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The metasomatic development of zoned ultramafic balls from Fiskenaesset, West Greenland

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ABSTRACT. This paper presents new data on the metasomatic development of zoned ultramafic balls from Fiskenaesset, West Greenland. Field and petrographic evidence indicate retrogression of original ultrabasic inclusions in acid country rock gneisses to serpentine-magnesite assemblages, followed by regional metamorphism and consequent development of the zonal structure upon metasomatic re-equilibration via a supercritical aqueous fluid phase confined to grain boundaries. The balls show varying degrees of deviation from an ideal sequence (antigorite-talc-tremolite-hornblende-chlorite-country rock) intimated by non-equilibrium thermodynamics, the currently accepted conceptual framework for the discussion of diffusion metasomatism.

Major and trace-element variations behave in a similar manner to those reported from other zoned ultramafic balls but fail to define the original country rock ultrabasic discontinuity unambiguously. It is tentatively suggested that application of the apparently systematic deviations from ideality may provide additional evidence.

The presence of a hornblende zone and absence of a continuous biotite zone are two significant differences from other zoned ultramafic bodies. The former may suggest increased mobility of the aluminium species at Fiskenaesset, the latter a lower temperature of formation or smaller K_2O content of the gneissic hosts.

ELEMENTAL transport via a fluid phase in crustal materials is currently gaining much attention (e.g. Fyfe *et al.*, 1978). In contrast to crustal-scale transport, metasomatism on a limited scale provides dimensional constraints which allow quantification of element migration. Here we provide new data on the metasomatic development of zoned ultramafic balls within Archaean gneisses from the Fiskenaesset region of West Greenland (Bridgwater *et al.* 1973). These rocks are particularly well suited for such a study, showing a regular, concentric mineralogical zonation, which enables chemical variations and migrations to be defined precisely. The system may be compared to an 'ideal' zonal sequence constructed from a well-developed theoretical background. Several previous studies of a similar nature are reported in the literature (see Brady, 1977 for references), but at Fiskenaesset the mineral zonation is distinctive.

The Greenlandic zoned balls are derived from ultrabasic inclusions in amphibolite-facies quartzofeldspathic gneisses, generally of granodioritic to tonalitic composition. The samples come from three localities, marked A, B and C on fig. 1. The Eskimo names to be found on most local topographic maps are as follows. A = Akugdlinguit, B = Mardlulukat, and C = Marrardlugtoq.

The gneisses were derived from acid igneous precursors during a late Archaean metamorphic-deformational event. There is no evidence that those at the above localities were ever in the granulite facies. The zoned balls range in diameter from *c*.60 cm to *c*.10 m and at each locality there are a dozen or more. The ideal sequence passes outwards from an antigorite core through zones of talc, light green tremolite and hornblende to an outer zone of chlorite, with only local development of a biotite skin. Fig. 2 shows the relationships of the outer zones. The 'white' zone at the top of the figure (marked as zone '3') is due to a decrease in the grain size of tremolite, and is not considered as a mineralogically distinct zone. Incomplete or partial metasomatism has commonly given rise to various combinations of mineralogical zones (*cf.* Read, 1934).

Mineral identification was assisted by X-ray diffraction, but the main analytical methods used in the study were X-ray fluorescence spectrometry

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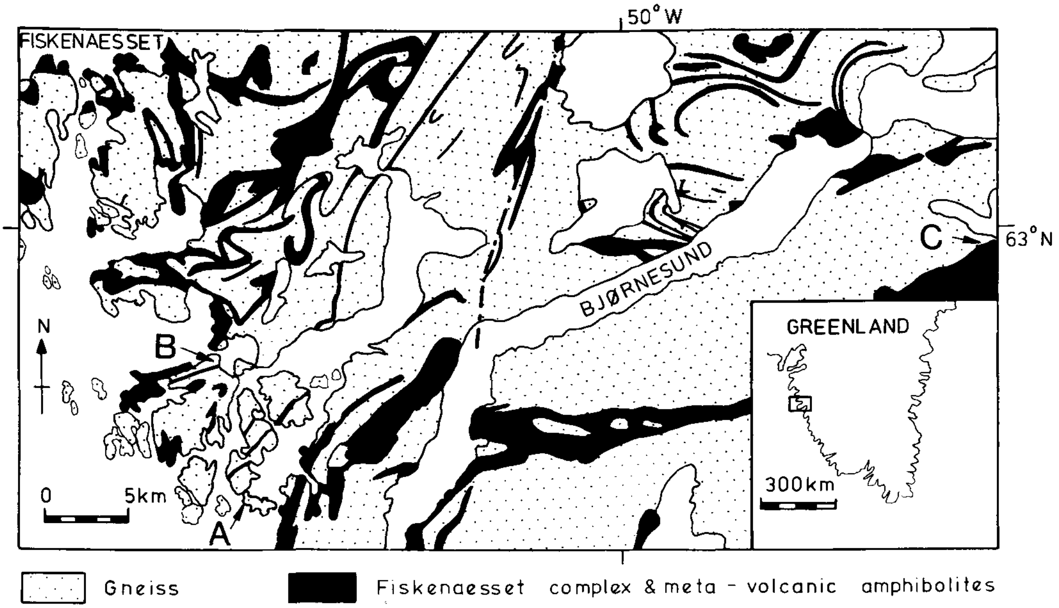


FIG. 1. Geological map of the Fiskenaesset region, showing the position of localities A, B, and C referred to in the text—modified after Kalsbeek and Myers, 1973.

at Birmingham University, using fusion discs for major elements and pressed powder pellets for trace elements, and electron probe microanalysis using the Microscan 5 electron probe at Leicester University. The operating conditions for the latter were 20 mA beam current at 15 kV; and the counts were processed by the Magic Correction programme, implementing full ZAF correction procedures.

Theoretical considerations. The spherical symmetry of the bodies is sufficient to suggest that metasomatic transport occurred by diffusion in a pervasive fluid phase (Hofmann, 1972), and textural evidence indicates that this was probably confined to grain boundaries. Therefore the effects of infiltration metasomatism (Korzhinskii, 1970) may be discounted. A brief review of the current theoretical treatment of diffusion metasomatism is therefore in order.

The conceptual framework favoured at present for the consideration of zonal metasomatism is the formalism of non-equilibrium thermodynamics. It has the advantage of considering diffusive transfer of material in terms of chemical potential gradients, which are more easily determined than the concentration gradients of Fick's Laws. Little can be added here to the detailed theoretical treatment of the subject—the reader is referred to the works of Weare *et al.* (1976), Frantz and Mao (1976, 1979), Fisher (1977), and Joesten (1977) for development of the basic concepts and specific theoretical models. Brady (1977) approached the problem in a different manner, utilizing chemical potential diagrams and mass-balance relationships to predict possible zonal sequences from given original compositions. He includes a brief review of previously reported zoned ultramafic bodies.

Both the direct manipulation of Fick's Laws of diffusion, and the formalism of non-equilibrium thermodynamics predict that if the reaction rate exceeds that of material transfer, (i.e. local equilibrium maintains), then the rate of the over-all process will be dependent upon the latter (Crank,

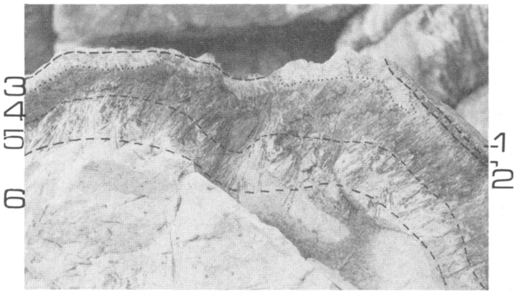


FIG. 2. Zonation of ball from locality A, showing white talc zone (6), passing outwards into green tremolite zone (4) through a transitional zone (5). Hornblende and chlorite zones (2 and 1 respectively) follow further outwards. (3) is a 'zone' of fine-grained tremolite. Width of visible zonation = 20 cm.

1975, p. 326). Hence the re-equilibration of chemically distinct rock units by diffusion via an intergranular fluid phase will produce a spatially organized series of zones with sharp boundaries arranged such that chemical potentials rise or fall in an orderly manner (Fisher, 1977, p. 384).

Mineralogy and petrology. The major components of the mineral species present in the ideal sequence are as follows: MgO, SiO_2, H_2O, CaO, Al_2O_3. Consideration of their relative abundances allows the construction of a simple representation of species mobility, fig. 3, based upon speciation in aqueous solution at 25 °C, 1 atmosphere and generally assumed to be applicable to higher temperatures and pressures in the absence of contradictory data (e.g. Curtis and Brown, 1969). The diagram is based on the assumption that an antigorite mass was the immediate forerunner of the zonal minerals. Unzoned serpentinite masses at all three localities support this assertion, but there is also field evidence for hornblendite or dunite as the ultimate ultrabasic precursors. Fyfe *et al.* (1978, p. 167) suggest that a common sequence of events is hydration to serpentinite under low-grade conditions, followed by regional metamorphism and associated zonal metasomatism. The mineralogical associations produced by the second metasomatic phase are described in detail below.

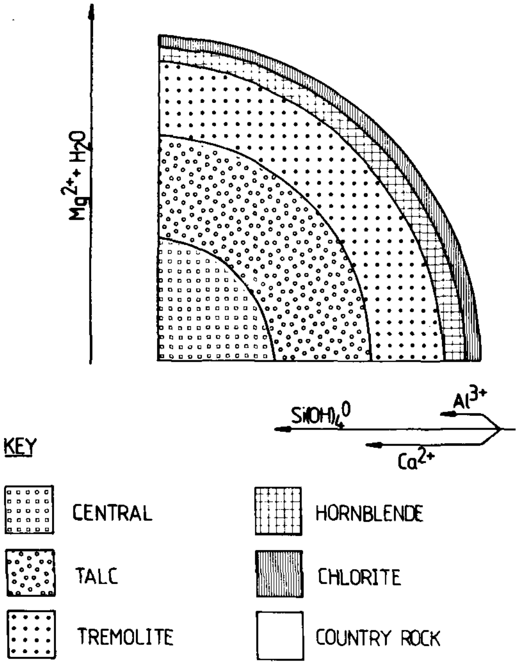


FIG. 3. Schematic representation of 'ideal' system showing over-all extent of component mobility, into and out of the balls. Here the central zone is pure antigorite.

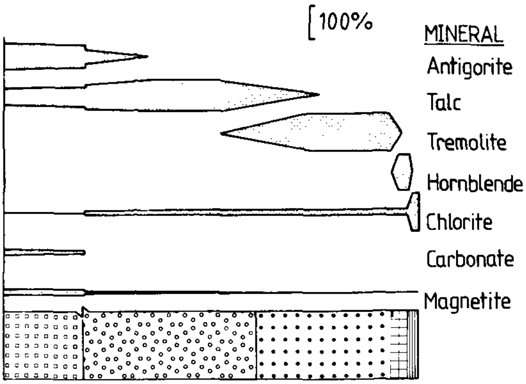


FIG. 4. Diagram representing the mineralogy of a ball from locality A, showing inward increase in zone transition width and number of minerals per zone. Key as in fig. 3.

The zonal mineralogy of the ball from locality A, as determined by optical microscopy and X-ray diffraction spectrography, can be most succinctly expressed in the form of a diagram, fig. 4. The central zone consists of a flaky aggregate of talc plates in which relic antigorite laths are randomly scattered, sometimes as isolated radiating masses. Magnetite polyhedra are abundant, nests of pale brown chlorite are not uncommon, and granular associations of a rhombohedral carbonate, probably magnesite, are widespread. The proportion of antigorite and magnesite falls with increasing radial distance, until the mineralogy represents the talc zone proper. There is no sharp boundary. The flaky talc matrix has a texture similar to that of the central zone, but antigorite and carbonate are absent. Isolated, elongate crystals of tremolite are present, and magnetite, though still quite abundant, has diminished.

The transition from the talc zone to the tremolite zone is *c*.5 cm wide (fig. 2), tremolite increasing rapidly to form a fibrous, interpenetrating mass. Chlorite and magnetite again form accessory minerals, but the habit of chlorite suggests that it is a late-stage alteration product. This zone terminates abruptly against stumpy, tabloid crystals of a dark green pleochroic hornblende with common chlorite and rare magnetite. The soft nature and thinness of the chlorite zone caused its absence from thin sections, and likewise the sporadic biotite skin. However, field and hand specimen observations indicate that the closest approximation to the monomineralic condition occurs in this outer chlorite zone.

Examples from locality B exhibit a less well-defined zonal sequence, most samples yielding multimineralic assemblages of minerals similar to those at locality A. The suite from locality C displays features which may be reconciled with more limited fluid activity in both metasomatic episodes; central relict pyroxenes with common dunites and thin zones forming only reaction rims. Biotite is more common here, due either to a higher K_2O content of the associated gneissic host rocks, or perhaps to a higher temperature of metasomatism. Some balls exhibit veins of tremolite-actinolite, caused by metasomatism at flat boundary zones, i.e. along fractures in the ultrabasic inclusion.

From the above descriptions it will be apparent that the samples deviate from a theoretically ideal situation (i.e. monomineralic zones with sharp boundaries) in varying degrees. These deviations may be categorized as follows:

(a) Truly monomineralic zones are rare, but the closest approximation is achieved in the outer, chlorite zone.

(b) There is an increase in the total number of mineralogical phases per zone towards the centre of the balls.

(c) There is a concomitant reduction in the sharpness of the replacement fronts.

Features similar to these were noted by Curtis and Brown (1969), Matthews (1967), and Read (1934).

Geochemistry. The results of electron probe microanalysis of the zonal minerals are presented in Table I, and those of X-ray fluorescence analysis of serial whole rock slices in Table II and figs. 5 and 6. Country-rock values are numbered only where they lie outside the range depicted, and are average values taken from Cheesman (1973).

The stability limits of the zonal minerals indicate that the temperature of formation was below ~ 500 °C, where serpentine becomes unstable in favour of forsterite + talc + H_2O (Winkler, 1974, p. 158). Authors of accounts of similar zonations (e.g. Curtis and Brown, 1969), have suggested that the fluid phase was supercritical in nature. These rocks display no features which require an alternative interpretation.

Figs. 5 and 6 reflect the chemical variations resultant upon diffusion-metasomatic reequilibration via such a medium. The culminatory behaviour of these major and trace element profiles is similar to that reported by Curtis and Brown (1969, 1971) and Matthews (1967). However, the MgO profile is anomalous in this respect, declining smoothly with only a small peak in the chlorite zone. Noticing a similar feature in rocks from Skye, Matthews (1967) attributed over-all control of the reaction sequence to the MgO concentration, but added that this factor may be over-ridden. However, the formation of the zonal sequence proceeds in order to produce smooth chemical potential gradients, which are not directly comparable with concentration profiles such as these.

Comparison of the trace and major element profiles reveals several examples of geochemical coherence—especially Sr with Ca, Rb with K, and Nb with Ti. These may be rationalized by consideration of the similarity in charge and ionic radius of the pairs, with crystal-field effects influencing only the Nb–Ti relationship.

The profiles reveal no 'inert markers' (Brady, 1977) which remain constant throughout the zonal sequence and hence identify the location of the original boundary between inclusion and country rock. Similarly, there are no constant elemental ratios, even those that generally show close geochemical coherence such as K/Rb, Ca/Sr, Al/Cr, Al/Ni. Thus precise identification of the original boundary is difficult on this basis. In Brady's (1977) discussion of ultramafic zonation he noted that when plotted on an AMS triangular diagram ($A = Al_2O_3 + Fe_2O_3$, $M = MgO + FeO + MnO$, $S = SiO_2$) the zonations show a marked discontinuity in relative A content between the actinolite and biotite (or chlorite) zones, and suggests that this might reflect the original boundary. However, the hornblende zone in the Fiskenaesset balls would appear to bridge the gap, and might indicate that here Al_2O_3 became a diffusing component. This further hampers determination of the original contact.

In recording deviations from ideality similar to those discussed here, Curtis and Brown (1969) proposed that they are a statistical effect with a Boltzmann distribution dependent upon the breakdown of local equilibrium, and that the original boundary must remain sharp. The sharpest boundaries in the Fiskenaesset balls lie either side of the chlorite zone. Thus, the evidence for the location of the original ultrabasic-country rock boundary is equivocal, and it is upon this that any proposed mass-balance calculations depend. Further work on these balls is planned, which may constrain the original boundary, when it should be possible to quantify migration in terms of mass-balance equations.

It is evident from the ideal zonal sequence (fig. 4), the electron-probe mineral analyses (Table I), and the whole-rock XRF results (Table II) that most zonal boundaries have a unique component species whose concentration abruptly increases at that boundary. This effect is most apparent at the outermost zonal boundaries, the abrupt increase being progressively blurred towards the centre of the ball. These species are analagous to the 'critical

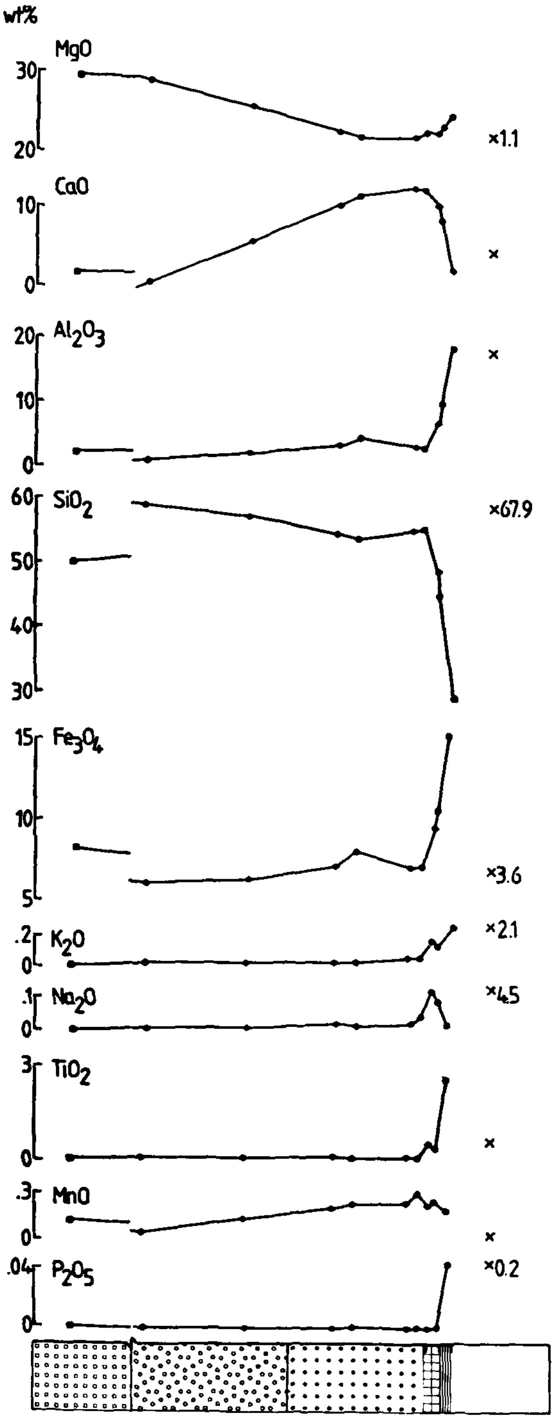
Table I. Average analyses of individual mineral species - by microprobe analysis except chlorite (XRF of virtually monomineralic zone).

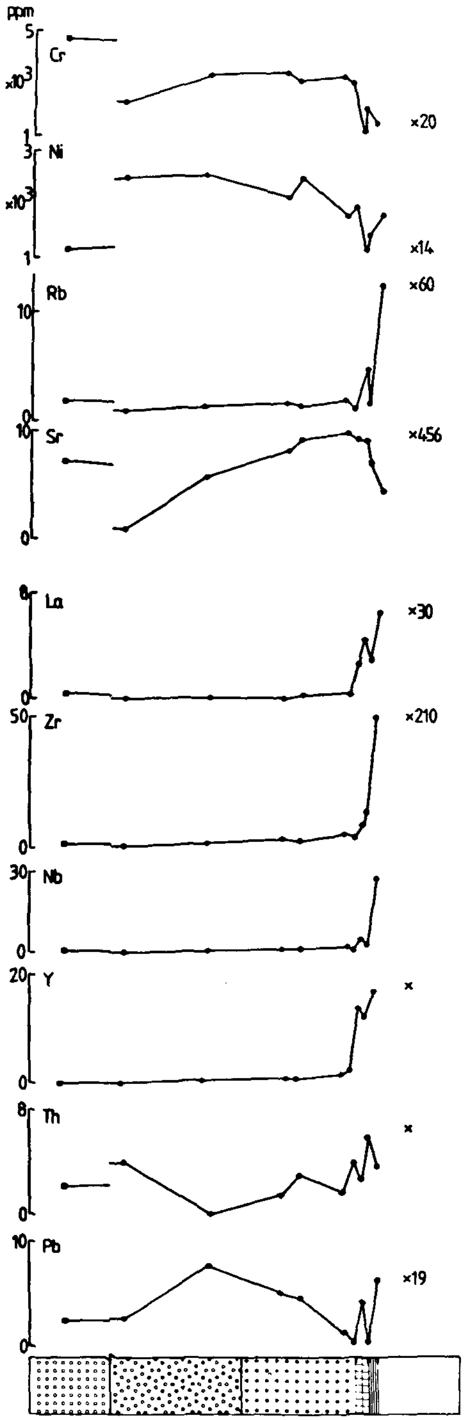
	Antigorite	Talc	Tremolite	Hornblende	Chlorite
SiO_2	42.84	61.38	56.01	53.95	28.72
TiO_2	0.03	0.01	0.03	0.08	2.41
Al_2O_3	0.87	0.06	0.53	2.71	17.11
FeO	1.66	3.28	5.59	7.31	14.84
MnO	0.08	0.05	0.22	0.27	0.18
MgO	40.66	28.20	20.20	19.47	24.28
CaO	0.04	0.04	12.97	12.37	1.46
Na_2O	-	-	0.10	0.44	0.00
K_2O	-	-	0.03	0.18	0.20
NiO	0.11	0.23	0.18	0.06	-
Total	86.29	93.25	95.86	96.80	89.28
Number of ions on the basis of (x) O,OH					
	(9)	(24)	(24)	(24)	
Si	2.130	7.988	7.814	7.634	
Ti	0.001	0.001	0.004	0.007	
Al	0.051	0.011	0.087	0.452	
Fe	0.069	0.357	0.661	0.864	
Mn	0.003	0.004	0.026	0.032	
Mg	3.021	5.470	4.200	4.106	
Ca	0.003	0.007	2.042	1.875	
Na	-	-	0.025	0.122	
K	-	-	0.005	0.032	
Ni	0.005	0.025	0.020	0.007	

Table II XRF analyses of a ball from locality A.

Sample no.	GGU68551	GGU68552/i	/ii	/iii	/iv	/v	GGU68553/i	/ii	/iii	/iv
SiO_2	50.37	58.89	53.14	54.77	44.13	28.72	56.96	54.32	54.48	48.35
TiO_2	0.07	0.02	0.03	0.03	0.30	2.41	0.04	0.04	0.06	0.41
Al_2O_3	2.06	0.68	3.46	2.13	8.78	17.11	1.54	2.36	2.50	6.17
Fe (total)	8.32	5.92	7.88	6.85	10.35	14.84	6.20	6.96	6.91	9.26
MnO	0.11	0.04	0.22	0.29	0.23	0.18	0.13	0.19	0.22	0.21
MgO	29.47	28.99	21.68	22.16	22.38	24.28	25.78	22.52	21.58	21.80
CaO	1.73	0.46	10.60	11.24	7.58	1.46	5.83	9.88	11.53	9.42
Na_2O	0.00	0.00	0.03	0.03	0.08	0.00	0.00	0.01	0.01	0.11
K_2O	0.00	0.00	0.00	0.02	0.08	0.20	0.00	0.00	0.02	0.11
P_2O_5	0.01	0.01	0.01	0.01	0.01	0.04	0.01	0.01	0.01	0.01
LOI	8.57	5.46	3.10	2.60	6.56	10.84	3.83	3.94	2.80	4.40
Total	100.71	100.47	100.15	100.07	100.48	100.04	100.32	100.23	100.12	100.25
Cr	4721	2321	3146	3021	2062	1529	3308	3471	3202	1154
Ni	1112	2483	2435	1830	1355	1714	2490	2051	1670	1056
Rb	2	1	1	1	3	12	1	1	2	4
Sr	7	1	9	9	7	4	6	8	10	9
Y	0	0	1	2	13	17	1	1	2	14
Zr	2	0	2	4	13	49	2	4	5	9
Nb	0	0	0	0	2	26	0	0	0	3
La	0	0	0	3	3	6	0	0	0	4
Pb	2	2	5	0	0	6	8	5	1	4
Th	2	4	3	4	5	3	0	1	1	3

68551 = central zone, 68552,3i = talc zone, ii = inner tremolite zone
iii = outer tremolite zone, iv = hornblende zone, v = chlorite zone.





FIGS. 5 and 6. FIG. 5 (*left*). Major elements variation diagram based on XRF analyses of locality A ball. FIG. 6 (*right*). Trace element variation diagram based on XRF analyses of locality A ball. Country rock average values are plotted from Cheesman (1973). Note the break in the scale between the central and talc zones—necessary for the inclusion of central analysis and those of the perimeter zonal sequence. Key as in fig. 3.

front-determining ions' of Carswell *et al.* (1974), and are as follows: antigorite-talc (Si(OH)$_4^0$); talc-tremolite (Ca^{2+}); tremolite-hornblende (Al^{3+}).

Carswell *et al.* (1974) gave an implicit definition of the front-determining ion in the following statement:

> 'The essential nature of a boundary (front) is that it separates (at any point in time) a region of flux from a region of zero flux for one component.'

In order to find a species conforming to this definition for the chlorite zone, it must be assumed that this zone is derived from the country rock due to the expulsion of material from the ball; Mg^{2+} then adequately fills this role. This suggests that the country rock-ultramafic discontinuity was originally located between the tremolite-hornblende and chlorite-country rock boundaries, though its exact position remains in doubt.

Conclusions. It seems likely that the zonal sequence observed in the Fiskenaesset balls is the result of re-equilibration under regional metamorphic conditions, probably in the upper greenschist or epidote-amphibolite facies, of a homogeneous antigoritic mass derived by hydration from pre-existing ultrabasic inclusions set in the gneissic host rocks. Comparison of these examples with other zoned ultramafic balls reveals many similarities in form and mode of formation—by grain boundary, diffusion-controlled reaction via a supercritical fluid phase. The presence of a hornblende zone is anomalous, and may reflect an increase in mobility of the Al species. Matthews (1967) noted the presence of interstitial hornblende in the biotite zone of zoned bodies on Skye. The limited appearance of biotite, as a sporadic surface skin to the chlorite zone, suggests either a lower temperature of formation, or perhaps a lower K_2O content of the tonalitic gneiss host at Fiskenaesset. The persistence of chlorite as an accessory mineral through the zonal sequence may be due to low-temperature alteration of the original zonal minerals.

It is worth emphasizing the apparently systematic departures from the ideal zonal sequence, in the locality A ball, which may be extended to encompass the low zonality and multimineralic nature of samples from locality B. This may have a bearing on the location of the original contact, which on geochemical grounds is equivocal, if boundary sharpness in reality decreases away from it.

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REFERENCES

Brady, R. (1977). *Geochim. Cosmochim. Acta*, **41**, 113-25.

Bridgwater, D., Watson, J., and Windley, B. F. (1973). *Phil. Trans. R. Soc. Lond. A*, **273**, 493-512.

Carswell, D. A., Curtis, C. D., and Kanaris-Sotiriou, R. (1974). *J. Petrol.* **15**, 383-402.

Cheesman, G. C. (1973). M.Sc. thesis Univ. of Birmingham. (Unpub.).

Crank, J. (1975). *The Mathematics of Diffusion.* Clarendon Press. Oxford.

Curtis, C. D. and Brown, P. E. (1969). *Contrib. Mineral. Petrol.* **24**, 275-92.

————(1971). Ibid. **31**, 87-93.

Fisher, G. W. (1977). *In*: Fraser, D. G. (ed.), *Thermodynamics in Geology.* D. Reidel, Dordrecht, Holland, pp. 381-403.

Frantz, J. D. and Mao, H. K. (1976). *Am. J. Sci.* **276**, 817-40.

————(1979). Ibid. **279**, 302-23.

Fyfe, W. S., Price, N. J., and Thompson, A. B. (1978). *Fluids in the Earth's Crust.* Elsevier, Amsterdam.

Hofmann, A. (1972). *Am. J. Sci.* **272**, 69-90.

Joesten, R. (1977). *Geochim. Cosmochim. Acta*, **41**, 649-70.

Kalsbeek, F. and Myers, J. S. (1973). Rapp. Grønlands geol. Unders. **51**, 5-18.

Korzhinskii, D. S. (1970). *Theory of Metasomatic Zoning.* Oxford University Press, Oxford.

Matthews, D. W. (1967). *Scott. J. Geol.* **3**, 17—33.

Read, H. H. (1934). *Mineral. Mag.* **23**, 519-40.

Weare, J. H., Stephens, J. R., and Eugster, H. P. (1976). *Am. J. Sci.* **276**, 767-816.

Winkler, H. G. F. (1974). *Petrogenesis of Metamorphic Rocks.* Springer-Verlag, New York.

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