Fluorapatites from the Skaergaard intrusion, East Greenland

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SUMMARY. The compositions of apatite crystals from seven Skaergaard rocks were obtained by electron-probe microanalysis. These span the range of occurrence from the base to the top of the exposed zones of the layered series. Apatite occurs as an intercumulus phase in the lower zones, but becomes a cumulus phase at a structural height of 1850 m (c. 98 % crystallized), defining the base of Upper Zone b. All apatite analyses show a high F:Cl ratio. There is a slight but significant increase in F and decrease in Cl when the apatite becomes a cumulus phase, the F/Cl values changing from < 10 to > 30. Variations in F:Cl:OH are attributed to differential volatile migration from trapped intercumulus liquid sites. The apatite data provide new support for ferrodiorite-granophyre liquid immiscibility.

THE petrological, mineralogical, and chemical properties of the Skaergaard intrusion have been studied extensively, up to and subsequent to the summary in Wager and Brown (1968). However, analyses of the apatite phase have not previously been made except for a study of the cumulus apatite from one Upper Zone (UZb) rock, EG4312, for rare-earths and other trace elements (Paster, Schauwecker, and Haskin, 1974). The electron microprobe permits analysis of low-abundance mineral phases and a reconnaissance of Skaergaard polished sections indicated that the compositional range could be obtained from a representative suite of seven samples.

Apatite occurrence. The 'cryptic' variation in the Skaergaard layered series of igneous cumulates consists of both continuous and discontinuous variations in the mineral compositions and assemblages, respectively, with fractionation. Whereas the continuous variation is reflected chiefly in the solid–solution compositions of the plagioclase, olivine, and pyroxenes, the discontinuous variation is characterized by the entrance and exit of particular mineral phases. One such example is the apatite phase, which did not separate as a euhedral cumulus phase (and thus participate in the crystal-sorting of the rhythmic layering) until a late stage in the fractionation of the basaltic magma body. It was estimated by Wager (1960) that this stage (UZb) was not reached until about 98 % of the body had crystallized. Although this model is in need of reassessment, there is no doubt that the magma did not become sufficiently saturated in phosphorus to precipitate apatite until it had advanced to the composition of a ferrodiorite representing a residual liquid with only about 10% or less of the original tholeiitic basalt volume. The maximum temperature of apatite crystallization would vary according to bulk magma compositions but the value proposed for Hawaiian tholeiite of about 1000 °C (Peck, Wright, and Moore, 1966) is of the right order for this stage of Skaergaard crystallization.

The gravity-deposited crystals of the layered series would have been enclosed by contemporary liquid, which, in many cases, crystallized as 'trapped liquid' (i.e. the orthocumulates of Wager, Brown, and Wadsworth, 1960). Hence, in the lower layered series (Lower Zone, LZ; Middle Zone, MZ; Upper Zone a, UZa), where apatite was absent as a cumulus phase, it could crystallize as an intercumulus, anhedral phase in the pore material produced during

advanced-stage crystallization of the trapped intercumulus liquid (*c.* 1000 °C). If this were so, one would not expect any difference in composition between the UZb and UZc (cumulus) apatites and the LZ, MZ, and UZa (intercumulus) apatites of the underlying layered series, since they would be precipitated at the same levels of phosphorus saturation and trace-element chemistry of the fractionating liquid.

In regard to phosphorus saturation, Henderson (1968) and Wager and Brown (1968) have postulated that P_2O_5 in the liquids increased progressively from about 0·2 % at the base of the exposed layered series until, when the amount had reached about 1·7 %, cumulus apatite separated from the liquid. Subsequently the liquid became depleted in P_2O_5, although cumulus apatite continued to form in the overlying UZc, and the later residual-liquid rock of the Sandwich Horizon (EG4330) and a melanogranophyre of the overlying Upper Border Group (EG5264) contain euhedral apatites suggestive of a relatively high P_2O_5 content in these liquids. The abundance patterns of P_2O_5 are illustrated by Wager and Brown (1968, tables 5, 6, and 10, figs. 109 and 115, plate 10). The habits of apatite, both intercumulus and cumulus, are illustrated by Wager and Brown (1968, figs. 50a, 61, 62). Modal apatite, where a cumulus phase, amounts to about 2 % of each rock.

Apatite analyses. Samples were analysed by electron microprobe (Appendix) from samples at various structural heights within the layered series and representative of LZa (100 m) and UZa (1650 m and 1800 m) for the range of intercumulus apatites, and UZb (2050 m), UZc (2350 m) and SHR (2500 m) for the range of cumulus apatites. A further sample was analysed from an Upper Border Group (UBGγ) melanogranophyre because, although the silicate mineralogy suggests an equivalence with the Upper Zone layered rocks (Wager and Brown, 1968, figs. 24, 90), such granophyres can more probably be viewed as the latest liquid fraction of the intrusion (*op. cit.*, p. 137) and may have crystallized from a siliceous liquid that was immiscible with the ferriferous SHR liquid (McBirney, 1975).

The analyses are given in Table I, from which it will be observed that the only chemical variables of major significance are the amounts of fluorine and chlorine and the F/Cl ratios. There is also a fairly sharp increase, in the latest differentiates, in the total rare-earth oxides.

The levels of abundance of the rare-earth oxides are appropriate to the apatites of generalized igneous rocks (e.g. Cruft, Ingamells, and Muysson, 1965; Stormer and Carmichael, 1971; Puchelt and Emmermann, 1976) although published apatite compositions from basaltic rocks are very rare and most data are for alkalic, granitic, and pegmatitic suites in which the abundances of the rare-earth elements (lanthanons) in the apatites are much higher than in the Skaergaard samples. Paster *et al.* (1974) detect 3000 ppm of Ln (chiefly Ce and Nd) in a Skaergaard UZb apatite, which is twice the abundance in apatite of metamorphic gneisses, about half the abundance in apatite of granites, phonolites, and carbonatites, and closest to a monzonite apatite with 3700 ppm (Puchelt and Emmermann, 1976). Our data suggest a range in total rare-earth element abundances of 1300 to 6200 ppm, the one low value for UZb (400 ppm) seeming anomalous although modal apatite is more abundant in this rock than in the others. The sharp rise to about 5000–6000 ppm of Ln in the apatites of the two latest differentiates indicates that since apatite is the only significant carrier of Ln in the Skaergaard mineral-phase assemblage, the precipitation of apatite at a slightly earlier stage (UZb and UZc) was not sufficient to deplete strongly the residual liquids in Ln. Paster *et al.* (1974, table 4) calculate about 240 ppm of Ln in the UZb parental liquid, whereas the average 2 % of modal apatite (3000 ppm of Ln) in the UZb rocks would only abstract about 60 ppm of Ln. Their calculations for the UZc parental liquid show about 500 ppm of Ln, which confirms that Ln enrichment has continued beyond the stage of apatite precipitation. Our data suggest that removal of about 2 % apatite (6000 ppm of Ln) from UZc liquids would only abstract at the level of about 120 ppm of Ln,

TABLE I. *Compositions (by electron probe) and formulae of fluorapatites from the Skaergaard intrusion*

	EG5107 LZa (100m)	EG4306 UZa (1650m)	EG5181 UZa (1800m)	EG4316 UZb (2050m)	EG4471 UZc (2350m)	EG4330 SHR (2500m)	EG5264 UBG
SiO_2 %	0.13	0.25	0.20	0.10	0.10	0.38	0.34
FeO	0.24	0.31	0.51	0.38	0.51	0.60	0.32
MnO	0.08	0.02	0.06	0.03	0.10	0.14	0.04
MgO	0.10	0.07	0.03	0.05	n.d.	n.d.	0.01
CaO	55.00	55.17	54.73	54.91	55.12	54.11	54.52
Na_2O	0.07	0.02	0.08	n.d.	0.01	0.07	0.13
P_2O_5	41.78	41.99	42.04	42.12	42.02	42.26	42.30
Ln_2O_3	0.39	0.16	0.41	0.05	0.15	0.61	0.73
Cl	0.42	0.25	0.35	0.05	0.04	0.06	0.11
F	2.81	2.58	2.65	3.64	3.14	3.30	3.54
H_2O^+	0.34	0.50	0.44	0.04	0.29	0.21	0.09
Total	101.36	101.32	101.50	101.37	101.48	101.74	102.13
Less O	1.28	1.14	1.19	1.54	1.33	1.40	1.52
Total	100.08	100.18	100.30	99.83	100.14	100.34	100.61
Unit formula							
Si	0.011	0.021	0.017	0.009	0.009	0.032	0.029
Fe	0.017	0.022	0.036	0.027	0.036	0.042	0.023
Mn	0.005	0.002	0.005	0.002	0.007	0.010	0.003
Mg	0.013	0.009	0.004	0.007	–	–	0.001
Ca	4.966	4.960	4.925	4.948	4.961	4.857	4.885
Na	0.012	0.004	0.013	–	0.002	0.012	0.021
P	2.981	2.983	2.989	2.999	2.989	2.998	2.995
Ln*	0.012	0.005	0.013	0.002	0.005	0.019	0.023
Cl	0.060	0.036	0.050	0.008	0.006	0.008	0.017
F	0.749	0.685	0.704	0.968	0.834	0.875	0.936
OH†	0.191	0.279	0.246	0.024	0.160	0.117	0.047
O	12.000	12.000	12.000	12.000	12.000	12.000	12.000
F/Cl (wt.)	6.7	10.3	7.6	72.8	78.5	55.0	32.2
Ln* (p.p.m.)	3300	1350	3500	400	1300	5200	6200

*Total rare earths expressed as Ln_2O_3 with Ln recalculated as elemental content (in p.p.m.) for comparisons in text.
†Hydroxyl (OH) by difference (F+Cl+OH = 1). H_2O^+ calculated from (OH).
First 3 analyses are intercumulus, and other 4 analyses are cumulus apatites.
The tabulated values are the averages of 1–7 grains analysed in each sample.
n.d. = not detected.

so there is abundant potential for Ln concentration in low-temperature, residual vein solutions from magma bodies of this type.

The halogen contents of the Skaergaard apatites (all of which are fluorapatites) provide an interesting pattern. The intercumulus apatites show a range of 2·37–2·81% fluorine and 0·25–0·52% chlorine. In contrast, the range for the cumulus apatites is 3·14–3·64% fluorine and 0·04–0·11% chlorine. The differences between the two assemblages are sufficiently large and consistent to be significant. The F/Cl values (by weight) differ appreciably as between 5 to 10 for the intercumulus, and 32 to 79 for the cumulus apatites. The hydroxyl values shown in Table I are, of course, not determinable by electron microprobe but are obtained by difference (F+Cl+OH = 1 for oxygen = 12). If the rule that (F+Cl+OH) = 1 is valid, then the calculated OH values become significant. The data in Table I indicate a reverse trend for (OH)

compared with F, such that the cumulus apatites show a marked fall in (OH) content compared with the intercumulus apatites.

Discussion. Apatite compositions have generally been considered in relation to isolated igneous bodies of strongly contrasted composition. In terms of apatite participation in crystal–liquid fractionation, this phase has been neglected relative to the silicate and oxide phases.

The Skaergaard intrusion provides evidence for the compositional variation of mineral phases, during progressive cooling from basaltic to ferrodioritic liquid, in the sequence of mineral layers upwards from the Lower Zone (LZ) and Middle Zone (MZ), through the sub-zones of the Upper Zone (UZa→UZb→UZc) to the residual ferrodioritic liquid of the horizon (SHR) sandwiched between UZc and the downward-crystallized Upper Border Group (UBG); the sandwich-horizon rock (SHR) contains pure fayalite and an Mg-free pyroxene on the Wo–Fs compositional join. Hence the only other residual liquid, apart from SHR, would be the one rich in silica and alkalis that gave rise to the melanogranophyres. Apatites from this extensive fractionation series have, up to now, been assumed to be isochemical and not affected by crystal–liquid fractionation. Exchange reactions between apatite and phlogopite, involving F–(OH) equilibrium distribution, have been used by Stormer and Carmichael (1971) to provide geothermometry data for certain igneous rocks, but there is no evidence for the coexistence of another hydroxyl-bearing phase with apatite in most of the Skaergaard sequence. Even so, their data on free-energy differences for fluorides, chlorides, and hydroxides would suggest that subtle variations in mineral F:Cl:OH ratios could occur as certain cation proportions vary in a fractionating magma body (i.e. Ca, Mg, Al, Na, K, Li, H).

Because apatite was not a separating cumulus phase through most of the Skaergaard cooling history, and because the other separating phases would not accept much of the available Ln from successive liquid fractions, such successive liquids would be expected to become enriched in Ln. This is not reflected in the abundances of Ln in the intercumulus apatites of the higher zones (UZa), and particularly not in the first cumulus apatites to precipitate (UZb, UZc). Presumably the level of acceptance of Ln in the apatites is controlled by temperature, oxygen fugacity, or other factors. The residual liquids, influenced by this low acceptance in earlier apatites and the low volume of apatite precipitation, must have become strongly enriched in Ln and this is ultimately reflected in the doubled Ln content of the SHR and granophyric apatites. Hence the apatites do show some compositional variation, but not significantly in regard to the refractory lithophile elements.

The volatile components show quite a different, variable distribution pattern. This causes us to consider that a process operated that was not simply related to crystal–liquid fractionation. There is a sharp distinction between the intercumulus and cumulus apatites in terms of their F:Cl:OH ratios. Since the precipitating crystal phases in the bulk of the layered series would reject F, Cl, and OH, simple crystal–liquid fractionation would increase these components in successive residual liquids. Apatite can only accept a fixed content of F+Cl+OH, and there is no experimental or theoretical evidence that can be used to suggest that the solid phase would discriminate between chlorine and fluorine, relative to the liquid phase. Available free-energy data that show a stronger preference for the calcium cation by the fluoride ion, compared with the preference by the chloride and hydroxyl ions, relate only to solid–solid partitioning (Stormer and Carmichael, 1971, table 1). In any case, differences in solid–liquid partitioning for F and Cl would not account for the sharp change in the F/Cl value and the (F+Cl):OH ratios between, say, intercumulus UZa apatite and cumulus UZb apatite, which crystallized at closely spaced layered horizons from liquids that would contain similar contents of F, Cl, and OH.

The critical distinction between the two types of halogen distribution does not, therefore,

seem related to fractionation stage but to the physico-chemical environment of apatite crystallization. In one group, the apatites crystallized late in the interstices of the crystal cumulates, after an appreciable fall in temperature of the crystal mush and in the presence of very little liquid. Migration of volatile components could have occurred by then, and if this were variable for F, Cl, and H_2O the apatite would reflect the $F:Cl:OH$ ratios only at the stage of final residuum crystallization. In contrast, the other group of apatites crystallized from the main bulk of contemporary magma at near-liquidus temperatures and would thus have $F:Cl:OH$ ratios unaffected by differential volatile migration (providing F did not migrate from the system into the roof rocks). If this reasoning is correct, then the analytical data suggest that the diffusion of volatile components from the intercumulus liquids was in the order $F > H_2O \gg Cl$.

A different aspect of the Skaergaard crystallization history is related to the apatites of the ferrodiorite (SHR) rock and the melanogranophyre (UBGγ) rock. Whereas the ferrodiorite is generally accepted as the residual product of Skaergaard fractionation, the melanogranophyre has been variously considered as due to incorporation of remelted country-rock gneiss or to silica-metasomatism of upper border group rocks that crystallized contemporaneously with the upper-zone layered rocks. Neither process would account for the close similarity of the SHR and UBG apatites in terms of Ln, F, and Cl contents compared with the other apatites (Table I). The alternative hypothesis, that the ferrodiorite and melanogranophyre liquids formed as immiscible liquid fractions at a simultaneous crystal–liquid fractionation stage (McBirney, 1975), cannot yet be confirmed from other mineral data but receives support from the apatite data.

Appendix. The electron-probe analytical procedures, standards, and ZAF corrections were as outlined by Sweatman and Long (1969) with the following additions:

Fluorine. The advent of thin-window detectors for electron-probe microanalysis now allows fluorine to be determined routinely in the quantitative analysis of minerals such as apatites or micas. Although the often-used Heinrich mass-absorption coefficients do not extend to fluorine $K\text{-}\alpha$ radiation, there are several published tables. For this study, the coefficients of Veigele *et al.* (in Birks, 1972) were used and fluorite (F = 48·7 %) was used as a standard. As a check on the internal consistency of these coefficients and of the ZAF procedure for such a long wavelength, a secondary (Norwegian apatite) standard was analysed both by electron probe and

TABLE II. *Comparison between wet-chemical analysis and electron-probe microanalysis for the halogen and hydroxyl contents of an apatite crystal*

Component	Method	Wt %	Standard deviation	Number of determinations
Fluorine	colorimetric	3.29	0.055	6
	probe	3.33	0.025	8
Chlorine	colorimetric	0.16	0.010	6
	probe	0.18	0.010	8
Water	gravimetric	0.11	0.015	4
	calculation†	0.18	—	—

† See footnote to Table I.

by wet chemistry. The colorimetric method of Huang and Johns (1967) was used for the halogens and the modified Penfield-tube method for water (> 105 °C). The results, tabulated below (Table II), show good agreement. The use of a PbO flux in the Penfield tube should aid water release at low temperatures but the gravimetric value quoted (Table II) may still err on the low side. The lower limit of electron-probe detection for fluorine is 230 ppm.

Rare-earth elements. These elements were analysed by electron probe using synthetic oxides as standards and the total amount is recorded as Ln_2O_3. The relative abundance of the individual rare-earth elements was Ce > Nd ⩾ Sm ⩾ La > rest. The individual and total concentrations were too low and therefore inaccurate, by this method, to be worth presenting as a chondrite-normalized pattern. The total Ln_2O_3 content is accurate to 25 % relative.

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