

Rare earth and other trace element mobility accompanying albitization in a Proterozoic granite, W. Bergslagen, Sweden

J. H. BAKER

Geologisch Instituut, University of Amsterdam, Nwe. Prinsengracht 130, 1018 VZ Amsterdam, The Netherlands

ABSTRACT. Zones of albitization 20 m wide are developed in the peraluminous, undeformed Proterozoic Bastfallshöjden granite, W. Bergslagen, central Sweden. During albitization Na, Si, Mg, Ni, Zn, and Ga are added, while Fe^{2+} , Fe^{3+} , Mn, K, Sc, Rb, Cs, Ba, Pb, U, and F are lost, together with the rare earth elements (*REE*) in decreasing amounts with increasing atomic number. Ti, Al, P, and Y were immobile. Trace element data for chlorites separated from hydrothermally altered country rocks and from a quartz-chlorite vein in the albitized granite show similar *REE* patterns indicating a common origin: the most altered granite has a similar *REE* pattern, probably resulting from interaction with the same hydrothermal fluid which produced the chlorites, in which seawater is thought to have been an important constituent.

KEYWORDS: rare earth elements, trace elements, albitization, Proterozoic, granite, Bergslagen, Sweden.

THE mobility of trace elements, in particular the *REE* and *HFS* (high field strength) elements such as Ti, Zr, Y, and Nb, during low-grade metamorphic and hydrothermal alteration processes is currently the subject of much debate. Discrimination between different magma types and/or their tectonic settings is often based on a supposed immobility of certain elements (e.g. Floyd and Winchester, 1978; Winchester and Floyd, 1976; Pearce and Norry, 1979). Nevertheless a growing body of evidence indicates that under certain, often extreme conditions of alteration, these elements are clearly mobile (Kerrick and Fryer, 1979; Hynes, 1980; Taylor and Fryer, 1982; Ludden *et al.*, 1982; Baker and de Groot, 1983a).

The Svecokarelian Bastfallshöjden granite is a small, high-level pluton, intrusive in a series of mainly submarine acid metavolcanic rocks (fig. 1), and has undergone partial hydrothermal alteration (albitization) under low water/rock mass ratios. A number of whitish albitization zones up to 20 m wide, and dyke-like in appearance, run approximately E.-W. through the pinkish granite, but

except for the difference in colour, they are macroscopically indistinguishable from the granite proper.

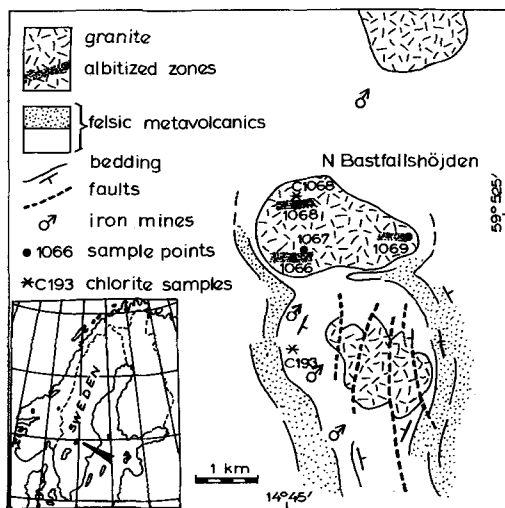


FIG. 1. Geological sketch-map of the area around Bastfallshöjden, showing whole rock and chlorite sampling points. Based on mapping by M. Melkert (unpubl. data).

Chemical data for the granite and the hydrothermal alteration zones presented here indicate varying degrees of mobility for the *REE* and some other elements during the albitization process, though there is no direct link between major element and trace element behaviour. The similarity in chemical data from chlorites separated from a quartz-chlorite vein in the albitized granite, and from adjacent hydrothermally altered felsic metavolcanics indicate a genetic link between the chlorites, and by analogy with sub-seafloor alteration zones near Hjulsjö, suggest an important

seawater role in the fluid causing the albitization of the granite.

Geological setting

The Bastfallshöjden granite with a surface area of approximately 3 km² belongs to a group of Proterozoic granites in W. Bergslagen which yield ages of about 1850 Ma (Åberg *et al.*, 1983 [U-Pb zircon]; Oen *et al.*, 1984 [Rb-Sr whole rock]). These Svecofennian granites have generally been referred to as Older Granites (Urgraniter) (Magnusson, 1925; Magnusson and Lundqvist, 1932) to distinguish them from the approximately 1700–1600 Ma Younger Granites (Welin *et al.*, 1977; Oen, 1982, 1983).

The granites intrude a thick succession of mainly submarine, acid pyroclastic rocks, recently called the Bergslagen Supracrustal Series, subdivided into three groups by Oen *et al.* (1982). The similar radiometric ages for the acid metavolcanic rocks (Welin *et al.*, 1980; Oen, in prep.), the granites (Oen and Verschure, 1982), greenstone dykes and skarn mineralization in the Hjulsjö area (Moorman *et al.*, 1982) led Oen *et al.* (1982) to suggest that the metamorphism of basic dykes, skarn formation, and the development of shear and schistose zones were all related to sub-seafloor metamorphic processes operating during the development of the supracrustal volcano-sedimentary sequence 1.9–1.8 Ga ago.

The stratigraphy of the metavolcanics around the Bastfallshöjden granite is still under investigation. The granite is intrusive in the subvertically dipping sequence, though in some places the contact runs parallel to the strike of the metavolcanics.

Petrography of the Bastfallshöjden granite

In the field the granite is pinkish, medium to coarse grained, and massive. Reddish feldspar predominates over colourless quartz and biotite, this latter being the only mafic phase, forming less than 5 vol. %. Except for their whitish colour, the alteration zones show the same macroscopic features as the pink host granite. The contacts between the zones and granite proper are diffuse, being gradational over about 10 cm.

In thin section the normal facies of the granite is seen to comprise large irregular microcline-microperthites up to 5 mm, and subhedral plagioclase, both partly replaced by newly formed microcline. Quartz forms large, recrystallized masses up to 5 mm, and is also interstitial. Grain boundaries between the older feldspars, and between these feldspars and the quartz are irregular and sutured. Progressive static recrystallization is apparent

throughout the granite, with the development of areas comprising equidimensional quartz and microcline aggregates, with a grain size of 0.1–0.2 mm, and triple junctions developing at the expense of the older parageneses. Oxidized, or locally greenish biotite is present as subhedral grains up to 0.5 mm, or forms poikiloblasts enclosing quartz and feldspar. Magnetite, generally associated with biotite, is abundant, and often has sphene rims developed around the edges. Sphene is also enclosed in biotite. Epidote and sericite are present in the plagioclase; zircon and apatite are accessory phases.

Narrow quartz-feldspar zones of recrystallization, 0.1 mm wide are weakly developed crossing the feldspars (fig. 2a).

One metre from a white alteration zone no major textural or mineralogical changes are apparent, though the feldspars are partly sericitized and more epidote is present. The number of small zones of recrystallization cutting the rock is seen to increase however.

In the albitized, whitish zone the feldspars are either chessboard albite or relict plagioclase, both partially sericitized. Some greenish biotite is present, mostly altered to chlorite which also fills cracks in, and replaces, the feldspar. Magnetite is virtually absent, and sphene is present along the chlorite cleavage planes. Calcite is also developed along some grain boundaries (fig. 2b).

In the most altered sample the feldspars are clouded, with blurred twin planes. Chessboard albite forms irregular grains up to 3 mm. Albitized plagioclase, up to 5 mm, forms an- to subhedral grains with sutured boundaries. The nucleation of new feldspar grains between mutually adjoining older feldspars is common. Relict, partially recrystallized granophyric intergrowths can also be recognized, testifying to the lack of a penetrative deformation. Quartz is anhedral, recrystallized, with sutured grain boundaries. Mafic phases are virtually absent. Biotite has been totally chloritized and occurs as small (0.2–0.5 mm), fine grained aggregates together with sphene. The narrow quartz-feldspar zones, sometimes containing chlorite, are abundant. Veins of quartz and chlorite up to 2 cm wide form discontinuous fracture fillings in outcrops of the most altered granite (fig. 2c), the chlorite also developed as impregnations in the granite.

Sample selection and analytical techniques

Two samples (1066a, 1069a) were selected for analysis from albitized zones, together with samples from the adjacent apparently unaltered granite (1066b, 1069b) for reference. In addition one sample of unaltered granite

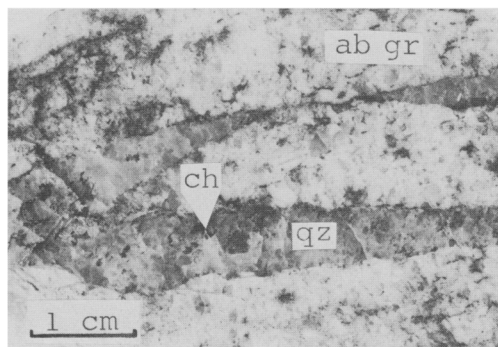
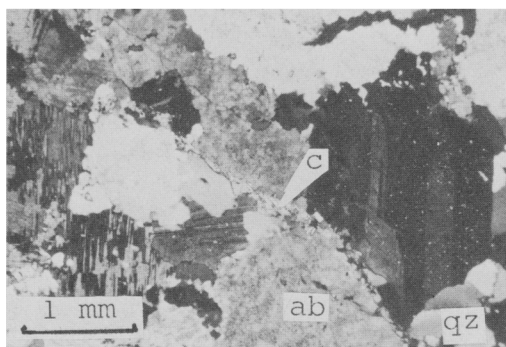
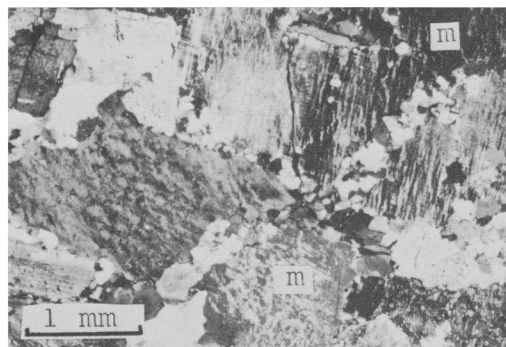


FIG. 2. (a), top (Bj 1066b, x-nicols) zone of fine grained quartz and albite crossing microcline microperthite in granite near to albitization zones. (b), centre (Bj 1066a, x-nicols) vein with calcite in albitized granite. (c), bottom (Bj 1068). Hand sample showing quartz-chlorite vein cutting albitized granite; ab, albite; ab gr, albitized granite; c, calcite; ch, chlorite; qz, quartz; m, microcline microperthite.

(1067) and one sample from another narrow, albitized zone (1068b) were also analysed.

Major elements were analysed on glassbeads prepared from powdered samples using standard XRF techniques. The trace elements Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, and Pb were analysed on pressed powder tablets using the

method of ViéLeSage *et al.* (1979). Sc, Co, As, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th, and U were analysed by INAA using the Interuniversity Reactor Institute (IRI) facilities in Delft. The relative accuracy for the INAA analyses can be found in Baker and de Groot (1983a). F was measured by standard addition using an ion selective anode. Accuracy is estimated to be within 5%. Chlorite samples were separated from crushed, washed, and sieved rock samples using a Franz isodynamic separator, and analysed for trace and some major element by INAA. Major elements were analysed in the chlorites with a Cambridge Instruments Geoscan microprobe operating at 20 kV, using silicate standards. Data reduction was done with an on-line ZAF correction program.

Major element chemistry

Six whole rock and trace element analyses for the Bastfallshöjden granite are presented in Table I, which is peraluminous with a high silica, and low Ca content. Specific gravity data are also given, essential for mass balance calculations to distinguish real from apparent gains and losses of elements during the alteration process. The three albitized samples show a gain in Si and Na, and loss of total Fe, Mn, and K. Looking at the albitized-unalbitized sample pairs (1066a, b and 1069a, b) it is apparent that there is also a slight gain in Mg, while Ti, Al, and P remain more or less constant. Ca is variable, gained by one sample, lost from the other. The effects of albitization on the alkali elements is best shown by the 'igneous spectrum' of Hughes (1972), where the samples are displaced out of the normal range of igneous values into the Na-enriched field (fig. 3). There is also a slight decrease in total Na-K content. The effect of albitization on the position of the samples in the Q-Ab-Or diagram of Tuttle and Bowen (1958) is equally pronounced (fig. 4a) displacing the altered samples to the Q-Ab join. In an AFM plot (fig. 4b) the samples are not greatly displaced if measured FeO is used, but if total iron is plotted as FeO, as is done by many workers, the loss of Fe in the altered samples drives them towards the A-corner, thereby developing a pseudo-calcalkaline trend. Albitization leads not only to a decrease in total iron, both FeO and Fe₂O₃, but also a modification of the oxidation ratio FeO/(FeO + Fe₂O₃) (fig. 5). Samples of ostensibly unaltered granite taken a few metres away from the albitized zones, though not showing significant petrological or other major element differences compared to the unaltered sample 1067, show a strong modification of the oxidation ratio, though total iron has not decreased significantly. From fig. 5 it is apparent that relative to unaltered sample 1067, the samples adjacent to the alteration zones show an increase in Fe₂O₃ and decrease in FeO, resulting in a decrease in oxidation ratio from

Table I.

Whole rock and trace element data: albitized samples 1066a, 1069a derived from 1066b, 1069b respectively; 1067 unaltered granite, 1068b is albitized. For locations see Fig. 1.

	1066a	1066b	1067	1068b	1069a	1069b
(wt%)						
SiO ₂	79.76	77.84	76.89	79.73	79.44	76.97
TiO ₂	0.106	0.109	0.136	0.082	0.110	0.111
Al ₂ O ₃	12.36	12.15	12.31	12.52	12.47	12.57
Fe ₂ O ₃	0.14	0.92	0.69	0.11	0.16	0.91
FeO	0.23	0.44	0.77	0.23	0.48	0.45
MnO	0.005	0.012	0.012	0.005	0.007	0.008
MgO	0.18	0.14	0.18	0.25	0.33	0.21
CaO	0.65	0.39	0.78	0.71	0.18	0.42
Na ₂ O	6.40	3.41	3.25	6.26	6.87	3.49
K ₂ O	0.24	4.59	4.42	0.30	0.14	4.39
P ₂ O ₅	0.021	0.020	0.028	0.042	0.035	0.042
Total	100.09	100.02	99.47	100.24	100.22	99.57
(ppm)						
Sc	1.487	2.166	2.374	1.406	1.91	2.09
Co	0.237	0.832	1.376	0.783	1.06	0.89
Ni	4.4	3.2	3.7	4.3	3.9	2.6
Cu	7.0	5.3	6.3	7.9	5.5	6.2
Zn	15.1	12.1	13.4	14.9	13.3	9.5
Ga	14.5	13.9	14.3	13.2	13.2	12.4
As	2.02	-	-	-	-	0.92
Rb	11.7	146.0	142.0	14.8	12.3	121.0
Sr	38.2	30.4	57.0	59.6	19.5	38.6
Y	42.0	42.0	32.6	34.1	27.3	27.7
Zr	88.0	105.0	106.0	85.7	96.0	94.7
Nb	10.3	12.9	7.6	9.6	7.4	6.0
Sb	0.82	0.396	1.19	-	0.218	-
Cs	-	0.734	1.219	-	0.233	0.564
Ba	-	663.3	675.7	87.2	62.0	800.0
La	36.68	60.66	57.01	2.12	43.56	88.06
Ce	61.86	82.54	85.76	2.64	103.40	107.30
Sm	4.46	7.35	5.87	0.57	4.75	10.20
Eu	0.468	0.612	0.571	0.174	0.366	0.923
Tb	0.791	0.970	0.683	0.321	0.623	0.943
Yb	4.251	4.847	3.288	3.285	2.936	2.623
Lu	0.698	0.647	0.579	0.575	0.504	0.469
Hf	3.954	4.332	3.970	4.155	3.60	3.56
Ta	1.08	1.163	0.796	1.043	0.804	0.676
Pb	4.4	10.5	9.3	5.0	8.7	9.5
Th	18.85	21.00	16.00	18.54	16.70	15.00
U	1.79	3.49	1.13	2.03	2.56	2.73
F	40.0	80.0	775.0	70.0	65.0	115.0
Specific Gravity						
	2.632	2.609	2.620	2.615	2.625	2.610

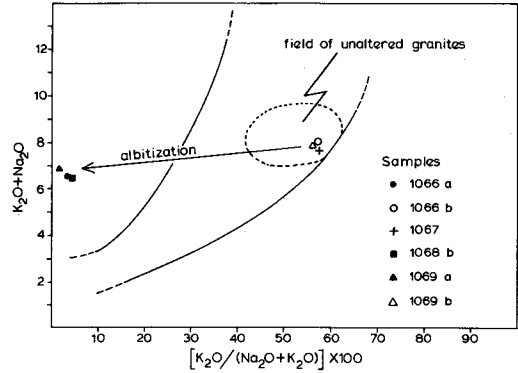


FIG. 3. Effects of alteration shown on the 'igneous spectrum' of Hughes (1972) where unaltered igneous rocks define a funnel shaped area. Albitized samples are displaced out of the field of unaltered granites.

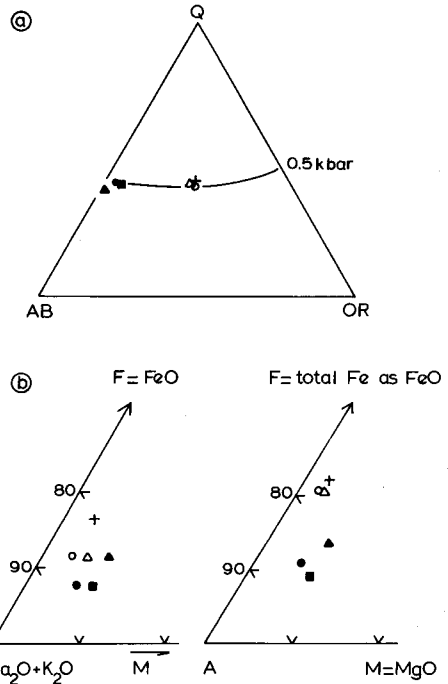


FIG. 4. (a) Q-Ab-Or plot (Tuttle and Bowen, 1958), for normative minerals, in which albitized samples are displaced to the Q-Ab join. (b) Expanded A-corner of AFM plot, for measured FeO, and for total iron calculated as FeO. Symbols as in fig. 3.

0.55 to 0.35, which increases to 0.65 in the albitized zones. Thermodynamic calculations (Jasiński, pers. comm.) for the dissolution reactions of magnetite and hematite to iron chlorides or hydroxides (using

the thermodynamic data of Robbie *et al.*, 1978), in the range $P \sim 2$ kbar, T 300–500 °C indicate that if Fe is being complexed with $(OH)^-$ it is removed as Fe^{2+} , with removal of $Fe^{2+} \gg Fe^{3+}$, but that

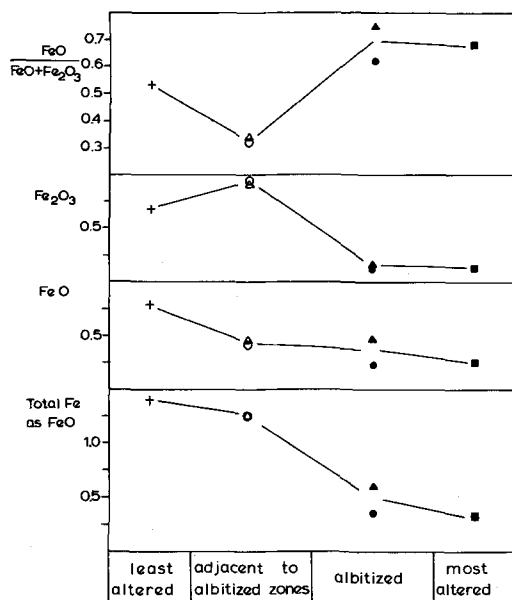


FIG. 5. Schematic diagram showing variation of FeO, Fe_2O_3 , total iron and the oxidation ratio $\text{FeO}/(\text{FeO} + \text{Fe}_2\text{O}_3)$, from least altered to most altered granite samples. Symbols as in fig. 3.

significant oxidation of Fe^{2+} to Fe^{3+} , will take place. If Fe is being complexed with Cl^- , the removal of $\text{Fe}^{2+} > \text{Fe}^{3+}$, both complexed as Fe^{2+} (i.e. Fe^{3+} is first reduced) though at higher temperatures the rate of complexing tends to be the same for both Fe^{2+} and Fe^{3+} . The granite samples adjacent to the albitized zones show higher SiO_2 and lower CaO values than the unaltered granite sample 1067.

Trace element chemistry of the granite

During the albitization process Ni, Zn and possibly Ga were added to the rock, while Pb was removed along with Sc, Rb, Cs, Ba, F, and U. The elements Y and possibly Hf were immobile. Of the REE, La, Ce, Sm, Eu and Tb were clearly leached; Yb and Lu were apparently less mobile. Other elements Co, Cu, Sr, Zr, Nb, Ta, and Th show no definite behaviour. If it can be assumed that sample 1067 has an unmodified chemistry and that this can be taken as approximately representative for the Bastfallshöjden granite (though elements such as Y indicate there are variations within this small pluton), then some generalized trends can be seen for certain elements, passing from least altered to albitized samples. Sc, Cs, and F show a decrease, Ni, Zn, and Ga decrease then increase, while U, La, Sm, Eu, and Tb increase then decrease into the albitized

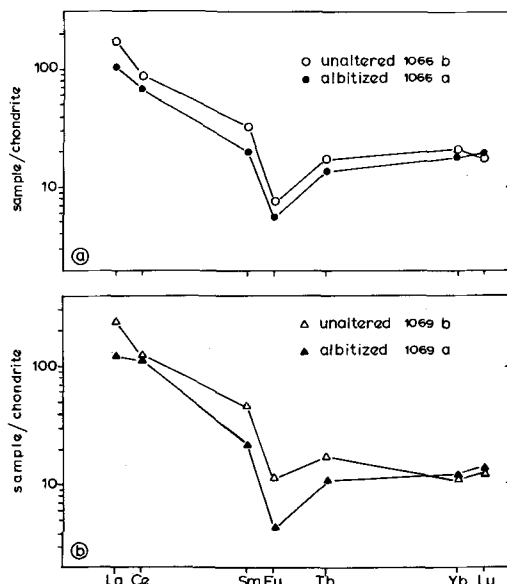


FIG. 6. Rare earth element plots normalized to chondrite (values of Evenson *et al.* (1978) $\times 1.5$) for albitized-unalbitized granite sample pairs.

zones. The chondrite normalized REE patterns are shown in fig. 6a, b. The albitized sample 1066a shows an overall depletion in REE, though Yb and Lu are more constant. 1069a shows a similar depletion pattern with a stronger retention of Ce. Replicate analyses of samples 1069a and 1069b were made to confirm the Ce values. 1068b is the most strongly depleted (assuming an original composition similar to the normal, unaltered granite), with light rare earth elements (LREE) more depleted than heavy rare earth elements (HREE) (see fig. 7). Alderton *et al.* (1980), in a detailed study of alteration in the SW England granite, observed an overall depletion of REE, except for Eu, which together with Zr, Y, and Ti remained constant during K-silicate alteration. An identical pattern of alteration was seen by Ludden *et al.* (1982) to result from K-metasomatism of pillow basalts from Abitibi. During K-mica formation Alderton *et al.* (1980) noted only a decrease in Eu. Bowden and Whitley (1974) noted an HREE enrichment during albitization in peralkaline Nigerian granites, while Zielinski (1982) records a greater depletion of LREE over HREE during the alteration of a rhyolitic ash to montmorillonite in which all the alkalis are depleted. The similarity in REE pattern produced during Na-enrichment (this work) and K-enrichment (Alderton *et al.*, 1980) indicates that the pattern produced is not specifically dependent

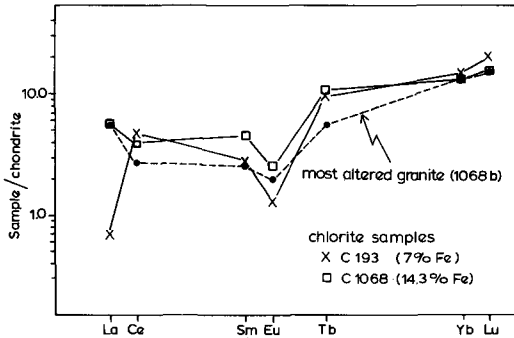


FIG. 7. Rare earth element plots normalized to chondrite (values of Evenson *et al.* (1978) $\times 1.5$) for the two chlorite separates C 193, C 1068, and the most altered granite sample 1068b.

upon the presence or absence of one of the alkalis Na or K, a point borne out by Martin *et al.* (1978) who note that REE were added in decreasing amounts with increasing atomic number during the fenitization of the Borralan quartzite, irrespective of whether Na or K was the alkali being added.

Discussion

Two extremes of hydrothermal fluid can be distinguished; the internally derived, purely magmatic-hydrothermal fluid, and the externally derived meteoric-hydrothermal fluid, with all transitions between. In the absence of stable isotope data any discussion concerning the origin of the albitizing fluid in the Bastfallshöjden granite is speculative. However, it is unlikely that the fluid was purely magmatic, and the relatively high level intrusive nature of the granite, intruding a wet pile of dominantly submarine felsic volcanics strongly suggests that a large if not dominant part of the hydrothermal fluid was externally derived. The narrow, poorly developed contact-metamorphic aureole around this and other older granites testifies to a rapid removal of latent heat from the crystallizing pluton by an external hydrothermal system (Helmers, 1984). The development of Mg-enriched alteration zones in the felsic volcanic rocks near Hjulsjö has been ascribed to hydrothermal processes involving the interaction of heated seawater with the volcanic rocks, whereby Mg-chlorite is extensively developed, the system being driven by the heat of the cooling Hjulsjö granitic complex (Baker and de Groot, 1983a) and the hot brines flowing out of the system on to the sea-floor being responsible for the formation of synsedimentary-exhalative iron ore deposits (Baker and de Groot, 1983b).

Origin of the hydrothermal fluid: evidence from chlorites. One chlorite sample (C 1068) was extracted from a quartz-chlorite vein seen cutting an outcrop of albitized granite. A second chlorite sample (C 193) was extracted from a sample of felsic metavolcanic rock 1.5 km to the southwest of the granite (fig. 1), where chlorite is developed as fracture and vein fillings. These whitish metavolcanics show the same microscopic evidence of hydrothermal alteration as that described from Hjulsjö, 10 km to the south (Baker and de Groot, 1983a). Poor exposure means that these hydrothermally altered rocks cannot be traced up to the granite.

Table II.

Electron microprobe analyses of chlorite separates C 193 and C 1068. d.l.= value less than detection limit of system. * total iron as FeO.

	C-193			C-1068		
	1	2	3	1	2	3
SiO ₂	27.28	27.02	27.44	28.77	28.56	26.80
TiO ₂	d.l.	0.02	0.02	0.15	0.22	0.13
Al ₂ O ₃	21.04	21.20	19.89	16.59	17.21	17.69
FeO*	9.64	8.88	8.69	18.73	19.27	19.77
MnO	0.14	0.11	0.07	0.19	0.20	0.19
MgO	26.38	26.50	27.39	19.79	19.17	19.17
CaO	d.l.	0.01	0.03	0.08	0.10	0.08
Na ₂ O	0.02	0.02	d.l.	0.04	0.02	0.05
K ₂ O	d.l.	d.l.	0.01	0.44	0.26	0.06
	84.50	83.76	83.54	84.78	85.01	83.94
on the basis of 28 oxygens						
Si	5.484	5.458	5.557	6.065	6.011	5.750
Al ^{IV}	2.516	2.542	2.443	1.935	1.989	2.250
Al ^{VI}	2.471	2.507	2.305	2.188	2.281	2.224
Ti	0.000	0.003	0.003	0.024	0.035	0.021
Fe ²⁺	1.621	1.500	1.472	3.302	3.392	3.547
Mn	0.024	0.019	0.012	0.034	0.036	0.035
Mg	7.904	7.979	8.266	6.217	6.013	6.129
Ca	0.000	0.002	0.007	0.018	0.023	0.018
Na	0.008	0.008	0.000	0.016	0.008	0.027
K	0.000	0.000	0.003	0.118	0.070	0.016
Σ[VI]	12.03	12.02	12.07	11.92	11.86	12.02
Fe/(Fe+Mg)	0.17	0.16	0.15	0.35	0.36	0.37

Representative microprobe analyses of the two chlorites are given in Table II. The chlorite from the hydrothermally altered metavolcanics (C 193) is Mg-rich, with an Fe/(Fe+Mg) ratio of 0.16, and according to the classification of Hey (1954) is a sherdanite, with the general formula $(Mg_{8.0}Al_{2.5}Fe_{1.5})(Si_{5.5}Al_{2.5})O_{20}(OH)_{16}$. The chlorite from the quartz-chlorite vein in the albitized granite (C 1068) has a slightly higher TiO₂ and MnO content, contains small amounts of alkalis, and approximately twice as much Fe as the other chlorite, with an Fe/(Fe+Mg) ratio of 0.36. The general formula is $(Mg_{6.1}Al_{2.2}Fe_{3.5})(Si_{6.0}Al_{2.0})O_{20}(OH)_{16}$.

Table III. Trace element data for chlorite separates: C 1068 from quartz-chlorite vein in albitized granite; C 193 from hydrothermally altered felsic metavolcanics 1.5 km SW of the Bastfallshöjden granite (see Fig. 1).

	C 193	C 1068
(ppm)		
Na	422.30	739.0
K	687.40	6220.0
Sc	12.57	44.80
Cr	3.62	15.50
Fe	7.0×10^4	14.30×10^4
Co	6.61	48.70
Ni	~	88.89
Cu	57.40	126.0
Zn	85.10	155.0
Ga	44.73	64.8
As	~	1.27
Rb	~	60.1
Sb	0.46	0.81
Cs	0.384	3.803
Ba	~	71.8
La	0.260	2.07
Ce	4.540	4.00
Sm	0.622	1.04
Eu	0.109	0.216
Tb	0.560	0.589
Yb	3.629	3.32
Lu	0.764	0.609
Hf	1.519	0.97
Ta	0.164	2.03
W	~	3.32
Th	3.292	2.46
U	0.817	5.43

Trace element data for the two chlorite separates are given in Table III. In addition to containing a higher amount of Fe, chlorite C 1068 also has higher concentrations of Na, K, Sc, Cr, Co, Cu, Zn, Ga, Sb, Cs, Ta, and U. Most element pair ratios are dissimilar though Th/Hf and Cu/Zn are approximately the same. However, looking at the REE, there are striking similarities (fig. 7). The HREE patterns are almost identical, the only significant difference in LREE is the extreme low La value of the chlorite C 193 from the hydrothermally altered metavolcanics. Duplicate analysis of C 193 has confirmed this pattern. The similarity in REE patterns of the chlorites and the most altered granite sample is striking (fig. 7). The similarity in REE patterns of the chlorites suggests they developed from a hydrothermal fluid with the same chemical characteristics, and the similar pattern in the most altered granite suggests this too was determined by the same hydrothermal fluid. The relative HREE enrichment seen in a chlorite from a sub-seafloor hydrothermal system near Hjuljö, with HREE ratios similar to those of seawater has been taken as evidence for a dominant seawater role in the hydrothermal fluid there (Baker and de Groot, 1983a). Similarly it can be inferred that the REE patterns of the chlorites from the hydrothermally

altered metavolcanics and from the quartz-chlorite vein in the altered granite, as well as that of the most altered granite itself, were determined by a hydrothermal fluid in which seawater was the dominant component. If this is correct then simple mass balance calculations relating the excess of Na in the albitized granite samples to the Na content of unmodified seawater indicate that the albitization occurred under water/rock mass ratios of 2 to 3. This value probably only represents a lower limit, since trace element depletion is variable for approximately constant Na input (see Table I). Though the albitized zones do not contain large amounts of Mg, an increase of 30–60% MgO relative to the unaltered granite is apparent, further evidence for a seawater role in the alteration process.

REE complexing in the hydrothermal fluid. The Na-rich hydrothermal fluid which also added Mg and Si to the granite, while removing Fe and K had variable effects on the trace elements in different parts of the system (see fig. 6).

It has been demonstrated experimentally that the REE form complexes with F^- (Mineyev, 1963), Cl^- (Flynn and Burnham, 1978), and it is generally considered that the HREE complex with F^- (Fryer and Edgar, 1977) and CO_3^{2-} (McLennan and Taylor, 1979; Kerrich and Fryer, 1979), while the LREE complex preferentially with Cl^- (Flynn and Burnham, 1978; Taylor and Fryer, 1982). Based on extrapolations of the experimental data of Flynn and Burnham (1978), Vidal *et al.* (1982) model the effects of F and Cl complexing on the REE to account for variations seen in a Himalayan leucogranite. An overall depletion was produced by F-complexing, and a strong increase in the size of the negative Eu anomaly with Cl-complexing coupled to a progressive decrease in the other REE (La > Lu). The Eu melt/fluid partition coefficient is, however, of critical importance in their Cl-complexing and it should be noted that Eu behaviour is strongly dependent upon f_{O_2} in the fluid (Drake, 1975), and temperature (Sverjensky, 1984).

The albitized (1066a, 1068b) samples of Bastfallshöjden granite show a depletion of the REE with the LREE depleted more than the HREE (figs. 6 and 7), indicating that Cl was the main complexing anion in the hydrothermal fluid. Whilst it has been demonstrated that highly concentrated Cl-enriched brines can be produced during the separation of water from a crystallizing magma at low pressure (Kilinc and Burnham, 1972), seawater is also Cl-enriched, and considering the geological setting of the Bastfallshöjden granite, the LREE depletion cannot be considered as evidence for a magmatic-hydrothermal fluid.

The slight depletion of the *HREE* in 1066a, 1068b suggests that another ionic species was also forming complexes, i.e. F^- or CO_3^{2-} . The presence of carbonate along grain boundaries, mentioned above, can be taken as good evidence for the presence of CO_3^{2-} in the fluid (Taylor and Fryer, 1982), a species also considered to have played an important role in the alteration of felsic volcanics to Mg-rich rocks in the Hjuljö area (Baker and de Groot, 1983a). It is likely that this too was seawater derived, rather than mantle derived as was suggested by Taylor *et al.* (1981) for some peralkaline systems. Other factors being constant, the variation in amount of depletion seen between for example 1066a and 1068b is probably a result of higher water/rock mass ratios (Mottl, 1983). The narrow quartz-feldspar \pm chlorite zones of fine grained, recrystallized material clearly served as channels through which material was added to, or removed from the system by the hydrothermal fluid. 1069a differs from the other albitized samples in retaining Ce. In behaving like an *HREE* it could be that the cerium was present as Ce^{4+} in that part of the system, though this idea cannot yet be substantiated.

Conclusions

A strong negative correlation between Na and K in the acid metavolcanics results in the development of Na- and K-extreme types (Sundius, 1923; Magnusson, 1970), but this is not considered to represent a primary magmatic variation (Frietsch, 1982; Baker and de Groot, 1983a, Lagerblad and Gorbatshev, 1983). In the light of the data presented here it is clear that the major element chemistry of Na-rich granitoids such as the 'Urgranit' near Silvergruvan (Sundius, 1923; Magnusson, 1970), or the Hjuljö granophyre (Baker, in prep.) is unlikely to be primary, and also probably resulted from modification by late stage, sub-seafloor hydrothermal-metasomatic processes.

During the albittization of parts of the Bastfallshöjden granite, extreme Na-rich rocks are produced. Nevertheless there is no obvious relationship between the variations seen in major element chemistry and trace element chemistry, probably reflecting variations in the water-rock mass ratio (Mottl, 1983). It seems that a maximum input of Na is achieved by combining with Al and Si to form feldspar. Once this has happened a 'saturation level' as regards Na-input has been reached. Leaching of trace elements may well continue, but this is not reflected in the Na content of the rock. For the above reasons the Na/K ratio in the granites or acid meta-volcanics is on its own a poor guide to use to trace enrichment or depletion of minor elements,

and is unsatisfactory to use when prospecting for alteration zones associated with, for example, porphyry-type molybdenum or wolfram deposits, which in Bergslagen have been shown to be linked to granites of this type (Hellingwerf and Baker, in prep.).

Acknowledgements. This paper has benefited from discussion with Professor Dr I. S. Oen and the comments of an anonymous reviewer. Thanks are due to M. de Bruin and co-workers of the Interuniversity Reactor Institute (IRI) in Delft for use of INAA facilities. Microprobe facilities were made available by WACOM, a working group for analytical geochemistry, subsidized by The Netherlands Organization for the Advancement of Pure Research (ZWO), who also provided financial support for the author with AWON grant 18.21.09 to Professor Dr I. S. Oen. The figures were drawn by F. Kievits and J. Wiersma took the photographs.

REFERENCES

- Åberg, G., Bollmark, B., Björk, L., and Wiklander, U. (1983) *Geol. För. Förh.* **105**, 78–81.
- Alderton, D. H. M., Pearce, J. A., and Potts, P. J. (1980) *Earth Planet. Sci. Lett.* **49**, 149–65.
- Baker, J. H., and de Groot, P. A. (1983a) *Contrib. Mineral. Petrol.* **82**, 119–30.
- (1983b) *Terra Cognita* **3**, 167 (abstract).
- Bowden, P., and Whitley, J. E. (1974) *Lithos*, **7**, 15–21.
- Drake, M. J. (1975) *Geochim. Cosmochim. Acta*, **39**, 55–64.
- Evenson, N. M., Hamilton, P. J., and O'Nions, R. K. (1978) *Ibid.* **42**, 1199–212.
- Floyd, P. A., and Winchester, J. A. (1978) *Chem. Geol.* **21**, 291–306.
- Flynn, R. T., and Burnham, M. (1978) *Geochim. Cosmochim. Acta*, **42**, 685–701.
- Frietsch, R. (1982) *Sver. Geol. Unders. Ser. C*, 791.
- Fryer, B. J., and Edgar, A. D. (1977) *Contrib. Mineral. Petrol.* **61**, 35–48.
- Helmerts, H. (1984) *Neues Jahrb. Mineral.* (in press).
- Hey, M. H. (1954) *Mineral. Mag.* **30**, 277–92.
- Hughes, C. J. (1972) *Geol. Mag.* **109**, 513–27.
- Hynes, A. (1980) *Contrib. Mineral. Petrol.* **75**, 79–87.
- Kerrick, R., and Fryer, B. J. (1979) *Can. J. Earth. Sci.* **16**, 440–58.
- Kilinc, I. A., and Burnham, C. W. (1972) *Econ. Geol.* **67**, 231–5.
- Lagerblad, B., and Gorbatshev, R. (1983) *Sver. Geol. Unders. Rapporter och Meddelanden*, **34**, 58–175.
- Ludden, J., Gélinas, L., and Trudel, P. (1982) *Can. J. Earth. Sci.* **19**, 2276–87.
- McLennan, S. M., and Taylor, S. R. (1979) *Nature*, **282**, 247–50.
- Magnusson, N. H. (1925) *Persbergs Malmtrakt. Kungl. Kommers-kollegium*.
- (1970) *Sver. Geol. Unders. Ser. C*, no. 643, 364 pp.
- and Lundqvist, G. (1932) *Ibid. Ser. Aa*, no. 175.
- Martin, R. F., Whitley, J. E., and Woolley, A. R. (1978) *Contrib. Mineral. Petrol.* **66**, 69–73.
- Mineyev, D. A. (1963) *Geochemistry* **12**, 1129–49.

- Moorman, A. C., Andriessen, P. A. M., Boelrijk, N. A. I. M., Hebeda, E. H., Oen, I. S., Priem, H. N. A., Verdurmen, E. A. Th., Verschure, R. H., and Wiklander, U. (1982) *Geol. För. Förh.* **104**, 1-9.
- Mottl, M. J. (1983) *Geol. Soc. Am. Bull.* **94**, 161-80.
- Oen, I. S. (1982) *Geol. Mijnbouw*, **61**, 305-7.
- (1983) *Ibid.* **62**, 301-3.
- Helmers, H., Verschure, R. H., and Wiklander, U. (1982) *Geol. Rundschau* **71**, 182-94.
- and Verschure, R. H. (1982) *Geol. Mijnbouw*, **61**, 301-4.
- Verschure, R. H., and Wiklander, U. (1984) *Ibid.* **63**, 85-8.
- Pearce, J. A., and Norry, M. J. (1979) *Contrib. Mineral. Petrol.* **69**, 33-47.
- Robbie, R. A., Hemingway, B. S., and Fisher, J. C. (1978) *U.S. Geol. Surv. Bull.* 1452.
- Sundius, N. L. (1923) *Sver. Geol. Unders. Ser. C*, no. 32.
- Sverjensky, D. A. (1984) *Earth Planet. Sci. Lett.* **67**, 70-8.
- Taylor, R. P., and Fryer, B. J. (1982) In *Metallization associated with acid magmatism* (A. M. Evans, ed.), 357-65. J. Wiley & Sons.
- Strong, D. F., and Fryer, B. J. (1981) *Contrib. Mineral. Petrol.* **77**, 267-71.
- Tuttle, O. F., and Bowen, N. L. (1958) *Mem. Geol. Soc. Am.* no. 74.
- Vidal, Ph., Cocherie, A., and LeFort, P. (1982) *Geochim. Cosmochim. Acta*, **46**, 2279-92.
- ViéLeSage, R., Quisefit, J. P., Dejean de la Bâtie, R., and Faucherie, J. (1979) *X-ray Spectrometry* **8**, 3, 121-8.
- Welin, E., Gorbatshev, R., and Lundegardh, P. H. (1977) *Geol. För. Förh.* **99**, 363-7.
- Wiklander, U., and Kähr, A. M. (1980) *Ibid.* **102**, 269-72.
- Winchester, J. A., and Floyd, P. A. (1976) *Earth Planet. Sci. Lett.* **28**, 459-69.
- Zielinski, R. A. (1982) *Chem. Geol.* **35**, 185-204.

[Manuscript received 5 June 1984;
revised 9 October 1984]