The Canadian Mineralogist
Vol. 32, pp. 149-158 (1994)

THE BEHAVIOR OF RARE-EARTH ELEMENTS IN HIGH-TEMPERATURE Cl-BEARING AQUEOUS FLUIDS: RESULTS FROM THE ØDEGÅRDENS VERK NATURAL LABORATORY

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ABSTRACT

The apatite from the ancient mines at Ødegården, northeast of Kragerø, South Norway, is known to be chlorapatite. Alteration during metamorphism involved the replacement of chlorapatite by hydroxyapatite and rare-earth phosphates, while hornblende developed elsewhere in the veins and in the country rocks. Ti-in-hornblende thermometry indicates *ca.* 700°C for this assemblage. The apatite provides a natural laboratory for the study of the behavior of the *REE* in high-temperature Cl-bearing aqueous solutions. La, Ce, Dy, Y, Na and Fe are leached from apatite, together with Cl. Coleaching of *REE* and Na indicates their coupled substitution in apatite. A different behavior is indicated for heavy and light *REE*, the latter being less depleted in Cl-poor apatite. Relatively more *LREE* precipitated as monazite than *HREE* as xenotime. The *HREE*-bearing complexes with Cl seem to have been more stable under the conditions described.

Keywords: apatite, rare-earth elements, mobility, hydrothermal, ore deposits, Ødegården, Norway.

SOMMAIRE

L'apatite des anciennes mines à Ødegården, au nord-est de Kragerø, dans le sud de la Norvège, a une composition proche de la chlorapatite. Une altération contemporaine du métamorphisme a causé le remplacement de celle-ci par une apatite riche en hydroxyle et des phosphates riches en terres rares, tandis que la hornblende s'est développée ailleurs dans le milieu, dans les veines aussi bien que dans les roches hôtes. La teneur de l'amphibole en Ti mène à une évaluation géothermométrique d'environ 700°C pour cet assemblage. Les cristaux d'apatite fournissent donc un laboratoire naturel pour étudier le comportement des terres rares en présence d'une phase fluide chlorée à température élevée. Les éléments La, Ce, Dy, Y, Na et Fe ont été lessivés de l'apatite, en même temps que le Cl. La cohérence des terres rares et du Na témoigne de leur couplage dans l'apatite. Nous démontrons un comportement différent pour les terres rares lourdes et légères, ces dernières étant moins fortement appauvries dans l'apatite à faible teneur en Cl. Une proportion relativement plus importante des terres rares légères a été fixée sous forme de monazite que de terres rares lourdes sous forme de xénotime. Les complexes chlorés responsables de la mobilité des terres rares lourdes seraient plus stables dans les conditions décrites.

(Traduit par la Rédaction)

Mots-clés: apatite, terres rares, mobilité, hydrothermal, gîtes minéraux, Ødegården, Norvège.

INTRODUCTION

The mobility, complexation and transport of elements, such as the rare earths, which commonly are used as petrogenetic indicators, are still some of the unsolved questions in geochemistry. Answers are far from unequivocal, and are mainly based on whole-rock chemical studies [see Table 1 in Grauch (1989)]. Knowledge of exchange with fluid and of breakdown of rare-earth-element-bearing minerals is fundamental to an understanding of such processes at the whole-rock scale.

Primary apatite from the old mines at Ødegården, southern Norway, approaches the Cl end-member. Along cracks, it is replaced by OH-apatite. The apatite is rare-earth-element-bearing and, therefore, provides an ideal opportunity to study the behavior of the rare-earth elements in the Cl–OH system in a natural laboratory. We studied the rocks by optical and cathodoluminescence microscopy, and analyzed apatite and coexisting minerals for major elements, halogens and rare-earth elements by instrumental neutron-activation techniques and electron microprobe. Results indicate different behavior of light (La, Ce, Nd) and heavy rare-earth elements (Dy and Y).

GEOLOGICAL SETTING

The Bamble Sector is part of the Mid-Proterozoic Southwest Scandinavian Domain (Gaál & Gorbatschev 1987). The lithologies and structural relations of the Bamble Sector have been elaborately described by Starmer (1990, 1991). A more detailed description of the geology of the Kragerø area is given by A. Bugge (1965). The area underwent amphibolite-facies metamorphism during the Gothian (Kongsbergian, 1.75–1.5 Ga) and Sveconorwegian (Grenvillian, 1.25–0.9 Ga) orogenies.

A century ago, this South Norwegian Precambrian coastal region, between Kristiansand and the Oslo Rift, was dotted with many small and some larger apatite mines (Helland 1874, Brøgger & Reusch 1875, Sjögren 1883, C. Bugge 1922). Among them was the ancient Ødegårdens Verk, to the northeast of Kragerø. The Ødegårdens Verk apatite deposits are situated in the eastern part of the Bamble Sector (Fig. 1); they were discovered in 1872, and were at that time the largest known phosphate deposits. The mines were jointly exploited by the Compagnie Française de Mines de Bamle, and Norwegian A/S Bamble Apatittgruber, and closed in 1918 (C. Bugge 1922).

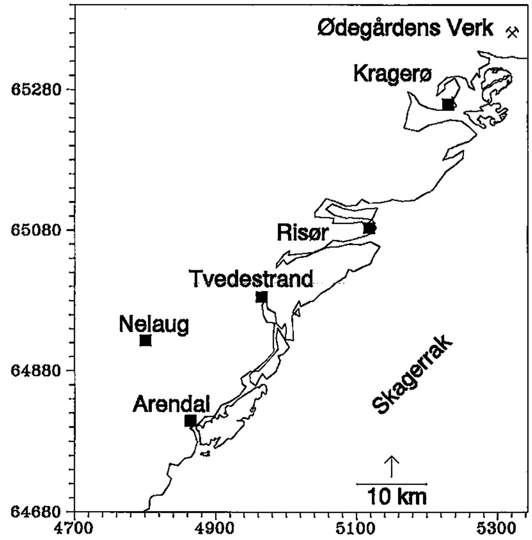

FIG. 1. Map of the Bamble Sector, southern Norway, with the ancient Ødegårdens Verk indicated. Coordinates are according to the grid of the Norges geografiske oppmåling. The precise coordinates of the Ødegårdens Verk are 5321, 65361.

At Ødegårdens Verk, apatite occurs in veins with phlogopite and orthopyroxene. The veins cut across scapolitized metagabbro, ("ødegårdites" in the sense of Brøgger 1934). Hornblende from the apatite veins has been dated at 1.03 ± 0.02 Ga (K–Ar; O'Nions *et al.* 1969). This most likely represents a cooling age, as dolomitic veins cutting across the apatite veins (A. Bugge 1965) have been dated at 1.18 ± 0.04 Ga (Sm–Nd; Dahlgren *et al.* 1993). Both the apatite and dolomite veins are intersected by microcline-bearing granitic pegmatites (A. Bugge 1965).

PETROGRAPHY AND EVOLUTION OF THE APATITE VEINS

The apatite-bearing veins, ranging from about 1 to 50 cm in width, have an outer zone of fine-grained phlogopite and an inner zone of coarse-grained phlogopite, with large crystals of apatite and aggregates in the center. Orthopyroxene and minor rutile occur dispersed throughout the veins (Fig. 2). Fragments of country rock occur in the veins (Brøgger & Reusch 1875). Orthopyroxene has generally been pseudomorphously replaced by talc (the "water-bearing enstatite" in the old Norwegian literature). Accessory phases are allanite, scapolite, nickeliferous pyrrhotite, chrysotile, titanite, hornblende, monazite, xenotime, carbonate-hydroxylapatite, whitlockite, woodhouseite and several unidentified phosphates (Neumann *et al.* 1960, Morton 1961, A. Bugge 1965, this study). The apatite veins are cut by late veinlets filled with calcite,

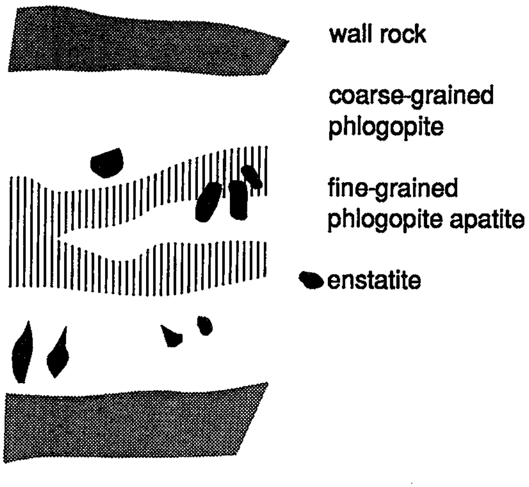

FIG. 2. Schematic drawing of an apatite – phlogopite vein. Modified after Brøgger & Reusch (1875).

chlorite, albite, chalcopyrite, quartz, pyrite, magnetite and tourmaline (Neumann *et al.* 1960).

The following successive assemblages of minerals occur in the veins: 1) chlorapatite – phlogopite – enstatite, 2) hydroxylapatite – hornblende – xenotime – monazite, and 3) chlorite – talc – albite – calcite.

Primary apatite (assemblage 1) consists of the Cl end-member, which is replaced by assemblage-2 apatite along fractures. The latter is a solid solution between Cl and OH end-members (Morton 1961, Morton & Catanzaro 1964). In thin sections, both types of apatite can clearly be distinguished by optical as well as cathodoluminescence microscopy (Fig. 3). The Cl-rich apatite is clear in transmitted light and is biaxial negative; it is light grey luminescent. Along cracks, the clear grains of Cl-rich apatite are recrystallized to a polygonal fabric of dusty, brownish apatite. This is the Cl-poor variety. This apatite is uniaxial negative and has a dark grey luminescence. The brownish color is due to precipitation of Fe-hydroxides. Very small grains of monazite and xenotime occur in the center of the cracks. Monazite is usually much more abundant. The replacement of chlorapatite occurred according to the reaction: chlorapatite + H_2O = hydroxyapatite ± rare-earth phosphates + Cl.

FIG. 3. Microphotograph of apatite from sample DL127. The Cl-rich apatite is clear, whereas the OH-rich apatite is dark and dusty. Width of field of view: *ca.* 2.5 mm.

Flakes of phlogopite have a preferred orientation and may be kinked. It has sporadically been altered to aggregates of talc and chlorite. The accessory hornblende is yellow to orange brown pleochroic. Hornblende overgrows the phlogopite.

A rutile – phlogopite – scapolite rock occurs in association with the veins, but the exact relationships are unclear.

The origin of the apatite veins has not definitively been established, but they are most likely magmatic, either as melts or as pneumatolytic deposits (A. Bugge 1965). A carbonatitic affinity has been suggested by Touret (1985). Exley & Smith (1982) demonstrated that "apatite – amphibole" liquids may result from fractionation of gabbroic magmas below the continental crust.

Assemblage 2 reflects the influence of amphibolite-facies metamorphism, which also caused the growth of hornblende in the surrounding gabbro (see below). The third assemblage reflects fluid infiltration under greenschist-facies conditions. Preliminary stable isotope data on calcite from this assemblage ($\delta^{13}C$ = –4.8 ‰, $\delta^{18}O$ = 10.9 ‰; M.A.T.M. Broekmans, T.G. Nijland, & J.B.H. Jansen, unpubl. data) are only slightly higher than those of the dolomitic veins in this area (Dahlgren et al. 1993); hence, assemblage 3 may be considered to be related to their formation.

PETROGRAPHY OF THE COUNTRY ROCKS

The surrounding country-rock, *i.e.*, the gabbro, has largely been transformed into a hornblende – scapolite rock. Locally, a subophitic texture has been preserved, with plagioclase laths and relict clinopyroxene (enclosed by hornblende). Aggregates of talc plus magnetite also occur, and are presumably pseudomorphic after orthopyroxene. Abundant rutile, and accessory apatite, zircon, ilmenite and phlogopite, also occur. Hornblende is altered to actinolite at its margin. Late epidote and chlorite also are present.

MINERAL CHEMISTRY

Analytical methods

The mineral analyses were performed with a JEOL JXA 8600 Superprobe at the Department of Geochemistry, Utrecht University. During a first session, the concentrations of Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, S, Cl and F were established; operating conditions were 15 kV, 10 nA and a counting time of 30 seconds. The concentrations of Ti, Mn, Na and F were established by wavelength-dispersion spectrometry (WDS), and the other elements, by energydispersion spectrometry (EDS). Natural and synthetic standards were used. As electron microprobe analysis of samples for the rare-earth elements (*REE*) requires operating conditions that prevent accurate analysis of those samples for the lighter elements like F and Na, the concentrations of the rare earths were measured during a second session. During this session, the samples were analyzed for the rare earths La, Ce, Nd, Dy, and Y, as well as for Si, Fe, Mn, Ca, P, S and Cl. Operating conditions were 25 kV, 40 nA and a counting time of 40 seconds. The beam was rastered and moved over a small area. Concentrations of the *REE* were determined by WDS. *Lα* peak positions were used for all *REE* determinations, and *REE* peak-overlap interferences were corrected for. Commercially available synthetic *REE*-oxide standards were used. Results of *REE* analyses were found to agree well with the expected values for the standards. Data were corrected with a Tracor Northern PROZA correction program. Selected results of mineral analyses are presented in Tables 1 and 2 for the major-element and *REE* sessions, respectively.

Trace elements were also sought from mineral separates using instrumental neutron-activation analytical (INAA) techniques at the Interfaculty Reactor Institute, Delft University of Technology. Nine separates of apatite, one of scapolite and one of phlogopite were analyzed (Table 3). Coarse grains were ground and purified by handpicking, and subsequently milled in a tungsten carbide mill. Details regarding INAA techniques can be found in De Bruin (1983). Concentrations of the *REE* have been normalized to the chondrite values of Sun & McDonough (1989).

The separates used were analyzed by conventional X-ray-diffraction techniques. The X-ray patterns confirm the existence of two types of apatite, a Cl-rich and a Cl-poor one. Both types of apatite can be distinguished by the method of Ekström (1973).

Neutron-activation results

Results of neutron-activation analyses indicate that the *REE* are present in considerable amounts (up to 1 wt.%) in the apatite from Ødegårdens Verk, whereas

TABLE 1a. CHEMICAL COMPOSITION OF PHLOGOPITE AND APATITE IN SAMPLE DL127I FROM THE APATITE VEINS

Mineral	Phl	Phl	Cl-Ap	Cl-Ap	OH-Ap	OH-A
Assembl.	1	1	1	1	2	2
SiO_2 wt.%	40.01	39.75	0.00	0.00	0.00	0.00
TiO_2	3.37	3.32	0.00	0.02	0.03	0.00
Al_2O_3	16.00	15.49	0.13	0.00	0.00	0.00
FeO	2.47	2.68	0.22	0.27	0.00	0.24
MnO	0.00	0.00	0.00	0.00	0.00	0.00
MgO	24.09	23.86	0.28	0.23	0.00	0.23
CaO	0.00	0.21	52.27	52.76	55.80	54.54
Na_2O	1.54	1.48	0.40	0.39	0.18	0.24
K_2O	7.83	7.49	0.10	0.00	0.00	0.00
P_2O_5	0.00	0.00	40.83	41.09	42.09	42.57
SO_3	0.15	0.00	1.45	0.95	0.27	0.42
F	0.71	0.75	0.37	0.08	1.00	0.19
Cl	0.15	0.16	5.64	5.32	0.59	1.38
Total	96.32	95.19	101.69	101.11	99.96	99.81
Si	5.57	5.60	0.00	0.00	0.00	0.00
Ti	0.35	0.35	0.00	0.01	0.01	0.00
Al	2.62	2.57	0.03	0.00	0.00	0.00
Fe	0.28	0.31	0.03	0.04	0.00	0.03
Mn	0.00	0.00	0.00	0.00	0.00	0.00
Mg	5.00	5.01	0.07	0.06	0.00	0.06
Ca	0.00	0.03	9.53	9.64	9.98	9.72
Na	0.42	0.41	0.12	0.12	0.06	0.08
K	1.39	1.35	0.02	0.00	0.00	0.00
P	0.00	0.00	5.88	5.93	5.95	6.00
S	0.02	0.00	0.18	0.12	0.03	0.05
F	0.31	0.33	0.19	0.04	0.53	0.10
Cl	0.03	0.04	1.63	1.54	0.17	0.39

Electron-microprobe data. The composition of apatite and phlogopite has been normalized to 25 and 23 atoms of oxygen, respectively.

TABLE 1b. CHEMICAL COMPOSITION OF CLINOPYROXENE, HORNBLENDE AND ACTINOLITE FROM COUNTRY-ROCK SAMPLE DL139

Mineral	Cpx	Hbl	Act
SiO_2 wt.%	52.14	41.05	47.26
TiO_2	0.00	1.43	0.77
Al_2O_3	0.00	9.07	5.67
FeO	12.02	24.11	19.81
MnO	0.21	0.15	0.19
MgO	10.94	7.06	10.55
CaO	23.27	10.51	11.07
Na_2O	0.70	2.18	1.32
K_2O	0.00	1.26	0.57
P_2O_5	0.00	0.00	0.00
SO_3	0.00	0.40	0.00
F	0.00	0.07	0.00
Cl	0.00	1.49	0.58
Total	99.28	98.78	97.79
Si	2.00	6.46	7.17
Ti	0.00	0.17	0.09
Al	0.00	1.68	1.02
Fe	0.39	3.18	2.52
Mn	0.01	0.02	0.03
Mg	0.63	1.66	2.39
Ca	0.96	1.77	1.80
Na	0.05	0.66	0.38
K	0.00	0.25	0.11
P	0.00	0.00	0.00
S	0.00	0.05	0.00
F	0.00	0.04	0.00
Cl	0.00	0.40	0.15

Electron-microprobe data. The composition of clinopyroxene and the amphiboles has been normalized to 6 and 23 atoms of oxygen, respectively.

TABLE 2. CHEMICAL COMPOSITION OF APATITE, MONAZITE AND XENOTIME

Mineral	Cl-Ap	Cl-Ap	Cl-Ap	Cl-Ap	OH-Ap	OH-Ap	OH-Ap	Mnz	Xen
Sample	TN174II	TN174II	DL129	DL129	TN174II	TN174I	DL129	TN174II	DL136
Assem.	1	1	1	1	2	2	2	2	2
SiO_2 wt.%	0.00	0.00	0.04	0.00	0.09	0.21	0.00	2.33	0.02
CaO	50.86	50.92	50.37	50.69	52.16	51.17	50.67	3.33	0.69
FeO	0.09	0.09	0.09	0.09	0.05	0.21	0.01	0.00	0.00
MnO	0.04	0.00	0.03	0.00	0.01	0.00	0.05	0.00	0.01
La_2O_3	0.07	0.04	0.14	0.09	0.07	0.04	0.06	21.80	0.00
Ce_2O_3	0.32	0.27	0.30	0.32	0.26	0.19	0.30	28.35	0.00
Nd_2O_3	0.19	0.19	0.28	0.30	0.22	0.21	0.21	7.00	0.30
Dy_2O_3	0.06	0.06	0.08	0.00	0.08	0.11	0.09	0.00	6.47
Y_2O_3	0.43	0.42	0.43	0.36	0.39	0.39	0.43	0.22	40.96
P_2O_5	40.28	40.92	39.82	39.71	39.99	39.30	40.72	29.72	29.17
SO_3	0.10	0.10	0.00	0.10	0.07	0.10	0.05	0.50	0.02
Cl	5.88	5.35	6.17	6.47	0.21	0.57	0.66	0.00	0.00
Total	98.32	98.36	97.75	98.13	93.60	92.50	93.25	93.25	77.64

Electron-microprobe data. The low totals for monazite and xenotime are due to lack of data for some of the REE.

Sc, V, As, Th and U occur in minor amounts (Table 3); Σ*REE* ranges from 6375 to 8875 ppm. $(La/Sm)_N$ and $(La/Yb)_N$ ratios vary between 0.8 and 1.3 and between 2.1 and 4.9, respectively. The Sc content of the apatite separates (≤2.8 ppm) is considerably lower than that obtained by Neumann (1961) for both red (10 ppm) and green (500 ppm) apatite from the same locality; the reason for this is unclear.

TABLE 3. CONCENTRATION OF TRACE ELEMENTS IN MINERAL SEPARATES

	Ap	Scp	Phl
Sc ppm	0.12 - 2.77	0.30	44.3
V	41 - 92	-	3160
Mn	46 - 299	-	24.1
Br	≤ 12.1	328	-
As	7.1 - 87	-	-
Sr	180 - 400	100	-
La	670 - 825	8.5	2.23
Ce	2250 - 2670	20.3	5.1
Pr	380 - 480	-	-
Nd	2030 - 2640	11	-
Sm	381 - 640	2.83	0.70
Eu	43.6 - 80.7	0.94	0.22
Gd	≤ 470	-	-
Tb	53.7 - 120	0.44	0.15
Dy	386 - 837	-	-
Ho	≤ 135	-	-
Er	≤ 330	-	-
Yb	108 - 268	1.17	0.4
Lu	16.5 - 42.7	0.21	0.07
Th	34 - 170	0.65	0.50
U	4.7 - 40.7	-	-

Results of instrumental neutron-activation analyses. Symbols: Ap apatite, Scp scapolite, Phl phlogopite.

Data on levels of Br in apatite are very scarce in literature, but tend to range between 1.3 and 5.5 ppm for phosphate apatite (Behne 1953, Reed & Van Allen 1966, O'Reilly & Griffin 1992). The maximum Br-content of the Ødegårdens Verk apatite (≤12.7 ppm) is relatively high. Carbonaceous apatite, however, may contain similar or even higher amounts of Br (5–40 ppm; O'Reilly & Griffin 1992). Scapolite from the associated rutile – phlogopite – scapolite rock, which is a nearly 100% Cl end-member, also contains minor amounts of Br (Lieftink *et al.* 1993). In the apatite – phlogopite veins, both primary apatite and phlogopite contain trace amounts of iodine (6.3 and 1.8 ppm, respectively; de Fellenberg & Lunde 1927).

Chondrite-normalized *REE* patterns of the Ødegårdens Verk apatite all have a convex shape (Fig. 4). They show a negative europium anomaly; Eu/Eu^* ratios vary from 0.38 to 0.96. It should be kept in mind that the separates analyzed are bulk samples, and contain both Cl-rich and Cl-poor apatite, as is confirmed by the X-ray study. The most important feature in Figure 4 is the lower content of *HREE* in the samples DL139, DL134 and DL127. These three samples contain a larger modal proportion of Cl-poor apatite than the other six samples.

The *REE* contents of the phlogopite and scapolite are considerably lower than that of the apatite. The chondrite-normalized *REE* pattern of phlogopite is rather flat (Fig. 4), as is commonly observed in phlogopite and biotite (*e.g.*, Roaldset 1975). The *REE* pattern of scapolite is similar to that of phlogopite, but displaced downward (Fig. 4). The absence of a

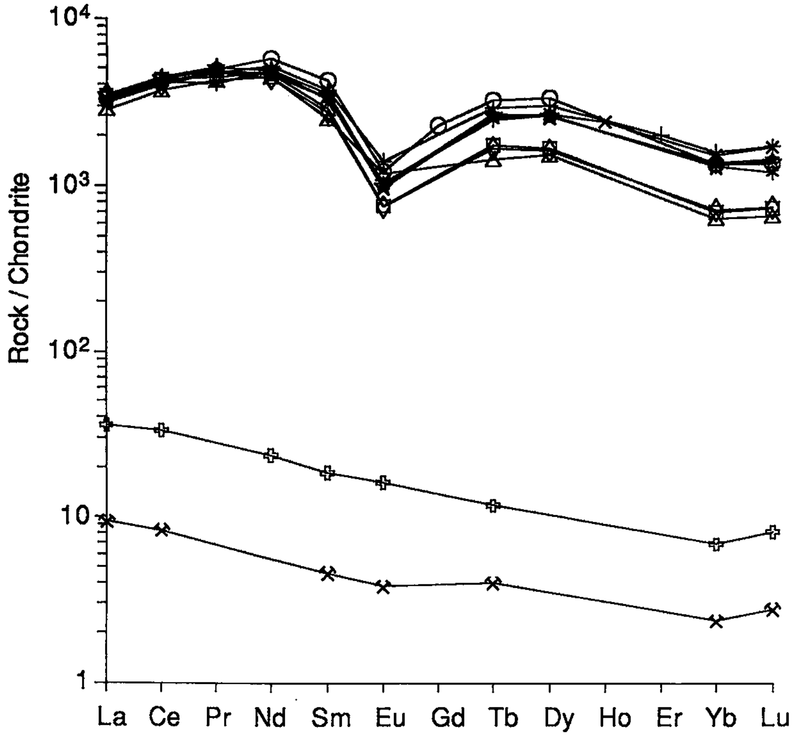

FIG. 4. Chondrite-normalized *REE* patterns for apatite, phlogopite (mine symbol) and scapolite (Swiss cross).

europium anomaly in the pattern for scapolite is remarkable, as it is commonly developed in most Ca-silicates (Lieftink *et al.* 1993).

Electron-microprobe data

The analyses of apatite show a large variation in chlorine content, from 0.21 to 6.74 wt.%. Fluorine varies from 0.08 wt.% in Cl-rich apatite (assemblage 1) to 1.14 wt.% in Cl-poor apatite (assemblage 2). A histogram of the Cl-contents of apatite shows a distinctly bimodal distribution (Fig. 5). Al, Fe, Ti, Na, Mn, Si, K and S are present in small amounts (Table 1a).

Electron-microprobe analyses obtained during the *REE* session have totals that are slightly too low (Table 2) owing to the extreme operating conditions. Some volatilization occurred, but the inferred stoichiometry of the minerals is good, considering the Ca/P ratios. The analyses show the presence of La, Ce and Y in all separates, whereas Nd and Dy are common (Tables 2, 4). The Dy and Y contents of the Ødegårdens Verk apatite ($Dy_2O_3 \leq 0.17$ wt.%, $Y_2O_3 \leq 1.09$ wt.%) are relatively high with respect to apatite from other rock types (Table 4). The *REE* contents obtained by electron microprobe are similar to those obtained by neutron activation.

To study the relation between the *REE* contents of apatite and the replacement of Cl-rich by Cl-poor apatite, profiles have been analyzed over alteration zones in which this replacement occurs. A profile from Cl-rich to Cl-poor and back to Cl-rich apatite along a traverse on Figure 3 is shown in Figure 6. In the first diagram (Fig. 6a), the normalized levels of Cl of the apatite are shown. They show a considerable drop in the percentage of chlorapatite. The La, Ce, Nd, Dy, Y, Fe and Na-contents are shown in Figure 6b. All clearly decrease with decreasing Cl-content.

As with apatite, the *REE* phosphates also show low totals (Table 2). For the latter, this may partly be because not all *REE* have been determined (*e.g.*, Pr, Sm, Eu). The Nd content of monazite is unusally low, but lower values have been reported (Table 4). The Dy and Y contents are relatively high, as has been observed in the apatite (Table 4). The composition of xenotime does not differ significantly from that analyzed from other rock types (Table 4). The Ce and Nd contents are very low, and La has not been detected.

The phlogopite has a Mg# [= Mg/(Mg+Fe)] of 0.94.

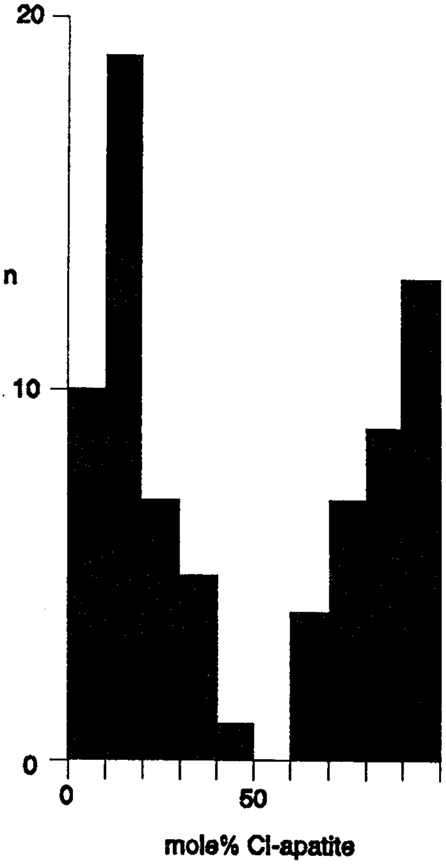

FIG. 5. Histogram of the Cl contents of apatite. The data used were obtained from both the "major" and "RE element" sessions ($n = 75$). The mole % of Cl-end member apatite was calculated as Cl/6.8.

TABLE 4. COMPARISON OF REE CHEMISTRY OF APATITE, MONAZITE AND XENOTIME

Apatite	1	2	3	4
La_2O_3	≤ 0.14	0.03 - 0.80	0.22 - 0.35	nd
Ce_2O_3	0.09 - 0.37	0.07 - 1.49	0.52 - 0.65	0.04 - 0.10
Nd_2O_3	0.09 - 0.33	0.05 - 0.52	0.11 - 0.18	≤ 0.18
Dy_2O_3	≤ 0.17	nd	nd	0.10 - 0.14
Y_2O_3	0.15 - 1.09	0.02 - 0.25	nd	0.09 - 0.71

Monazite	1	2	3	4	5
La_2O_3	9.91 -13.78	13.25 -31.24	2.80 -17.80	6.88 -17.98	9.38 -11.05
Ce_2O_3	26.20 -29.80	3.70 -32.09	15.60 -33.80	25.49 -33.73	30.77 -32.19
Nd_2O_3	7.00 -14.72	5.41 -19.31	1.20 -30.50	10.96 -26.49	17.73 -20.83
Dy_2O_3	0.22 - 1.13	nd	nd	nd	0.20 - 0.27
Y_2O_3	0.17 - 2.25	nd	0.10 - 4.70	nd	0.87 - 0.96

Xenotime	1	2	3
La_2O_3	nd	nd	nd
Ce_2O_3	≤ 0.04	nd	nd
Nd_2O_3	0.03 - 0.49	nd	≤ 0.38
Dy_2O_3	4.23 - 6.47	1.80 - 7.60	3.58 - 7.02
Y_2O_3	40.38 - 40.96	38.80 - 55.10	42.48 - 47.88

Apatite: 1 Ødegårdens Verk, 2 Gabbroic intrusions and alkali basalts (Nash 1976, Exley & Smith 1982, Boudreau et al. 1986, Boudreau & Kruger 1990, Drinkwater et al. 1990), 3 Selligdar-type ores (Entin & Tyan 1989), 4 Gloserhei pegmatites (Åmli 1975). Monazite: 1 Ødegårdens Verk, 2 Selligdar apatite ores (Entin & Tyan 1989), 3 Alpine veins (Mannucci et al. 1986, Demartin et al. 1991a), 4 Fen carbonatite (Andersen 1986), 5 Gloserhei pegmatites (Åmli 1975). Xenotime: 1 Ødegårdens Verk, 2 Alpine veins (Demartin et al. 1991b), 3 Gloserhei pegmatite (Åmli 1975).

It contains significant amounts of Na, the sum of K+Na+Ca varies around 1.80 atoms per 22 atoms of oxygen, and the Na/K ratio is 0.30. The Cl content is low, approximately 0.16 wt.%; F ranges from 0.71 to 0.75 wt.%.

The clinopyroxene in the country rock is Al-free, with trace amounts of Na (*ca.* 0.7 wt.% Na_2O). The Mg# is 0.61. The replacing hornblende is Cl-, Ti- and alkali-rich (Table 1b). Cl and TiO_2 vary between 1.49 and 1.71 wt.%, and between 1.28 and 1.48 wt.%, respectively; F is less than 0.09 wt.%. The *A* site is almost entirely filled with Na + K. The hornblende contains traces of SO_3 (0.20–0.43 wt.%), and has a Mg# of 0.31 to 0.34. Along its margin, the hornblende is zoned outward into Al- and alkali-poor actinolitic hornblende to actinolite, with F less or equal to 0.04 wt.%, Cl in the range 0.06–0.58 wt.%, and TiO_2 less or equal to 0.77 wt.%. Mg# shows a large spread between 0.49 and 0.67.

DISCUSSION

The timing of alteration in the Ødegårdens Verk apatite veins cannot be determined absolutely. However, it involved the influx of an aqueous fluid phase that caused the growth of some hornblende in the veins. It seems likely that this same fluid phase was responsible for the widespread amphibolitization of the surrounding metagabbros. Hornblende from these metagabbros indicates temperatures of *ca.* 700°C, using the Ti-in-hornblende thermometer of Otten (1984). This finding indicates that the alteration of the Ødegårdens Verk apatite took place under relatively high-grade conditions. Remarkably, the effects documented are similar to the results from the low-temperature alteration of chlorapatite described by Boudreau & McCallum (1990; see below).

The convex shape of the chondrite-normalized *REE* patterns of apatite (Fig. 4) is due to the ionic radii of the *REE*. The ionic radii of Nd and Pr are closest to the ionic radius of Ca (*cf.* Shannon 1976). The apatite shows a negative europium anomaly, which indicates that the apatite veins crystallized from a differentiated magma, rather than from a hydrothermal fluid (Ayers & Watson 1992).

Microprofiles over alteration zones in apatite (Fig. 6) demonstrate that the *REE*, Fe and Na decrease simultaneously with Cl. The coleaching of the *REE* and Na indicates that they probably were incorporated

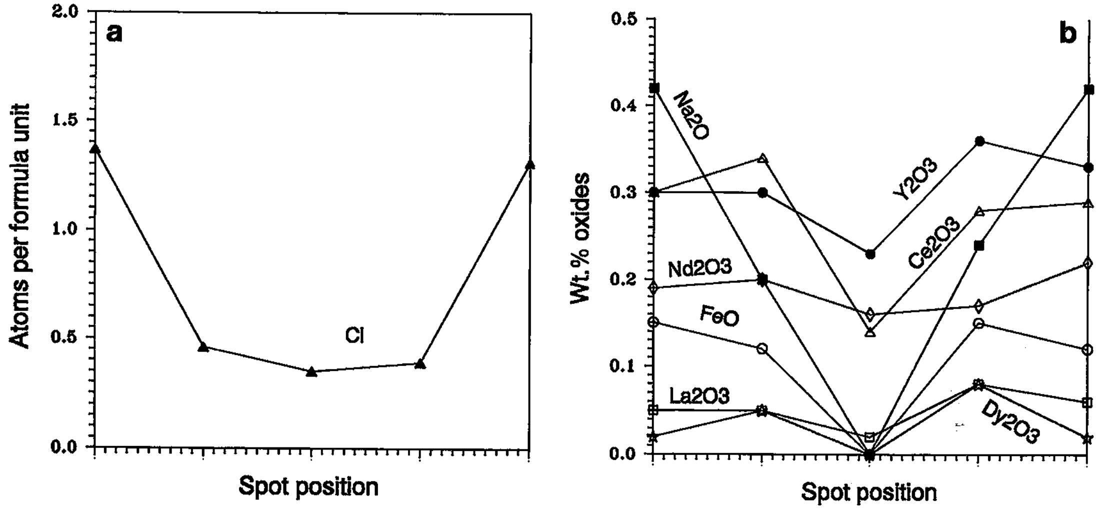

FIG. 6. Chemical profiles over a crack in apatite in Fig. 3. a. The Cl content of apatite, expressed in atoms per formula unit (calculated on the basis of 25 atoms of oxygen). b. The amounts of La, Ce, Nd, Dy, Fe and Na, in wt.% of the oxides.

by coupled substitution (*cf.* Rønsbo 1989, Hughes *et al.* 1991). As F contents are low in both primary and secondary apatite, the alteration mainly involved the replacement of Cl by hydroxyl groups. It is unlikely that the *REE* were complexed by OH groups. However, replacement of Cl by OH, and infiltration of a neutral aqueous fluid phase, will eventually result in an increasingly acid solution, at least within the cracks along which alteration took place. This locally increased acidity was responsible for the leaching of the *REE*.

Similar alteration has been described in low-temperature environments. Boudreau & McCallum (1990) described the leaching of chlorapatite in the Stillwater Complex (Montana); they observed a decrease of La and Si, and an increase in Fe and Mg with the replacement of Cl by OH. Soubiès *et al.* (1991) reported supergene alteration of primary F–OH-bearing apatite in P–Ti ores from Minas Gerais (Brazil). In this case, the secondary apatite is strongly enriched in F, and depleted in the *REE*. The sharp reaction-fronts and the location of the leached zones along cracks in all cases indicate that halogen re-equilibration in apatite occurs by recrystallization and not by solid-state diffusion (*cf.* Tacker & Stormer 1989, Boudreau & McCallum 1990).

No differences are observed in the behavior of the *LREE* and *HREE* in the microprofile (Fig. 6). However, INAA analyses of bulk separates show a difference in *REE* content between samples with a major component of Cl-rich apatite and those which mostly consist of Cl-poor apatite. The *LREE* are present in equal amounts in both types of apatite, but the *HREE* are more abundant in the samples that contain more Cl-rich apatite. This points to a preferred loss of *HREE* with leaching of Cl from apatite.

The leached *REE* are partly precipitated in the rare-earth phosphates monazite and xenotime, which are common in the central zones of the cracks. Monazite is more abundant than xenotime. This implies that the *LREE* were less mobile than the *HREE* under the same conditions of pressure, temperature, and activity of Cl and P. This is in marked contrast to the trend expected from partition coefficients for the *REE* between an aqueous fluid and apatite, which are much lower for Yb than Ce (Ayers & Watson 1992).

ACKNOWLEDGEMENTS

Ms. T. Bouten and Dr. R.P.E. Poorter assisted with the electron-microprobe analyses. T. van Meerten performed the INA analyses. H.M.V.C. Govers performed the X-ray-diffraction analyses. We thank Drs. R.F. Martin, R.N. Abbott, J.M. Hughes and A.E. Boudreau for their constructive comments. Financial support was provided by AWON (NWO 751.353.023, TGN).

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Received December 9, 1992, revised manuscript accepted April 22, 1993.