

# TRACE ELEMENTS IN A PRECAMBRIAN GABBRO INTRUSION, HIÅSEN, BAMBLE AREA, SOUTH NORWAY

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A small gabbro intrusion has been analysed for 16 trace elements to see their behaviour under magmatic differentiation, scapolitization, and regional metamorphism.

V and Cr were concentrated in the later members of the magmatic differentiation series. Mn, Ga, Sr, and Ba were leached during the scapolitization, while no trace element seems to have been introduced. During the regional metamorphism Rb was introduced while Mn was removed.

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The Hiåsen gabbro intrusion, Bamble area, south Norway, has previously been systematically studied (Frodesen 1968). Thirty-five specimens were sampled according to a quadratic grid, and each was studied microscopically and chemically. All the samples were analysed for all major elements by X-ray fluorescence, flame photometry, and atomic absorption.

The same 35 samples have now been analysed for certain trace elements by spark source mass spectrometry, using an AEI/MS 702 mass spectrometer. The isotopes  $^{47}\text{Ti}$  and  $^{57}\text{Fe}$  were used as internal standard, as Ti and Fe had already been analysed by X-ray fluorescence. Relative sensitivity factors are based on USGS standards W-1, BCR-1, and G-2. Data from Flanagan 1969 and Fleischer 1969. Mean values are given.

The rock samples had previously been crushed in a stainless steel swinging mill (Sieb Technik) and had a grain size of less than 200 mesh. The rock powders had been stored in glass jars for approximately 3 years, so each jar was homogenized in a Turbula mixer for 10–15 minutes before a sample was taken out. 500 mg of the sample was mixed with 20 % (weight) soda (Johnson, Matthey & Co., 'specpure') in agate mortar for 10 minutes, fused in Pt-foil at 1150 °C for 20 minutes, quenched in distilled water, ground in agate mortar, and thoroughly mixed with 60 % (weight) graphite powder (Spektralkohle-Pulver, Höchster Reinheit, Ringsdorff Werke) in agate mortar for 10 minutes. From this mixture electrodes were pressed in a die, stainless steel, Ringsdorff Werke. Photographic detection was used (Ilford Q2 plates). Optical densities were measured with a Joyce Loebel double beam microdensitometer equipped with a digital voltmeter and a printer. The method used to calculate concentrations is described by Perkins & Pollack (1962).

Each sample was run in duplicate and concentrations computed. Some of the runs were rejected and repeated due to:

Poor agreement between the duplicates.

Poor agreement between values based on  $^{47}\text{Ti}$  and  $^{57}\text{Fe}$ .

Mishaps during procedure caused poor photoplates.

In the given results the difference between the duplicates and the difference between values based on  $^{47}\text{Ti}$  and  $^{57}\text{Fe}$  are less than 20 % rel. except for 2 samples. Fig. 1 shows the agreement between values of  $\text{TiO}_2$  obtained by mass spectrometry and by X-ray fluorescence. The values from X-ray fluorescence can be considered 'true values', as this method is by far superior at this relatively high concentration level.

The chemical variations of the Hiåsen gabbro were unexpectedly great (Frodesen 1968). It was demonstrated that the variations are mainly primary (magmatic), but secondary processes like scapolitization and regional metamorphism have caused certain chemical transformations.

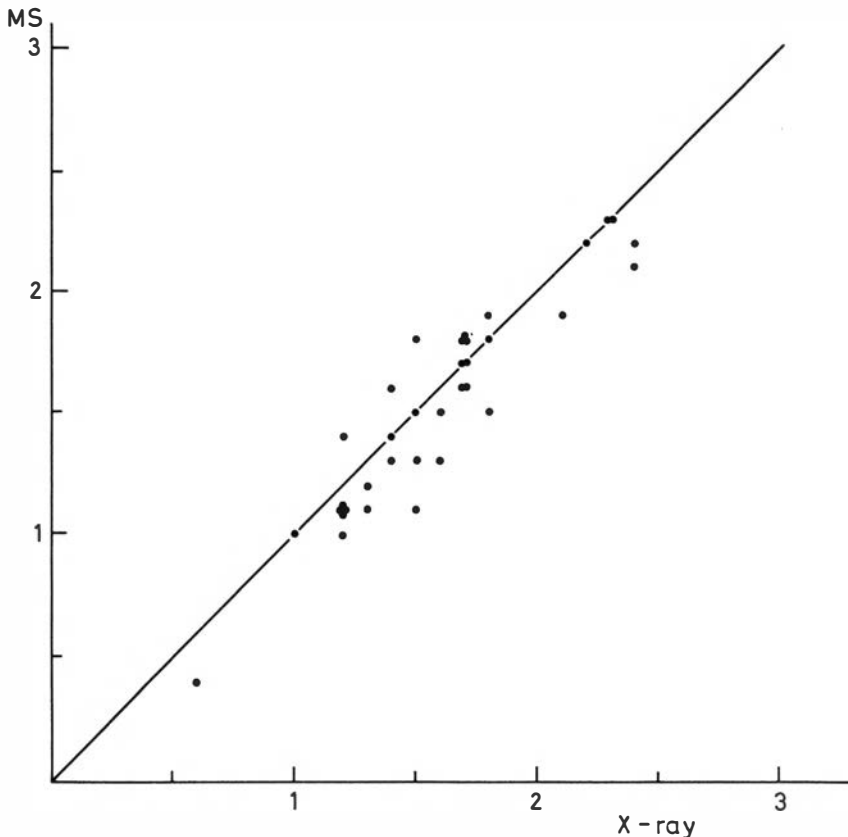


Fig. 1. Concentrations of  $\text{TiO}_2$  obtained by mass spectrometry versus 'true values' obtained by X-ray fluorescence.

Table 1. Concentrations (ppm) of 16 trace elements in 35 samples from the Hiåsen gabbro.

Sample	TiO <sub>2</sub> %	V	Cr	Mn	Co	Cu	Zn	Ga	As	Rb	Sr	Y	Zr	Nb	Ba	La	Ce
C4	1.5	250	56	640	59	67	150	11	27	11	130	27	55	14	47	8.3	16
C10	2.1	240	35	380	35	15	68	8.3	14	9.4	150	31	63	14	62	12	23
D4	1.3	140	42	1200	45	29	170	11	51	8.3	280	24	55	19	160	6.5	15
D5	1.8	240	34	750	50	41	100	8.8	37	11	230	29	56	12	140	8.8	18
D9	1.6	220	75	1200	52	25	78	11	15	9.7	160	41	62	24	250	15	27
D10	1.0	140	58	1300	65	32	140	15	60	7.2	170	18	33	7.9	250	8.4	19
E2	1.5	150	46	240	43	35	120	7.2	60	6.8	110	25	39	10	49	13	24
E3	1.7	220	49	600	47	50	110	15	11	49	320	47	82	25	180	26	42
E4	2.3	350	160	910	60	30	110	11	17	7.1	160	46	61	16	100	19	39
E4-1	1.7	190	56	780	50	15	59	7.9	14	7.9	130	17	42	14	58	5.1	8.5
E5	2.2	250	60	1700	34	28	56	9.0	13	11	140	25	49	17	120	13	20
E6	1.6	320	81	1100	58	43	250	13	54	16	240	38	49	15	230	12	26
E7	1.1	200	70	1700	33	52	110	12	28	22	260	26	39	15	210	14	19
E8	2.3	180	37	2200	46	53	95	14	27	15	230	29	56	13	220	10	18
E9	2.1	390	160	1700	39	31	120	13	18	9.4	170	20	39	8.5	160	6.1	10
F2	1.2	120	38	1500	40	24	140	9.5	23	13	230	16	37	11	150	7.3	10
F4	1.1	230	88	1300	65	51	120	13	59	12	230	25	41	12	250	14	21
F5	1.8	210	43	2000	61	62	92	17	19	26	230	43	79	28	260	22	27
F6	2.2	170	15	1900	50	41	57	15	28	18	260	33	54	18	180	16	27
F7	1.3	160	81	1000	60	42	200	11	48	35	340	41	70	23	200	27	39
F8	1.9	230	140	960	31	42	93	10	8.1	34	170	50	73	21	130	18	25
G2-1	1.4	140	54	660	43	30	140	8.1	28	12	210	21	45	12	99	12	18
G3	1.1	140	64	960	61	36	150	16	16	35	230	25	48	14	280	16	23
G4	1.0	150	47	660	53	20	150	7.6	52	4.2	200	16	33	9.4	90	7.7	13
G5	1.1	160	29	820	54	12	110	12	15	33	270	32	48	8.8	370	14	28
G6	0.4	110	61	1500	79	46	220	12	66	9.1	190	10	16	4.8	280	8.8	15
G7	1.8	160	56	1400	50	33	110	11	40	16	190	26	51	24	150	11	17
H3	1.1	180	51	1600	58	88	120	14	45	7.8	140	18	32	11	110	9.3	13
H4a	1.5	180	55	750	64	49	120	17	22	60	190	41	67	25	220	26	40
H4b	1.4	130	40	1300	46	31	130	10	17	9.1	230	16	32	10	100	9.1	11
H7	1.6	200	54	640	56	39	150	11	28	6.8	210	31	51	13	110	10	17
H8	1.1	100	41	1700	49	39	68	9.2	19	6.1	170	12	21	7.7	200	7.0	10
I4	1.8	140	67	140	42	22	130	8.1	20	6.0	53	21	36	12	46	10	16
I5	1.8	190	77	840	51	21	160	11	28	3.9	200	22	45	16	98	11	16
I8-1	1.3	120	50	1100	43	29	95	10	16	8.7	180	29	58	14	110	16	26

From the series of 35 samples two subseries were selected based on microscopic studies: The 5 samples which are completely scapolitized (ødegårdites), and the 8 samples containing most modal pyroxene, as they were considered to be the ones least altered by secondary processes. It was proved that 4 of these 8 samples are early and 3 late members of the differentiation series. One sample is intermediate (Frodesen 1968).

The main purpose of this work was to study the behaviour of various trace elements during the 3 processes. The gabbro was analysed for the following trace elements: Ti, V, Cr, Mn, Co, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Ba, La, and Ce. The results are given in Table 1.

### Magmatic differentiation

It has been demonstrated that a slight magmatic differentiation took place within this small intrusion, at an early stage, when only plagioclase had started crystallizing. This caused a detectable increase in Fe and Ti and a decrease in Al in the later members.

As the differentiation was so slight, little was expected to be seen from the rather inaccurate trace element data. However, it is obvious that the later members are enriched in V and probably Cr. See Fig. 2 in which the analyses of V and Cr are displayed in histograms where the 8 least altered samples are ruled to stand out in the 'normal distribution'.

During crystallization both  $V^{3+}$  and  $Cr^{3+}$  ions will be preferred to the  $Fe^{3+}$  ion in a crystal structure, and they are rapidly removed from the magma

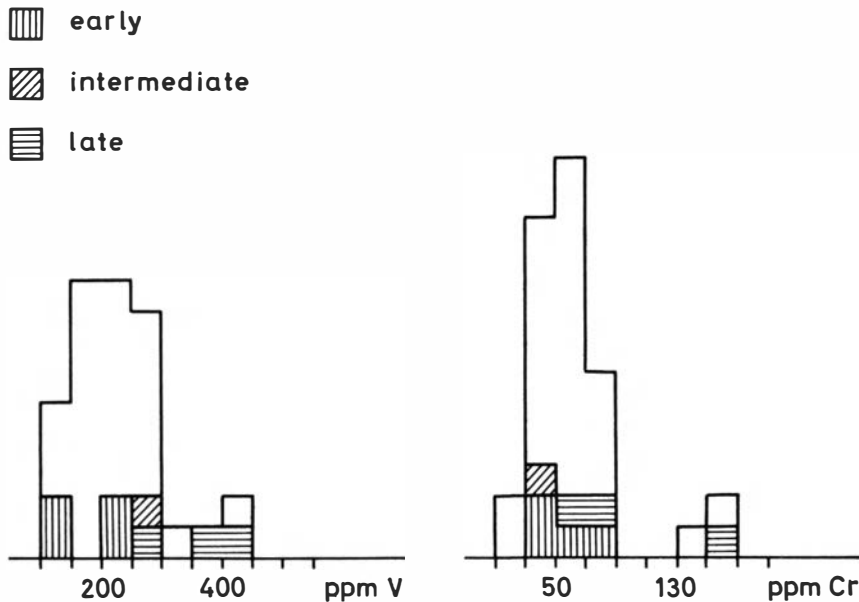


Fig. 2. Analyses of V and Cr in histograms. The 8 least altered samples are ruled. V and probably Cr are concentrated in the later members of the differentiation series.

as soon as a mineral with  $\text{Fe}^{3+}$  in definite crystal sites starts to crystallize (Ringwood 1955). They stay in solution in the magma until this happens. In this case this particular mineral is probably magnetite, which therefore must have been a rather late mineral in the crystallization course.

### Scapolitization

Scapolitization of the gabbros and their surroundings is a very common feature in the Bamble area. It is caused by the introduction of vapours and solutions rich in Cl and  $\text{CO}_2$ , during which plagioclase is replaced by scapolite. It is a post consolidation, high temperature process, and is considered to be related to the magmatic activity itself. The process is accompanied by the replacement of pyroxene by hornblende, and the end product of the metasomatism is a pure scapolite-hornblende rock without plagioclase or pyroxene. In 1884, W. C. Brøgger introduced the name 'ødegårdite' for such rocks.

It was demonstrated that during the scapolitization of the Hiåsen gabbro Cl, Na, and Mg were added, while Si and  $\text{Fe}^{2+}$  were removed (Frodesen 1968). This is in contrast to the scapolitization of the gabbro at the Ødegården Mines (some 40 km to the NW), where there has also been a marked addition of  $\text{SiO}_2$  during the metasomatism (Brøgger 1934).

As the scapolitization is caused by fluids percolating through the rock, one might expect an addition of different trace elements along with the major elements mentioned above. However, this investigation proves that this is not at all the case.

It is obvious from Fig. 3 that Mn, Ga, Sr, and Ba are leached from the rock during the recrystallization. If the other elements are presented in the same way, they do not reveal any clear relation between the ødegårdite and the original rock. But if the mean values of the ødegårdites are compared with the mean values of the rest of the samples, it is seen that the ødegårdites have a somewhat higher content of Zn and As, but a lower content of all the other elements (V, Cr, Co, Cu, Rb, Y, Zr, Nb, La, Ce) (Table 2). A leaching of trace elements therefore seems to be a general feature.

The four elements that are leached from the rock to a large extent during the pneumatolysis occur mainly in isomorphous solid solution at lattice sites in the minerals which took part in the recrystallization. In the magmatic crystallization Ga will substitute for Al (Si) and Sr and Ba for Ca in plagioclase, while Mn will substitute for  $\text{Fe}^{2+}$ , mainly in the pyroxene (olivine).

Vestiges of the ophitic texture of the original gabbro can be seen even in these completely recrystallized rocks, so it is believed that the amount of scapolite after recrystallization roughly equals the amount of the original plagioclase. Hence the amount of hornblende equals the amount of pyroxene. The original rock contained relatively small amounts of olivine, but this was very shortly after the consolidation essentially isochemically replaced by pyroxene, and is neglected in this discussion.

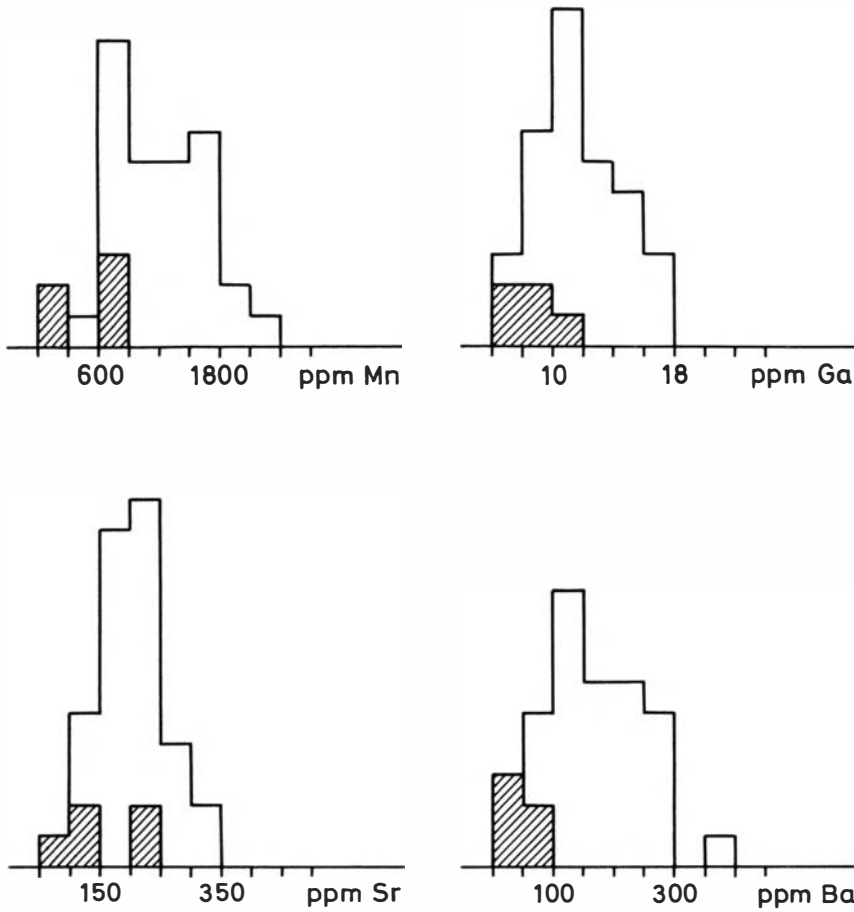


Fig. 3. Analyses of Mn, Ga, Sr and Ba in histograms. The 5 ødegårdites are ruled. All 4 elements were leached during the scapolitization.

The original plagioclase is highly zoned, but according to calculated norms the average composition is close to  $An_{50}$ . The scapolite, however, is a dipyre,  $Me_{35}$ . This implies that the excess of Al and Ca derived from the replacement of plagioclase by scapolite must have been accepted by the hornblende, as the chemical analyses show that the gabbro and the ødegårdite have the same content of  $Al_2O_3$  and CaO. In return the transformation pyroxene-hornblende has provided more Si than necessary for the formation of the more acid scapolite, as some  $SiO_2$  has been leached from the rock.

Ga is reported to be found in similar concentrations in plagioclase, scapolite, and hornblende (Shaw et al. 1963). Almost all the Al (hence also the Ga) was originally in the plagioclase, but after recrystallization it is divided between two minerals (according to a very rough calculation: approximately 20%  $Al_2O_3$  in the scapolite, 13%  $Al_2O_3$  in the hornblende), and yet all the Ga cannot be accommodated by the two. Similarly, by the redistribution of the Ca, the trace elements Sr and Ba were lost.

Table 2. Mean values (ppm) of trace element contents of ødegårdites compared with the rest of the gabbro. The ødegårdites have lower contents of all elements except Zn and As.

	Mean ødegårdites	Mean all samples – ødegårdites
V	166	196
Cr	54	70
Mn	468	1230
Co	48	51
Cu	31	38
Zn	138	120
Ga	8.7	11.9
As	35	29
Rb	8.0	17
Sr	141	210
Y	22	29
Zr	42	50
Nb	12	15
Ba	66	174
La	10	13
Ce	17	22

Shaw et al. also found that skarn minerals (metasomatic) are as a rule purer than the same minerals from magmatic rocks. This may be because they have crystallized more slowly at a lower temperature, so the crystals are more perfect with fewer dislocations and inclusions where trace elements can be sited. Besides, if they are in a higher state of order, they might also reject trace elements which form isomorphous solid solution.

The 5 samples of ødegårdite are almost identical and exhibit a very typical granoblastic texture with, especially in the scapolite, triple points and straight grain boundaries with approximately 120° between them (Fig. 4). This represents the lowest possible energy (Spry 1969) and indicates crystallization under equilibrium conditions.

The amounts of trace elements taken up by minerals crystallizing under such conditions will be a function mainly of temperature and pressure (Shaw et al.), besides, of course, of the properties of the minerals. As the scapolitizing fluids were probably of magmatic origin, they probably contained large amounts of trace elements. But the chemical composition of the existing rock and the introduced solutions was such that under the governing conditions it gave rise to a two-mineral rock consisting of almost equal amounts of scapolite and hornblende with low concentrations of trace elements. It therefore seems impossible from these data to say anything about the composition of the fluids.

The other trace elements for which the Hiåsen gabbro has been analysed may of course have been sited in the major minerals (plagioclase and pyrox-

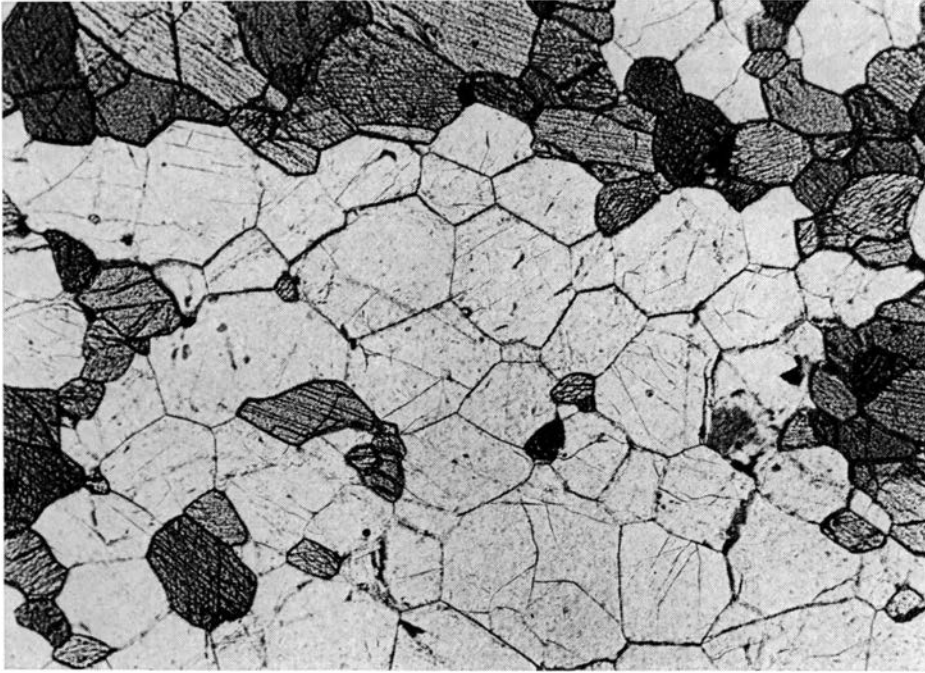


Fig. 4. Typical texture of ødegårdite. Note triple points and straight grain boundaries with  $120^\circ$  between them. Sample I4. Plane light,  $\times 50$ .

ene), in isomorphous solid solution, on imperfections in the crystal lattice, or as inclusions. They would then of course have been excluded during a recrystallization under equilibrium conditions. But most of them are probably found in the accessory minerals such as apatite, sphene, and iron ores. It does not seem unlikely that these accessories were to a certain degree dissolved by the scapolitizing fluids. This is definitely the case with the iron ores (Brøgger 1934).

### Regional metamorphism

During the regional metamorphism, pyroxene has been replaced by common hornblende, while the plagioclase has partly recrystallized and is highly sericitized and albitized in places. The chemical transformations during this process are a certain oxidation of iron and an introduction of Na, K, and  $H_2O$  (Frodesen 1968).

The metamorphism has affected two trace elements only, Mn and Rb (Fig. 5).

Mn has undoubtedly been in the original pyroxene (at  $Fe^{2+}$  sites) but it was not allowed to enter the hornblende at  $Fe^{3+}$  sites. It could not enter the recrystallizing plagioclase, nor could it form a new mineral phase, so it was carried away in solution.

The distribution of Rb indicates a secondary introduction of the element.



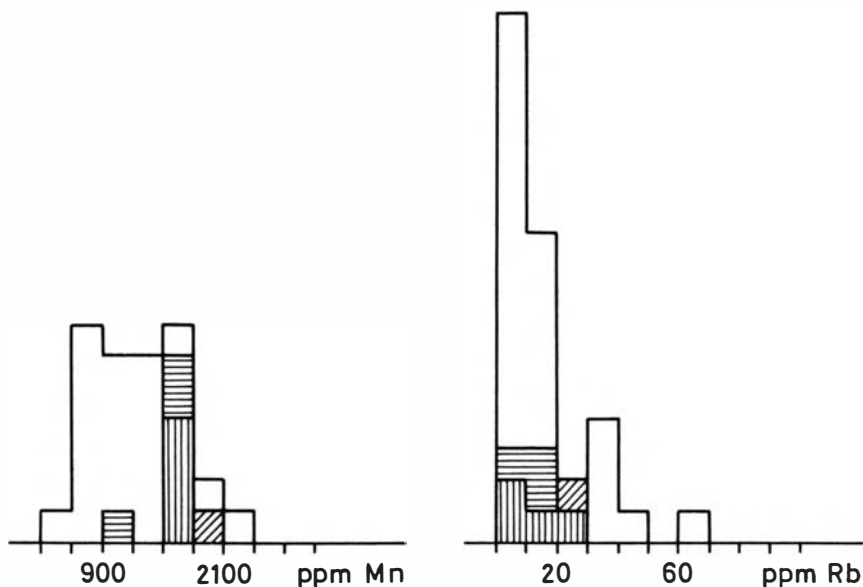


Fig. 5. Analyses of Mn and Rb in histograms ( $\phi$ degårdites excluded from diagram of Mn). The 8 least altered samples are ruled. Mn was leached and Rb introduced during the regional metamorphism.

The majority of the samples contain less than 15 ppm, while a few (six) contain between 30 and 60 ppm Rb. These extreme samples are also rich in  $K_2O$  and  $H_2O$ . Two of them were taken close to a quartz-albite pegmatite dyke which is believed to have been formed during the regional metamorphism, and they carry some stray grains of secondary biotite which can accommodate the Rb. The other extremes do not differ from the rest in any respect, so the secondary Rb is probably sited in the sericite.

### Conclusion

The chemical variations of the Hiåsen gabbro are the result of three processes: magmatic differentiation, chlorine pneumatolysis (scapolitization), and regional metamorphism. The purpose of this work was to study the behaviour of various trace elements during these processes. The gabbro was analysed for Ti, V, Cr, Mn, Co, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Ba, La, and Ce.

During the magmatic differentiation, V and Cr were concentrated in the later members, probably sited in magnetite.

The scapolitization caused a marked leaching of Mn, Ga, Sr, and Ba, while no trace element seems to have been introduced. A recrystallization under equilibrium conditions is suggested as an explanation.

The regional metamorphism also caused a leaching of Mn, as Mn could not pass from  $Fe^{2+}$  sites in pyroxene to  $Fe^{3+}$  sites in hornblende. Rb was introduced under this metamorphism.

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