, Mn, Cr, Na, K, and trace element contents have been determined by ITNAA with the exception of K, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Cs, Ba, W, Ir, Au, U, and REE in samples Ka 103 and Ka 168 which have been determined by RNAA. Accuracies for the analysis of Mn, Na, and Cr are estimated to be 2%. For the K analyses accuracies are generally lower (5-10%) and depend on the K content of the samples. Accuracies of trace element determinations are given in the last column of Table 3 (see WÄNKE *et al.* 1977b, for detailed discussion). Major and minor element contents of minerals have been determined by electron microprobe X-ray analysis (KURAT *et al.*, 1979).

RESULTS AND DISCUSSION

A bulk compositions

Basanite (Ka 170). The Kapfenstein basanite is very similar in composition to several nepheline basanite lavas from the Styrian volcanic arc, such as those from the Steinberg near Feldbach (STINY, 1923), and from the Kindsbergkogel and Klösch (SCHOKLITSCH, 1932, 1933, 1935b). Major and trace element contents of the Kapfenstein basanite (Tables 2 and 3) are very similar to those reported from basanites of San Carlos, Arizona (FREY and PRINZ, 1978). The degree of REE fractionation (Fig. 1), however, is much higher in the Kapfenstein basanite as compared to the San Carlos basanites: The La/Yb ratio for the Kapfenstein basanite is 28.9 whereas for San Carlos the same ratio varies between 14.2 and 19.2. This is due to a stronger enrichment (factor of 2) of light rare earth elements

Table 2. Major element contents of host basanite and ultramafic xenoliths from Kapfenstein, Austria, in wt% (IFNAA and XRF)

	Ka 170	Ka 103	Ka 167	Ka 125	Ka 105	Ka 155	Ka 111	Ka 168
	Basanite	Websterite	Harzburg	Lherzolite	Hbl-Lherz	Hbl-Lherz	Hbl-Lherz	Lherzolite
SiO ₂	45.41	47.49	41.92	42.78	43.21	43.64	43.21	43.42
TiO ₂	1.95	0.47	0.008	0.03	0.08	0.07	0.08	0.12
Al ₂ O ₃	14.39	12.85	0.96	1.55	2.74	2.98	2.38	4.45
Cr ₂ O ₃	0.038	0.184	0.183	0.303	0.396	0.418	0.479	0.535
FeO ¹⁾	9.70	7.49	8.57	8.09	9.57	7.75	8.18	8.14
MnO	0.197	0.165	0.125	0.133	0.164	0.129	0.134	0.130
MgO	8.28	19.9	46.26	43.28	39.80	40.46	41.29	39.63
CaO	9.44	9.93	0.59	1.75	2.01	2.36	2.35	3.04
Na ₂ O	4.14	0.961	0.081	0.127	0.469	0.225	0.291	0.285
K ₂ O	2.18	0.0054	0.0048	0.017	0.025	0.006	0.0088	0.0012
Total	95.73	99.44	98.70	98.06	98.46	97.85	98.40	99.75
100 Mg / Mg + Σ Fe	60.3	82.6	90.6	90.5	88.1	90.3	90.0	89.7

¹ Total Fe as FeO.

Table 3. Trace element contents of host basanite and ultramafic xenoliths from Kapfenstein, Austria

Element	Ka 170	Ka 103	Ka 167	Ka 125	Ka 105	Ka 155	Ka 111	Ka 168	Accuracy %
	Basanite		Websterite	Harzburg.	Lherzolite	Hbl-Lherz.	Hbl-Lherz.	Hbl-Lherz.	
Sc (ppm)	16.3	39.6	6.5	9.1	11.8	13.4	14.4	14.7	2
Co (ppm)	36.5	53.3	125.0	113.0	109.0	114.0	113.0	106.0	2
Ni (ppm)	190.0	560.0	2750.0	2270.0	2010.0	2400.0	2360.0	2250.0	5
Cu (ppm)	...	41.5	6.4	5
Zn (ppm)	22.2	40.8	60.0*	75.0*	96.0*	70.0*	94.0*	46.1	5
Ga (ppm)	...	10.6	...	1.4*	2.8*	...	3.4*	2.43	5
Ge (ppm)	...	1.7	1.1	15
As (ppm)	7.2	0.8	0.22*	0.35	0.18	5
Se (ppm)	...	0.09	0.25	15
Rb (ppm)	82.7	0.24	0.12	15
Sr (ppm)	1100.0	18.6	8.9	5
Cs (ppm)	1.53	0.006	0.006	20
Ba (ppm)	924.0	9.0	2.3	10
La (ppm)	68.6	0.44	0.19	0.25	0.78	0.11	0.34	0.18	5
Ce (ppm)	124.5	1.77	2.5*	0.69	5
Sm (ppm)	8.8	1.15	0.033	0.088	0.28	0.18	0.24	0.27	3
Eu (ppm)	2.79	0.45	0.017	0.037	0.11	0.06	0.093	0.10	5
Tb (ppm)	1.07	0.40	0.06*	0.06*	0.075	5
Dy (ppm)	5.71	3.0	0.48*	0.54	5
Yb (ppm)	2.37	1.83	0.090	0.16	0.25	0.25	0.35	0.37	5
Lu (ppm)	0.33	0.29	0.015	...	0.036	0.037	0.053	0.056	5
Hf (ppm)	6.28	0.65	0.08*	0.064*	0.12	...	0.18	0.15	10
Ta (ppm)	5.61	0.014	10
W (ppb)	...	23.0	8.9	10
Re (ppb)	...	0.14	<0.28	10
Ir (ppb)	4.0	6.0	4.0	4.0	4.5	5
Au (ppb)	...	2.6	0.67	5
Th (ppm)	8.28	0.21	...	0.03	10
U (ppm)	2.70	0.52	0.009	10

* Accuracy reduced by a factor of 2.

(LREE) relative to the heavy rare earth elements (HREE) which have the same abundance in both basanites. Since the Mg/Mg + Fe ratio of the Kapfenstein basanite (0.603) and its contents of Ni and Co are high, the strong enrichment of the LREE cannot be attributed to fractional crystallization but rather indicate a primitive liquid derived by a small degree of partial melting of upper mantle rocks. Also the Ni/Co ratio is in accordance with this view and fits theoretical calculations based on experimental distribution coefficients (IRVING, 1978). The high degree of REE fractionation clearly places the site of melt generation into the deeper parts of the upper mantle where garnet peridotites are stable (KAY and GAST, 1973).

Spinel-lherzolite-harzburgite main series

The major element composition of spinel lherzolite and harzburgite xenoliths from all over the world is rather similar (compare MAALØE and AOKI, 1977) and varies in between rather narrow limits. Differences in bulk chemical compositions are mainly confined to variations in Al, Ca, Ti, Na, and K contents (for a general discussion see RINGWOOD, 1975). In Tables 2 and 3 our analyses have been arranged in the order of increasing Yb and Sc contents. Apparently, Ka 105 does not fit the sequence in several instances. Thus,

the main harzburgite-lherzolite series consists of the samples Ka 167, Ka 125, Ka 155, Ka 111, and Ka 168 in the order of increasing 'primitiveness'. In that order the CaO contents vary from 0.59% (Ka 167) to 3.04% (Ka 168). Al, Ti, Cr, Na, Sc, and Yb increase in the same order in a parallel pattern. Although variations of the Mg/Mg + Fe ratios in the lherzolite series are rather small, they continuously decrease with increasing Ca, Al, Sc etc. contents. As mentioned before, hornblende lherzolite Ka 105 does not completely fit into that sequence. This can be explained by a wet, basaltic metasomatism which led to the formation of amphibole and caused considerable contamination of the original (probably rather strongly depleted) lherzolite (see discussion below). Hornblende lherzolites Ka 111 and Ka 155, however, completely fit our main series in spite of secondary hornblende being present (see discussion below). They, therefore, will also be included into the discussion of the main lherzolite series.

Comparison of the lherzolite suite from Kapfenstein with data for xenoliths from other localities reveals some remarkable features of the Kapfenstein samples:

(1) Most Kapfenstein samples have extremely low K contents. Ka 168 contains only 10 ppm K in spite

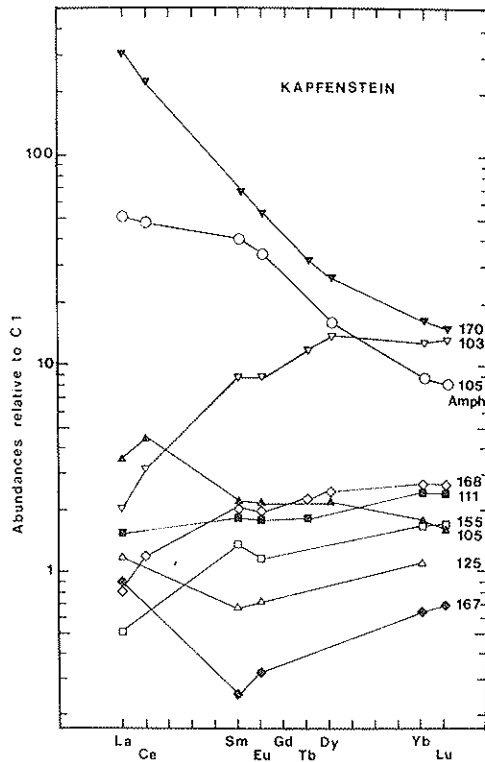


Fig. 1. REE pattern (normalized to C1) of samples from Kapfenstein, Austria. 170: host basanite; 103: websterite; 168, 111, 155, 105 and 125: lherzolites; 167: harzburgite. Discussion in the text.

of its rather high modal clinopyroxene content of more than 10% (Table 1). Only some lherzolite xenoliths from Victorian basanites have comparable low K-contents (GREEN *et al.*, 1968). These K contents enable us to place an upper limit for the contamination of xenoliths by the host basanite. In the case of Kapfenstein only 5.5×10^{-4} parts of the host basanite (Ka 170) could account for the K content of Ka 168. A dilution of that order of magnitude of a basaltic liquid by a solid rock appears to be physically unfeasible. Even minor contaminations of our xenoliths by the host basanite appear to be remote.

(2) Spinel lherzolite Ka 168 has the lowest Mg/Mg + Fe ratio and the highest Al and Ca contents of the Kapfenstein main lherzolite series. Its CaO content (3.04%) is among the highest reported so far from lherzolites (compare MAALOE and AOKI, 1977). Except for a depletion of highly incompatible elements, Ka 168 closely approaches the composition of postulated mantle material (RINGWOOD, 1975; PALME *et al.*, 1978).

Trace element contents in the main harzburgite-lherzolite series in most cases are clearly correlated to the major element concentration trend but there are some peculiarities. In order to facilitate the discussion of trace elements, we separate them into three groups:

(a) Elements which are incompatible with respect to olivine, orthopyroxene, clinopyroxene, and spinel. These are the LIL (large ion lithophile) elements K, Rb, Cs, Ba, Sr, U, Th, and the LREE and elements which are incompatible because of their high charge like Ta, Hf, and Nb.

(b) Elements which are to some degree accepted by clinopyroxene and to a lesser degree by orthopyroxene and which are almost completely rejected by olivine: Na, Sc, V, Ti, Cr (under upper mantle conditions) and the HREE.

(c) Elements which enter the olivine lattice like Zn, Co, Ni, and Mn. These three groups will be discussed separately:

(a) *Highly incompatible elements.* From Tables 2 and 3 and Fig. 1 it is apparent that the concentrations of highly incompatible elements, especially that of the LREE, do not follow the trends of Ca, Sc or the HREE within the sequence Ka 167 to Ka 168. Potassium behaves very similar and rather unpredictable. For example, Ka 168 which has the highest contents of Ca, Al, Sc, etc. has the lowest K content encountered. It is obvious that the highly incompatible elements are not present in the expected abundances and that the amounts present are the result of at least one contamination process. This inconsistent behaviour of incompatible elements has been observed in samples from many localities and has been attributed to varying degrees of contamination by the host lava or an undefined "phase". The latter conclusion was, for example, reached by FREY and GREEN (1974) in a study on ultramafic xenoliths from Victorian basanites. BASU and MURTHY (1977) showed that the concentrations of K, Rb, Sr, and Ba in mineral fractions from lherzolites can be considerably reduced by washing the samples in diluted HCl. We have performed a similar leaching experiment on Ka 167, a harzburgite which is the most depleted sample of our suite but shows an enrichment of La over Lu (Fig. 1). The bulk sample Ka 167 was leached in 0.5 N HCl for 10 min. The leached fraction was highly enriched in incompatible elements. Our results are summarized in Table 4. Although determination of the mass of the leached fraction causes some problems, the enrichment factors derived are out of the range of a possible

Table 4. INAA of solution leached from lherzolite Ka 167 (0.5 N HCl, 10 min) and distribution ratio solution/bulk.

	% Fe ppm	Mn	Co	Na	Sc	Cr	As	Br	Ba	K	La	Sm	Eu	Yb	Lu
Solution	11.6	1720	201	990	3.6	350	11	5	250	1100	6.08	0.75	0.24	0.5	0.06
Solution/Bulk	1.75	1.82	1.61	1.71	0.55	0.28	-	-	116 ¹	27.5	32	25	14	5	4

¹ Assuming a chondritic Ba/La ratio in bulk Ka 167.

error in mass determination. In addition to the normal LIL elements, As and Br are also enriched in the leachable fraction. However, we do not have data for these elements from the bulk sample.

During mineral separation we observed in sample Ka 111 'black dots' on freshly broken grain surfaces. Inspection of Ka 167 showed that similar dots are present. Because of these dots being much more abundant in Ka 111 than Ka 167 we investigated samples of Ka 111 by electron-scanning microscopy, electron microprobe analysis, and INAA. An example of a 'black dot' is shown in Fig. 2. These dots are between 50 and 500 μm in diameter, have a smooth surface but leave—if removed—an etched imprint on the surface of olivine but not on pyroxenes. The nature of this material has not yet been identified. Electron microprobe analysis showed that these black dots contain high amounts of Mn (around 24% MnO), Ni (4% NiO), and Ba (0.6% BaO). The latter is enriched 1000 times above the lherzolite level. A partial analysis is given in Table 5. The totals of the analyses are always low implying the presence of probably carbonates (HCl leachable) which appear to be mixed with silicates. In order to ascertain that the 'black dots' are indeed the contaminating phase which contains the highly incompatible elements, a few olivine grains especially rich in 'black dots' were analysed separately. The results (Table 5) show a strong enrichment of La and Sm in 'black dot'—rich olivines as compared to the bulk olivine fraction. We believe that we have found the mysterious phase which is the carrier of the highly incompatible elements in our lherzolite samples and will try to fully characterize this phase in the near future.

These black dots could contain the key to an understanding of contamination and enrichment processes by vapor and fluid transport in the upper mantle. Three modes of formation can be envisaged:

- (1) Weathering processes,
- (2) Deposit from emanations of the host basanite during ascent, and
- (3) Deposit from emanations from deeper parts of the mantle.

The composition and the very high contents of incompatible elements (Ba, La) and Mn, as well as the etching phenomena observed suggest transportation by a vapor or high temperature liquid phase. The formation of round, droplike deposits instead of a continuous cover of grain surfaces, suggests liquid immiscibility or condensation processes which are likely to occur in $\text{H}_2\text{O} + \text{CO}_2$ mixtures.

(b) *Pyroxene-compatible elements.* The concentrations of several elements increase in a regular way with increasing modal clinopyroxene contents and decreasing Mg/Fe ratios. This trend can best be demonstrated by using the Yb/Sc ratio as a fractionation index as has been suggested by PALME *et al.* (1978). Thus, the harzburgite with very low concentrations of Ca, Al, Sc, etc. also has the lowest Yb/Sc ratio. This ratio increases with decreasing degree of depletion and Ca, Al, Ti, Yb, Sc, Cr, and Na systematically increase in the same direction. Chromium which is generally considered to be a refractory element does not behave that way and decreases continuously from Ka 168 to Ka 167. Obviously, the distribution coefficient $D_{\text{liq.}-\text{lherz.}}^{\text{Cr}}$ must be larger than unity. This finding is in agreement with observed and experimentally determined mineral-liquid distribution coefficients (IRVING, 1978) which can be used to calculate rock-liquid distribution coefficients. The $D_{\text{liq.}-\text{lherz.}}^{\text{Cr}} > 1$ implies, that primitive melts from the upper mantle should be enriched in Cr as compared to upper mantle residual rocks. This is indeed the case for ultramafic liquids like komatiites (NESBITT and SUN, 1976; ARNDT *et al.*, 1977; NISBET *et al.*, 1977) where

Table 5. Partial analyses of 'black dots' and olivine rich in 'black dots' from lherzolite Ka 111, Kapfenstein, Austria. Accuracies for La and Sm determinations in olivines rich in 'black dots' are 13 and 15%, respectively

Electron microprobe analysis of "black dots" in weight-%									
SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	V ₂ O ₃	FeO	NiO	CaO	CuO	MnO
23.9	0.7	10.9	<0.02	<0.02	10.5	4.1	0.9	0.8	23.5
ZnO	MgO	CaO	BaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	Total	
<0.02	1.4	2.8	0.6	0.2	0.2	1.0	0.7	82.2	
INAA of bulk olivine (106 mg) in ppm									
Fe	Co	Mn	Cr	La	Sm				
71000	132	1035	67	0.032	0.0063				
INAA of olivine rich in "black dots" (1.9 mg) in ppm									
Fe	Co	Mn	Cr	La	Sm				
68000	131	1005	68	0.26	0.026				

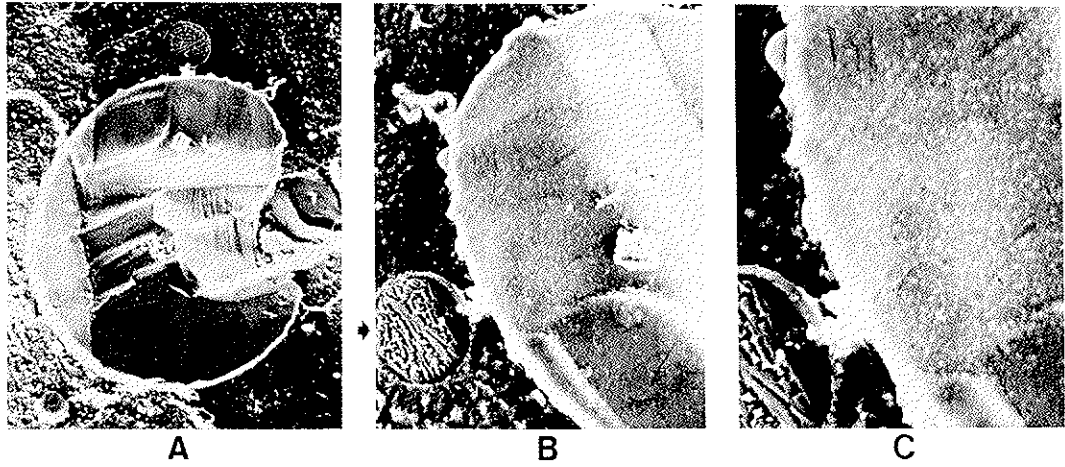


Fig. 2. Secondary electron image of a 'black dot' from sample Ka 111 and etched imprint (arrow) of a removed 'black dot' at surface of olivine. Widths of pictures are: A: 0.57 mm; B: 0.23 mm; C: 0.11 mm. Images B and C are enlargements of upper part of picture A.

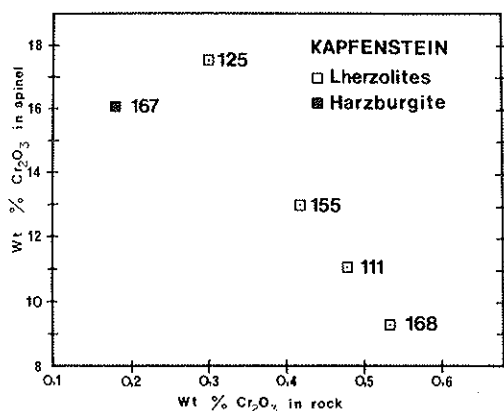


Fig. 3. Plot of wt% Cr₂O₃ in bulk vs wt% Cr₂O₃ in spinel of rocks of the main harzburgite-lherzolite series from Kapfenstein, Austria. Note the strong anticorrelation which also shows up in any mineral-rock plot.

the Cr contents also tends to be independent of the total MgO content. Experimental data also support this observation (BICKLE *et al.*, 1977). Kimberlites (STUEBER and GOLES, 1967; GURNEY and EBRAHIM, 1973), some oceanites (LE MAITRE, 1962; GUNN *et al.*, 1970; UPTON and WADSWORTH, 1972) and a few continental basalts (HIGAZY, 1954; CLARKE, 1970) have Cr contents comparable to that of the most depleted sample of the Kapfenstein residual sequence (like Ka 167). If they have been produced by partial melting of a fertile mantle material like Ka 168 they must have lost about half of the original Cr by fractionation during ascent. The overwhelming majority of basalts is strongly depleted in Cr (compare PRINZ, 1967) and therefore appears to be strongly fractionated. Apparently Cr is quickly used up by very early crystallization of chromite from basaltic melts and most basalts still considered being 'primitive' have fractionated Cr abundances. Spinell-liquid distribution coefficients for Cr (under low-p conditions) are very large (up to ~1000, HILL and ROEDER, 1974) and rather small amounts of early crystallizing chromite will take up most Cr present in the primitive basaltic liquid. With increasing ultramafic character of basaltic liquids Cr-spinel apparently is no longer a liquidus phase and therefore no Cr fractionation does occur. Chromium therefore appears to be the most sensitive element in basaltic liquid fractionation.

With decreasing Cr-content of the Kapfenstein residual rock suite the Cr-contents of the minerals increase (see Fig. 3 and discussion on mineral compositions). Ytterbium shows the opposite behaviour. The bulk contents of Yb increase parallel to Cr from Ka 167 to Ka 168 and the minerals become successively richer in Yb. Although the simple correlation of increasing clinopyroxene contents and increasing pyroxene compatible element contents offhand implies a simple mixing model, the regular and opposite behaviour of Cr and Yb contradicts this view as do the regular changes of mineral compositions with the Yb/Sc bulk ratio. Thus, the series from Ka 168 to Ka

167 represents a sequence of residues from different and increasing degrees of partial melting.

The fractionation index Yb/Sc can be used to estimate the limit composition for the Earth's mantle (e.g. PALME *et al.*, 1978). The almost chondritic Yb/Sc ratio of Ka 168 implies that it is the most primitive sample encountered in Kapfenstein.

(c) *Olivine-compatible elements.* Since olivine is the most abundant mineral in all samples, concentrations of olivine-compatible elements are not likely to change considerably in a residual sequence as represented by Ka 168 to Ka 167. With decreasing Yb/Sc (the fractionation index) only the Mg/Fe ratio increases regularly. Cobalt, Ni, Zn, and Mn do not show any regular variation within our residual lherzolite suite. The rather high variability of bulk Zn contents is probably due to sampling because small amounts of (the rather irregularly distributed) spinel will undoubtedly strongly influence the bulk Zn content.

Of some interest is the Ni/Co ratio. Although both Ni and Co are depleted by a factor of about 5 relative to chondrites, the Ni/Co ratio is almost exactly chondritic. The mean Ni/Co ratio of the harzburgite-lherzolite series is 21.06 ± 0.28 which is very close to the mean Ni/Co ratio of nine carbonaceous chondrites of 22.21 ± 1.12 found by applying the same analytical procedures (unpublished data, MPI Mainz). The uniform Ni/Co ratios of lherzolites have been used by FREY and GREEN (1974) as an argument against a cumulate origin of these rocks. Although Ni/Co ratios of cumulate dunites can be indistinguishable from residual dunites, lherzolites (containing appreciable amounts of opx and cpx) formed by gravitational fractionation generally can not have a chondritic Ni/Co ratio because the distribution coefficients of Ni and Co between liquid and olivine are different (e.g. IRVING, 1978). As a consequence, after a certain degree of fractional crystallization the Ni/Co ratio of the liquidus phases must change and be different from the chondritic ratio.

Amphibole-lherzolites Ka 111 and Ka 155

These amphibole lherzolites have major, minor and trace element contents which fit the main lherzolite-harzburgite series (Table 2 and 3). The REE have almost chondritic abundances in Ka 111 and give a flat, unfractionated pattern (Fig. 1). Ka 155 shows an overall stronger depletion with a pronounced relative depletion in LREE. The slight depletion of LREE over HREE in Ka 111 may be the result of contaminating a rock with a strong depletion in LREE by a LREE-rich phase, such as the black dots (see discussion above). The content of incompatible elements in Ka 111 is close to the less depleted end whereas Ka 155 is in intermediate position in the lherzolite-harzburgite series. The petrological evidence for late formation of hornblende by reaction of spinel, clinopyroxene and water in Ka 111 is supported by trace

element data. Although the REE data indicate a contamination by a phase rich in LREE a contamination by a wet basaltic liquid can be excluded. The formation of amphibole probably was solely caused by water metasomatism. This conclusion is supported by the low K-contents of both the amphibole and the bulk rock Ka 111. For Ka 155 a similar genesis followed by a partial melt formation can be envisaged. The overall major and trace element contents, which fit the normal series, exclude a contamination of this rock by a basaltic liquid. Since hornblende is not generally associated with spinels the latter probably reacted away during formation of a liquid. This event could also have caused the pronounced depletion of LREE.

Amphibole—lherzolite Ka 105

This amphibole lherzolite fits in most elemental contents (Tables 2 and 3) 'normal' lherzolites such as the series Ka 168 to Ka 167 which has been discussed above. However, the Fe/Mg ratio, the alkali content, and the abundance of LREE are significantly higher in Ka 105 as compared to the normal lherzolite series. The REE abundance pattern (Fig. 1) shows practically unfractionated HREE at about chondritic abundances. The LREE are irregularly enriched over the HREE. On the basis of these geochemical data, we suggest that Ka 105, a previous 'normal' lherzolite, has been impregnated by a wet basaltic liquid of a composition similar to the composition of the amphibole present. Under the prevailing high pressure conditions this liquid or almost all of this liquid crystallized as amphibole similar to what has been suggested by CONQUÉRÉ (1971) for comparable rocks from Lherz. A subsequent metamorphism of the contaminated rock led to a redistribution and equilibration of elements from both partners. Thereby the Fe/Mg ratio and the alkali contents of all phases increased.

This view is supported by the presence of a hornblende layer in sample Ka 105. Hornblende in this vein has a composition very similar to hornblende in the hbl-lherzolite 105. An analysis of that pargasite is given in Table 7. Since the hornblende contains only very minor amounts of other minerals beside pargasite, its composition very closely approaches that of the bulk hornblende. As is evident from Table 7 its chemical composition corresponds to an alkali olivine basalt. Minor and trace elements mostly fit the major element chemistry: The REE are highly fractionated and show the pattern of a typical liquid of alkali olivine basalt composition. The LREE, however, indicate loss of the final liquid (taking along the most incompatible elements) caused by restricted acceptance by the amphibole lattice (for distribution coefficients see IRVING, 1978). Alkali contents are high as are the contents of Ta and Hf relative to the HREE. The Ni content and the Ni/Co ratio are high and indicate some subsolidus equilibration with the host lherzolite during the post-magmatic metamorphic event. In conclusion we suggest, that the hornblende vein in

sample Ka 105 almost completely represents a wet alkali-basaltic liquid which partially impregnated the host lherzolite. Subsequent subsolidus recrystallization led to an elemental exchange between the host lherzolite and the amphibole leading to (beside others) a high Fe/Mg ratio of the host lherzolite and to a high Ni/Co ratio of the hornblende.

Garnet-spinel-websterite (Ka 103)

The major element chemistry of Ka 103 is that of a picritic basalt. This composition is exceptional for pyroxenites (compare AOKI and SHIBA, 1974; FREY and PRINZ, 1978). Only a few analyses reported in the literature are comparable to the analysis of Ka 103. KORNPROBST (1969) reports pyroxenites from Beni Bouchera of somewhat similar compositions and JACKSON and WRIGHT (1970) describe comparable pyroxenites from Hawaii.

Websterite Ka 103 is depleted in LREE as compared to the HREE (Fig. 1). This REE pattern typically characterizes a residue after extraction of a liquid produced by a small degree of partial melting. The low K, Ba, and Sr contents of Ka 103 strongly support this view. The HREE, however, are enriched by about a factor of 10 relative to CI chondrites. Since a residuum of picritic composition cannot be enriched in REE over the starting material (see IRVING, 1978, for crystal-liquid partition coefficients) and since the Earth's mantle may only have 1–3 times the amount of REE in CI chondrites (see discussion in RINGWOOD, 1975) the websterite Ka 103 definitely represents a liquid. This view is strongly supported by its high, almost unfractionated (!) Cr, Ni, and Co contents and its Ni/Co ratio, which fits the calculated ratio for partial melts derived from upper mantle material. The Cr content is high and comparable to depleted mantle rocks (like Ka 167). All these parameters indicate that Ka 103 represents a liquid which was formed by a high degree of partial melting of upper mantle rocks.

The overall composition of Ka 103 can, however, not be explained by one single fractionation process. At least two fractionation steps are necessary in order to enrich the HREE and deplete the LREE and other highly incompatible elements. The most probably genetic model appears to be the following: Ka 103 represents a liquid which crystallized within the upper mantle. During the latter stage of crystallization or during a subsequent partial remelting event it lost a small amount of partial melt. This second event caused the observed deficit in incompatible elements like K and LREE. The HREE contents probably did not change significantly during the partial melting event and indicate an original liquid composition of tholeiitic type. These liquids are characterized by a rather 'primitive', unfractionated abundance of REE (FREY and HASKIN, 1964; FREY *et al.*, 1968; GAST, 1968; PUCHELT and EMMERMANN, 1977) with an overall abundance of 5–15 times chondritic. From such a rock extraction of a partial melt highly enriched in

Table 6. Partial analyses of oxidized sulfides from websterite Ka 103, Kapfenstein, Austria

Microprobe analysis (average of 10 different areas)							
Weight-%	Fe	Ni	S				
	40.0	3.7	4.6				
σ	± 12.0	± 5.4	± 5.5				
INAA (0.3 mg)							
Weight-%	Fe	Ni	Co	Cu			
	40.0	2.7	0.062	0.66			
ppm	Sc	Ga	As	Sb	W	Au	U
	10.0	17.0	190.0	25.0	13.0	0.9	230.0

LREE can produce the pattern observed in Ka 103. This loss of the low temperature melting portions could either have occurred during the later stage of crystallization of Ka 103 from the melt or during a later partial melting process. The latter appears to be more plausible because of the almost complete extraction of K. MASUDA and JIBIKI (1973) report some very similar REE abundances from Mid-Atlantic-Ridge gabbros which they interpret as an indication for liquid-solid separation during the late-stage crystallization phase. Since garnet is present in Ka 103 only in small amounts and is clearly of secondary origin (exsolution from clinopyroxene), the REE pattern cannot be the result of a cumulate origin of Ka 103. An origin by accumulation of pyroxenes is also clearly impossible because even clinopyroxenes crystallizing from a melt rich in incompatible elements like Ka 170 should contain three times lesser amounts of HREE than rock Ka 103.

All major and trace element data are compatible with the two stage genesis model except U which is much too high (0.52 ppm). This high U content causes very unusual K/U (87) and Th/U (0.40) ratios (e.g. GREEN *et al.*, 1968). The sample obviously has been contaminated by a U-rich phase either before or after eruption. In order to clarify this a second sample from inside the nodule has been analyzed for U and Th with the result that the Th content was the same and the U content was 1.46 ppm, three times higher than in our first sample. Thus, the high U-content was confirmed and evidence for an inhomogeneous distribution of U was obtained. Further studies showed, that in this xenolith U is highly concentrated in an Fe- and Ni-rich phase. Microscopy and electron microprobe analysis showed this phase to be a finegrained and recrystallized mixture of Fe oxides and sulfides, obviously the oxidation products of former sulfides. Analytical data for separates of this material are given in Table 6. The extremely high U content (230 ppm) is readily apparent and the bulk composition is consistent with a derivation from former sulfides. The most plausible explanation is weathering whereby oxidized U from groundwater became trapped in the more reducing local environment of decaying sulfides. As

shown by our data this process is very effective. It certainly takes place at many xenolith (and other) localities, thus being a major source of contamination of ultramafic rocks.

B mineral compositions

Mineral compositions for all samples investigated in this study have been determined by electron microprobe analysis. In addition, mineral separates from some rocks have been analysed for major, minor and trace element contents. Data for those samples (Ka 168, Ka 111, Ka 105, and Ka 167) are given in Table 7. Mineral chemical data for the remaining samples can be found in KURAT *et al.* (1979).

Major and minor element compositions in all samples, except Ka 105, are homogeneous as measured with the electron microprobe. The homogeneity extends beyond the scale of a thinsection (~1 cm) as is shown by the excellent accordance between microprobe analyses and INAA for which samples have been taken from different portions of each rock. Since major elements are in equilibrium between different phases, minor and trace element distributions may also be in equilibrium.

Trace element contents of minerals change, as expected, according to the distribution trends of the bulk rock samples. This provides clear evidence for real bulk compositional variations between different rocks and contradicts mixing models which explain bulk compositional variations by different proportions of minerals rich in trace elements (e.g. clinopyroxene) and minerals poor in trace elements (e.g. olivine). This relationship is clearly evident in Fig. 4. The HREE abundances in pyroxenes clearly reflect the degree of fractionation of each sample in the same order as it is shown by the bulk rock samples. The LREE are strongly variable and in several samples show positive anomalies. Obviously, different minerals are contaminated by a phase rich in LREE to different degrees. From modal mineral contents of Ka 167 and Ka 168 (Table 1) and from data in Table 7 it is evident that mass balance has been achieved for all trace elements except the highly incompatible elements. Thus the major portion of the trace elements

Table 7. Electron microprobe and INAA analyses of minerals from ultramafic xenoliths from Kapfenstein, Austria. Accuracies of REE and Hf determinations are in all cases less than a factor of two lower than those given in Table 2

	Ka 168 Sp-lherzolite				Ka 111 Hbl-sp-lherzolite			Ka 167 Harzburgite			Ka 105 Hornblendite	
Electron microprobe analyses												
	Ol	Opx	Cpx	Sp	Ol	Cpx	Sp	Ol	Opx	Cpx	Sp	Amph. 2)
SiO ₂	40.3	54.4	51.8	0.09	40.2	52.4	0.12	40.4	53.8	51.9	0.14	44.1
TiO ₂	<0.02	0.13	0.60	0.12	0.03	0.42	0.09	<0.02	0.07	0.27	0.10	2.50
Al ₂ O ₃	<0.02	4.6	6.9	57.0	0.04	0.58	55.0	<0.02	4.1	5.6	50.4	11.6
Cr ₂ O ₃	<0.02	0.37	0.79	9.3	<0.02	0.81	11.1	<0.02	0.53	1.06	15.1	0.14
FeO ¹⁾	9.7	6.1	2.76	11.1	9.3	3.0	12.4	9.2	5.8	2.67	11.3	6.8
MnO	0.11	0.15	0.11	0.11	0.13	0.09	0.12	0.12	0.13	0.09	0.13	0.12
MgO	49.4	33.9	15.8	21.3	48.4	15.9	21.1	49.7	34.0	16.3	20.4	17.4
CaO	0.07	0.74	20.1	<0.02	0.08	19.8	<0.02	0.06	0.78	19.9	<0.02	10.6
Na ₂ O	<0.02	0.10	1.60	<0.02	<0.02	1.36	<0.02	<0.02	0.11	1.44	<0.02	2.93
Total	99.92	100.59	100.46	99.02	98.18	99.60	99.93	99.48	99.32	99.23	98.57	97.44 2)
Instrumental neutron activation analysis of mineral separates												
% Fe	7.53	4.90	2.13	7.85	7.09	2.52		6.85	4.44	2.30	7.3	4.93
ppm												
Na	108	808	11976	129	130	12850	...	139	865	9830	63	20400
Sc	2.16	17.5	67.5	1.12	2.28	69.3	...	2.55	17.6	56.5	0.5	21.1
Cr	52	2255	5047	56100	67	5860	...	114	3315	7150	103800	1250
Mn	1054	1100	698	702	1035	746	...	962	980	672	20	980
Co	137	59	20.1	208	132	25.5	...	132	58.5	30.0	210	53.2
Ni	2950	750	340	3270	2990	2920	850	520	2600	990
Zn	40	24	...	740	39	44	40	...	740	50
Ga	...	3.8	5.0	4.0	2.6	...	40	14
La	0.03	0.12	0.80	...	0.032	1.3	...	0.04	0.09	2.53	...	11.3
Sm	0.003	0.05	1.75	...	0.0063	1.6	...	0.005	0.021	0.53	...	5.38
Eu	0.005	0.03	0.69	0.67	0.26	...	1.79
Yb	0.047	0.29	2.0	...	0.043	2.11	...	0.025	0.21	1.27	...	1.21
Lu	0.015	0.046	0.32	...	0.0062	0.34	...	0.013	0.032	0.20	...	0.18
Hf	...	0.16	1.18	0.94	0.42	...	4.1

¹ Total Fe as FeO.

² K₂O 1.25%; Rb 42.3, Sr 310, Cs 0.28, Ba 380, Ce 34, Tb 0.61, Dy 3.5, Ta 3.4, Au 0.019, Th 0.5, U 1.3—all in ppm.

of the second and third groups (pyroxene and olivine compatible respectively, see above) is residing in the four main minerals. Contributions from minor phases like the black dots are negligible. Textural and major element chemical equilibrium of the lherzolite mineral assemblages are the result of a high temperature and high pressure metamorphism. Major element distributions between different minerals (mainly pyroxenes) indicate that the whole suite of ultramafic xenoliths has equilibrated between 940 and 1100°C and 15–27 kb (see KURAT *et al.*, 1979). Thus the whole collection has been sampled by the basanite liquid from a depth interval of approximately 50–80 km within the upper mantle.

Since major elements clearly show a temperature dependent distribution between the main minerals (KURAT *et al.*, 1979), it can be expected, that trace elements will behave in a similar way. First, however, it has to be ascertained that the trace elements indeed have equilibrium distributions between different phases. Figure 5 demonstrates that this is indeed the case for Cr and Yb which have been chosen as examples. The general distribution of Cr and Yb between different minerals is by and large the same in both rocks. Differences in bulk Yb contents of the

rocks are reflected in the Yb contents of the minerals. This is, however, not the case for Cr, which has a lower abundance in Ka 167 (0.183 wt% Cr₂O₃) as compared to Ka 168 (0.535%). With increasing residual character of lherzolites (our main series) the bulk Cr content gradually decreases because the $D_{\text{liq.}, \text{rock}}^{\text{Cr}}$ is larger than unity and consequently Cr enters preferentially the liquid (compare Fig. 3). On the other hand the spinels become increasingly Cr-rich with increasing residual character of the rock. This happens because of $D_{\text{liq.}, \text{rock}}^{\text{Al}} > D_{\text{liq.}, \text{rock}}^{\text{Cr}}$ and because the $D_{\text{sp.}, \text{liq.}}^{\text{Cr}}$ increases with increasing Cr content of spinel from about 20 for Al-spinel ($D_{\text{sp.}, \text{cpx}}^{\text{Cr}} \sim 12$, Table 7; $D_{\text{cpx}, \text{liq.}}^{\text{Cr}} \sim 1.6$, IRVING, 1978) up to 1000 for chromite (HILL and ROEDER, 1974). Thus, the amount of spinel decreases with increasing loss of partial melt and the Cr content of spinel increases. This high Cr content of spinel causes higher Cr concentrations in all other phases of the residual rock.

The apparent mineral-mineral distribution coefficients for trace elements in different rocks should be of the same order of magnitude but should also reflect different equilibration conditions as do the major elements. In Fig. 6 this fine-structure of apparent distribution coefficients is readily visible. There is a

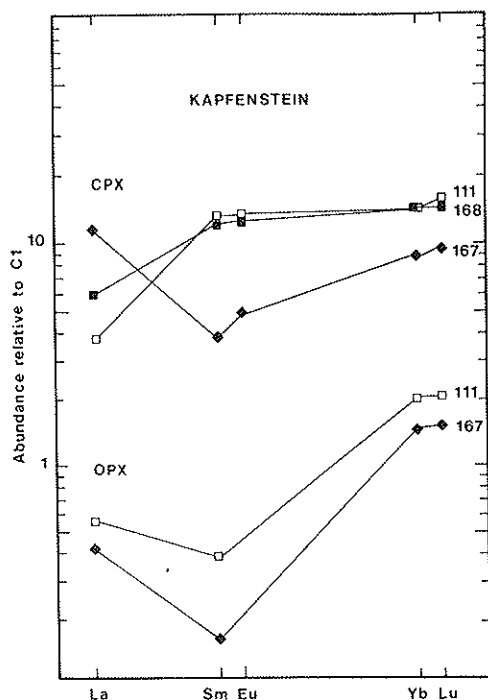


Fig. 4. REE pattern (normalized to CI) of clinopyroxene and orthopyroxene separates from ultramafic xenoliths from Kapfenstein, Austria.

systematic difference in these distribution coefficients in samples Ka 168 and Ka 167. Distribution coefficients larger than unity decrease from Ka 168 to Ka 167 whereas distribution coefficients smaller than 1 increase. Furthermore, the numerical differences between distribution coefficients from Ka 168 and Ka 167 increase with increasing deviation from unity. Since these trends are in perfect accordance with the trends of the major element distribution coefficients, the different trace element distribution coefficients must reflect different physical environments of equilibration. Because volume changes with changing pressure in solids are small compared to thermal expansion, the influence of pressure on distribution coefficients can be neglected (compare RAMBERG and DEVORE, 1951; THOMPSON, 1955). Therefore, the variations in distribution coefficients in the Kapfenstein samples are probably due to differences in equilibration temperatures. Correlation with equilibration temperatures estimated from the composition of coexisting pyroxenes (DAVIS and BOYD, 1966; NEHRU and WYLLIE, 1974) is perfect. Ka 168—according to the pyroxene geothermometer—equilibrated at 960°C and Ka 167 equilibrated at 1100°C. The direction of change in distribution coefficients is correct, because they should tend to approach unity with increasing temperature. Unfortunately no calibrations for a trace element geothermometer are available. Comparison with experimental data (IRVING, 1978; LINDSTROM and WEILL, 1978) reveals that only the distribution coefficient for Ni agrees in order of magnitude and direc-

tion. Large discrepancies are encountered in $D_{\text{Cpx-OpX}}^{\text{Sc}}$ (experimental ~15, in nature ~4), $D_{\text{Cpx-Ol}}^{\text{Cr}}$ (experimental ~14, in nature ~100!) and $D_{\text{Cpx-OpX}}^{\text{Cr}}$ (experimental ~0.3!, in nature ~2). The Cr distribution causes the largest problems and experimental data do not fit at all the reality in upper mantle rocks.

CONCLUSIONS

Petrological analyses of a suite of 36 ultramafic xenoliths from Kapfenstein, Austria, suggest that the upper mantle below Kapfenstein has been sampled by the basanite lava between approximately 50–80 km below the surface (KURAT *et al.*, 1979). In spite of the approximately 30 km sampling profile, the upper mantle below Kapfenstein appears to be of a rather monotonous composition with lherzolite being by far the most common rock type. Furthermore, these lherzolites generally show little variation in mineral composition which implies little variation in bulk composition for a large proportion of lherzolite samples investigated. The overall range of modal compositions reaches from lherzolite to dunite and is characterized by continuously changing mineral compositions. The most apparent variables are the Fe/Mg ratio of the silicates and the Cr content of spinel. The Cr content of spinels tends to systematically increase with decreasing Fe/Mg ratio of the silicates. Within this suite of rocks ranging from high $(\text{Fe/Mg})_{\text{Ol}}$ and low $(\text{Cr/Al})_{\text{Sp}}$ to low $(\text{Fe/Mg})_{\text{Ol}}$ and high $(\text{Cr/Al})_{\text{Sp}}$, bulk major, minor and trace element contents vary similarly in a regular manner. According to our data presented above this suite represents a residual sequence formed by different degrees of partial melting in the upper mantle. Samples Ka 168, Ka 111, Ka 155, Ka 125, and Ka 167 represent such a sequence from a

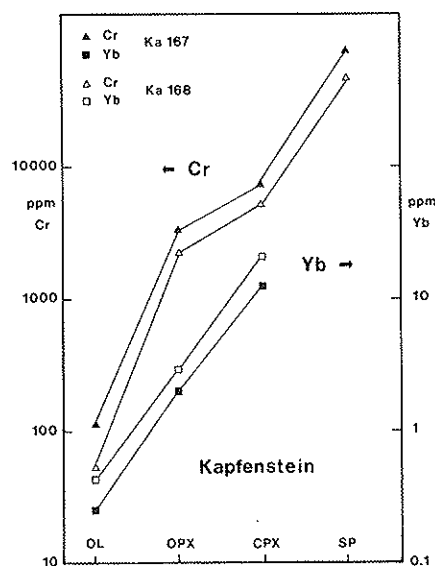


Fig. 5. Distribution of Cr and Yb between different minerals in samples Ka 167 and Ka 168.

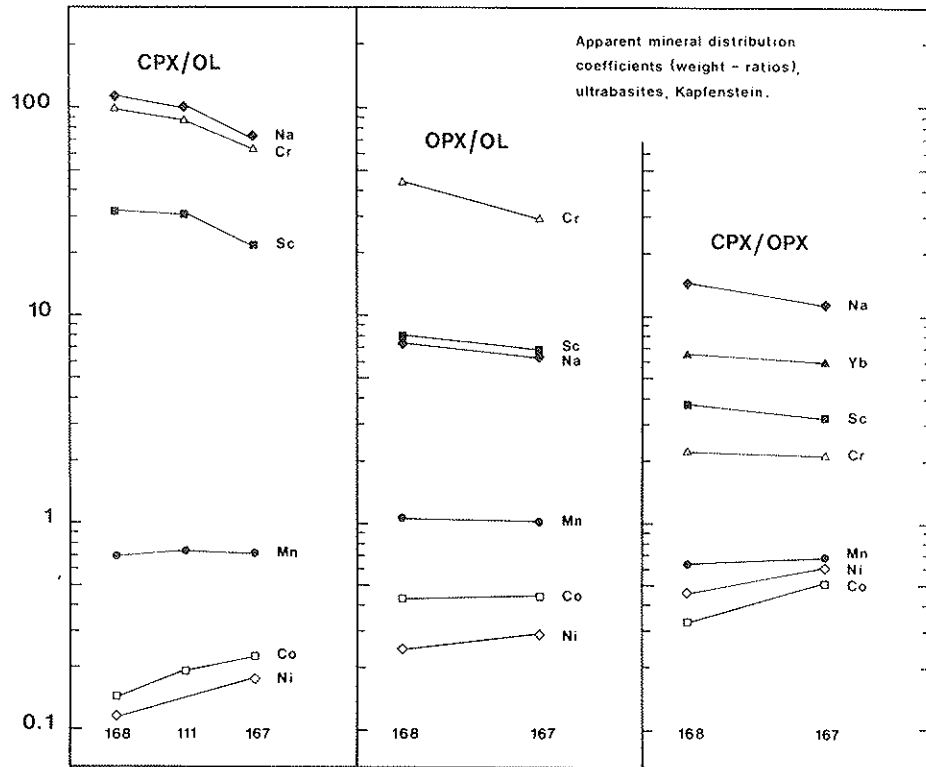


Fig. 6. Apparent distribution coefficients for Na, Cr, Sc, Mn, Co, and Ni between clinopyroxene and olivine, orthopyroxene and olivine, and clinopyroxene and orthopyroxene in different ultramafic rocks from Kapfenstein, Austria.

'primitive' lherzolite to a highly depleted harzburgite. Characteristically, Al, Ca, Ti, Na, Sc, V, Cr, and the HREE contents decrease systematically within this depletion sequence Ka 168 to Ka 167. Simultaneously the Mg/Fe ratio increases and the Yb/Sc ratio, a fractionation index introduced by PALME *et al.* (1978), decreases. Although all samples of this depletion sequence are depleted in highly incompatible elements and consequently no real 'primitive' mantle rock was found, the less depleted endmember of our suite (Ka 168) very closely approaches the chondritic Yb/Sc ratio. Ka 168 is therefore a rather primitive sample of the Earth's mantle which escaped large-scale partial melting processes (e.g. PALME *et al.*, 1978).

Chromium has been found to be a non-refractory element and bulk contents of lherzolites-harzburgites decrease with decreasing Yb/Sc ratio. Simultaneously the Cr contents of the minerals increase. The distribution coefficient for Cr between a partial liquid and lherzolites according to our data is larger than unity. Consequently, partial melts (e.g. basalts) should be much richer in Cr than they normally are. We suspect, that Cr of most basalts is fractionated by early crystallization and separation of chromite. Only lunar basalts (e.g. TAYLOR, 1975) and some terrestrial basic and ultrabasic igneous rocks appear to be really unfractionated with respect to Cr.

Only very few samples bear evidence for local inhomogeneities as well as evidence for mobilization processes taking place within the upper mantle:

(1) the hornblendite Ka 105 represents a wet *alkali-basaltic mobilisate* which crystallized within the upper mantle. This basaltic mobilisate not only formed the hornblendite but also caused

(2) a *basalt metasomatism* of a normal lherzolite which led to formation of the amphibole-lherzolite Ka 105. This amphibole-lherzolite formerly was probably a normal member of the lherzolite-dunite sequence but because of the addition of an alkali-basaltic component deviates in several compositional parameters from that sequence. For example, the Fe/Mg ratio, the overall alkali contents, and the abundance of the LREE are significantly higher in Ka 105 as compared to the normal lherzolite series.

(3) Two amphibole-lherzolites (Ka 111 and Ka 155) give evidence for *H₂O metasomatism* taking place within the upper mantle. The overall bulk and mineral compositions of these rocks fit perfectly the normal lherzolite-dunite sequence. Amphibole in these samples has been formed by reaction of spinel with clinopyroxene and water. No contamination of these samples by larger amounts of incompatible elements is detectable. Thus, addition of solely water to a normal lherzolite, causing formation of amphibole

characteristically poor in K, is responsible for the formation of these rocks.

(4) The garnet-spinel websterite sample Ka 103 provides evidence for formation and *trapping of tholeiitic liquids* within the upper mantle below Kapfenstein. Furthermore, Ka 103 has experienced a subsequent partial melting event which led to a strong depletion of incompatible elements. This rock is an important example of *partial mobilization of a former mobilisate*.

(5) Behaviour of highly incompatible elements is generally very irregular and there is ubiquitous evidence for contamination. We have identified a contamination phase which in some samples can be found as 'black dots'. Although the origin of these dots has not yet been ascertained, they could represent condensates rich in Mn, Ni, Ba, La, and other highly incompatible elements from vapors diffusing through upper mantle rocks. These gases could have originated within the deeper mantle and therefore could represent *degassing products* of the deeper mantle.

(6) Another source of contamination is weathering. In Ka 103 we found clear evidence for a strong U—contamination caused by percolating groundwater. The U dissolved in groundwater thereby becomes trapped by decaying sulfides in the rock. In the case of Ka 103, U contamination by weathering caused the extremely high U content within partly oxidized sulfides of 230 ppm. This process obviously is very efficient and probably affected all samples to some degree.

Investigation of trace element distributions between different minerals not only revealed that the lherzolite-dunite series is indeed a depletion series but also showed that several trace element distribution coefficients are strongly dependent on equilibration temperature and thus are suitable for geothermometry. Unfortunately, experimental data on trace element partitioning are scarce and in many cases contradict our observed distribution coefficients. We hope that our data stimulate more experimental efforts which eventually should lead to well calibrated geothermometers based on trace element distributions between minerals.

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REFERENCES

- AOKI K. and SHIBA I. (1974) Petrology of websterite inclusions of Itinome-Gata, Japan. *Sci. Rep. Tohoku Univ. Ser.* **3**, 395–417.
- ARNDT N. T., NALDRETT A. J. and PYKE D. R. (1977) Komatiitic and iron-rich tholeiitic lavas of Munro Township, northeast Ontario. *J. Petrol.* **18**, 319–369.
- BASU A. R. and MURTHY V. R. (1977) Trace elements and Sr-isotopic geochemistry of the constituent minerals in ultramafic xenoliths from San Quintin, Baja California. *Second Intern. Kimberlite Conf.*, Santa Fe, NM, abstract.
- BICKLE M. J., FORD C. E. and NISBET E. G. (1977) The petrogenesis of peridotitic komatiites: evidence from high-pressure melting experiments. *Earth Planet. Sci. Lett.* **37**, 97–106.
- CLARKE D. B. (1970) Tertiary basalts of Baffin Bay: possible primary magma from the mantle. *Contrib. Mineral. Petrol.* **25**, 203–224.
- CONQUÉRE F. (1971) Les pyroxénolites à amphibole et les amphibololites associées aux lherzolites du gisement de Lherz (Ariège, France): Un exemple du rôle de l'eau au cours de la cristallisation fractionnée des liquides issus de la fusion partielle de lherzolites. *Contrib. Mineral. Petrol.* **33**, 32–61.
- DAVIS B. C. T. and BOYD F. R. (1966) The join $Mg_2Si_2O_6$ - $CaMgSi_2O_6$ at 30 kilobars pressure and its application to pyroxenes from kimberlites. *J. Geophys. Res.* **71**, 3567–3576.
- FREY F. A. and HASKIN L. (1964) Rare earths in oceanic basalts. *J. Geophys. Res.* **69**, 775–780.
- FREY F. A., HASKIN M. A., POETZ J. A. and HASKIN L. A. (1968) Rare earth abundances in some basic rocks. *J. Geophys. Res.* **73**, 6085–6098.
- FREY F. A. and GREEN D. H. (1974) The mineralogy, geochemistry and origin of lherzolite inclusions in Victorian basanites. *Geochim. Cosmochim. Acta* **38**, 1023–1059.
- FREY F. A. and PRINZ M. (1978) Ultramafic inclusions from San Carlos, Arizona: Petrology and geochemical data bearing on their petrogenesis. *Earth Planet. Sci. Lett.* **38**, 129–176.
- GAST P. W. (1968) Trace element fractionation and the origin of tholeiitic and alkaline magma types. *Geochim. Cosmochim. Acta* **32**, 1057–1086.
- GREEN D. H., MORGAN J. W. and HEIER K. S. (1968) Thorium, uranium and potassium abundances in peridotite inclusions and their host basalts. *Earth Planet. Sci. Lett.* **4**, 155–166.
- GUNN B. M., COY-YILL R., WATKINS N. D., ABRANSON C. E. and NOUDIER J. (1970) Geochemistry of an oceanitic-ankaramite-basalt suite from East Island, Crozet Archipelago. *Contrib. Mineral. Petrol.* **28**, 319–339.
- GURNEY J. J. and EBRAHIM S. (1973) Chemical composition of Lesotho kimberlites. In *Lesotho Kimberlites*. (ed. P. H. Nixon), pp. 280–284. Lesotho National Development Corp., Maseru.
- HAUSER A. (1954) Der steirische Vulkanbogen als magmatische Provinz. *Tschermaks Mineral. Petrog. Mitt.* **4**, 301–311.
- HERITSCH F. (1908) Über einige Einschlüsse und vulkanische Bomben von Kapfenstein in Oststeiermark. *Zentralbl. Min.* **1908**, 297–305.
- HERITSCH H. (1963) Exkursion in das oststeirische Vulkangebiet. *Mitt. Naturwiss. Ver. Steiermark* **93**, 206–226.
- HERITSCH H. (1965) Das oststeirische Vulkangebiet. *Fortschr. Mineral.* **42**, 165–169.
- HERITSCH H. (1967) Über die Magmenentfaltung des steirischen Vulkanbogens. *Contrib. Mineral. Petrol.* **15**, 330–344.
- HIGAZY R. A. (1954) Trace elements of volcanic ultrabasic potassic rocks of south-western Uganda and adjoining part of the Belgian Congo. *Geol. Soc. Am. Bull.* **65**, 39–70.
- HILL R. and ROEDER P. (1974) The crystallization of spinel from basaltic liquids as a function of oxygen fugacity. *J. Geol.* **82**, 709–729.
- IRVING A. J. (1978) A review of experimental studies of crystal/liquid trace element partitioning. *Geochim. Cosmochim. Acta* **42**, 743–770.
- JACKSON E. D. and WRIGHT T. L. (1970) Xenoliths in the Honolulu volcanic series, Hawaii. *J. Petrol.* **11**, 405–430.

- KAY R. W. and GAST P. W. (1973) The rare-earth content and origin of alkali-rich basalts. *J. Geol.* **81**, 653-682.
- KOLLMANN K. (1964) Jungtertiär im steirischen Becken. *Mitt. Geol. Ges. Wien*, **57**, 479-632.
- KORNPROBST J. (1969) Le massif ultrabasique des Beni Bouchera (Rif Interne, Maroc): Etude des peridotites de haute température et de haute pression, et des pyroxénites, à grenat ou sans grenat, qui leur sont associées. *Contrib. Mineral. Petrol.* **23**, 283-322.
- KURAT G. (1971) Granat-Spinell-Websterit und Lherzolit aus dem Basaltuff von Kapfenstein, Steiermark. *Tschermaks Mineral. Petrog. Mitt.* **16**, 192-214.
- KURAT G., KRACHER A. und SCHARBERT H. G. (1976) Petrologie des oberen Erdmantels unterhalb von Kapfenstein, Steiermark (Abstract). *Fortschr. Mineral.* **54**, 53-54.
- KURAT G., KRACHER A. und SCHARBERT H. G. (1977a) The Earth's upper mantle below Kapfenstein (Eastern Styria, Austria) (Abstract). *Min. Soc. Bull.* **34**, 6.
- KURAT G., PALME H. und SPETTEL B. (1977b) Zur Geochemie des Erdmantels unterhalb von Kapfenstein, Steiermark (Abstract). *Fortschr. Mineral.* **55**, 170-171.
- KURAT G., KRACHER A. und SCHARBERT H. G. (1979) Petrology of ultramafic xenoliths from Kapfenstein, Austria, in preparation.
- LE MAITRE R. W. (1962) Petrology of volcanic rocks, Gough Island, South Atlantic. *Geol. Soc. Am. Bull.* **73**, 1309-1340.
- LINDSTROM D. J. and WEILL D. F. (1978) Partitioning of transition metals between diopside and coexisting silicate liquids. I. Nickel, cobalt, and manganese. *Geochim. Cosmochim. Acta* **42**, 817-831.
- MAALOE S. and AOKI K. (1977) The major element composition of the upper mantle estimated from the composition of lherzolites. *Contrib. Mineral. Petrol.* **63**, 161-173.
- MASUDA A. and JIBIKI H. (1973) Rare-earth patterns of Mid-Atlantic Ridge gabbros: Continental nature? *Geochim. J.* **7**, 55-65.
- NEHRU E. C. and WYLLIE P. J. (1974) Electron microprobe measurement of pyroxenes coexisting with H₂O-undersaturated liquids in the join CaMgSi₂O₆-Mg₂Si₂O₆-H₂O at 30 kilobars, with applications to geothermometry. *Contrib. Mineral. Petrol.* **48**, 221-228.
- NESBITT R. W. and SUN S. (1976) Geochemistry of Archaean spinifex-textured peridotites and magnesian and low magnesian tholeiites. *Earth Planet. Sci. Lett.* **31**, 433-453.
- NISBET E. G., BICKLE M. J. and MARTIN A. (1977) The mafic and ultramafic lavas of the Belingwe greenstone belt, Rhodesia. *J. Petrol.* **18**, 521-566.
- PALME C. and JAGOUTZ E. (1977) Application of the Fundamental Parameter Method for the determination of major and minor elements on fused geological samples with X-ray fluorescence spectrometry. *Anal. Chem.* **69**, 717-712.
- PALME H., BADDENHAUSEN H., BLUM K., CENDALES M., DREIBUS G., HOFMEISTER H., PALME C., SPETTEL B., VILCSEK E., WÄNKE H. and KURAT G. (1978) New data on lunar samples and achondrites and a comparison of the least fractionated samples from the earth, the moon and the eucrite parent body. *Proc. Lunar Sci. Conf. 9th*, 25-57.
- PRINZ M. (1967) Geochemistry of basaltic rocks: trace elements. In *Basalts* (eds H. H. Hess and A. Poldervaart), pp. 271-323. Interscience.
- PUCHELT H. and EMMERMANN R. (1977) REE characteristics of ocean floor basalts from the MAR 37°N (Leg 37 DSDP). *Contrib. Mineral. Petrol.* **62**, 43-52.
- RAMBERG H. and DEVORE D. G. W. (1951) The distribution of Fe²⁺ and Mg²⁺ in coexisting olivines and pyroxenes. *J. Geol.* **59**, 193-210.
- RINGWOOD A. E. (1975) *Composition and Petrology of the Earth's Mantle*. 618pp. McGraw-Hill.
- ROSS C. S., FORSTER M. D. and MYERS A. T. (1954) Origin of dunites and of olivine-rich inclusions in basaltic rocks. *Am. Mineral* **39**, 693-737.
- SCHADLER J. (1913) Zur Kenntnis der Einschlüsse in den südsteirischen Basaltuffen und ihre Mineralien. *Tschermaks Mineral. Petrog. Mitt.* **32**, 485-511.
- SCHOCKLITSCH K. (1932) Beiträge zur Kenntnis der oststeirischen Basalte. 1. Teil. *Neues Jahrb. Mineral. Geol.* **A**, **63**, 319-368.
- SCHOCKLITSCH K. (1933) Beiträge zur Kenntnis der oststeirischen Basalte. 2. Teil. *Centralbl. Mineral.* **1933**, 348-359.
- SCHOCKLITSCH K. (1935a) Pyrometamorphose an Einschlüssen in Eruptiven am Alpen-Ostrand. *Tschermaks Mineral. Petrog. Mitt.* **46**, 127-152.
- SCHOCKLITSCH K. (1935b) Gläser und Nephelinakkumulationen vom Steinberg bei Feldbach. *Centralbl. Mineral.* **1935**, 368-382.
- SCHULTZ R., KURAT G. and KRACHER A. (1979) Contribution to the petrology of alkali-basaltic rocks from SE Austria, in preparation.
- SIGMUND A. (1899) Die Basalte der Steiermark. 6. Die Basaltuffe. *Tschermaks Mineral. Petrog. Mitt.* **18**, 377-407.
- STINY J. (1923) Gesteine vom Steinberg bei Feldbach. *Verh. Geol. Bundesanst. (Austria)* **1923**, 132-140.
- STUEBER A. M. and GOLES G. G. (1967) Abundances of Na, Mn, Cr, Sc and Co in ultramafic rocks. *Geochim. Cosmochim. Acta* **31**, 75-93.
- TAYLOR S. R. (1975) *Lunar Science: A Post-Apollo View*. 372pp. Pergamon.
- TESCHKE F. and WÄNKE H. (1974) Major element analysis of extraterrestrial rock samples with 14 MeV neutrons. *Radiochem. Radioanal. LeH.* **18**, 341-348.
- THOMPSON J. B. (Jr) (1955) The thermodynamic basis for the mineral facies concept. *Am. J. Sci.* **253**, 65-103.
- UPTON B. G. J. and WADSWORTH W. J. (1972) Aspects of magmatic evolution on Reunion Island. *Phil. Trans. Roy. Soc. London, Ser. A*, **271**, 105.
- WÄNKE H., BADDENHAUSEN H., JAGOUTZ E., PALME C., SPETTEL B., THACKER R. and VILCSEK E. (1977a) On the chemistry of lunar samples and achondrites. Primary matter in the lunar highlands: A re-evaluation. *Proc. Lunar Sci. Conf. 8th*, 2191-2213.
- WÄNKE H., KRUSE H., PALME H. and SPETTEL B. (1977b) Instrumental neutron activation analysis of lunar samples and the identification of primary matter in the lunar highlands. *J. Radioanal. Chem.* **38**, 363-378.