

# The distribution of Cu across three basaltic lava flows from the Faeroe Islands

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The distribution of Cu across lava flows has been investigated by using a combination of several different analytical methods on samples taken along two profiles across each of three flows: one from the lower series, one from the middle series, and one from the upper series of the Faeroe Islands basalts. The profiles comprise 97 samples, all of which have been investigated by X-ray fluorescence analysis, atomic absorption analysis, and microscopic analysis. Furthermore some of the samples have been investigated by microchemical analysis, spectral analysis, and electron microprobe analysis. Spectral analysis has also been carried out on separates from selected samples.

The total amount of Cu present in the samples has been determined by X-ray fluorescence analysis. The amount of Cu lattice-bound in Fe-Ti-oxides, pyroxenes and plagioclases has been determined as the difference between total Cu and Cu values obtained by atomic absorption analysis carried out on solutions obtained by using weak solvents which do not dissolve lattice-bound Cu in minerals not having Cu as a major element. Electron microprobe analysis has shown that the amount of Cu lattice-bound in Fe-Ti-oxides, pyroxenes and plagioclases increases with increasing oxidation, with an abrupt increase coincident with the formation of pseudobrookite. Where pseudobrookite is present most of the Cu is lattice-bound, but where the oxidation during initial cooling has not resulted in the formation of pseudobrookite, most of the Cu ends up loosely held in the rock in the same manner as cations in zeolites, but in many of the samples a smaller part of the Cu forms native copper and Cu-bearing sulphides.

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## Introduction

The petrology of the 3000 m thick sequence of early Tertiary flood-basalt lavas that make up the Faeroe Islands has been described by Noe-Nygaard & Rasmussen (1968), and a geological map of the Faeroe Islands was issued in 1969 (Rasmussen & Noe-Nygaard 1969). The 3000 m pile of basaltic lavas is divided into three series: the lower series, the middle series and the upper series (Noe-Nygaard 1962). The lower series comprises 900 m of mainly aphyric quartz tholeiitic basalts and is separated from the middle series by a 15 m thick sedimentary coal-bearing sequence. The average thickness of single lava flows in the lower series is about 20 m, whereas the single flows of the middle series, which comprises 1350 m of mainly porphyritic quartz tholeiitic basalts, are considerably thinner, having thicknesses down to 10 cm. The upper series comprises 675 m of mainly olivine tholeiitic basalts, the single flows being about 10 m in thickness.

The material investigated comprises 97 sam-

ples collected from two profiles across three lava flows, one from each of the three lava series. The average distance between the two profiles of the same flow is 5 m, and the maximum distance between samples within each profile is 2 m.

The lower series is represented by 41 samples. However, only 30 samples are from the same flow, the second uppermost flow of the lower series, taken at a locality where the flow is estimated to be 17 m thick, but where the lowermost 2 metres are not exposed and it is estimated that the uppermost 1½ m have been eroded away. This main profile has therefore been supplemented by profiles through the lowermost 2 metres of the third uppermost flow and through the uppermost 1½ m of the fourth uppermost flow, in order to be able to follow variations close to the contacts.

The middle basalt series is represented by 32 samples from an 11 m thick flow which is completely exposed from lower to upper contact.

The upper series is represented by 24 samples from an approximately 18½ m thick flow. The

lower contact is represented, but although very little of the flow is missing at the top, the actual upper contact is not represented.

The mineralogy and geochemistry of these three flows have been dealt with in two previous papers (Jensen 1978, 1980). In the present investigation S and Cu determinations by X-ray fluorescence analysis, Cu determinations by atomic absorption analysis on solutions not affecting Cu lattice-bound in Fe-Ti-oxides, pyroxenes and plagioclases, and microscopic determinations of the amounts of Cu present as native copper and in Cu-bearing sulphides have been carried out on all 97 samples. The results obtained are shown in figs 1, 2, 3 together with the C-values of the oxidation stage of the Fe-Ti-oxides (Haggerty 1976) taken from Jensen (1980).

It can be seen from figs 1, 2, 3 that the Cu which is not bound in native copper and in sulphides occurs in two different ways: Cu which is soluble in the weak solutions used for atomic absorption analysis, and Cu not affected by these solvents. The occurrence of the soluble Cu has been further investigated by microchemical methods used on selected samples, and the occurrence of the insoluble Cu has been further investigated by spectral analysis of separates from selected samples and electron microprobe analysis of selected samples. Furthermore spectral analysis, microchemistry, and atomic absorption analysis have also been used to determine the total amount of Cu in some of the samples for comparison with the values for total Cu obtained by X-ray fluorescence analysis.

## Analytical methods

### Determinations by X-ray fluorescence

Values of the total amounts of Cu and S present in the samples have been obtained by X-ray fluorescence analysis. The Cu values have a precision of  $\pm 2-3\%$  and an accuracy of  $\pm 5\%$ . The S values have a precision of  $\pm 15\%$  and an accuracy of  $\pm 15\%$ .

### Determinations by atomic absorption spectrometry

Atomic absorption determinations have been carried out on solutions obtained by using less active fluids than hydrofluoric acid, so that the Cu lattice-bound in Fe-Ti-oxides, pyroxenes and plagioclases would not be affected by the solvents used. After crushing until a grain size less than 5  $\mu\text{m}$  was obtained, the powders were treated with a mixture of ascorbic acid and hydrogenperoxide as described by Lynch (1971).

Cameron, Siddeley & Durham (1971) deal with the minerals which go into solution in the above-mentioned mixture. These include the sulphide species present in the Faeroe Islands basalts, but native metals were not mentioned. However, experiments have been carried out which show that grains of native copper less than 50  $\mu\text{m}$  are completely dissolved in the above-mentioned solution in less than 5 hours. (The standard procedure of Lynch (1971) is 18 hours).

The average deviation between atomic absorption values for duplicate samples is 1.6% when the Cu content is above 50 ppm, while the average deviation is 5.0% for Cu contents below 50 ppm. Measurements of the standard UM 4 of Cameron (1972), which is stated to contain 538 ppm Cu soluble in ascorbic acid and hydrogenperoxide, gave the values: 530, 549, 541 and 528 ppm.

Atomic absorption analysis has also been used to determine the total amount of Cu in some of the samples. The results are shown in table 1 together with the corresponding values from X-ray fluorescence analysis. The coefficient of correlation ( $r$ ) is 0.974. The equation for the line is  $y = 1.14x - 28.24$ . The values used in figs 1, 2, 3 are those from X-ray fluorescence.

### Microscopic determinations of native copper and Cu-bearing sulphides

The determination of native copper has been carried out by measuring the total area of native copper in freshly polished sections of known area as described earlier (Jensen 1975).

Concerning the precision of the method it is found that the average deviation between values obtained when the same polished section is

Table 1

Comparison of total Cu determinations by X-ray fluorescence analysis with results from atomic absorption analysis.

Sample number	Values in ppm.	
	Total Cu from X-ray fluorescence analysis	Total Cu from atomic absorption analysis
63005	199	163
63013	221	220
63014	238	221
63023	146	116
63141	81	71
63147	111	119
63171	204	242
63177	322	338
63183	215	215
63187	351	372
63188	208	219
63194	224	229

measured more than once is 5%, whereas the average deviation between values obtained by measuring different polished sections cut from the same hand-specimen is 22% in samples with more than 5 ppm Cu, while with lower content of Cu the values can vary between 1 and 5 ppm. Deviations in the values for different polished sections of the same hand-specimen do not, however, express only precision, but also express genuine differences inside a single hand specimen. Although the native copper generally seems to be rather homogeneously distributed over the polished sections, it is sometimes clearly seen that the one end of a polished section is richer in native copper than the other. The highest values obtained for native copper are about 50 ppm, and as the content can drop from this maximum value to zero in a sample taken one metre away, differences in contents of native copper between different polished sections cut from the same hand-specimen are to be expected. Thus deviations between different polished sections from the same hand-specimen above 5% are believed to express inhomogeneities within the hand-specimen.

The amounts of Cu-bearing sulphides have been determined in the same way. However, because of the small grain-size one cannot be certain that chalcopyrite and pyrite have not in some cases been mistaken for each other. Therefore the determination of the Cu content in sulphides must be considered less reliable than the determination of native copper.

Figs 1, 2, 3 show only the amounts of native copper found, whereas the amounts of Cu in sulphides are too small to be shown. If the amounts of Cu in sulphides are added to the amounts of native copper, such a curve for microscopically determined copper will not be visibly different from the curve for native copper in figs 2, 3 on account of the extremely small amounts of sulphides in these flows. In fig 1 the effect of adding Cu in sulphides will be to smoothen the curve for native copper somewhat, but the general shape will not be changed.

#### Occurrence of native copper and sulphides

Most of the grains of native copper have a diameter smaller than or about 3  $\mu\text{m}$ , and grains with a diameter larger than 15  $\mu\text{m}$  are extremely scarce. The largest grain found has a diameter of 25  $\mu\text{m}$ .

Native copper is very seldom found enclosed in Fe-Ti-oxides, less seldom in pyroxenes, and most frequently in green alteration product, plagioclase, and zeolites. Native copper is rather frequently found together with digenite or covellite (blaubleibender), but native copper is also found in many samples which do not contain Cu-bearing sulphides at all.

The grain size of the sulphides is similar to that of native copper, and there is no noticeable difference in grain-size between the different sulphides.

The flow from the lower series is the one richest in sulphides, and sulphides are found in all the samples. The Cu-bearing sulphides are chalcopyrite, digenite, covellite (blaubleibender), and bornite. Chalcopyrite is the most abundant, averaging about 3 ppm. Next come digenite and covellite each averaging about 2 ppm. These three sulphides are found in practically all the samples, but in strongly varying amounts. The occurrence of bornite is more scattered, and many samples lack bornite completely. The average content of bornite is less than 2ppm. Non-Cu-bearing sulphides are scarce and comprise mainly pyrrhotite, whereas pyrite is very subordinate. The average content of non-Cu-bearing sulphides is well below 1 ppm. They are mainly restricted to the lower half of the flow.

The average content of Cu-bearing sulphides in

the flow from the middle series is below 1 ppm. The Cu-bearing sulphides are covellite (blaubleibender), digenite and chalcopyrite, whereas bornite is not seen. There is some tendency for covellite and digenite to be concentrated in the middle of the flow, whereas the upper part of the flow does not contain Cu-bearing sulphides. The only non-Cu-bearing sulphide found is pyrite the average content of which is well below 1 ppm.

The flow from the upper series is extremely poor in sulphides. Chalcopyrite is practically the only Cu-bearing sulphide, as digenite is found in only one sample, and covellite and bornite are not seen at all. Non-Cu-bearing sulphides comprise pyrite and pyrrhotite and are present in about the same amount as the Cu-bearing sulphides. The average content of total sulphides is well below 1 ppm.

The amounts of sulphides found can only ac-

count for a small part of the total S determined by X-ray fluorescence. The amounts of total S found at the lower contact in the upper series, at the upper contact in the middle series, and at both contacts in the lower series are considerably higher than the estimated value of juvenile sulphur in basalts given by Moore & Fabbi (1971), and the average content of S in the three flows is 4-7 times as high as the value for subaerially-erupted basalts found by Moore & Fabbi (1971).

#### Microchemical investigations

It can be seen from figs 1, 2, 3 that the amount of Cu soluble in the mixture of ascorbic acid and hydrogenperoxide used for atomic absorption analysis, but not detectable in the microscope as either native copper or Cu-bearing sulphides,

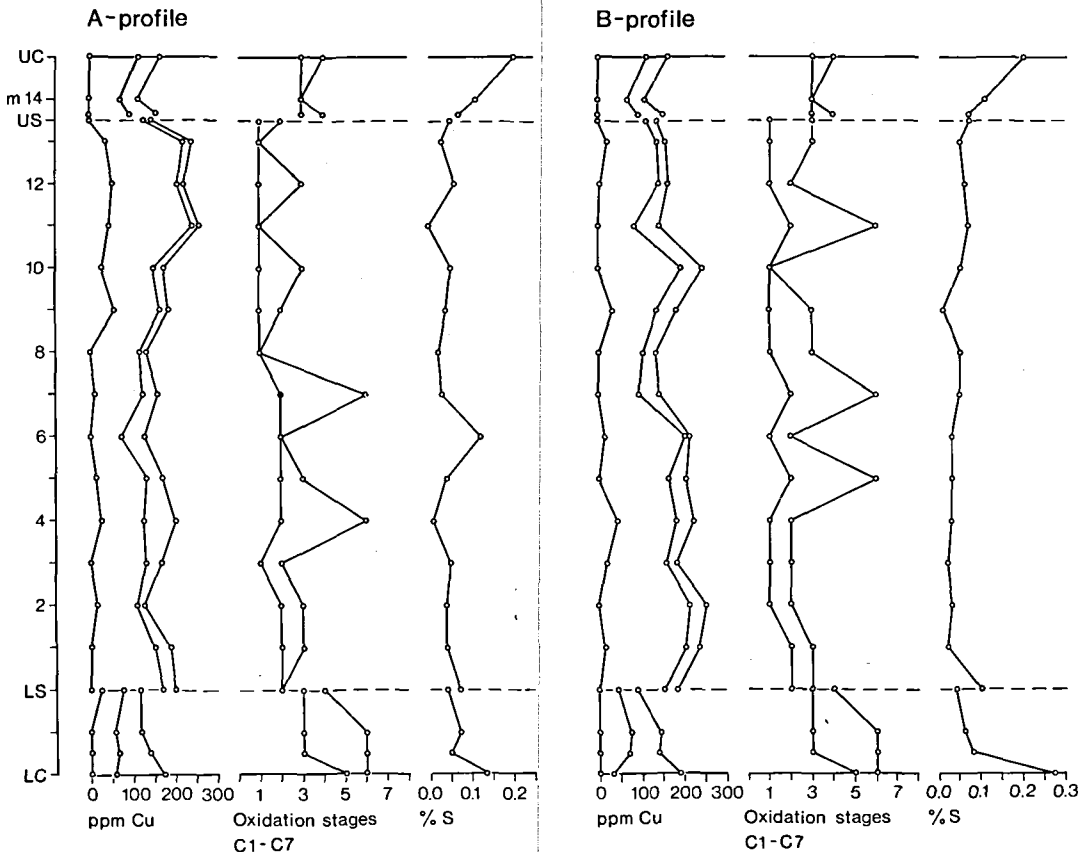


Fig. 1. Variations in native copper (first curve), soluble Cu (in ascorbic acid and hydrogenperoxide, second curve), total Cu (third curve), oxidation stages, and S in the flow from the lower series. LC = lower contact. UC = upper contact. LS = lowermost sample of main profile. US = uppermost sample of main profile. Figures on ordinate are metres above lowermost sample of the main profile.

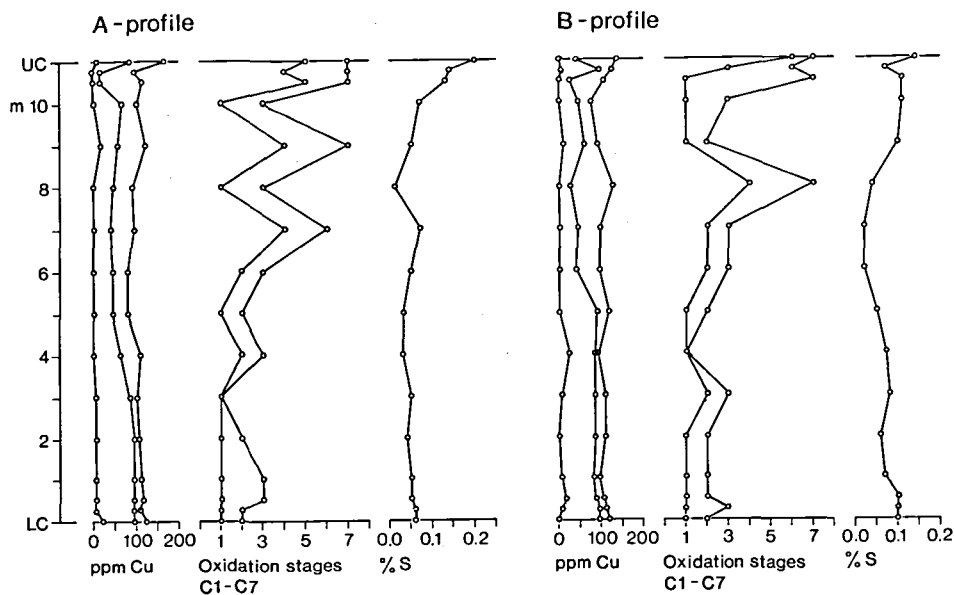


Fig. 2. Variations in native copper, soluble Cu, total Cu, oxidation stages, and S in the flow from the middle series. LC = lower contact. UC = upper contact. Figures on ordinate are metres above lower contact.

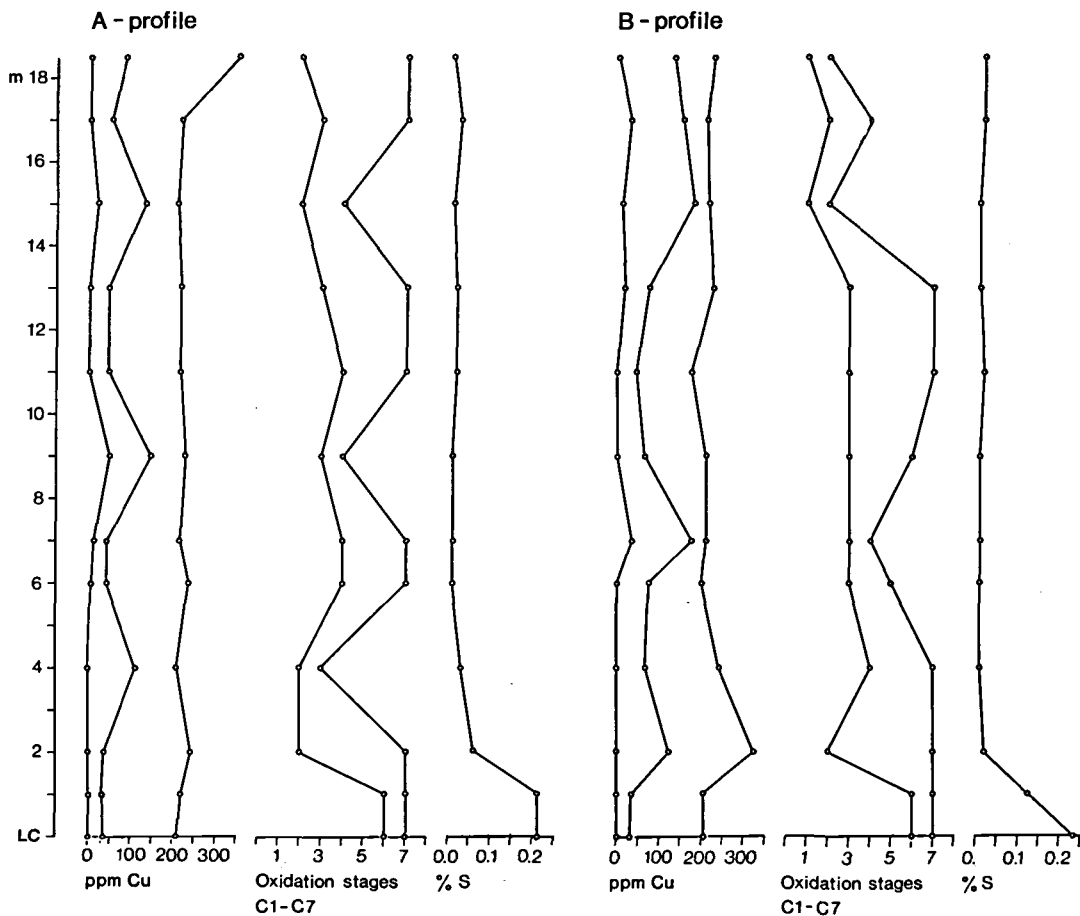


Fig. 3. Variations in native copper, soluble Cu, total Cu, oxidations stages, and S in the flow from the upper series. LC = lower contact. Figures on ordinate are metres above lower contact.

Table 2

Comparison of amounts of Cu soluble in ascorbic acid and hydrogenperoxide (atomic absorption analysis) with amounts of Cu soluble in sodium acetate ( $\text{Na}^+=1\text{M}$ ,  $\text{Ac}^-=1.5\text{M}$ ,  $\text{pH}=5.4$ ). The microscopically determined amounts of native copper and of Cu present in sulphides are also given. Values in ppm.

Sample number	63018	63175	63176	63182
Soluble Cu from atomic absorption analysis	216	32	109	146
Cu extractable with sodium acetate	180	22	82	129
Native copper	< 1	< 1	< 1	46
Cu in sulphides	4	0	0	1

varies considerably. In order to find out how this Cu occurs, four samples with different amounts of Cu soluble in ascorbic acid and hydrogenperoxide were selected for microchemical investigations. These have shown that an appreciable amount of Cu, proportional to the amount of Cu soluble in ascorbic acid and hydrogenperoxide, can be extracted with sodium acetate ( $\text{Na}^+ = 1 \text{ M}$ ,  $\text{Ac}^- = 1.5 \text{ M}$ ,  $\text{pH} = 5.4$ ). The amounts of Cu extracted were determined by spectrophotometry. The results are shown in table 2 together with the values of soluble Cu from atomic absorption analysis, and the amount of Cu found as native copper and in sulphides.

Further experiments have shown that not only can Cu be extracted with as weak a solvent as water containing sodium acetate, but the Cu can be taken up again by the samples when these are left in contact with cupriferous solutions. Cu taken up this way can also again be extracted with sodium acetate. It was found that the samples can take up much more Cu than they originally contained. Thus for the sample 63018 it was found that this could take up 2000 ppm Cu.

It is therefore concluded that the Cu in question is bound in material with ion-exchange properties like those known for zeolites, and this Cu will in the following be referred to as 'Cu loosely held as in zeolites'. However, the amounts of zeolites found in the samples (Jensen 1980) are small, and the possibility remains that the material termed 'green alteration product' might also have ion-exchange properties.

The total amount of Cu in sample 63182 has also been determined by microchemistry; the value obtained was 238 ppm, whereas the corre-

sponding value from X-ray fluorescence was 222 ppm.

### Spectral analysis

As proposed by Wager & Mitchell (1951) it is to be expected that  $\text{Cu}^+$  substitutes to some extent for  $\text{Na}^+$  in feldspars and likewise  $\text{Cu}^{++}$  for  $\text{Fe}^{++}$  in Fe-Ti-oxides and Fe-Mg-silicates, but it is still a question how much of the Cu found by analysis of mineral fractions is actually lattice-bound and how much might be present as very small grains of Cu-bearing sulphides or native copper.

In the Faeroe Islands basalts investigated the plagioclase of the phenocrysts in the flow from the upper series is the only mineral it is considered possible to separate free of microscopically visible inclusions. Accordingly separates of plagioclase phenocrysts from four selected samples were hand-picked under the microscope from crushed unmounted thin sections. These separates were analysed for Cu with a Large Hilger Quartz spectrograph using emission spectrography. The results are shown in table 3. It is seen that the plagioclase phenocrysts are practically without Cu.

It has been found elsewhere that the iron ore fraction is the mineral fraction richest in Cu (Cornwall & Rose 1957, Tiller 1959, McDougall & Lovering 1963). Although pure separates of Fe-Ti-oxides could not be obtained from the present material, spectral analysis was also performed on magnetic concentrates from the same four samples from the upper series from which plagioclase phenocryst separates have been analysed, and from two samples selected from the flow from the middle series. These magnetic concentrates, however, are very impure and contain an appreciable amount of pyroxenes, and the degree to which Fe-Ti-oxides are concentrated in these magnetic concentrates depends on the amount of unaltered titanomagnetite present in the samples.

The results of the spectral analysis of the magnetic concentrates are shown in table 3. It is seen that four of the samples have a concentration of Cu in the magnetic concentrate, but two of the samples have a magnetic concentrate which is depleted in Cu relative to the whole rock. Thus the conclusion from spectral analysis is that there is practically no Cu in plagioclase phenocrysts, and

Table 3

Cu in separates of plagioclase phenocrysts and in magnetic concentrates and comparison of total Cu determinations by X-ray fluorescence with Cu in whole rock determined by spectral analysis; values are in ppm. The percentage of Cu bound in lattices is also given.

Sample number	63175	63178	63180	63192	63146	63147
Total Cu from X-ray fluorescence	238	241	200	216	100	111
Cu in whole rock from spectral analysis	205	227	152	200	90	60
Cu in separates of plagioclase phenocrysts	7	15 17	5 14	14 16		
Cu in magnetic concentrates	580	97	210	280	115	46
Percentage of Cu in lattices	87	72	61	18	33	86

in magnetic concentrates Cu can be either enriched or depleted. The two samples with magnetic concentrates depleted in Cu have a high proportion of Cu bound in lattices: 72% for 63178 and 86% for 63147. The Fe-Ti-oxides are mainly pseudobrookite, rutile and hematite, the C-values being 4–7 for 63178 and 5–7 for 63147.

Spectral analysis has also been used to determine the total amount of Cu present in the whole rock in the samples from which concentrates were made. The results are shown in table 3 together with the corresponding values from X-ray fluorescence analysis. The values from spectral analysis are throughout lower than those from X-ray fluorescence.

#### Electron microprobe analysis

From the spectral analysis it is found that Cu is enriched in the magnetic concentrates as long as unaltered titanomagnetite is present, but the two magnetic concentrates from samples where the lowest C-value is 4 and 5 respectively are depleted in Cu. Having got so far, it was decided that no further progress could be made with analysis of mineral concentrates, and interest turned to the electron microprobe.

Several workers have succeeded in using the electron microprobe for determination of trace elements. Thus for instance Häkli & Wright (1967) determined trace amounts of Ni, and

Brande & Bence (1977) obtained very low detectability limits for trace amounts of Na, Al, Ca, Ti, Cr, Fe, and Ni using an automated probe. Although no automated probe was available, a reasonably rapid procedure for measuring Cu in concentrations at least as low as 100 ppm was established. The Cu analysis was made with a Hitachi XMA-5B electron microprobe using 20.0 kV accelerating voltage and a sample current on a Faraday cage of 60.0 nA. When analysing for Cu in silicates Ca and Si were run simultaneously, and when analysing for Cu in Fe-Ti-oxides Ti and Si were run simultaneously in order to ensure which mineral was actually analysed. With the standard deviations generally obtained by this method the detectability limit, when using 8 replicate measurements of 100 seconds of Cu peak and Cu background, is about 70 ppm for the 95% confidence level, and about 100 ppm for the 99% confidence level.

No average values are given. High and low Cu-values for each of the minerals were deliberately sought for, and the range of Cu-values found for the different minerals is given in table 4 together with the C-values of the oxidation stages, the amounts of Cu in whole rock from X-ray fluorescence analysis, and the percentage of Cu which is bound in lattices.

In about half of the samples investigated Cu was not detected in the groundmass plagioclase, but in the other half up to 300 ppm was measured in some of the grains of groundmass plagioclase.

Cu is always found in some of the pyroxene grains. With the exception of 63175 where Cu is found in pigeonite but not in augite, and 63146 where Cu in pigeonite can be twice as high as in augite, there seems to be no substantial difference in the distribution of Cu between pigeonite and augite.

The Cu content of titanomagnetite and ilmenite seems to be slightly higher than that of the pyroxenes in the same samples. Ilmenite can be either richer or poorer in Cu than the corresponding titanomagnetite.

The highest amounts of Cu are found in Fe-Ti-oxides which have reached a high oxidation stage: C6 and C7. Such grains invariably contain Cu, and the amount can approach 2½%.

The range of Cu-values in the bronzite phenocrysts occurring in the flow from the middle series only (63146 and 63147) is found to be from not

Table 4

Range of ppm Cu in different minerals from electron microprobe analysis. nd=not detectable. C-values, ppm Cu in whole rock from X-ray fluorescence analysis, and percentage of Cu bound in lattices are also given.

Sample number	Titano-magnetite	Ilmenite	Pseudobrookite-hematite-rutile	Pigeonite	Augite	Plagioclase (groundmass)	C-values	ppm Cu in whole rock	% of Cu in lattices
63171			800- 2200		nd-200	nd	6-7	204	85
63175	nd-350	nd-350	600- 2200	nd-250	nd	nd	2-7	238	87
63176	nd-300	nd-250			nd-200	nd	2-3	209	48
63178	nd-300	nd-350	2000-24000	nd-250	nd-300	nd-300	4-7	241	72
63180	nd-300	nd-400		nd-300	nd-350	nd-300	3-5	200	61
63182	nd-300	nd-200		nd-200	nd-200	nd	3-4	222	34
63192	nd-300	nd-400		nd-200	nd-200	nd	1-2	216	18
63146	nd-250	nd-250		nd-200	nd-100	nd-100	1-3	100	33
63147			1700-15000	nd-200	nd-200	nd-200	5-7	111	86

detectable to 200 ppm but is not shown in table 4.

Although the plagioclase phenocrysts in the flow from the upper series are considered on the basis of the results from the spectral analysis to be without Cu, these were also investigated with the electron microprobe. With one exception the plagioclase phenocrysts showed no sign of Cu, but in 63175 one grain was encountered where two measurements gave 120 and 140 ppm Cu respectively. However, the standard deviation in these two measurements were such that only the 95% confidence level, not the 99%, was exceeded. The plagioclase phenocrysts are to all intents and purposes considered to be without Cu.

Thus it can be seen that the only real concentration of Cu is found in the highly oxidised Fe-Ti-oxides where C reaches 6 and 7, and the mineral assemblage is pseudobrookite, hematite and rutile. These three minerals are generally intimately intergrown, but the investigation shows that Cu is preferentially concentrated in pseudobrookite. This means that the oxidation of Fe-Ti-oxides during initial cooling, even to the highest stages with the formation of pseudobrookite, takes place at a time where a residual enriched in Cu is still in existence and able to supply the pseudobrookite with an appreciable amount of Cu.

Relations between the amounts of native copper, sulphide copper, lattice-bound copper, and copper loosely held as in zeolites.

Samples with oxidation stage C1 have an average of 10% of their Cu in lattices; the percentage of Cu that is lattice-bound rises gradually with oxidation stage to 40% at stage C6, while at C7 it reaches 80%. Thus the percentage of total Cu that goes into lattices is determined by the oxidation stage. The maximum percentage of Cu in lattices is 87.

The dependence of the amount of Cu in lattices on oxidation can also be seen from the  $Fe_2O_3/FeO$  ratio. The percentage of Cu in lattices increases with the increase in this ratio, until 85% of total Cu is in lattices when the ratio reaches 1.0; further increase in ratio does not increase the percentage of Cu in lattices. Fig. 4 shows the dependence of percentage Cu in lattices on the  $Fe_2O_3/FeO$  ratio for the upper series. Most of the Cu that escapes lattice binding goes into zeolites, or is as loosely held as cations in zeolites, but a smaller part can form native copper or Cu-bearing sulphides.

There can be seen to be a negative correlation between values for native copper and oxidation stages (figs 1, 2, 3). With two exceptions native copper is not found when the ratio  $Fe_2O_3/FeO$  exceeds 0.6. Although samples with native copper have low oxidation stages, there are many samples with low oxidation stages but without native copper. Low oxidation stages is thus a necessary

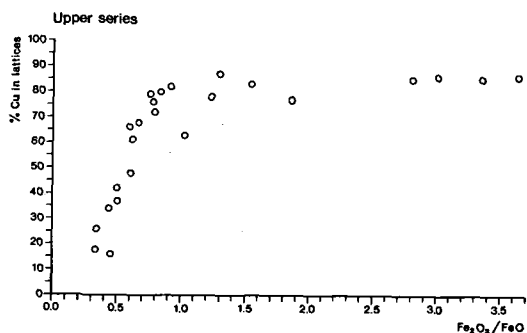


Fig. 4. Dependency of percentage Cu in lattices on the ratio  $\text{Fe}_2\text{O}_3/\text{FeO}$  for the flow from the upper series.

but not sufficient condition for the formation of native copper.

The amounts of Cu in sulphides show no correlation with oxidation stage, nor with total Cu or total S.

In the flow from the lower series the amount of total Cu fluctuates, and the curves for total Cu, soluble Cu, and native copper mainly show a positive correlation. This may be interpreted as if the amount of soluble Cu is more dependent on the total amount of Cu present than on the oxidation stage which determines how much of the Cu goes into lattices. However, in this flow the degree of oxidation is low (C7 is not reached at all), so the influence from oxidation is small. Most of the Cu in this flow (71%) is loosely held as in zeolites, and 18% is lattice-bound. Native copper amounts to 8%, and the remaining 3% is found in Cu-bearing sulphides.

In the flow from the middle series the amount of total Cu fluctuates less than in the flow from the lower series. In the lower part of the flow from the middle series, where oxidation is low, the amount of soluble Cu is determined by the amount of total Cu, whereas in the upper part of the flow the amount of soluble Cu seems to be determined by the oxidation stage. Also in this flow the largest part of Cu, 58%, is loosely held as in zeolites. 38% of Cu is lattice-bound, native copper constitutes 4%, while less than 1% is found in Cu-bearing sulphides.

In the flow from the upper series the amount of total Cu is almost constant apart from two exceptionally high values. The amounts of soluble Cu are clearly dependent only on oxidation stage. There is a positive correlation between the curve for soluble Cu and the curve for native copper,

expressing the dependence of both on the oxidation stage. In this flow most of the Cu, 64%, is lattice-bound, and only 33% is loosely held as in zeolites. The remaining 3% is native copper since Cu-bearing sulphides are practically absent.

## Conclusions

During the crystallisation of the lavas a small amount of Cu was taken up in the lattices of the groundmass plagioclase with  $\text{Cu}^+$  substituting for  $\text{Na}^+$ , while a somewhat larger amount of Cu was bound in the lattices of pyroxenes, ilmenite, and titanomagnetite, with  $\text{Cu}^{++}$  substituting for  $\text{Fe}^{++}$ ; when the oxidation of Fe-Ti-oxides during initial cooling resulted in the formation of pseudobrookite the major part of Cu was bound in lattices.

Besides the abrupt increase in lattice-bound Cu with the formation of pseudobrookite there is also a clear though less marked increase in percentage of Cu in lattices which accompanies increase in oxidation for the lower oxidation stages. This is probably due to increase in the ratio  $\text{Cu}^{++}/\text{Cu}^+$ , as it is believed that the substitution of  $\text{Cu}^{++}$  for  $\text{Fe}^{++}$  is easier than the substitution of  $\text{Cu}^+$  for  $\text{Na}^+$ , because the difference in electronegativity between  $\text{Cu}^{++}$  and  $\text{Fe}^{++}$  is much smaller than the difference in electronegativity between  $\text{Cu}^+$  and  $\text{Na}^+$ .

It is believed that the amount of Cu that enters lattices of plagioclase, pyroxenes, ilmenite, and titanomagnetite is so small that Cu is continuously enriched in the residual until pseudobrookite, if formed at all, starts to crystallise.

If the oxidation of Fe-Ti-oxides during initial cooling does not result in the formation of pseudobrookite most of the Cu ends up loosely held in the rock in the same manner as cations in zeolites, but in many of the samples a smaller part of the Cu forms native copper (5% on average) and Cu-bearing sulphides (1% on average).

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## Dansk sammendrag

Fordelingen af kobber på tværs af lavabænke er blevet undersøgt ved hjælp af en kombination af forskellige analysemetoder på prøver taget i to profiler på tværs af hver af tre bænke: en fra nedre serie, en fra mellemste serie, og en fra øvre serie. Profilerne omfatter 97 prøver der alle er analyseret for total kobber og svovl ved røntgenfluorescens, for opløselig (i ascorbinsyre og hydrogenperoxid) kobber ved atomabsorption, og for gedigen kobber og sulfidkobber ved mikroskopi. Resultatet heraf er vist i figs 1, 2, 3 sammen med oxidationsstadiene for Fe-Ti-oxidierne.

Blandingen af ascorbinsyre og hydrogenperoxid opløser gedigen kobber og sulfidkobber, men ikke kobber der er gitterbundet i plagioklaser, pyroxener og Fe-Ti-oxider. Der er langt mere opløseligt kobber end det der kan ses i mikroskopet som gedigen kobber og kobbersulfider. Mikrokemiske undersøgelser har vist at dette kobber kan ekstraheres med vand indeholdende natriumacetat (1 molær). Ydermere kan prøverne optage kobberet igen, når de kommer i kontakt med kobberholdige opløsninger, og prøverne kan optage langt mere kobber end de oprindeligt indeholdt. Det således optagne kobber kan igen ekstraheres med 1 molær natriumacetat. Dette viser at den opløselige kobber der ikke er til stede som gedigen kobber og kobbersulfid må forekomme løseligt bundet på samme måde som cationer i zeoliter. Zeoliter er imidlertid kun til stede i så ringe omfang, at dette næppe kan være forklaringen, og det formodes derfor at det såkaldte grønne omdannelsesprodukt, der er rigeligt til stede, har ionbytende egenskaber i lighed med zeoliter.

Forskellen mellem total kobber og opløseligt kobber repræsenterer kobber der er gitterbundet i plagioklaser, pyroxener og Fe-Ti-oxider. Mikrosondeundersøgelser har vist at der er et lille indhold af kobber i grundmasseplagioklasen og i pyroxenerne, og væsentligt mere kobber i Fe-Ti-oxidierne. Mængden af kobber i Fe-Ti-oxidierne stiger med stigende oxidationstrin, og der ses en ganske særlig kraftig stigning hvor oxidationen har været stærk nok til at der er fremkommet pseudobrookit. Det formodes at den mængde kobber der går ind i gitrene af plagioklas, pyroxen, ilmenit og titanomagnetit er så lille at kobber koncentreret i restfasen, indtil der eventuelt begynder at dannes pseudobrookit. Hvor pseudobrookit er til stede forekommer størstedelen af kobberet gitterbundet, men hvor oxidationen under afkølingen ikke har resulteret i dannelsen af pseudobrookit forekommer størstedelen af kobberet løseligt bundet på samme måde som cationer i zeoliter. I mange af prøverne findes en lille del af kobberet (gennemsnitligt 5%) som gedigen kobber, og en endnu mindre del (gennemsnitligt 1%) som kobbersulfider.

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