INVESTIGATIONS
IN THE CRYSTAL CHEMISTRY OF SILICATES

III. The Relation Haematite — Microcline.

BY

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Abstract. The relation between haematite and potash feldspar is discussed. These parageneses are often encountered in Norway. The solubility of Fe₂O₃ in microcline in solid state is determined by means of radioactive iron (fig. 5.) The solubility is normally low. It is concluded that e. g. the aventurine feldspar originally crystallized from a magma, poor in aluminum or rich in alcali. Thus the feldspars became rich in iron. A subsequent aluminum metasomatism replaced the iron atoms in the feldspar lattices. The iron thus expelled, formed the iron oxide lamellae in and between the feldspar crystals.

Pegmatites with microcline quartz and haematite as main constituents are rather frequent among the rocks of the Norwegian mountain chain. I found numerous pegmatites of this kind during my field work in the area between Opdal and Lesja. Rutile is often found as a minor constituent in them. The haematite occurs generally as plates, 0.5—2 mm thick, between the feldspar crystals. The microcline of the pegmatites is mostly light reddish, and contains very rarely inclusions of haematite or other dark minerals.

Also in the pre-Cambrian pegmatites in Østfold, in the Kongsberg—Bamble formation and in the Telemark formation similar parageneses are encountered. But these pegmatites from Southern Norway generally carry muscovite, biotite and a great variety of other minerals, also minerals containing Fe.

It seems to be a general feature that the feldspar minerals have only very slight iron content although minerals containing iron either as oxides or as silicates, are frequent in the rock. Chemical analyses of these feldspars often give an iron content as low as 0.01 % Fe₂O₃. It is, however, possible that the real content is still lower, as the microscopical examination unveils fine inclusions of dark minerals in the feldspar. The true iron content can consequently not be determined merely through a chemical analysis of a cleavage piece of the feldspar.
In the rocks of the Oslo-region, nearly opaque feldspar filled with fine dust of iron ore minerals is frequent. According to R. Selmer-Olsen (1): microcline crystals of a deep wine reddish colour are frequent in the breccia of the Kongsberg—Bamble formation. The colour is caused by a nearly sub-microscopical dust of haematite. He interprets these crystals as formed by late hydrothermal activity in the fault zones.

The two syenite varieties, tonsbergite and larvikite are nearly identical, both as to mineralogical and chemical composition. The feldspar from the tonsbergite is deep-red coloured from fine inclusions of iron oxide, whereas the feldspar from the typical larvikite is a dark labradorizing cryptoperthite.

The aventurines are a well known group of feldspar containing haematite. They were much used as cheaper gem stones. In Norway oligoclase aventurines are known from localities in the Kongsberg—Bamble formation. Olaf Andersen (2) has examined aventurines both as to their optical and thermical properties. The minerals examined came from localities in Norway, USA and Canada and included both plagioclases and potash feldspar. I summarize his results as follows.

The ferric iron primarily occurred in solution in the feldspar crystals, either as a surplus of Fe₂O₃ or as a dissolved compound of ferric iron. Due to a change in the equilibrium conditions after the crystallization, the Fe₂O₃ was expelled and formed small haematite lamellae in the feldspar crystals. This change was mainly a change in temperature. The lamellae crystallized along certain structural planes, and Andersen has identified several of these.

Some 2.5 km North to North-East of the mountain Snøhetta, by Dovre in central Norway, I found a pegmatite with haematite lamellae between the feldspar minerals. This pegmatite carries abundant rutile and several iron-bearing minerals. I analysed a single haematite lamella, 2 mm thick, and found only slight traces of aluminum in it. The titanium content found in the lamellae may come from rutile. Although the paragenesis is rich in iron, the feldspar does not contain measurable amounts of iron, nor does the haematite contain any aluminium.

It might have been expected that feldspars containing iron should crystallize from a pegmatite magma of a composition as mentioned above. Further we might expect alumina minerals as corundum, sillimanite or others.
Numerous chemical analyses, referred to in the geological literature, indicate the presence of iron in feldspar. But a close examination very often shows that the iron comes from inclusions or impurities. Potash feldspars with undoubted content of iron are best known from the papers of Lacroix (3). Seto (4) has given the results of several chemical analyses, carried out by him on iron feldspars. Among these is a light orthoclase from Madagascar, containing 2.93% $\text{Fe}_2\text{O}_3$, the highest figure. Calculated as $\text{KFeSi}_3\text{O}_8$, this gives 11.2% of iron orthoclase. A flesh coloured orthoclase from Arendal, Norway, quoted by Seto, is more dubious. I do not feel convinced that this is a real homogeneous mineral. It is possible that this mineral corresponds to the red feldspar dusted with haematite, described by Selmer-Olsen. As to the iron content of plagioclases, Seto gives some values slightly exceeding 0.4%. But neither here I feel convinced that these results come from homogeneous minerals. In an antiperthitic albite from Seiland, Barth (5, 6) found 0.4% iron feldspar.

By an unfortunate misprint, Barth says that the feldspar contains ferrous iron and gives the formula for the iron feldspar as $\text{FeAl}_2\text{Si}_2\text{O}_8$. In a letter to G. T. Faust (7) quoted on page 762 in Fausts paper, Barth, however, states that it is a misprint and that the iron is found as ferric iron, replacing aluminium. This is the only natural interpretation. Faust (op. cit.) arrived at the same conclusion in his work on the system $\text{K}_2\text{O}-\text{Fe}_2\text{O}_3-\text{Si}_2\text{O}_5$. Faust found that iron orthoclase was formed by crystallization of these components. As to the analogous system $\text{Na}_2\text{O}-\text{Fe}_2\text{O}_3-\text{Si}_2\text{O}_5$, Bowen, Schairer and Willems (8) did not succeed in getting an iron albite. They always got aegirine and quartz. Neither was it possible to obtain iron anorthite synthetically. Homogeneous plagioclases, with iron replacing some of the aluminum, must consequently have been formed under physical and chemical conditions different from those that allowed iron orthoclase to crystallize from supercooled melts.

It is not very probable, however, that the orthoclase from Madagascar crystallized from dry melts. Most likely volatiles and flux were active by the formation of the Madagascar pegmatites. The temperature probably was lower than the solidus temperatures observed by Faust for dry melts.

Anyhow, there seems to be no doubt about the fact that under certain geological conditions minerals of an isomorphic series
KAlSi₃O₈—KFeSi₃O₈ may form. It is further reasonable that to a certain degree minerals from the isomorphic composition NaAlSi₃O₈—NaFeSi₃O₈ may be found.

The ionic radius of Fe³⁺ is 0.67 Å and the ionic radius of Al³⁺ is 0.57 Å. This makes it reasonable that the steric conditions for the formation of NaFeSi₃O₈ is more difficult than the formation of KFeSi₃O₈. The orthoclase cell containing the large K⁺ ion R = 1.43 Å is less compact than the albite cell with the small Na⁺ ion R = 0.96 Å.

Andersen's hypothesis for the exsolution of haematite from albite by cooling, is not proved by his own experiments. It is correct that the transparent haematite lamellae disappeared by heating the aventurines to 1235° C. By heating these minerals for 45 hours at 1050°, however, opaque lamellae reappeared at the same place as the original haematite lamellae. Andersen interprets these observations in the logical way that thin light coloured ferric glass lamellae are formed at 1230° in the feldspar. At 1050° this glass devitrifies, forming albite and haematite. Taking a fresh aventurine and heating it for 45 days at 1050°, he finds only a very slight resorption of the haematite lamellae. It is beyond doubt that the aventurines had never previously been heated to such a temperature.

Barth (op. cit. 6) has among other examinations also examined the optical conditions of the orthoclases rich in iron from Madagascar. He finds that these minerals have optical constants characteristic for minerals formed by low temperature. Heating of the minerals for a very short time changed the angle of the optical axis from 50° to 25°. The symmetry and colour, however, remained unchanged.

According to these investigations it seems to me that we have no indication for the theory that the feldspars containing iron in solid solution should be typical high temperature minerals.

**Laboratory investigations.**

The rather frequent parageneses of microcline and iron oxide offers a problem of physico—chemical nature. It seems possible to solve this problem only by experimental investigations. It is, for instance, necessary to know the real solubility of Fe₂O₃ in potash feldspar at different temperatures. This solubility depends, of course, on the concentration of alcali, alumina and iron oxide. Such an in-
vestigation, taking all variable factors into account, would be very helpful, but a complete study of the system is at the moment beyond the possibilities of our laboratory. I therefore choose, only to determine the equilibrium concentration of iron in feldspar heated together with equal amounts of iron oxide, and with a mixture of \( \text{Fe}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \). The laboratory investigation was carried out in the manner described below.

Radioactive iron oxide was prepared from radioactive iron, containing \( \text{Fe}^{55} \) and \( \text{Fe}^{59} \). The total radioactivity was of the order 30 \( \mu \) C per gram. This radioactive iron was delivered once a month from Isotope Division A E R E, Harwell, Didcot, England. I should like to bring them my best thanks for the good service.

The radioactive iron oxide was mixed with a fine crushed feldspar powder. The feldspar powder was prepared from a light pink microcline microperthite from Einerkilen, near Evje. The feldspar apparently was specially poor in iron. The melted feldspar glass was quite colourless. From the fine crushed feldspar powder only the fraction passing sieve no. 325 (Tyler) i.e. 44 \( \mu \) was used. The feldspar powder thus obtained was mixed with a concentrated solution of iron chloride. To this mixture amonia was added, thus precipitating the iron hydroxide. The amount of iron oxide precipitated was in each case equal to the amount of feldspar. In this way the most effective mixture of iron hydroxide and feldspar was obtained. This mixture was filtered off, washed and dried at 200\(^\circ\) C. After cooling the mixture was pressed to tablets, using a pressure of 3000 kg/cm\(^2\). The tablets had a good consistence and could be handled fairly roughly.

The tablets obtained, were placed in furnaces in order to be tempered to equilibrium. Mostly 4 tablets were tempered at various temperatures. It was easily controlled that diffusion equilibrium really had taken place. This was done by removing the tablets from the furnaces at different times. After cooling, the tablets were crushed and heated with aqua regia till all iron oxide was dissolved. The iron content of the feldspar is only to a minor amount affected by this treatment.

The tablets treated in this way showed at the beginning an increasing radioactivity in the feldspar phase. After a certain time, however, the radioactivity reached a maximum and further tempering did not increase the radioactivity of the feldspar to any measurable
amount. This makes it probable that the equilibrium conditions had been reached. This means that the iron in the feldspar had the same percentage of Fe$^{55}$ and Fe$^{50}$ as the iron in the iron oxide. Because of the fine-grained feldspar material, the equilibrium is reached in a fairly short time (i.e.) less than two hours at 980° C, less than 12 hours at 780° C, less than 48 hours at 600° C and less than 168 hours at 480° C.

According to this, the times and temperatures mentioned were chosen for the experiments. The radioactivity of the feldspar residue after leaching with aqua regia, could be recalculated to the content of Fe$_2$O$_3$. The measurements were done in the following way:

The tablets of hot feldspar and iron oxide were leached for half an hour with aqua regia. The undissolved silicates were filtered off and the radioactivity of 100 mg was measured. After this, the sample was again leached with aqua regia for half an hour, and the radioactivity of the undissolved part of the sample measured. In this way leaching and measuring were repeated until the radioactivity remained constant. It proved, however, impossible to obtain absolutely constant radioactivity. The radioactivity always decreased a little by continuous treatment with aqua regia. It seems reasonable that this slow decrease in radioactivity is caused by leaching of the feldspar. In order to determine the iron content which has really existed in the
feldspar in equilibrium with the iron oxide, we therefore have to extrapolate from the last measurement back to the starting point, i.e. the radioactivity of the feldspar before the treatment by acid. The figures 1, 2, 3, 4 shows the measurements performed. Figure 5 shows a diagram where the temperature is along the X axis and the iron content of the feldspar along the Y axis. I think this iron content represents the amount of iron orthoclase which can be kept in stable solution in the microcline investigated at the corresponding temperature and chemical conditions. The equilibrium may be given by the following equations:

I. \[ 2\text{KAlSi}_3\text{O}_8 + \text{Fe}_2\text{O}_3 \underset{\text{600°C}}{\leftrightarrow} 2\text{KFeSi}_3\text{O}_8 + \text{Al}_2\text{O}_3 \]

\[ a^2(\text{KAlSi}_3\text{O}_8) \cdot a(\text{Fe}_2\text{O}_3) = K \]

II. \[ a^2(\text{KFeSi}_3\text{O}_8) \cdot a(\text{Al}_2\text{O}_3) \quad (\text{PT}) \]

We must be aware of the fact, that the law of the mass action cannot be used on a heterogeneous system without taking certain reservations. We must assume, that the equilibrium constant represents the equilibrium in a homogeneous phase in or between the grains of the tablets. In the case treated, however, we may use the law of mass action without any special precaution.
The values found in figure 5 represent equilibria. Iron microcline and aluminum microcline are completely isomorphous, and haematite and corundum are also isomorphous. We may hence treat the mixture, when in equilibrium, in the same way as uniphased systems. The amount of iron oxide which enters the feldspar lattice is equal to the amount of alumina which enters the haematite lattice. The determination of the iron oxide content of the microcline phase hence gives the equilibrium constant of the reaction, provided the activity coefficient of iron oxide in feldspars is constant at the concentrations and temperatures in question. Further we may assume that the activity coefficient of alumina in the haematite phase is constant and equal to unity. Basing on these suppositions we may calculate the equilibrium constant.

The first series of experiments were performed with equal amounts (by weight) of microcline and haematite. At a temperature of 980° C we find an

"equilibrium constant" = 1.48 \cdot 10^8.

In order to check the supposition mentioned above, some additional experiments were carried out. In these cases the equilibrium concentration of iron oxide in the microcline phase was determined, using a mixture of \( \frac{2}{3} \text{Fe}_2\text{O}_3 \) and \( \frac{1}{3} \text{Al}_2\text{O}_3 \) instead of pure iron oxide.

Under these conditions the iron oxide contents of the feldspar phases were much lower than in the first cases. At 980° C the iron oxide content was 0.02 %, which gives an

"equilibrium constant" = 0.87 \cdot 10^8.

At the lower temperatures the iron oxide content of the feldspar phase was still lower. Actually the radioactivity was so low, that it was impossible to measure it with any accuracy.

If the activity coefficient of iron oxide in the iron microcline phase should be calculated as a function of the temperatures, the corresponding activity coefficients of alumina in haematite must be known.

As far as I know, no statement of the activity coefficient of aluminum oxide in the haematite phase as a function of temperature and concentration is given in the literature.
The fact, that the two "equilibrium constants" observed at 980° C, i.e. $0.87 \cdot 10^8$ and $1.5 \cdot 10^8$, are nearly the same, although the concentration of aluminum oxide in the haematite phase varied from 0.2%—33.3%, indicates that no important differences in the activity coefficient of iron oxide in potash feldspar occurs in the concentration interval 0.02%—0.2%.

We may calculate the "equilibrium constant" at the lower temperatures in the same way. The measurements give at

- 780° C "equilibrium constant" = $9.0 \cdot 10^8$
- 600° C "equilibrium constant" = $2.6 \cdot 10^{10}$
- 480° C "equilibrium constant" = $1.1 \cdot 10^{11}$. 
Supposing the activity coefficient of iron oxide in the feldspar phase to be \( = 1 \) at this and lower concentrations, we may calculate the amount of iron oxide which will exist in the feldspar phase in equilibrium with a haematite phase consisting of \( \frac{2}{3} \) \( \text{Fe}_2\text{O}_3 \) and \( \frac{1}{2} \) \( \text{Al}_2\text{O}_3 \). The concentrations will be

\[
\begin{align*}
900^\circ \text{C} & \quad C = 0.02 \% \text{Fe}_2\text{O}_3 \text{ (measured)} \\
780^\circ \text{C} & \quad C = 0.0063 \% \text{Fe}_2\text{O}_3 \text{ (calculated)} \\
600^\circ \text{C} & \quad C = 0.0011 \% \text{Fe}_2\text{O}_3 \\
475^\circ \text{C} & \quad C = 0.0005 \% \text{Fe}_2\text{O}_3
\end{align*}
\]

From the figures above we may conclude; if a feldspar crystallizes with any noticeable amount of iron oxide, the iron oxide activity in the surrounding magma from which the feldspar crystallizes must be extremely higher than the aluminium oxide activity. We assume that pegmatite feldspar crystallizes at a temperature around \( 600^\circ \text{C} \). The ratio between the iron oxide activity and the aluminium oxide activity must be \( 2 : 1 \) if a microcline containing \( 0.001 \% \text{Fe}_2\text{O}_3 \) shall crystallize. Feldspar containing so little iron is most probably not found in our pegmatites, and we may therefore assume that the ratio between the iron oxide and the aluminium oxide activity has been higher.

From the amount of iron oxide entering the feldspar phase and the amount of aluminium oxide liberated, we find that at \( 600^\circ \text{C} \) the ratio between the iron oxide activity and the aluminium activity in the magma bordering to the growing crystal must have been \( 2500 : 1 \) if a feldspar with an iron oxide content \( = 0.04 \% \) has crystallized. The ratio between the iron oxide activity and the aluminium activity must increase beyond this limit if a crystal of potash feldspar richer in iron is going to crystallize. According to this we must conclude that the homogeneous feldspars rich in iron crystallized from a surrounding phase where the \( \text{Fe}_2\text{O}_3 : \text{Al}_2\text{O}_3 \) ratio was extremely high. This is the case even when the feldspar only contains some \( \frac{1}{100} \) of a per cent iron oxide.

Most of the pegmatites where potash feldspar is found, contain more aluminium oxide than iron oxide. This is, however, no contradiction to the statement given above. We must assume, that a feldspar crystallizes from a magma in the following way.

At first a tiny seed crystal forms. This seed crystal will contain much more aluminium than iron. In this way nearly all aluminium
ions disappear from the immediate surroundings at the seed crystal. Consequently the adjacent magma layer will be enriched in iron relatively to aluminum. If the crystal shall continue to grow, aluminum ions from adjacent parts of the magma must diffuse through this layer.

Such a diffusion is a very slow process, and it will always result in an equilibrium between the iron oxide content and the aluminum oxide content in the magma layer nearest to the crystal surface. It seems probable that this equilibrium generally must be represented by a high Fe$_2$O$_3$—Al$_2$O$_3$ ratio, as most aluminium ions reaching the crystal surface will precipitate on it, while only very few iron ions will precipitate.

We must consequently assume that if aluminum oxide is added to a feldspar, rich in iron, the feldspar will embody the aluminum ions and expel the iron ions as haematite. This replacement will continue until the feldspar has only so much iron left as corresponds to the equilibrium feldspar: haematite. This equilibrium is according to my opinion represented by figure 5 provided a pressure of one atmosphere and a ratio Al/Alk = 1. The influence of pressure of this equilibrium is unknown. We may, however, assume that the equilibrium by increasing pressure may shift against higher iron content of the feldspars by an equal Fe$_2$O$_3$/Al$_2$O$_3$ ratio in the magma. Ordinary the Fe$_2$O$_3$ content probably is of the same order of magnitude as found by one atmosphere.

From the above we may conclude that feldspar containing iron ore minerals e. g. the aventurines are formed from a homogenous feldspar. The exsolution, however, is not caused by a change of temperature, as stated by Olaf Andersen, but by a replacement. I think that feldspar rich in iron at first crystallized from a magma or a solution with an aluminium deficit. Under these conditions, a feldspar may crystallize where a part of the aluminum positions of the lattice is occupied by iron ions. After the crystallization has taken place, we may assume that the aluminium: alcali, or the Fe$_2$O$_3$: Al$_2$O$_3$, ratio changed in such a way, that the iron substituting aluminum was replaced by aluminum. The iron thus expelled formed the haematite lamellae.

I think that the iron ore content so frequently found in potash feldspars very often is a result of aluminum metasomatism. It was to elucidate this point I prepared the tablets consisting of microcline
powder with $\frac{2}{3}$ iron oxide and $\frac{1}{3}$ aluminum oxide. As previously mentioned these experiments proved the effect of increasing $\text{Al}_2\text{O}_3$ activity.

In many cases it is probable that the alcali activity of the rock has decreased after the crystallization. Such decrease in the alcali activity will of course, lead to the same exolution of iron as an addition of aluminum. This conclusion gives an explanation of the deep red colour of, for instance, the tônsbergite syenite. The common opinion among the Norwegian petrologists, seems to be that the red colour of the tônsbergite is caused by oxydation of ferrous iron. This opinion has been hold up by W. C. Brøgger in his courses in petrology by the University of Oslo and later the same opinion has been hold by V. M. Goldschmidt. It seems, however, to be very uncertain that the $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$ ratio is any higher in the tônsbergite than in the larvikite. Moreover it is difficult to understand how a rock can obtain a red colour by atmospheric oxydation hundreds of meters below the surface. The explanation given in this paper seems to me, more probable and in accordance to the laboratory observations.

At last I will bring my best thanks to Guri Taraldrud, Chr. Sundre Lauritzen and Øystein Tuntland for the very helpful assistance they have rendered during the experiments. The experimental part of this paper is done in the laboratories of the Norwegian Defence Research Establishment.

List of literature.

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3. A. Lacroix: Mineralogie de Madagascar.