A comparison between the parageneses of Fennoscandian limestone contact minerals and those of the Alnö alkaline rocks, associated with carbonates

By Harry von Eckermann

(Stockholm).

PARGAS in Finland and Mansjöand and Tennberg in Sweden are the only three Fennoscandian contact metamorphic limestone occurrences of which systematic accounts have been published; in the first case by A. Laitakari (1) and in the two latter ones by the present author (2, 3). A more complete analytical programme would have been desirable, and unfortunately many of the analyses are incomplete, especially as regards the determination of the valency of the iron. Nevertheless, the available data, and a few I have been able to add later, may suffice to give us a general idea of the paragenetical and chemical differences between these Archaean mineral parageneses and those of much younger age which occur in connexion with the limestone masses associated with the alkaline occurrence of Alnö in Sweden.

What adds special interest to such a comparison is that we have here an example of two radically different behaviours of the carbonic acid during the metamorphic growth of the minerals. In the case of the Archaean limestone contacts the CO_2, bound as calcite, is at the beginning of operation a 'sleeping partner' stirred to life by the energy of an external 'active partner' which forces it to sever its connexion with the lime and imbues it with an energy of its own. On the other hand, in the case of the Permian (?) alkaline carbonatitic rocks the carbonic acid has been the acting partner from the beginning, or in any case as far back as we can trace the genesis of the ascending alkaline extrusion, while the surrounding country rocks have played the part of the sleeping partner to which the CO_2 distributed part of its energy.

When discussing the source of energy of the first-named 'active partner', the granites around Pargas, Mansjö, and Tennberg, one cannot help but get into the firing-line of the two belligerent armies: the 'magmatists' and the 'emanation-frontists'; and especially so as one of the foremost leaders of the latter has strongly advocated the granitization of the limestone at the said localities by a diffusive process at temperatures supposedly far below the fusion-point (5).

Originally the present author treated the granite both at Mansjö and Tennberg as truly magmatic at the time of its interaction with the limestone. Whether its magmatic habit was the outcome of the crystal-differentiation of a regenerated (palingenetic) mother-magma or of the direct mobilization of down-faulted sediments is of small importance; the thing that really matters is that even if the said sediments were 'stewed' in emanations from unknown depths and chewed in orogenic convulsions, the result at the time of the brecciating of the limestone was a brew with a thermal energy of its own and the consistency of a magma. How the granite has acquired its homogeneity and thermal energy and from whatever nebulous depths the emanations may have come which may have called the granite to life need not be discussed in this connexion as long as we agree that the brecciation and the contact metamorphism of the still preserved part of the limestone cannot have been contemporaneous with the 'emanation-birth' of the granite itself. No acceptable evidence to the contrary, able to explain the actually existing structural features, has been presented so far.

Before entering upon any comparison between the two types of metamorphism, however, it may be necessary to give a condensed review of the Pargas, Mansjö, and Tennberg localities. The limestone body at Pargas is part and parcel of a petrologically varying metamorphosed pack of sediments of which comparatively narrow layers of amphibolite- and pyroxene-schists are still bordering on or intercalated with the limestone. The sedimentary formation as a whole is enclosed by migmatites, consisting of gneiss and granite, from which latter pegmatite dikes have penetrated the limestones. The Mansjö occurrence is of similar type, only on a much smaller scale, while at Tennberg the limestone is a fragment without any visible connexion with other sediments and totally surrounded by a practically homogeneous granite.

The chief distinction between Pargas and Mansjö lies in the rich occurrence of pargasite as compared with pyroxene at the former place, whereas the pyroxene is the dominating femic mineral at Mansjö. At Tennberg both kinds of paragenesis occur, the former being the result of a secondary transformation of primarily formed pyroxene. On the other hand, Tennberg is singularly lacking in chondrodite, one of the most conspicuous minerals of Pargas and Mansjö, as well as in apatite, the two minerals being only accessories. While the adjoining sediments at Pargas and Mansjö to some extent obscure the metamorphic action of the granite upon the limestone, and introduce an element of doubt when tracing the movements of the different atoms or ions taking part in

the reactions, the mineral 'skarn'-zones formed around the Tennberg limestone derive their material from the granite and limestone only. In consequence we may use the Tennberg paragenesis as the most typical of its kind when making a comparison with that of the alkaline carbonatitic rocks.

When describing the Tennberg occurrence I have previously used the simile of the hedgehog. Attacked by the thermal energy of the granite the limestone has resisted annihilation by surrounding itself with a radial growth of silicate minerals of successively decreasing acidity and increased density: wollastonite (sp. gr. 2·992)—diopside (sp. gr. 3·201–3·375)—idocrase (sp. gr. 3·381–3·421)—grossular (sp. gr. 4·076). Before that, however, some lime must undoubtedly have been assimilated by the granite, the evidence being a conspicuous increase of the anorthite component of the plagioclases within an aureole around the limestone. This, on the other hand, must have increased the viscosity of the granite and slowed down or finally prevented the ionic movement of excess silica towards the limestone contact. This migration of silica may have been accompanied by some soda as proved by a fairly high soda content of the wollastonite and pure albite at the actual contact, and must have been counterbalanced by the emigration of lime and carbonic acid at the initial stages of the metamorphosis and of CO_2 alone from the time the 'hedgehog' began forming.

As previously shown by the present author (3), the carbonic acid, released on decomposition of the calcite, raised the oxidation ratio of the contact minerals, while the resulting carbon monoxide escaping radially through the granite moved towards regions of higher temperature and acquired increased thermal energy. This was later spent by reducing the trivalent iron of the hornblende in the granite, creating a narrow zone of hastingsite-bearing granite around the limestone. Finally the precipitation of the anorthitic felspar at some distance from the contact and the binding of silica as a solid phase in the mineral growth at the contact is supposed to have accelerated the development of a pegmatitic phase between the two. The limestone deposit at this point may be visualized as floating in a hydatogenous liquid inside a solidified or, at least, extremely viscous granite shell. The ultimate consolidation of this liquid led to the thin zone of partly pure quartz, partly a graphic intergrowth of secondary calcite, quartz, albite, topaz, and tourmaline, which separates the contact mineral shell proper from the plagioclase-diopside aureole of altered granite. Lately some scheelite has been found, too, in veins originating from this zone.

This pegmatitic end-stage must of course have developed gradually, and the accompanying concentration of volatiles, especially water, around the limestone may be taken as mainly responsible for the breaking off of the primary crystallization of wollastonite and the ensuing alternating growth of idocrase and garnet. Unfortunately the lack of a systematic control of the valency of the iron content of the minerals prevents any attempt of a co-ordination between volatiles and oxidation ratios. In table I are compiled the meagre data at our disposal. They show that, with the exception of two phlogopites, the oxidation ratio is the lowest at Mansjö, as may be expected when taking into consideration the pegmatitic and low-energy character of the local Mansjö granite. The phlogopites in question occur in the pyroxenite-mansjöite dikes, where the concentration of fluorine and water must have been exceptionally high. At Tennberg the oxidation ratios are generally higher and at Pargas they reach in most cases, except in the case of the phlogopites, maximum values.

TABLE I. Atomic oxidation ratio, $Fe^{...}$: $Fe^{..}$, of the minerals of the Mansjö, Tennberg, and Pargas parageneses.

	Mansjö.	Tennberg.	Pargas.
Diopside	0·07	0·00–0·05	0·41
Mansjöite	0·11	—	—
Pyrallolite	—	—	0·36
Grossular	0·00–0·10	2·04	2·61
Idocrase	0·11–0·16	0·47–0·91	—
Chondrodite	0·36*	—	0·54
Phlogopite	0·45–0·76	—	0·11–2·41
Phlogopite in pyroxenite dikes ...	3·36–13·50	—	—
Biotite	0·08	—	—
Clintonite	—	—	1·18
Pargasite	0·42	0·44*	0·05–0·45
Alkali-spinel	0·29	—	—

* From a previously unpublished analysis by the present author.

Of the oxidation ratios of the minerals within the contact zone of the granite itself, metamorphosed by the interchange with the limestone, no analyses are available, the only guidance being the approximate compositions as deduced from the optical data and some rock analyses. The hastingsite character of the amphibole around Tennberg has already been emphasized as evidence of reducing atmosphere in the vicinity of the contact. The pyroxene-gneiss, which at Mansjö replaces the amphibolite at the tapering ends of the limestone layer, shows an atomic oxidation ratio of 0·09 against 0·11 for the amphibolite; and that of the Mansjö granite drops from 0·03 to 0·00 at the contact. At Pargas the

'lime-gneiss', which according to Laitakari adjoins the limestone, consists mainly of diopside and plagioclase and shows a very low oxidation ratio of 0·03. It grades outwards into amphibolites, however, of ratios ranging up to 0·86.

We may now turn to the parageneses of the alkaline limestones. Since the report on the alkaline rocks of the alkaline district of Alnö was published two years ago by the present author (4), the minerals have been subjected to continued research, partly in order to collect more evidence sustaining the petrogenetic hypothesis presented in the above-mentioned paper, and partly to fill a gap in our general knowledge of the composition of the minerals occurring in a well-defined alkaline rock suite. More than 60 new analyses have been executed and will give the base for a systematic account of the mineralogy of this region to be published next year. They furnish at the same time interesting data for a comparison with the previously treated Archaean parageneses. Before pointing out, however, conformities and differences we may shortly recapitulate what is known about the origin of the alkaline parageneses.

As previously emphasized, the active carrier of the energy is here the carbonate, which at about a depth of 6 miles below the erosion surface at that time forced its way upwards in the shape of a liquid of dolomitic composition rich in CO_2 and F. It was suggested by the present author that the gradual change to a calcitic carbonate at a depth of 2 miles resulted from a metasomatic exchange between the liquid carbonate and the solid wall-rocks, producing a desilication of the latter and a silication of the carbonatitic magma.

In consequence we have to deal with two different types of mineral parageneses: the one of the wall-rocks and the other of the intrusive. The latter in turn may be subdivided into four main groups, viz. those of the deep-seated rocks: alnöites, kimberlites, ouachitites, and beforsites; those of intermediate depths (3–4 miles): jacupirangites and vibetoides; and those at the focal depth of the first shattering brecciation of the overlying rocks (2 miles): sövites, alvikites, nepheline-syenites, and foyaïtic dikes. One must, however, keep in mind that there is no sharp limit between the different subdivisions, but that they grade into each other as follows: alnöites → kimberlites → beforsites –> alvikites and jacupirangites → vibetoides → nepheline-syenites → sövites.

The ionic flow across the intrusion contact is characterized by the movement of CO_2, OH, F, Ti, Ca, P, Ba, and K into the wall-rock and Si and Na in the opposite direction. This is quite the opposite of what

took place at Tennberg, where the silica and soda moved away from the source of energy and not towards it. If, however, we look at the phenomenon from a reaction viewpoint we find that in both cases the lime attracts the silica and soda irrespectively of its being the 'active' or the 'sleeping partner' of the metamorphosis, whereas the carbonic acid, liberated at the dissociation of the carbonate (or carried as such by the magmatic solution), behaves differently in the two cases. Set free at the Archaean limestone contacts at a temperature at which it carries a minimum of acquired energy, its oxidation power will necessarily be at the beginning very low but will increase as it moves towards the source of energy, viz. the granite. The resulting carbon monoxide will then acquire more thermal energy and exercise a reducing action on the femic minerals of the granite. This is quite in accordance with what may be deduced from the scanty data of the oxidation ratios of the Archaean contact occurrences.

On the other hand, the CO_2 of the Alnö carbonatite, charged from the beginning with the high thermal energy of the volcanic vent, may be expected to exercise a much stronger oxidizing influence on the minerals of the wall-rock, especially as its internal pressure at the same time must be supposed to have been very much higher than at a simple contact between fluid granite and solid limestone, where there should be plenty of room for the gas to escape through the granite.

As, however, the carbon dioxide is travelling in a direction away from the source of energy, its oxidizing power may be supposed to weaken fairly quickly. At the same time the carbon monoxide, resulting from the oxidation, will not carry enough energy but be chemically dead and unable to create any reduction zones within the migmatites constituting the wall-rocks. The adiabatic cooling of the gases, CO_2, F, and H_2O, will contribute to putting a comparatively early limit to the distance within which metasomatic reactions could take place. In other words, the depth of the fenitization zone depends largely upon the original energy (temperature + pressure) of the hyper-fusibles of the alkaline intrusion, and the minerals may be expected to show a radial reduction of oxidation values.

The oxidation of the minerals within the alkaline rocks of the intrusion may also, in consequence, be expected to stand in a certain relation to the dissociation of the carbonate, viz. to the presence of free carbonic acid. This means that the deep-seated dolomitic dikes should show comparatively low ratios and the rocks at the upper 'explosion'-focus, sövites and nepheline-syenites, comparatively high ones. This is verified

and borne out by the compilation of the oxidation ratios of the new mineral analyses, presented in table II. The highest average values are found in the nepheline-fenite, closely followed by those of the ultrabasic

TABLE II. Atomic oxidation ratio, $Fe^{...}$: $Fe^{..}$, of the minerals of the Alnö parageneses.

	Sövites and alvikites.	Pyrochlore-bearing sövite dike.	Nepheline-syenites, dikes included.	Ultrabasic alkaline rocks.	Alnöites and kimberlites.	Beforsites.	Ouachitites.	Nepheline-fenites, inner zone.	Nepheline-fenites, outer zone.
Andradite	—	—	2·50	—	—	—	—	5·25	—
Melanite	—	—	3·21	3·12–5·16	—	—	9·44	—	—
Aegirine-augite ...	0·63–2·17	2·44	0·89–1·03	0·85–1·55	—	1·56	—	2·56	0·70–1·02
Hornblende ...	—	—	—	1·59	0·65	—	—	—	—
Serpentine	—	2·92	—	—	—	—	—	—	—
Phlogopite	1·15	1·96	—	—	—	—	—	—	—
Biotite	0·20–0·82	—	—	0·89	0·37	0·40	—	—	—
Soda-orthoclase ...	2·50	—	4·55–5·50	—	—	—	—	9·10–0·00	3·42
Altered felspar* ...	—	—	—	—	—	—	—	4·50–4·94	2·23–3·57
Nepheline	—	—	2·23	3·01	—	—	—	5·05	—
Altered nepheline†	—	—	1·76	—	—	—	—	—	—
Cancrinite ...	—	—	5·10	—	—	—	—	—	—
Wollastonite ...	0·27	—	0·05	—	—	—	—	0·78	—
Sphene	2·16	—	—	—	—	—	—	4·52	—
Apatite	0·35–0·55	—	—	0·56	—	—	—	—	—
Titano-magnetite ...	2·03	2·15	1·32	2·02	—	—	—	—	—
Pyrochlore	—	9·04	—	—	—	—	—	—	—
Knopite	0·00	—	—	—	—	—	—	—	—

* Altering into montmorillonite → natrolite · → nepheline.
† Altering into haüyne and nosean.

rocks. As the latter were generated by crystal precipitation at an early epoch of the intrusion, the minerals reflect the very high concentration of CO_2 and comparatively high temperature ruling at that period. The average oxidation level then drops in the case of the nepheline-syenites and still more so in the sövites. This last fact is at first glance somewhat puzzling, but may be explained if we recall that at the time of the 'blowing up' of the diatreme the partial pressure of the CO_2 may have been very high (at least a thousand bars), but that at the same time the temperature was probably rather low. An outstanding exception is the very high oxidation ratio of the pyrochlore, which occurs in a sövite-dike together with phlogopite and aegirine-augite of exceptionally high ratios, 1·96 and 2·44 respectively. Exceptional circumstances must in this case have been responsible for the increased oxidation.

Another interesting feature is the remarkably high oxidation of the

melanite of the ouachitite dike intersecting the sövite of the central cone (Eckermann 4, p. 95). The chemistry of the dike is alnöitic, but the main mineral paragenesis quite different and very simple—melanite, biotite, and calcite. Of the original, probably dolomitic, carbonate nothing remains, but the calcite carries the indication of an earlier dissociation of the magnesite component in the shape of minute vesicles enclosing carbonic acid. The excess of CO_2, in consequence trapped in the dike, may satisfactorily explain the high oxidation ratio of the melanite. Probably the partly greenish biotite is highly oxidized too.

There are good reasons for supposing that in the different run of the oxidation process, viz. the different parts played by the carbonic acid at Archaean limestone contacts and in volcanic vents, may be found one of the answers to the question why in no single instance an alkaline trend of development has been encountered at the thousands of limestone-granite contacts observed in Fennoscandia. Another one may be given by the different behaviour of that most important of hyper-fusibles, the water. Round the 'passive' limestone it is concentrated at low tempera-ture in the pegmatitic rest-solutions, 'provoked into existence'—as I used to express myself in earlier papers—by the premature crystalliza-tion of the granite as a result of its enrichment with CaO, while in the case of the active carbonate it is forced by the CO_2 pressure at higher temperature into the surrounding rocks, establishing a 'hydration front' which advances as long as the energy supply from the volcanic vent is maintained. One should therefore expect conspicuous differences in the succession of minerals in the two instances, which is also found to be the case when compiling the parageneses, as has been done in table III.

The silicates of table III have been classified according to atomic structures and their 'dry' (D) or 'hydrous' (H) nature. Dominant minerals are given without brackets; one pair of brackets signifies that the mineral occurs frequently, but in comparatively small amounts, while two pairs denote it as rare. Several minerals have not yet been satisfactorily classified by X-ray studies, as for instance the epidote, where Ito's solution with two linked polyhedra of O and OH around Ca may need confirmation. In the meantime I have adopted Strunz's classification of the mineral. Another doubtful item is the wollastonite, in which case the parawollastonite only has been investigated. The structure of prehnite is actually unknown, but may, according to Strunz, be a complex one. Its classification, together with the idocrase, is in consequence a symbolic one only. Finally, one may challenge the posi-tion of the analcime as it contains Si_4O_{12}- and Si_6O_{18}-rings in its three-

dimensional framework. All these minerals are marked in the table by a sign of interrogation.

Table III brings out the dominance of hydrous minerals in the case of the Archaean contact parageneses, especially within the silicates containing separate SiO_4 groups. But also within the silicates of silicon-oxygen chains and framework structures a close attention to the 'brackets' will lead to the same conclusion. Only in the case of the sheet structures, viz. the micas, clays, and chlorites, is the frequency of the minerals about equal.

Unfortunately the compilation of the minerals is in one respect not complete. The occurrence of sulphides includes several more species than is given in the table, as for instance blende, marcasite, and chalcopyrite, but the present author was prevented by unforeseen circumstances from working out their distribution in time for this paper. The same applies to rutile, haematite, and goethite. As all these minerals, however, occur as accessories only, their absence does not distort the validity of the broad view of their parageneses and comparison, which table III is meant to give.

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