CONTRIBUTION TO THE GEOCHEMISTRY OF GRANITE PEGMATITE

By

IVAR OFTEDAL

Abstract. The behaviour of certain elements during the replacement of amazonite pegmatite by cleavelandite pegmatite is considered. In conclusion some remarks on the enrichment («capture») principle are added.

The following is based mainly on two occurrences of amazonite and cleavelandite pegmatite in Southern Norway (Tørdal), which have been briefly described some years ago (1). They are located some 2 km apart within and near the boundary of an area of gabbro and crystalline schists surrounded by the so called Telemark Granite. The pegmatites obviously are genetically connected with this granite. The cleavelandite pegmatite occurs within pre-existing amazonite pegmatite, and has clearly been formed by metasomatic replacement processes. In the one locality (Skarsfjell) these processes have only just started: the cleavelandite pegmatite forms irregular veins in the still quite predominating amazonite pegmatite. In the other locality (Høydalen) the amazonite pegmatite has nearly disappeared, being preserved in scattered lumps only, within a predominating mass of cleavelandite pegmatite. Chemical and mineralogical differences between the cleavelandite pegmatites of the two localities may be due to these differences in the stage of development.

Apart from the main constituents the a m a z o n i t e (in both localities) contains the following elements in spectrochemically significant concentrations: Rb, Cs, Tl, Pb, Sr, Ga, and traces of Mg, Fe, Mn.

Barium is absent, or nearly so. This is in accordance with the «capture» rule given by V.M. Goldschmidt. The Ba ion has a higher

charge than the K ion, and is also somewhat smaller in size: therefore it should be captured in alkali feldspars belonging to earlier stages of development. In the present case this process has worked very efficiently, having removed the Ba nearly completely before the formation of the pegmatite. The microcline of the nearby Telemark Granite exhibits quite normal contents of Ba, some hundred parts per million.

Strontium behaves in a similar way, but the difference between the granite microcline and the amazonite is here somewhat less marked. The Sr content of the granite microcline is hardly ten times that of the amazonite. It is probable that the Sr in the amazonite mainly replaces K, but part of it may possibly replace Na (or Ca) in the perthite lamellae. Facilities for very accurate trace element determination have not been at my disposal; I hope to be able to improve the measurements later. But assuming the age of the pegmatites to be something like 1 000 million years, my present approximate values for Rb and Sr may very well indicate that the Sr in the amazonite is mainly radiogenic. L. H. Ahrens (2) has found values between 40 and 80 % for the ratio Sr^{87}/Sr in amazonite. The ratio will depend on the extent to which «ordinary» Sr has been removed before the formation of the amazonite. It is probable that Sr has been no less effectively removed than Ba.

Lead and *thallium* occur in the Tørdal amazonites in concentrations which approach 1 000 p.p.m. The present writer has examined spectrochemically a large number of alkali feldspar samples from granites and granite pegmatites, and published part of the results(3). He never elsewhere came across Pb (or Tl) concentrations approaching those of the Tørdal amazonites. The feldspars containing appreciable amounts of Pb were all microclines, but the contents are highly variable. In some granite bodies in gneiss areas the Pb content may exceed 100 p.p.m., in others it may be ten times less. The same is true of archaean pegmatite bodies, but here it is possible to make a distinction between two types of different geological occurrence, as will be shown below. It appears that Pb enters preferentially into «late» microclines; in high temperature alkali feldspars (orthoclase) it does not seem to occur at all. This is contrary to what was expected by V. M. Goldschmidt (4, p. 399), and in fact it can hardly be for purely crystal chemical reasons. In spite of the similar ionic radii and charges, Sr

and Pb behave quite differently during the formation of granitic rocks. Sr strictly follows the rule of «early capture», Pb does not, at least as shown by numerous data from Southern Norway. Of course the chemical characters of Sr and Pb are different. The maximum observed Pb content increases very markedly along the series: orthoclase from granite (below 5 p.p.m.) — microcline from granite (over 100 p.p.m.) — microcline from granite pegmatite (about 1 000 p.p.m.), but on the other hand these maximum values are approached in a few cases only. It appears that in many cases Pb has not been available, or very scarce. Most striking is the fact that the Pb content of microcline may vary by a factor of 100 or more in different pegmatite bodies. This may be partly due to the strongly chalcophil character of Pb, which might sometimes lead to a concentration of Pb in galena outside the examined bodies. But the Pb-poor and the Pb-rich pegmatites in general seem to be genetically different. The former mostly are integrating parts of gneiss areas, probably formed by granitisation more or less in situ, the latter are clearly connected with large granite bodies and intrusive in adjacent rocks, so that a concentration of Pb (and other rarer elements) is to be expected. I think that generally the pegmatites rich in «rare» elements must have gathered these from larger parent granite bodies, while pegmatites of the former type must generally be barren. It may be pointed out in this connection that in Tørdal the Pb content has increased by a factor of about 10 from the microcline of the Telemark Granite to the amazonite of the pegmatites.

The process by which amazonite pegmatite has been replaced by cleavelandite pegmatite must have required addition (and also subtraction) of various materials. The a m a z o n i t e   p e g m a t i t e itself does not seem to contain anything but amazonite perthite, quartz, and perhaps some mica. The main constituents of the c l e a v e l a n d i t e   p e g m a t i t e are cleavelandite, quartz, various Li-rich micas, muscovite, topaz, beryls, cassiterite, fluorite. Some minerals containing Ta, Nb, Ce, Zr, etc. occur in quite small quantities.

Because of the large quantities of cleavelandite observed at Høydalen, it is obvious that much *sodium* must have been added; the perthite lamellae of the amazonite would by no means offer sufficient material. The cleavelandite may possible originate through

decomposition and redeposition of ordinary (graphic) albite pegmatite which is observed to occur as boundary zones between the amazonite pegmatite and the country rock.

On the other hand much *potassium* must have disappeared from the pegmatite, as the quantities of mica minerals are certainly not large enough to account for the K that must have been present in the decomposed amazonite.

The *rubidium* and *cesium* from the decomposed amazonite, however, may have been transferred nearly quantitatively to the micas of the cleavelandite pegmatite, as these are on the average considerably richer in Rb and Cs than the amazonite. Small quantities of Rb and Cs are also found in the beryls. Thus it is probable that the Rb and Cs quantities present have not been notably influenced by the replacement process.

All the micas contain *strontium* in small and nearly equal concentrations, similar to those in the amazonite. Of the other minerals only Rb-rich beryls contain Sr in detectable quantities. According to Ahrens (2) the Sr in micas (especially lepidolite) is almost exclusively Sr^{87}. Also, V. M. Goldschmidt has pointed out (4, p. 246) that micas do not seem to be able to incorporate Sr by ordinary capture. Even without a knowledge of these statements I should have supposed that the Sr in the Tørdal micas is mainly radiogenic. The Sr is always associated with much larger quantities of Rb; it does not occur in the cleavelandite; and finally, Ba is not detectable in the micas. A very accurate determination of the Rb/Sr ratio in these micas should thus give a good value for the age of the deposits. (There is obviously no geologically significant age difference between the amazonite pegmatite and the cleavelandite pegmatite. Therefore there was probably no Sr^{87} present in the amazonite at the time of replacement.)

The *lead* contents of the micas are on the average lower than those of the amazonite, and in other minerals of the cleavelandite pegmatite only insignificant amounts of Pb have been found. Thus no Pb seems to have been introduced by the replacement process, on the contrary, some Pb probably has been carried away.

Thallium behaves very much like Pb. Relatively very large quantities of Tl must have been supplied from the decomposing amazonite. In the cleavelandite pegmatite Tl is found in the micas only, mostly

in much lower concentrations than in the amazonite. The cleave-
landite pegmatite thus contains only a small fraction of the Tl origi-
nally present. The surplus Tl may have been fixed somewhere in
the environs, probably at higher levels now removed by denudation,
perhaps with Pb in galena. This is to be expected because of the
partly chalcophil nature of Tl, and in fact nearly all of the chalcophil
Tl is found in galenas.

As is well known, Rb^{1+} and Tl^{1+} are crystal chemically so closely
related that they never seem to part in minerals[5]. This is well demon-
strated in the Tørdal pegmatites. But it must be remarked that the
ratio Tl/Rb is 5 to 10 times higher in the amazonite than in the micas,
not counting some rare muscovites which are exceptionally rich in
Tl. The replacement process has clearly been able to separate Rb
and Tl to some extent. This does not seem to be due to the difference
in crystal structure between feldspar and mica, since the rare muscovite
just mentioned exhibits about the same Tl/Rb ratio as the amazonite.
A possible explanation might be that Rb is purely lithophil, Tl only
partly so.

The *gallium* content of the amazonite seems to have been preserved
fairly unchanged in the cleavelandite pegmatite. As usual, Ga is
found in all the Al-rich minerals. The average Ga content of these
is fairly high, probably in excess of 100 p.p.m., but there are some
notable deviations. It is not always possible to establish age relations
between the minerals of cleavelandite pegmatite, but in some cases this
could be done with certainty. Thus a white mica had grown in parallel
position on a dark mica as a core. The white (younger) mica here
turned out to be much poorer in Ga than the dark one. Also the very
abundant Li-micas («lepidolites»), which apparently belong to the very
latest minerals, are exceptionally poor in Ga. This does not agree
with the camouflage rule of V.M. Goldschmidt. But I think it indi-
cates that Ga was scarce during the latest stages of mineral formation.
Very striking are the low Ga contents of topaz as compared with
feldspars, beryls, and some of the micas. Topaz generally appears to
be one of the earliest minerals of the cleavelandite pegmatite. Low
contents of Ga seems to be a specific property of topaz in general.
I have examined topaz from a number of different deposits, and
never found higher Ga contents than about 10 p.p.m. (V.M. Gold-
schmidt (4, p. 324) has quoted a similar figure for Ga in topaz, but

this came from a deposit where also the micas were poor in Ga.).
It is obvious that this peculiarity is due to crystal chemical proper-
ties, but it is hardly possible at present to give a more definite expla-
nation. Another peculiarity of topaz is, as well known, that it contains
much more *germanium* than any other of the more common minerals.
In fact, the only pegmatite minerals in which I have myself found
Ge, are topaz and spessartite, and the higher concentration was
always in the topaz. And I never came across a topaz which did not
contain considerable quantities of Ge, mostly several 100 p.p.m.
Observations thus indicate that topaz tends to avoid Ga and collect
Ge. These tendencies may be interconnected. Tentatively I would
suggest that in this case Ge may replace Al (not Si), and that this
in some way may hinder further replacement of Al by Ga. (The
electric neutrality might be re-established e. g. by letting a little
O replace F.). As to the immediate source of the Ge, it may be the
spessartite which is observed to occur in the primary pegmatite (in
the albite pegmatite zones referred to above), and which is sometimes
found as partly decomposed nodules embedded in the cleavelandite
pegmatite.

Elements which have clearly been supplied during the replacement
process are F, Li, Sn, Be, Sc. Other elements, like Y and rare earths,
Nb, Ta, Ti, Zr, P, occur in very small quantities, and may have been
present in the primary pegmatite. This certainly applies to *yttrium*
and *rare earths*, since gadolinite occurs quite abundantly in the zones
of albite pegmatite and is found partly decomposed in the cleave-
landite pegmatite. Some *beryllium* is also accounted for by the decom-
position of gadolinite, but this does not seem to be sufficient for the
formation of the abundant giant crystals of beryl observed in the
cleavelandite pegmatite.

Fluorine has been very abundant, as shown by the large quantities
of topaz, micas, and fluorite.

Lithium is found in mica minerals, especially in the very abundant
varieties, which contain 3 to 5 % Li_2O, and further in colourless to
pink beryls, which are also fairly rich in Cs. On the whole Li appears
to have been concentrated especially in the very latest minerals of
the cleavelandite pegmatite.

Most of the *tin* is found in cassiterite. But Sn is also a characteristic
constituent of all the mica varieties. In some micas the Sn content

exceeds 100 p.p.m., in others it is hardly more than 10 p.p.m In some cases it can be shown quite definitely that the low Sn contents are characteristic of late micas, the high contents of earlier ones. Because of its ionic radius Sn must be supposed to replace Fe (or Mg or Li) in the mica structure. As this is a very pronounced case of «capture» the observed distribution of Sn between early and late micas is in accordance with Goldschmidt's rule.

Scandium has been found in the cassiterite, in some micas, and in some beryls. The concentrations in mica may reach values exceeding 1 000 p. p. m. The high Sc contents are found in micas which apparently belong to the earliest minerals of the cleavelandite pegmatite. In some cases it can be stated quite definitely that the Sc content decreased by a factor of at least 10 during the zonal growth of such a mica crystal. Also, the very Li-rich micas («lepidolites») and some other presumably very late micas did not show any Sc at all. This deficiency in Sc in the latest micas is probably not to be explained crystal chemically. It is much more probable that there was no Sc left at the latest stages of mineral formation. This is confirmed also by observations on the beryls. Sc was found in the earliest (yellow, partly corroded) beryls only, not in the later (bluish and pink) ones. Sc, like Sn, must be supposed to replace Fe in the micas (Mg is very scarce in all of them), and this would again be a case of capture. The above data might be interpreted as being in support of the capture rule. But it has been shown earlier (6) that there is really a very marked increase in the Sc content of biotite along the series: magmatic rocks — microcline granite and gneiss — granite pegmatite. The decrease observed in the Tørdal pegmatites is at the very end of the series, and is therefore given the above interpretation. Thus the behaviour of Sc in mica minerals is not in agreement with the capture rule.

In conclusion I might make some remarks on the capture principle in general. It has been argued that capture should not be any more probable than other kinds of diadochy, because capture of one element in a crystal structure must generally be coupled with admission of an other. D. M. Shaw (7) in particular has discussed this question in some detail, and arrives at the conclusion that the «enrichment principle» of V. M. Goldschmidt (including the capture rule) is not

valid: it is not possible to predict the distribution of a trace element between «early» and «late» crystals from its properties alone.

It is certainly true that the capture principle has no general validity, or at least that it does not operate alone. Every worker on trace elements in minerals will know this from his own experience; he frequently comes across «surprises». Thus also the above observational data in several cases clearly contradict the capture rule. V. M. Goldschmidt himself was fully aware of such exceptions from his rule, as I know from verbal discussions with him, but I think he never gave up the belief that the capture rule has a real background. The capture rule may be taken in a wider and a more restricted sense. We may consider the distribution of an element between early and late mineral associations, e. g. between early and late differentiates of a magmatic rock series, and we may consider the distribution between early and late fractions of one and the same mineral, or between early and late members of a series of isomorphous mixed crystals. These distributions may be quite different. Thus Sc is found mainly in pyroxenes and amphiboles of basic and intermediate rocks. In late differentiates (granites etc.) pyroxene and amphibole have usually disappeared, and the only ferromagnesian mineral is biotite, which is much poorer in Sc. Late differentiates thus contain only a small fraction of the Sc which was present in the earlier ones. On the other hand the biotites of basic and intermediate rocks are even poorer in Sc than those of the acid ones, even in equilibrium with very Sc-rich pyroxenes or amphiboles (6). It is obvious that the nature of the crystal is at least as important in determining the possibilities of diadochy as the properties of the ions, and it is clearly useless to compare the content of an element in an early mineral with that in a fundamentally different late mineral in order to get an understanding of the enrichment mechanism. (I also think that the system with the end members A and B and the minimum melting compound A_mB_n, considered by Shaw (l. c. Fig. 5), is not really relevant, as the two series of solid solutions are A_mB_n enriched in A, and A_mB_n enriched in B, that is: the «trace element» is not the same in the two series.)

I think that a profitable discussion may be possible only when the enrichment principle is taken in the restricted sense, i. e. as applied to genetically connected minerals belonging to the same species or

the same isomorphous series. Even so there is no doubt that Shaw is right in his criticism of the principle. The above statement that Sc is relatively enriched in late (low temperature) biotites is one instance that clearly contradicts it (Sc^{3+} and Fe^{2+} are equal in size, but Sc has the higher charge). On the other hand, the striking success of the capture principle in many important cases requires an explanation. If a crystal containing a trace element may be considered as a mixed crystal between two isomorphous end members, a case in which the «restricted» enrichment principle might be applied, then Shaw points out that the higher melting end member must be enriched in the earlier fractions. Apparent agreement with the enrichment principle would then mean that the higher melting member by chance contained the smaller cation. In simple systems I do not think this is merely by chance. Of two isomorphous crystals which have all elements but one in common, the one with the strongest bonds will most probably have the higher melting point.

Cases where ions of different charges are exchanged are not so easily explained. The exchange of Ca^{2+} for Na^{1+} in the plagioclase series is in agreement with the capture rule, but the «coupled» exchange of Al^{3+} for Si^{4+} is not. Obviously the tendency to capture Ca is here stronger than the resistance against the admission of Al. At first sight this is unexpected, since of course the changes in the charges exactly compensate each other, and in addition Al^{3+} is considerably larger than Si^{4+}. But the fact remains that in this coupled diadochy the capture process strengthens the bonds by a factor of 2, while the admission process weakens the bonds by a factor of 4/3 only. Thus the bonds inside the tetrahedral network are relatively less altered than the bonds outside it. Taking this view, Ca is actually more strongly «attracted» by the albite structure than Al is «repulsed». This would explain why the capture process seems to operate in the plagioclase series and in other similar cases, e. g. in alkali feldspar containing Sr, Ba, Pb, and probably also in micas containing Ba and Pb.

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Oslo universitet,
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