Oxidation of native copper in polished sections

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Basalts from the Faeroe Islands are frequently found to contain small grains of native copper, the size of which rarely exceeds 15 μ m in diameter. In polished sections these small copper grains are strongly oxidised in a few months, and repolishing of the sections often plucks out the oxidised grains so that the original content cannot be recovered by repolishing. The loss of native copper is serious and highly variable. It has not been possible to establish which factors govern the degree to which the copper is lost by oxidation and repolishing. Complete new-polishing, where the sections are brought back to the first grinding stage, will restore the original content of native copper.

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During an investigation of the opaque minerals in the basalts of the Faeroe Islands it was found that the basalts frequently contain small grains of native copper. Most of these grains have a diameter which is smaller than or about 3 μ m, and grains of native copper with a diameter larger than 15 μ m are extremely scarce.

The investigation was carried out on polished sections with an average size about 4 cm^2 , and the number and size of the grains of native copper within each polished section were noted, as long as the number of copper grains was reasonably limited, whereas the notation for the relatively copper-rich sections was simply: numerous grains of native copper within this or that size range.

In the course of the investigation the wish for a more exact determination of the amount of native copper expressed in ppm arose. For the copper-poor samples this could be done simply by calculation, based on the notation already made, whereas the copper-rich samples because of the procedure of notation just mentioned, had to be reexamined with full notation of the size and number of the copper grains, before calculation to content in ppm could be carried out.

For the copper-poor samples the total area in μ m² of native copper grains was calculated for each polished section. The variation in size

of the polished sections was considered to be too large to allow the use of the average 4 cm² as a factor for turning the established μ m² of native copper into ppm. Therefore the area of each polished section has been drawn on cardboard, which was cut out and weighed. The area of the polished sections was then obtained by correlating with the weight of 4 cm² of the same cardboard. Having thus established the area of the different polished sections the amounts of native copper hitherto expressed in μm^2 could now be turned into ppm values. The ppm values obtained in this way however are ppm by volume. These figures therefore were corrected for the difference in density between native copper and basalts, so that the ppm given in this paper are ppm by weight.

Reexamination of the copper-rich polished sections was first done without repolishing in the belief that the red tarnish obtained by the copper grains had made them more easily recogniseable than in freshly polished sections. The result of this reexamination however was that sections previously noted to contain numerous grains of native copper frequently showed up as copper-poor. Then the polished sections in question were repolished. This resulted in the removal of the red tarnish on the copper grains, but in no case was the amount of native copper increased substantially. Sections 63011, 63012 and 63014 can serve as an example. During the initial investigation these sections were all noted to contain numerous grains of native copper with diameters between 1 and 15 μ m, and to have clusters of native copper grains, the maximum diameter of clusters being 25 μ m.

Reexamination without repolishing resulted in less than 1 ppm in 63011 and 63012, whereas no native copper at all was detected in 63014. Examination after repolishing still gave less than 1 ppm in 63011, whereas the content in 63012 rose to about 3 ppm, and in 63014 native copper was now found but in an amount less than 1 ppm.

There is no possibility that the first notations made of the sections containing numerous grains of native copper were mistaken. That the samples 63011, 63012 and 63014 really are copper-rich is proved by the fact that completely new polished sections prepared from the hand specimens of these numbers all showed up to be copper-rich.

Thus it has now been established that small grains of native copper disappear from polished sections with time, and that they cannot be recovered simply by repolishing.

Having found that new polished sections prepared from the hand specimens of 63011, 63012 and 63014 were copper-rich, the original polished sections were completely newpolished by bringing them back to the first grinding stage. Reexamination of these freshly polished sections gave 35, 56 and 31 ppm respectively for 63011, 63012 and 63014.

Examination of these same sections $2\frac{1}{2}$ months later gave 5, 24 and 14 ppm without any polishing treatment, and 8, 29 and 14 ppm after repolishing.

Thus in 63011 only $14 \frac{0}{0}$ of the original copper content could be found after $2\frac{1}{2}$ months without repolishing and after repolishing $23 \frac{0}{0}$ of the original amount of copper could be found.

63012 had 43 0 of the original amount of copper left after 2¹/₂ months, and repolishing resulted in an increase to 52 0 /₀ of the original amount.

In 63014 45 % of the original amount of copper was left after 2¹/₂ months, but re-

polishing did not increase the detectable amount of copper.

It has now been shown that during $2\frac{1}{2}$ months the content of native copper decreases seriously, and that the effect of repolishing can vary from no gain at all, to an increase in copper of about $10\frac{0}{0}$ of the original amount. Furthermore it is seen that the decrease in copper can be different in different polished sections.

During the previous investigation the polished sections had not always been examined immediately after polishing, partly because it was found easier to recognise small grains of native copper after they had attained a reddish tarnish due to oxidation. However having now established that the lapse of time after polishing had a strong effect on the amount of native copper that could be detected, it was obvious that a serious quantitative determination of the native copper had to be carried out on freshly polished sections.

Up to this point the length of running on the different grinding and polishing discs had been determined by the appearance of the Fe-Ti-oxides which are the most frequent opaque minerals in the basalts. This meant that the grinding and polishing procedure had not been the same for all the sections, and as the detectable amount of native copper is dependent on the grinding and polishing procedure, the determination of native copper must be carried out on freshly polished sections which have all undergone the same grinding and polishing procedure.

The problem remaining then was to decide which procedure of preparation of the polished sections would give the most reliable results. While it should be obvious that insufficient polishing time will result in too low an amount of native copper, it is not obvious that the right time to use is that which results in the highest amount of detectable native copper, because there is the danger that extended polishing can tear loose parts of larger copper grains and later fasten them elsewhere in the polished section.

It was decided to use the standard procedure used in the polishing laboratory for basalts for the grinding stages and the first polishing stage, and then make experiments using different times on the two final polishing stages (ca. 3 μ m and ca. 1 μ m diamond spray respectively).

Extensive experiments with variation in the time taken on the two final polishing stages showed that slight extension or slight shortening of the polishing time had the least effect on the amount of native copper that could be found when the polishing time was 60 minutes for each of the two final polishing stages. Accordingly all the sections were so prepared and examined for native copper the same day or, in some cases, the day after the polishing.

These copper determinations are part of a future work concerning the distribution of the element copper between native copper. sulphides, and silicates within lava flows on the Faeroe Islands. Although the main results of these copper determinations will be published later, the same samples have been used for further elucidation of the disappearance of native copper from polished sections. So amongst the polished sections used in the above mentioned investigation, some were selected for repolishing, and the selection was made so that the repolishing covered a span of time from 5 weeks to 27 weeks after the original polishing.

The amount of native copper that could be found in these sections after repolishing varies from about 5 to about 75 % of the amount of native copper found in the freshly polished sections after the original polishing. The values however are so distributed that there is no relationship between the percentage of copper left and the time between the original polishing and the repolishing. For example the two marginal values of 5 and 75 % were both obtained on samples 21 weeks old.

Accordingly there must be some differences between the individual sections which have a stronger influence on the disappearance of the native copper than time has.

In the belief that the size distribution of the copper grains could be a determining factor, it has been calculated for each of the polished sections how large a percentage is present as small grains (less than 5 μ m in diameter) and how large a percentage is present as large

grains (10 μ m in diameter or larger). Comparisons between these percentages and the percentage of copper present after repolishing, however, show that there is no relationship between size distribution and the decrease in copper content.

The possibility that copper-rich sections lose copper grains faster or slower than copper-poor sections has also been looked into, but no relationship exists between the percentage of copper left after repolishing and the actual amount of original copper.

It was also thought that the different rates of decrease of copper might be dependent on the variable distribution of the copper grains, e.g. as inclusions in harder minerals like pyroxene and plagioclase or in softer materials such as zeolites and glass. This seems not to be the case.

Whereas the dependence of factors other than time is so strong that the relationship with time cannot be seen when different sections are repolished at different times after the original polishing, the time dependence can be seen when the same polished sections are repolished more than once. Thus sections 63011, 63012 and 63014, which were repolished $2\frac{1}{2}$ months after the original polishing as dealt with earlier, were repolished again 7 months later, that means $9\frac{1}{2}$ months after the original polishing.

Counting after this second repolishing gave 8,16 and 10 ppm respectively for 63011, 63012 and 63014. This means that section 63011, which showed the most serious decrease after $2\frac{1}{2}$ months, did not decrease further in the following 7 months but still had $23 \frac{0}{0}$ of the original amount left. The other two sections however show a substantial further decrease in copper: 63012 from 52 % to 28 %, and 63014 from 45 % to 32 % of the original copper content.

Concerning the length of time used in the repolishing, one minute is generally sufficient to give the copper grains a completely fresh appearance, but in a few cases the copper grains retained the red tarnish even after five minutes repolishing. Generally there is no difference in the amount of copper that can be found after one minute and after five minutes of repolishing, but extended repolishing (e. g. 15 minutes and more) always results in a decrease in copper.

The fact that extended repolishing always results in a decrease in copper content is taken as evidence for copper grains being plucked out during the polishing procedure. However it is believed that the decrease in copper is not solely due to the actual disappearance of copper grains by outplucking, but that some of the oxidised copper grains are still present in the polished section but fail to become polished. This idea is a result of a change in the conditions of the polishing experiments with sections 63011, 63012 and 63014. Except for these three sections all other sections mentioned in this paper have been polished (and repolished) using pellon cloth. However the original polishing and the repolishing after $2\frac{1}{2}$ and $9\frac{1}{2}$ months for the above mentioned three sections have been done with nylon cloth. These three sections were repolished a third time 12 months after the original polishing, but at that time the use of nylon cloth had been completely abandoned in the polishing laboratory and the repolishing was therefore carried out with pellon cloth. The results were astonishing. Instead of the expected further decrease, the copper content increased relative to the results obtained by repolishing 21/2 months earlier. The values of 23, 28 and 32 0 of the original copper content which were found after 91/2 months were now increased to 40, 37 and 45 % respectively. This increase in the visible amount of copper can be seen almost entirely to come from an increase in the number of small copper grains (up to 5 μ m). As the pellon cloth obviously is not able to restore copper grains already plucked out, it is believed that it causes a larger proportion of oxidised copper grains to become polished before outplucking occurs.

Therefore it can be concluded that a considerable, but highly variable amount of native copper can disappear from polished sections within a few months, and although pellon cloth is better suited than nylon cloth the lost copper content cannot be recovered by repolishing, but a completely new surface obtained by regrinding is necessary to restore the copper content. Acknowledgements. Thanks are due to John Bailey who kindly corrected the English manuscript.

Dansk sammendrag

Færø-basalterne indeholder ofte små korn af gedigen kobber. De fleste af disse korn er mindre end eller lig med 3 μ m i diameter, og korn med en diameter større end 15 μ m er yderst sjældne. I polerprøver bliver kornene af gedigen kobber i løbet af kort tid stærkt oxiderede, og ofte kan de da ikke længere identificeres i mikroskopet. Oppoleres polerprøverne ved få minutters polering med 1 μ m diamant spray løsrives en del af de oxiderede kobberkorn, inden de opnår polering. Det er derfor ikke muligt ved oppolering at få det oprindelige kobberindhold frem igen.

Tabet af gedigen kobber ved oxidation og oppolering er stort, men varierer stærkt. Af to prøver, der begge blev oppoleret 21 uger efter den oprindelige polering, havde den ene kun 5% af det oprindelige kobberindhold tilbage, medens den anden havde bevaret 75% af det oprindelige indhold. Det har ikke været muligt at fastslå hvilke faktorer, der afgør, hvor meget af kobberet, der forsvinder, men det har vist sig, at tabet er tydeligt mindre ved oppolering med pellonklæde end med nylonklæde, og nylonklæde anvendes ikke længere i polerlaboratoriet ved Institut for Mineralogi. Forlænger man oppoleringstiden ud over 15 minutter, falder kobberindholdet altid.

Medens det oprindelige kobberindhold ikke kan genvindes ved oppolering, har det vist sig, at en fuldstændig nypolering, hvor prøverne bringes tilbage til det første slibestadium, kan bringe den oprindelige mængde af gedigen kobber frem igen.