

RUDYARD FRIETSCH

THE OCCURRENCE
AND COMPOSITION OF APATITE
WITH SPECIAL REFERENCE
TO IRON ORES AND ROCKS IN
NORTHERN SWEDEN



STOCKHOLM 1974

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Abstract

The apatite from some iron ores and rocks in Northern Sweden has been chemically investigated, mainly with respect to the content of halogens. In the iron ores of the Kiruna type the apatite is fluorine-dominated with only small amounts of chlorine. In some deposits the apatite contains, however, a rather high content of chlorine. These chlorine-apatites occur in an environment with scapolitization and the possibility is discussed that the high chlorine content, if not primary, is related to this alteration. There is rather clear evidence in most cases when chlorine-apatites are formed, that they are due to the action of high-temperature, metasomatic solutions rich in chlorine.

The apatite found in some of the skarn iron ores in Northern Sweden is mostly a fluorine-chlorine-apatite. Even in this case the high chlorine content can possibly be attributed to the above mentioned scapolitization.

On the basis of the literature the chemical substitutions in apatite are discussed. Further, the changes in composition of apatite due to different modes of formation are reviewed. The elements and components of importance in genetic considerations are fluorine, chlorine, hydroxyl, carbonate, manganese, strontium, barium and the rare earth elements.

Introduction

Apatite is a common mineral occurring in small or accessory amounts in many types of rock and some types of ore. It is the main phosphorus-bearing mineral in the earth's crust. The chemical composition of apatite shows a rather wide range of variation which in many cases is related to the mode of formation of the rocks or ores in which the apatite is found. Apatite is thus fitted for genetic considerations. Chemical differences of major importance in this mineral, depending on different environments of formation, are variations in the content of fluorine, chlorine, hydroxyl and carbonate, which components in part substitute for each other. Most commonly the apatite is fluorine-dominated. Other elements of interest are barium, strontium, manganese and the rare earth metals.

Mineral deposits in which apatite forms an essential constituent are formed either by magmatic or sedimentary processes. The magmatic apatites deposits are connected with alkaline complexes, and occur in part in the carbonatites following these. The sedimentary apatite deposits, or the phosphorites, are mostly developed at the border of continental shelves, the apatite precipitated when cold, upwelling phosphate-saturated water meets warmer surface water. Besides these phosphorus deposits, which are economic because of their content of apatite and partly because of their content of rare earths, there are some iron ores types in which apatite occurs in subordinate amounts. The presence of the latter is here undesirable. Phosphorus forms an impurity in the metallurgical process and has to be removed in the blast-furnace. In the late-magmatic magnetite-hematite deposits of the Kiruna type, apatite is a common mineral. Further there are sedimentary iron ores, of Phanerozoic age and mostly oolitic, which have a rather high content of phosphorus. The apatite is in these of biogenic origin. The Precambrian iron formations are mostly low in phosphorus, but there are some with a relatively high content. The apatite is here of abiotic origin.

The principal purpose of the present investigation is to study the chemical composition of the apatite in different Precambrian types of iron ores in Northern Sweden. Within this area the ores of the Kiruna type dominate both quantitatively and economically. These ores always contain apatite in subordinate amounts. The apatite is commonly considered as a fluorine-apatite, but there are rather few analyses to support this statement. In Northern Sweden there occur further rather large amounts of skarn iron ores, built up of magnetite with masses or layers of calcium-magnesium-rich silicates. Most probably these ores are metamorphosed chemical sediments. Some of the deposits belonging to this type of ore contain small amounts of apatite, and their chemical composition has been investigated in the present work. Further

the apatite in some metasomatic iron ores, a gabbro, and a uranium-bearing sediment, all in Northern Sweden, has been investigated.

The main interest in the present work concerns the relationship between the halogens, namely fluorine and chlorine, in apatite, but also some other elements were determined. To better understand how the chemical composition of apatite varies with different modes of formation, apatite analyses published in the current literature have been reviewed.

Method of investigation

The localities in Northern Sweden from which apatite has been investigated in the present paper are shown in Fig. 1. The investigated material comprises rock samples and drill cores. All together there are 33 analyses of apatite. Of these 20 analyses are from 9 deposits of iron ores of the Kiruna type, 8 analyses from deposits of skarn iron ore, 3 analyses from 3 deposits of metasomatic iron ores, 1 analysis from a gabbro and 1 analysis from a uranium-bearing sediment.

Both the separation and the analytical treatment of the apatites were made

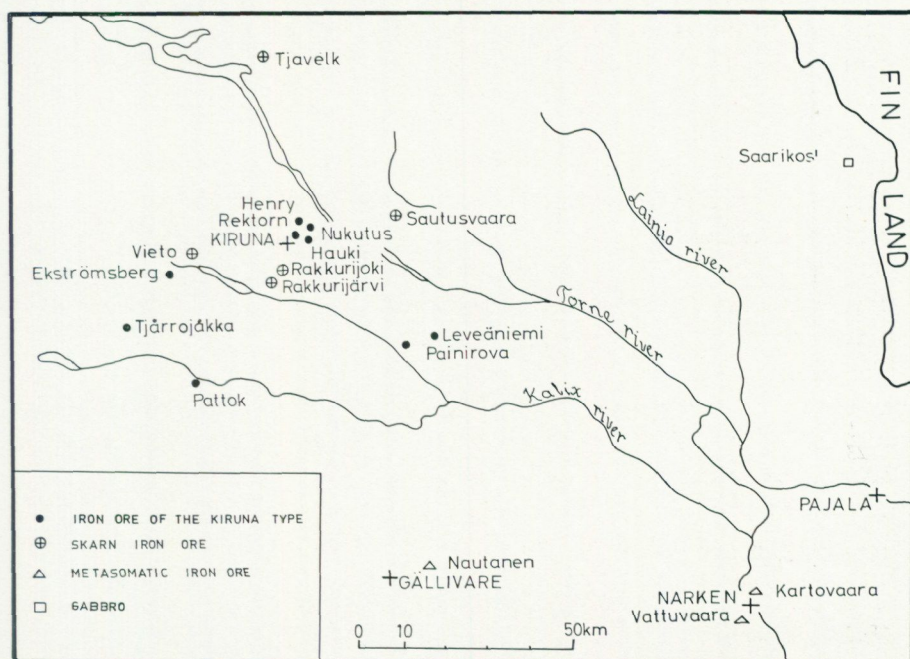


Fig. 1. Map showing the site of the different apatite-bearing iron ores and rocks investigated in Northern Sweden.

TABLE 1. PARTIAL CHEMICAL ANALYSES OF APATITE FROM DIFFERENT TYPES OF ORE AND ROCK IN NORTHERN SWEDEN. VALUES IN WEIGHT PER CENT.

Sample No.	Locality	P ₂ O ₅	CO ₂	SO ₃	F	Cl	H ₂ O >105°	H ₂ O <105°	Na
IRON ORE OF THE KIRUNA TYPE									
Normal P-content, <2 % P									
1828	Ekströmsberg				3.4	<0.2			0.04
1829	Ekströmsberg				2.8	0.6			0.02
1845	Leveäniemi	42.3	0.01		1.5	2.2	0.10	0.04	0.060
1846	Leveäniemi	42.3	0.14	0.05	2.3	0.9	0.12	<0.01	0.022
1847	Leveäniemi			0.36	1.7	2.0			0.053
1806	Painirova	40.7	0.06	0.15	2.6	0.2	0.24	<0.01	0.039
1807	Painirova				2.7	0.2			0.01
1800	Tjärrojåkka				2.4	0.7			0.02
1801	Tjärrojåkka				2.3	0.7			0.02
High P-content, >2 % P									
1808	Hauki	40.0		0.07	3.4	<0.2			0.05
1809	Hauki		0.02		3.6	<0.2	0.31	0.07	0.085
1813	Henry				2.7	<0.2			0.07
1814	Henry				3.3	<0.2			0.05
1810	Nukutus				2.9	<0.2			0.07
1811	Nukutus ¹⁾				3.2	<0.2			0.07
1812	Nukutus	39.5	1.94	0.35	3.3	<0.2	0.20	0.05	0.097
1802	Pattok				2.8	0.3			0.03
1803	Pattok ²⁾				2.1	<0.2			<0.01
1815	Rektorn	41.7	0.06	0.10	3.5	<0.2	0.22	0.05	0.071
1816	Rektorn				3.3	<0.2			0.1
SKARN IRON ORE									
1824	Rakkurijoki				1.8	1.7			0.05
1825	Rakkurijoki				2.1	1.3			0.05
1826	Sautusvaara S.				2.3	<0.2			0.05
1827	Sautusvaara N.				1.7	0.7			0.06
1830	Tjavelk				1.5	1.6			0.1
1831	Tjavelk	41.1	<0.01	0.17	1.3	2.3	0.22	0.01	0.089
1832	Vieto	42.3	0.01	0.29	2.9	0.3	0.12	<0.01	0.019
1833	Vieto				2.4	0.8			0.02
METASOMATIC IRON ORE									
1805	Nautanen				3.1	<0.02			<0.01
1823	Kartovaara				3.5	<0.02			0.06
1820	Vattuvaara				3.4	<0.02			0.03
GABBRO									
1839	Saarikoski				2.4	0.7			0.03
APATITE-RICH META-SEDIMENT									
1848	Påläng ³⁾				1.9	<0.2			0.8

¹⁾ Th and La in the unseparated sample ²⁾ Traces of Zr³⁾ 0.2 % U

n.d. = not determined

Mg	Al	Si	K	Ti	Mn	Fe	As	Sr	Y	Ce	Nd
IRON ORE OF THE KIRUNA TYPE											
Normal P-content, <2 % P											
0.05	0.05	0.3		0.01	0.02	0.06		n.d.	n.d.	n.d.	n.d.
0.03	0.03	0.07		0.01	0.02	0.15		0.03	0.05	-	-
0.01	0.07	0.3	0.008	<0.01	0.05	0.15		0.03	0.06	++	++
0.045	0.01	0.04	0.009	<0.01	0.012	0.073	0.016	0.017	0.04	+	+
0.026	<0.01	0.04		<0.01	0.037	0.14	0.009	0.024	0.05	++	++
0.019	0.03	0.07	0.013	0.01	0.025	0.14		0.029	0.04	-	-
<0.01	0.05	0.1		0.03	0.03	0.15		0.02	0.04	-	-
<0.01	<0.01	0.08		<0.01	0.01	0.07		0.04	0.04	++	++
0.02	<0.01	0.09		<0.01	0.01	0.09	0.017	0.04	0.04	++	++
High P-content, >2 % P											
<0.01	0.02	1.5		<0.01	0.02	0.1	0.008	0.03	0.06	+	+
0.010	<0.01	0.2	0.017	<0.01	0.015	0.057		0.032	0.06	++	+
<0.01	0.01	>3.0		<0.01	0.01	0.1		0.04	0.09	+	+
<0.01	<0.01	1.5		<0.01	0.02	0.08		0.04	0.08	++	++
0.04	0.02	1.5		<0.01	0.05	0.1	0.009	0.03	0.07	+	++
0.02	0.02	0.4		0.03	0.03	0.09		0.02	0.07	++	++
0.042	0.02	0.3	0.032	0.01	0.028	0.092		0.028	0.07	++	++
0.2	0.04	0.1		<0.01	0.07	0.1		0.04	0.07	+	+
0.2	0.2	>3.0		0.02	0.07	0.45		0.03	0.06	+	+
0.012	0.08	0.2	0.026	0.04	0.014	0.062		0.040	0.08	+	+
<0.01	0.25	3.0		<0.01	0.01	0.09	0.010	0.030	0.08	+	+
SKARN IRON ORE											
0.07	0.05	0.1		<0.01	0.01	0.15		0.03	0.05	++	++
0.05	0.04	0.2		<0.01	0.02	0.15		0.02	0.04	++	++
0.08	0.1	0.5		<0.01	0.02	0.2		0.03	0.03	n.d.	n.d.
0.5	0.06	0.7		<0.01	0.001	0.1		0.04	0.04	++	++
0.5	0.02	0.2		<0.01	0.09	0.15		0.07	0.03	++	++
0.19	<0.01	0.2	0.008	<0.01	0.060	0.086	0.005	0.094	0.04	++	++
0.035	0.05	0.05	0.008	<0.01	0.039	0.13	0.008	0.037	0.02	-	-
0.04	0.04	0.2		<0.01	0.02	0.15		0.02	0.04	-	-
METASOMATIC IRON ORE											
<0.01	0.05	0.2		0.05	0.1	0.08		0.03	0.01	-	-
0.01	0.07	0.9		<0.01	0.02	0.25		0.04	0.05	n.d.	n.d.
0.08	0.2	0.08		<0.01	<0.01	0.3		0.02	0.04	n.d.	n.d.
GABBRO											
0.03	0.05	0.09		<0.01	0.02	0.2		0.06	0.03	-	+
APATITE-RICH META-SEDIMENT											
0.9	>0.6	>3.0		0.2	0.04	0.6		0.02	0.01	+	+

DESCRIPTION OF SAMPLES

Iron ores of the Kiruna type

Normal P-content, $< 2\%$ P

- No. 1828 Ekströmsberg. Martite, mainly hematite, with 0.1–1 mm wide parallel bands of red-brown apatite.
- No. 1829 Ekströmsberg. Martite, mainly magnetite, with 0.1–0.2 mm wide parallel bands of white apatite.
- No. 1845 Leveäniemi. Magnetite dike, with crystals up to some centimetres long, of a yellowish or grey-white apatite, in biotite-schist.
- No. 1846 Leveäniemi. Magnetite dike, in magnetite ore with grains of grey-white apatite up to several centimetres in length.
- No. 1847 Leveäniemi. Magnetite ore, with veins up to 3–4 cm wide of a grey-red, fine-grained apatite and some skarn silicates and quartz.
- No. 1806 Painirova. Magnetite ore with euhedral grains of white or brown-white apatite up to 3 cm long.
- No. 1807 Painirova. Magnetite ore with euhedral grains of white apatite up to 1 cm long.
- No. 1800 Tjärrojjäcka. Magnetite ore with veins up to 5 cm wide of red-white apatite which brecciate the ore.
- No. 1801 Tjärrojjäcka. Magnetite ore with aggregates of red-white apatite up to 5 mm long.

High P-content, $> 2\%$ P

- No. 1808 Hauki. Hematite ore with small grains of grey-white apatite evenly distributed or as bands up to 2 mm wide.
- No. 1809 Hauki. Hematite ore with veins up to 4 cm wide of a white or pink apatite.
- No. 1813 Henry. Hematite ore with bands up to 2 cm wide of a pink apatite.
- No. 1814 Henry. As above. The apatite bands somewhat mobilized.
- No. 1810 Nukutus. Magnetite ore with bands of white apatite some mm wide.
- No. 1811 Nukutus. Magnetite ore with veins up to 90 cm wide of pink apatite which brecciate the ore.
- No. 1812 Nukutus. As above.
- No. 1802 Pattok. Hematite ore with veins up to 1 cm wide of red-white apatite in a diffuse banding.
- No. 1803 Pattok. Hematite ore with veins up to 2 cm wide of red-white apatite which brecciate the ore.
- No. 1815 Rektorn. Martite ore with veins up to 50 cm wide of red apatite which brecciate the ore.
- No. 1816 Rektorn. White-grey apatite with bands up to 4 mm wide of hematite.

Skarn iron ore

- No. 1824 Rakkurijoki. Magnetite ore with veins up to 4 mm wide of white-grey apatite and skarn silicate minerals.
- No. 1825 Rakkurijoki. Magnetite ore with veins up to 3 cm wide of green-grey apatite and skarn silicate minerals.
- No. 1826 Southern Sautusvaara. Magnetite ore with skarn silicate veins up to 2 cm wide in which occur 2–3 mm wide veins of apatite and calcite.
- No. 1827 Northern Sautusvaara. Skarn silicates (biotite and tremolite) with small grains of apatite evenly distributed.
- No. 1830 Tjavelk. Magnetite ore rich in skarn silicates and with veins of apatite up to 4 cm wide.
- No. 1830 Tjavelk. Grey-white apatite with aggregates of magnetite and skarn silicates.
- No. 1832 Vieto. Magnetite ore with bands up to 1 cm wide of skarn silicates and grey apatite.
- No. 1833 Vieto. Magnetite ore with diffuse veins up to 2 mm wide of skarn silicates and apatite.

Metasomatic iron ore

- No. 1805 Nautanen. Tremolite-actinolite skarn with some magnetite and thin parallel veins of apatite.
- No. 1823 Kartovaara. Epidote and hematite with small fragments of hematite and evenly distributed apatite.

- No. 1828 Vattuvaara. Epidote with small fragments of hematite and evenly distributed apatite.

Gabbro

- No. 1839 Saarikoski. Gabbro with sparsely occurring 0.5–1 cm long grains of yellow apatite.

Apatite-rich meta-sediment

- No. 1848 Påläng. Light-grey, fine-grained, non-schistose apatite rock.

in the laboratory of the Geological Survey of Sweden. In many samples the apatite-concentrate was obtained by the aid of heavy liquids. The analytical results are shown in Table 1, but they are only partial analyses. In all samples fluorine and chlorine were determined. In a small number of analyses the content of phosphorus was determined, mostly to find out the pureness of the samples, and the content of CO_2 , SO_3 and water, which components are of special interest for the substitutions in the apatite. All these main components were determined by traditional wet-chemical methods. For the determination of F and Cl an ion-selective electrode was used. The determination of most elements which occur only in lesser amounts (Mg, Al, Ti, Mn, Fe and Y) was made spectrochemically with the tape-method and direct reading. The content of As was obtained by the same method, but the sample was treated by sulphide-isoformation. The determination of Al and Mg must be considered as semi-quantitative with the greatest error for Al. For Mn and Ti the error is about ± 20 per cent. K and Na were determined by the atomic absorption method. Sr, Nd, Ce were determined by the X-ray fluorescence method which also was used to control the spectrochemically obtained values of Fe, Mn and Y. The contents of Ce and Nd are given in arbitrary units as "++", "+" and "-". The last sign means a content lower than the detection limit of the method.

The pureness of the samples, as judged from the analyses, is in most cases good. The impurities most difficult to get rid of by the separation are calcite and quartz. Both minerals occur together with apatite in relatively large amounts in the high-phosphorus iron ores of the Kiruna type. The highest contents of silicon are consequently found within this group. If the high CO_2 -content in sample No. 1812, from the Nukutus ore, is due to impurities of calcite, or ankerite which also belongs to the paragenesis, or if it is really sited in the apatite lattice, cannot be said. Further there are some analyses from the skarn iron ores (No. 1827 from N. Sautusvaara and No. 1830 from Tjavelk) which show relatively high contents of magnesium. Possibly this indicates that the samples still contain small amounts of Ca-Mg-silicates. The magnesium can, however, be sited in the lattice as there is a tendency for apatite in some cases, mostly when occurring in basic igneous rocks, to contain some magnesium. The iron content is in all samples low, meaning that the iron oxides have been removed completely.

The author wants to thank Dr. Allan Danielsson and Fil. mag. Bengt Rönholm, Chemical Laboratory, Geological Survey of Sweden, for their interest and support of the investigation. Mr. Frantisek Horwath, at the same laboratory, has made the mineral separations with great care. Mrs. Maj-Britt Mecklin, Geological Institute, Åbo Akademi, has drawn the illustrations. Dr. Micheal Wilson has kindly corrected the English.

Apatite-bearing iron ores and rocks in Northern Sweden

Iron ores of the Kiruna type

In the northern part of Sweden there occur somewhat more than 25 different deposits of iron ore of the Kiruna type (Frietsch 1970, 1973). The mineralogical composition of the ore is mostly simple with magnetite, and in many cases hematite, as the principal minerals. In minor amounts apatite, tremolite-actinolite and diopside occur. Some deposits are rather rich in calcite.

As apatite is a common mineral, the content of phosphorus is often relatively high, reaching 1–2 per cent, but there are parts of the deposits, or even whole deposits, which are poor in apatite or almost free of the mineral. In most cases there is a sharp border between parts rich and poor in phosphorus. The average content of phosphorus does mostly not exceed 1 per cent. In the deposits Hauki, Henry, Lappmalmen, Nukutus and Rektorn, which lie immediately NE of the town center of Kiruna, and in the Pattok deposit, 40 km SW of Kiruna, the phosphorus content is, however, rather high. The average content is between 2.5 and 5 per cent. These deposits differ from the "normal" apatite iron ores by having hematite as the main ore mineral, magnetite being absent or occurring in subordinate amounts. The gangue is not composed of tremolite-actinolite and diopside, but of quartz and carbonate (calcite or ankerite), with some tourmaline, muscovite and albite also.

The apatite iron ores are formed by a magmatic differentiation in which volatiles played an important role (Geijer 1931b, 1935). While the main part of the magma crystallized and formed the wall rock, the ore-material was kept in solution. After the solidification of the wall rock, the ore-material intruded and gave rise to rather big, massive bodies or, to a lesser degree, to a network of small ore-veins in the wall rock forming an "ore-breccia". The above mentioned high-phosphorus ores are formed by a similar magmatic activity that formed the main mass of the iron ores of the Kiruna type, but they intruded at a lower temperature and with a higher content of volatiles. The latter gave rise to a higher oxygen fugacity and this promoted the formation of hematite instead of magnetite (Frietsch 1967). Otherwise the chemical composition of the iron oxides in the high-phosphorus ores seems to be the same as in the main mass of the apatite iron ores (Frietsch 1970).

Geijer (1967) divided the apatite-bearing ores of the Kiruna type in two types: one with a fine-grained apatite and one with a coarse-grained apatite. In the fine-grained type the apatite forms grains from a few tenths of a millimetre up to about 1.5 mm in length. This type of the apatite occurs in any proportion with magnetite, from sporadic grains in pure ore to bodies of apatite rock. Most of the iron ores of the Kiruna type belong to the fine-grained type.

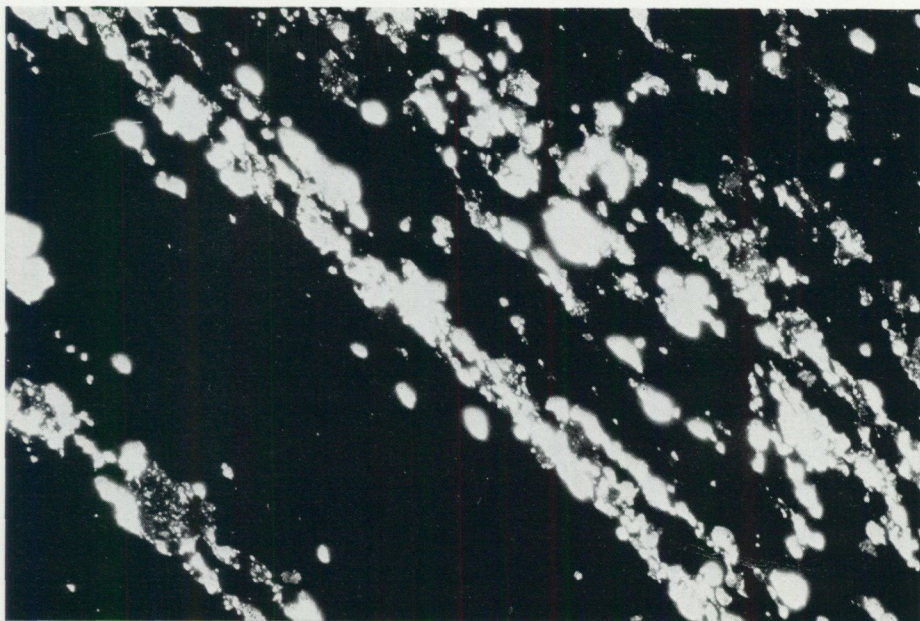


Fig. 2. Banding of apatite (white) in hematite ore. Ekströmsberg. Thin section. Nic. +, $\times 35$.

The fine-grained type shows in many cases a banding with more or less pure bands of apatite in an ore where the apatite content can vary from high to low. Geijer (*ibid.*) explains the banding as a fluidal phenomenon in the crystallizing ore magma or due to rhythmic crystallization.

In the coarse-grained type the apatite grains generally reach at least a couple of centimetres in length. The apatite is mostly unevenly distributed in the ore and does not form units of pure apatite rock in the ore. Parts of the ore are rich in apatite while other parts are almost free of this mineral.

The following apatite iron ores of the Kiruna type have been investigated in the present paper: (a) "normal" type (with the average phosphorus content less than 2 per cent P), Ekströmsberg, Leveäniemi, Painirova and Tjärrojåkka; and (b) high phosphorus-type (with the average phosphorus content higher than 2 per cent P), Hauki, Henry, Nokutus, Pattok and Rektorn.

Of the investigated apatite iron ores with a normal content of phosphorus all except Painirova have a fine-grained apatite which is evenly distributed or occurs as a thin banding in the ore (Fig. 2). The apatite forms subhedral to euhedral grains, which mostly are 0.1–0.5 mm long, but sometimes, as in Tjärrojåkka, up to 1 mm in size. In the Painirova deposit the apatite occurs partly as fine-grained, but in many cases forms rather coarse, prismatic crystals which grow perpendicular to the borders of the enclosing magnetite veins. The apatite in the Leveäniemi deposit has also in places a similar appearance,



Fig. 3. Apatite-banded magnetite ore surrounded and partly brecciated by apatite. Nukutus.

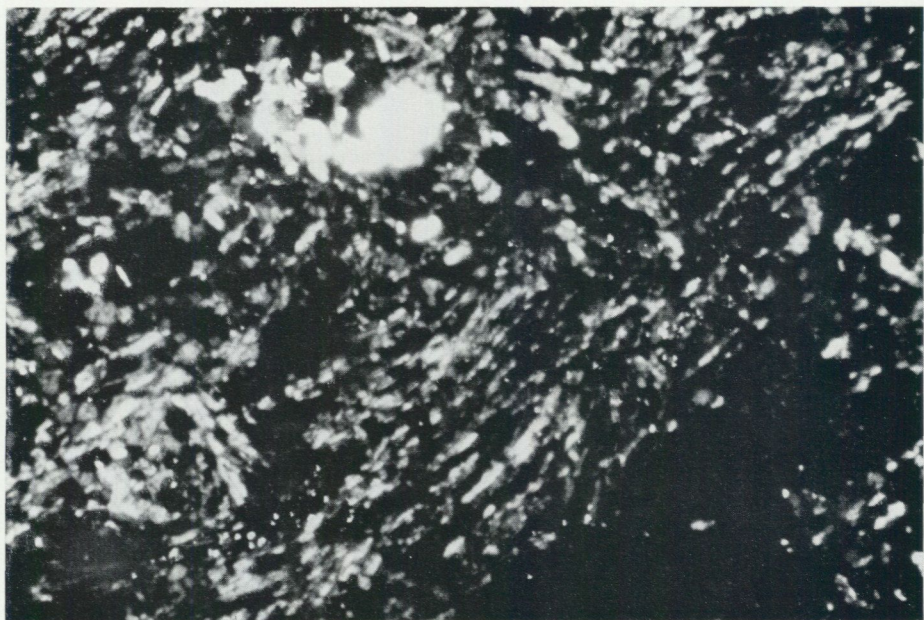


Fig. 4. Apatite (small white, grey or black laths) in hematite ore (larger black areas). White, larger grains are quartz. Hauki. Thin section. Nic. +, $\times 35$.

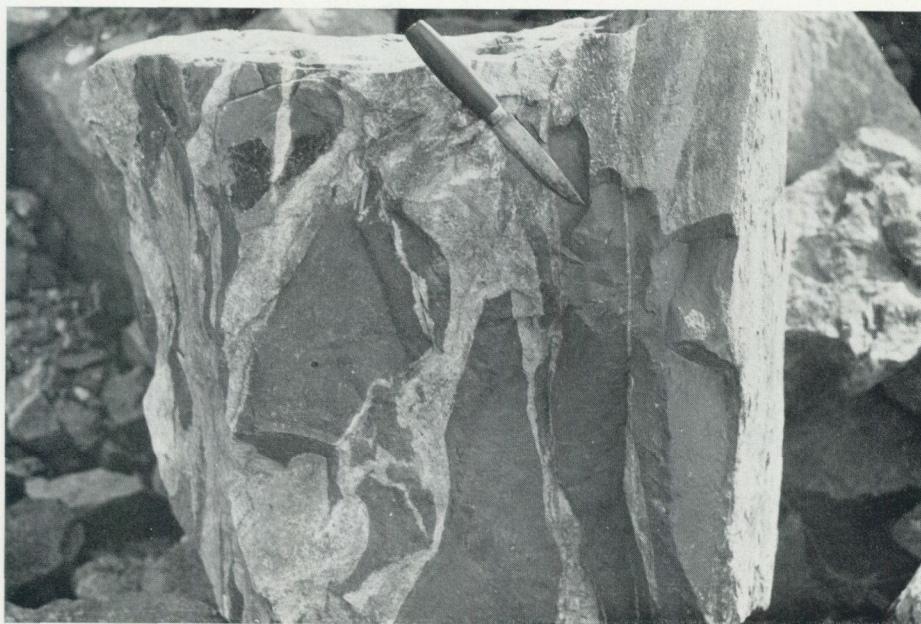


Fig. 5. Massive magnetite ore brecciated by apatite. Nukutus.

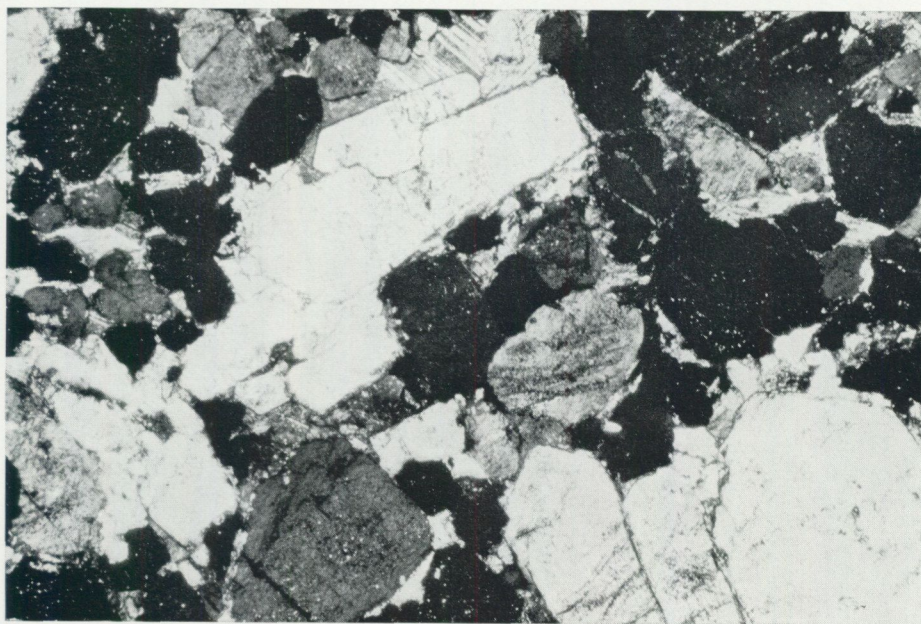


Fig. 6. Euhedral apatite grains (white, grey or black) in a fine-crystalline matrix of calcite. Nukutus. Thin section. Nic. +, $\times 35$.

but for the most part it is fine-grained and occurs in a manner typical for the "normal" type of apatite iron ores. The phosphorus content is generally rather low, less than 0.1, but in places it is between 0.1 and 0.8 per cent. The ore and the wall rock are cut by narrow veins, mostly less than 0.5 m wide, of a second generation of magnetite, which, however, is throughout relatively rich in coarse apatite. The apatite forms crystals up to some centimetres long which grow perpendicular to the direction of the veins. The phosphorus content in these veins is between 1 and 3 per cent. The appearance of the apatite is thus rather similar to that in parts of the Painirova ore. Presumably the apatite-rich magnetite dikes in Leveäniemi belong to the same ore forming activity that formed the main ore body except that in this somewhat later intrusion there was an increase in the phosphorus content of the magma.

In the high-phosphorus apatite iron ores the apatite often occurs as a very regular banding in the ore (Fig. 3). Sometimes the bands are very delicate, only some millimetres in width. In the bands the apatite forms 0.05–0.2 mm long subhedral laths, which in many cases are more or less subparallel (Fig. 4). Even if the samples investigated in the present work are few, there seems to be a tendency for the fine-grained apatite to be grey in colour, but when the apatite forms massive veins, sometimes up to one metre in width, which are brecciating the ore (Fig. 5), the colour of the apatite is mostly pinkish. The apatite in these veins has a coarser grain size, usually over 0.5 mm and sometimes up to 2 mm in diameter. The grains are anhedral to euhedral, and the apatite is often occurring together with calcite, which surrounds the apatite as a matrix (Fig. 6).

Skarn iron ores

In Northern Sweden there are found more than thirty deposits of skarn iron ore. They form lenses concordant with the surrounding wall rock which often is a limestone or some other sedimentary rock. These sediments occur always in volcanic sequences of basic composition. Sometimes the skarn ores lie directly in the volcanic rocks. The ore mineral is in almost every case magnetite, hematite occurring only rarely. The ore usually contains small amounts of iron sulphides, mostly pyrite or pyrrhotite and, in very small amounts, chalcopyrite. The ore is accompanied by large amounts of skarn minerals, either disseminated in the ore or as a banding. Further the skarn forms separate layers outside the ore. The skarn minerals are Ca-Mg-rich and are mainly tremolite-actinolite, diopside, phlogopite and serpentine. The skarn ores were formerly considered to be pyrometasomatic (Geijer 1931a, Geijer & Magnusson 1952) but are now considered to have a sedimentary origin, their present features being due to metamorphic processes (Frietsch 1970, 1973).

The content of phosphorus bound to apatite in these ores is in most cases lower than 0.1 per cent, but in some deposits the content is locally or on the whole higher, and reaches 1–2 per cent. Higher contents are known from

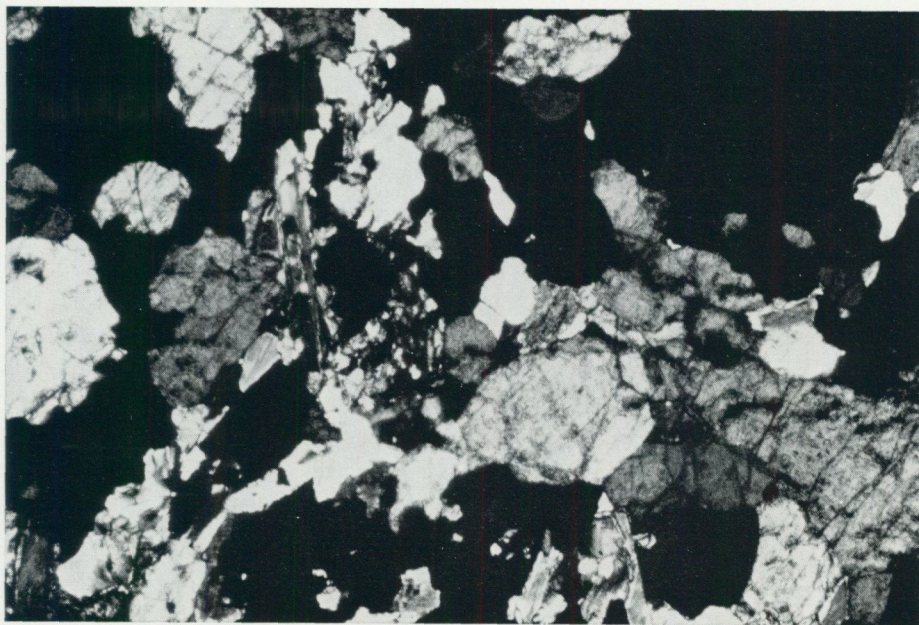


Fig. 7. Apatite (white-grey to grey, large grains with relief) surrounded by magnetite (black), tremolite-actinolite and phlogopite (both as white to white-grey laths). Tjavelk. Thin section. Nic. +, $\times 35$.

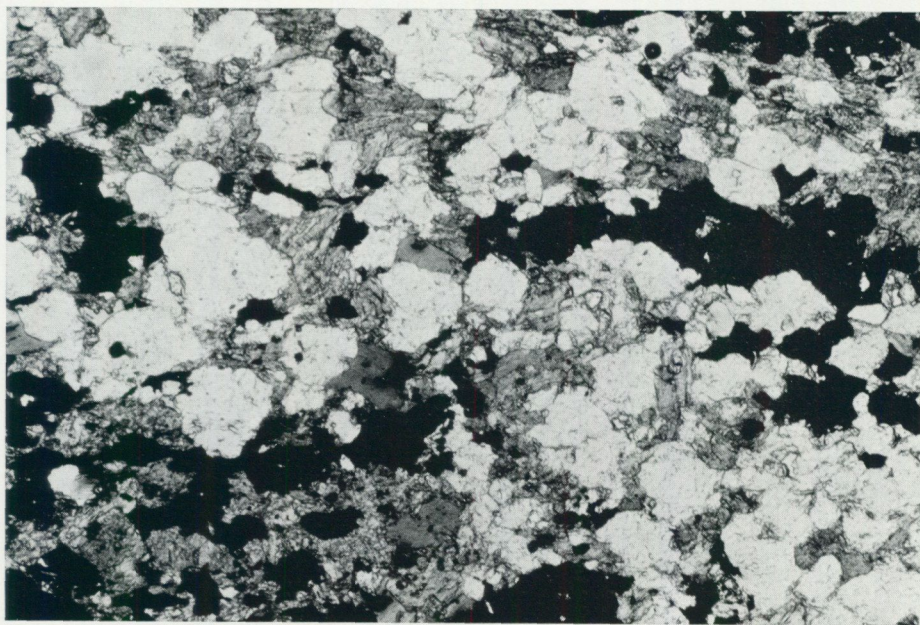


Fig. 8. Apatite (white) surrounded by tremolite-actinolite (grey) and magnetite (black). Vieto. Thin section. Ord. light, $\times 35$.

Karhujärvi, NW of Pajala: 0.1–0.8 % P; Laukujärvi, WSW of Kiruna: average 0.07 % P, locally 0.34 % P; Rakkurijoki, SW of Kiruna: mostly lower than 0.1 % P, locally 1–2 % P; Rakkurijärvi, SW of Kiruna: mostly lower than 0.05 % P, locally 0.4 % P; Tjavelk, N of Kiruna: average 1.3 % P; Vieto, W of Kiruna: mostly 0.1–0.3 % P, locally 1–2 % and Vuoma, at Masugnsbyn. 0.06–0.2 % P. The apatite occurs in many cases as a fine dissemination or forms narrow bands or veins together with the skarn silicates. In Rakkurijoki, Tjavelk and Vieto the apatite forms veins several centimetres in width. The apatite is possibly of primary origin and the thicker veins, which in some cases cut the original banding, are secondary enrichments due to mobilization processes. The apatite forms mostly anhedral to subhedral grains which are between 0.1 and 1 millimetres long (Fig. 7 and 8). Only in Rakkurijoki, Tjavelk and Vieto there are grains which are several millimetres in length.

Metasomatic iron ores

In Nautanen, ENE of Malmberget, occur some small, 1–2 metres wide, magnetite layers in meta-sediments rich in biotite and garnet (Frietsch 1970). The meta-sediments have been affected by a metasomatic alteration producing minerals such as scapolite, tourmaline, calcite, chalcopyrite, pyrite, bornite and molybdenite. According to Geijer (1918, 1931a) the ores of Nautanen area have been deposited by gaseous emanations in connection with the intrusion of the Late Archean Lina granite. The magnetite layers are rather rich in apatite and the skarn minerals tremolite-actinolite and epidote. The apatite forms veins some millimetres wide or aggregates in the skarn. The apatite occurs as 0.2–0.5 mm long subhedral grains.

The small hematite-(magnetite) ores in the Narken area (Frietsch 1972) are also of metasomatic origin. The ores at Kartovaara and Vattuvaara are built up of iron oxides as small fragments in a matrix of epidote and chlorite. The iron mineralization is mostly surrounded by epidote-quartz-rich or albite-extreme alteration rocks. A common constituent in the iron mineralization is apatite occurring as euhedral grains up to 0.5 mm long. The apatite has sometimes a kernel of orthite. Analyses from three different places show that the iron mineralization contains 0.18, 0.35 and 0.56 per cent phosphorus.

Gabbro

At Saarikoski, SW of Muodoslombolo at the Finnish border, occurs a gabbro which contains small amounts of apatite. The latter forms 1–2 cm long aggregates and has a yellow colour. The gabbro, which is in part anorthositic, is built up by andesine together with pyroxene (diopside and hypersthene), small amounts of biotite and opaque minerals. The apatite forms anhedral grains mostly around 1 mm in size.

Apatite-rich meta-sediment

At Påläng¹⁾, 45 km NE of the town of Luleå, there occur narrow apatite-rich intercalations in the sedimentary series which build up the area. Dominating are schists which often contain graphite and iron sulphides. Further, there are found quartzites, which are chemical precipitates, and limestones. The apatite-rich rock is light-grey in colour, non-chistose and rather dense. It is mainly built up of apatite occurring as sub- to anhedral grains about 0.008 millimetres in size. The origin of the apatite-rich rock is not accurately known, but is most probably sedimentary.

The sediments of the area are intruded by granodiorites and to a lesser degree gabbros, the age of which is about 1880 m.y. (Welin et al. 1970).

Substitutions in apatite

Apatite has been accorded special interest in geochemical considerations due to the complex composition which makes it possible for different elements to enter. The variation in composition is in many cases related to the mode of occurrence. The changes in composition and possible chemical substitutions will be reviewed as follows.

Fluorine, chlorine, hydroxyl and oxygen. Apatite has the formula $\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl}, \text{OH})$ where, according to many authors (i.a. Deer et al. 1962), the fluorine and hydroxyl ion can mutually replace each other to form almost pure end-members. The partition between these ions has been much discussed. According to other authors (e.g. Vasileva 1957) only the fluorine and hydroxyl ions are naturally interchangeable in the intermediate members of the continuous series fluorine-apatite hydroxyl-apatite. Without doubt the fluorine-apatite is the most common of these. It contains mostly some hydroxyl, but this ion is, like chlorine, sometimes missing or occurring only in small amounts. The fact that fluorine-apatite is the most common variety depends on the structural arrangement. At one level each F atom is surrounded by three Ca atoms, further there are Ca-O columns linked with PO_4 groups giving a hexagonal network (Deer et al. 1962). This gives a very stable structure to the fluorine-apatite. Hydroxy-apatite is transformed to fluorine-apatite even in an environment poor in fluorine (Goldschmidt 1954). This depends on the structure of hydroxy-apatite, which is little expanded compared to fluorine-apatite, and is thus relatively less stable. The chlorine-apatites and hydroxy-apatites contain on the other hand always small amounts of fluorine.

Taborszky (1962) showed that the ionic radii F^- (1.33 Å), OH^- (1.40 Å) and O^{2-} (1.40 Å) are so similar that a substitution between these does not have any effect on the apatite lattice. The greater size of the chlorine ion (1.81 Å)

¹⁾ The locality lies outside the map on Fig. 1, about 120 km S of Narken.

makes the substitution with these other ions not possible. The position of chlorine in the lattice is further different from that of fluorine, the chlorine ions are lying out of the plane with the calcium (and fluorine) ions (Strunz & Tennyson 1966).

Vasileva (1957), with the support of earlier work by Hendriks et al. (1932), also maintained that chlorine does not enter the place of fluorine and hydroxyl in the apatite structure. The chlorine ions are somewhat displaced in the direction of the c-axis compared to F and OH. According to Vasileva only one large ion such as chlorine is possible within the structure of apatite. The formula of apatite should thus be written as $\text{Ca}_{10}\text{P}_6\text{O}_{24}\text{Cl}(\text{OH}, \text{F})$, where $\text{Cl}/(\text{OH} + \text{F}) = 1$ and the maximum chlorine content is 3.5 per cent.

Vasileva (1957) and Taborszky (1972) pointed out that pure chlorine-apatites are extremely rare in nature. According to the latter author this rareness is due to the fact that chlorine-apatite is an unstable (monoclinic) modification which easily transforms to hydroxy- (or fluorine)-apatite. That chlorine-apatite appears only under special circumstances is shown by the fact that when apatite is formed in exogene conditions with excess of chlorine, viz. in seawater as phosphorite in coastal areas, a hydroxy-apatite and not a chlorine-apatite is precipitated.

Young et al. (1966) showed that oxygen replaces fluorine in apatite to a small degree, because the formula calculated from the chemical compositions shows too many positive valences and because the calculated density is closer to the measured density when oxygen is added to balance the valence.

Carbonate. That carbonate-fluorine-apatite is a distinct variety of apatite rather than a mixture of fluorine-apatite and a carbonate, seems more or less sure and has i.a. been shown on X-ray evidence by Altschuler et al. (1953). Whether or not CO_2 substitutes for the (OH, F, Cl) group, for Ca or the PO_4 -group is, however, less clear. McConnell (1971) showed that in the francolites (carbonate-apatite with more than one per cent fluorine) there is fluorine in excess above the two ions required for fluorine-apatite. On the whole francolites seem to show a rather complex pattern of substitution with C for P, F for oxygen, water for both Ca and P. The content of CO_2 can rise up to 5 %.

Manganese, strontium, rare earths. Ca may partially be replaced by Mn (up to 7.6 % MnO), Sr (up to 11.5 % SrO) and rare earths (up to 11 %) (Deer et al. 1962). Among the rare earths cerium, lanthanum and neodym are the most common, in some cases yttrium also. The content of rare earths does usually not exceed 2 per cent. As the replacement of Ca^{2+} by Ce^{3+} (or some other trivalent lanthanide) requires valence compensation, Denisov et al. (1961) have suggested heterovalent substitutions such as $2 \text{Ca}^{2+} = \text{Na}^+ + \text{Ce}^{3+}$ or $\text{Ca}^{2+} + \text{P}^{5+} = \text{Ce}^{3+} + \text{Si}^{4+}$. Further thorium and uranium are known to enter apatite. The content of uranium is, according to Altschuler et al. (1958), some hundredth of a per cent, being somewhat higher in sedimentary apatites compared to

igneous apatites. The content of thorium is several times as high as that of uranium. Other elements known to replace calcium, but less common, are iron, sodium, potassium and magnesium (Goldschmidt 1954, Taborszky 1962). Further, beryllium seems to occur in carbonate-apatite in limestone hornfelses (Grigoryev et al. 1969).

Sulphur, silicon, arsenic, vanadium. Phosphorus in apatite can, according to Goldschmidt (1954) be replaced by sulphur, silicon, arsenic and vanadium. Whether or not carbon enters is uncertain (Taborszky 1962). Vasileva (1958) has paid attention to the isomorphous replacement between phosphorus, sulphur and silicon. This necessitates in many cases paired substitutions with other elements such as Ca^{2+} , Na^+ and rare earth ions (Ce^{3+} , La^{3+} etc.).

Compositional variation of apatite due to different modes of formation

Apatite is the only rock-forming mineral that contains phosphorus and is thus very fitted for geochemical considerations. The many possibilities for substitution due to its complex chemical composition make it interesting in many respects, e.g. to study the partition of different elements such as halogens, rare earths etc. The composition of apatite is in many cases related to the mode of formation, i.e. the environment in which apatite is formed. Apatite occurs in basic to acid magmatic rocks, sedimentary rocks and metamorphic

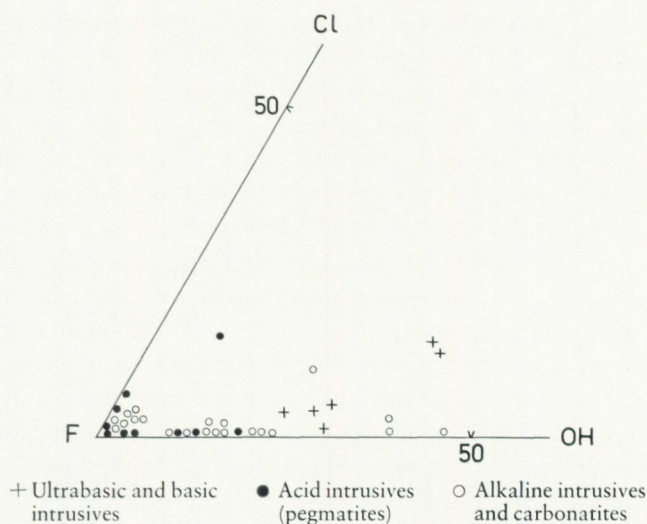


Fig. 9. Distribution of fluorine, chlorine and hydroxyl in different magmatic apatites.

rocks. A survey of the chemical composition of apatite according to the environment of formation is shown in Tables 2–7. In these are included somewhat more than 50 apatite analyses taken from the literature and a few were obtained by personal communication. Only partial analyses are given. The content of some elements such as P, Ca, Ti, Si etc. are considered of less interest for genetic consideration and are therefore omitted. As one of the main aims with the present work is to study the distribution of chlorine and fluorine in different apatites, the values of these elements together with the water-content, after recalculation to atomic proportions, have been plotted in Fig. 9.

Igneous rocks

As pointed out by Kind (1939) and Goldschmidt (1954) there is a gradual decrease of the phosphorus content with increasing acidity of magmatic rock. In both igneous and extrusive rocks the phosphorus content is highest in the basic members. High values are recorded from basalts. A high amount of phosphorus is, however, also encountered in granite pegmatites where not only apatite, but other phosphates such as triphylite-lithiophilite are found.

The number of analyses shown in Tables 2–4 is small which naturally hampers the drawing of reliable conclusions concerning the principal differences in compositions of the apatites in magmatic connection. Some differences can, however, be discerned. For the apatites in ultrabasic and basic rocks there seems to be a slight tendency for a relatively high content of magnesium. In the apatite from acid intrusives, i.e. the pegmatites, there is a clear predominance of manganese, which is in accordance with the common observation that this element is enriched in the late-stage products during magmatic crystallization.

Apatite is a typical mineral of most alkali complexes with carbonatites, and occurs in some types in such amounts that it is an economic source of phosphorus. According to Heinrich (1966) the apatite in these complexes is followed by magnetite and pyrochlore in or associated with ultramafic and mafic rocks. Further apatite is found in early carbonatitic deposits, where it occurs as disseminations and lenses in sövite and rauhaugite, and finally as postcarbonite veins within the carbonatite complexes. The apatites from the alkaline intrusives and the carbonatites are in many respects different from the other magmatic apatites. It is a well known fact that the apatite from these rocks is always relatively rich in rare earths. As seen from Tables 2–4 and as pointed out earlier by Cruft (1966), these apatites are further enriched in strontium and to some extent also in barium compared to the other magmatic apatites. Some of the apatites from the carbonatites are rather rich in carbonate and are in part francolites. This concerns especially the apatite from the Sokli alkaline deposit in Finland described by Paarma (1970).

TABLE 2. CHEMICAL ANALYSES OF APATITES FROM ULTRABASIC AND BASIC IGNEOUS ROCKS. WEIGHT PER CENT.

	1	2	3	4	5	6	7	8	9
SO ₃			0.50			0.08			
F		1.63	2.45	2.50		2.50	1.40-1.50	0.18	
Cl		0.16	0.34	0.06		0.25	0.74-0.79	5.70	
H ₂ O +		0.31	0.50	0.53		0.38	0.53-0.58	0.82	
Na ₂ O		0.11	0.14					0.5	
MgO		0.49	0.53	0.36					
Al ₂ O ₃		0.28		0.18			0.19-0.26		
K ₂ O		0.04	0.16					0.65	
MnO		tr.	0.01			tr.	tr.	0.003	
SrO		0.26	0.07	0.11		0.20	0.09-0.20	0.02	
BaO								0.28	
(REM) ₂ O ₃	0.26-0.35	0.45	0.94	0.84	0.49	0.25	0.0 -0.10	0.61	
Y ₂ O ₃								0.62	
Rare earth oxides, per cent	Ce 42-47 La 19-25 Nd 17-22 Y n.d. Σ Ce ¹⁾ 94-98 ²⁾	Y 26 Nd 24 Ce 13			Ce 39 Nd 23 La 13 Y n.d. Σ Ce 94 ²⁾			Y 30 Ce 23 Nd 11 La 10 Σ Ce 56	

¹⁾ In Tables 2-6 Σ Ce is calculated as $\frac{\Sigma (\text{La}-\text{Eu})}{\Sigma (\text{La}-\text{Lu}) + \text{Y}} \cdot 100$

²⁾ Yttrium not included

1. Peridotite-pyroxenite. Aldan, USSR. Lyakhovich & Barinskii (1961).
2. Peridotite. Alleretschen, USSR. Gontscharov (1965).
3. Gabbro-diabase. Norilsk, USSR. Gontscharov (1965).
4. Porphyrite. Norilsk, USSR. Gontscharov (1965).
5. Gabbro. Western Tuva, USSR. Lyakhovich & Barinskii (1961).
6. Gabbro-pegmatite. Kopan region, USSR. Vasileva (1957).
7. Amphibolite. Kusinsky, USSR. Vasileva (1957).
8. Gabbro. Bamble, Norway. Taborsky (1972).
9. Gabbro-norite. Rai-Iz, USSR. Vlasov (1966, p. 227).

TABLE 3. CHEMICAL ANALYSES OF APATITE FROM ACID (-INTERMEDIATE) IGNEOUS ROCKS. WEIGHT PER CENT.

	1	2	3	4	5	6	7	8	9	10	11	12	13
CO ₂				0.36-0.41	0.03	0.04							0.04-1.30
SO ₃					0.11	0.01							
F	1.35	2.57	3.01-3.68	3.64-3.75	2.40	3.25							2.4 -3.4
Cl	0.08	tr.	0.0-tr.	0.10-0.35	0.91	0.02							0.04-0.27
H ₂ O ⁺			0.07-0.34		0.12	0.04							
Na ₂ O		0.10	0.0 -0.65		0.17								
MgO	2.09	0.25	0.0 -0.04			0.01							
Al ₂ O ₃		0.38		0.46-0.58	0.04	0.08							
K ₂ O		0.02			0.01								
MnO	0.15	0.02	0.28-7.59		0.11	1.82							
SrO		11.6	0.0 -1.37		0.04	0.97							
BaO		0.06											
(REM) ₂ O ₃	3.13				1.79		0.19-0.82	1.03	0.4	0.05			
Rare earth oxides, per cent					Ce 45		Ce 17-45	Ce 44	Ce 43	Y 27	Ce 26	Y 50	
					La 22		Nd 15-29	La 29	La 29	Ce 19	Y 20	Dy 11	
					Nd 16		La 7-25	Nd 14	Nd 22	Nd 17	Nd 18	Er 10	
					Pr 10		Y n.d.	Y n.d.	Y n.d.	Gd 8	La 14	Yb 8	
					Y 3		ΣCe 74-100 ¹⁾	ΣCe 99 ¹⁾	ΣCe 99 ¹⁾	ΣCe 51	ΣCe 68	ΣCe 8	
					ΣCe 95								

¹⁾ Yttrium not included.

1. Granite. Lausitz, Germany. Kind (1939).
2. Syenite-dike. Montana, USA. Larsen et al. (1952).
3. Pegmatite. Different analyses, no 3-6, p. 325, Deer et al. (1962).
4. Pegmatite. Different analyses, no 1-2, p. 328, Deer et al. (1962)
5. Pegmatite. Crystal Lode, USA. Young & Munson (1966).
6. Pegmatite. Peerless, USA. Young et al. (1966).
7. Granite. Different localities, USSR. Lyakhovich & Barinskii (1961).

8. Quartz vein. Western Tuva, USSR. Lyakhovich & Barinskii (1961).
9. Pegmatite. Megrinskii, USSR. Lyakhovich & Barinskii (1961).
10. Granite. Kirovograd, USSR. Vlasov (1966, p. 229).
11. Granodiorite. Rai-Iz, USSR. Vlasov (1966, p. 243).
12. Granite. Slyudyanyaya, USSR. Vlasov (1966, p. 243).
13. Pegmatite. Different localities, Canada-USA. Walters & Luth (1969).

From Fig. 9 it is evident that in igneous rocks there is a dominance of fluorine-apatite, which, however, in many cases contains appreciable amounts of the hydroxyl ion. The content of chlorine is mostly less important. Kind (1939) stated that there is a tendency for the fluorine-content of the magmatic apatites to increase with the acidity of the rock, whereas the chlorine-content increases towards the basic igneous rocks. Even if the number of apatite analyses from basic rocks plotted in Fig. 9 is rather small the statement made by Kind does not seem fully justified. The fluorine-content is higher in the acid igneous rocks compared to the basic ones, but the apatite in the basic rocks has only a somewhat higher content of chlorine compared to the apatite in the acid rocks (mostly pegmatites) and the alkaline intrusions. In the acid igneous rocks there is one analysis with a higher chlorine content (0.91 per cent) described by Young & Munson (1966) from a pegmatite in a grano-diorite from Colorado (analysis No. 5, Table 3). This apatite is, however, deficient of halogens, and this is possible because of the substitution of oxygen for halogens, especially fluorine. The distribution of these ions is $F_{1.29} Cl_{0.26} (OH)_{0.14} O_{0.32}$.

In all igneous rocks, and in almost every type of rock, the fluorine content in apatite always dominates. Far more important than the chlorine-content is the hydroxyl-content, which in Fig. 9 shows a rather wide spread. Without doubt the apatites in the ultrabasic and basic igneous rocks have the highest content of this ion. The apatites in the acid igneous rocks have a low content of the hydroxyl ion. The apatites in the alkaline intrusives show a rather wide range of variation in the hydroxyl content.

TABLE 4. CHEMICAL ANALYSES OF APATITE FROM ALKALINE INTRUSIONS AND CARBONATITES. WEIGHT PER CENT.

	1	2	3	4	5	6	7
CO ₂							
SO ₃							
F	1.83	1.10					3.18-3.35
Cl	0.13	0.31					0.0-tr.
H ₂ O+	0.54	0.19					0.24-0.42
Na ₂ O	1.24	1.21					
MgO	1.06	0.10					
Al ₂ O ₃	0.89	0.68					
K ₂ O	0.68	0.06					
MnO	0.18						
SrO		2.00			1.06-2.66		2.02-14.33
BaO		0.04					0.0-0.08
(REM) ₂ O ₃		0.77	0.18-0.69 ²	0.22-0.98	0.98-1.23	0.32-2.41	0.83-2.25
Rare earth oxides, per cent			Ce 34-45 La 19-25 Nd 15-19 Y(+Tb) 6-12 ΣCe 82-91	Ce 38-49 La 15-24 Nd 15-29 Y(+Tb) 3-7 ΣCe 92-95	Ce 48-52 La 26-30 Nd 13-14 Y n.d. ΣCe 98-99 ¹	Ce 46-53 La 23-25 Nd 16-20 Y n.d. ΣCe 98-100 ¹	

¹) Yttrium not included.²) Metals, not oxides.

1. Ijolithe. Iivaara, Finland. Kind (1939).
2. Alkaline rock. Kola, USSR. Kind (1939).
3. Ultramafic alkalic massif. Koksharov, USSR. Rass (1964).
4. Ultramafic alkalic carbonatite massif. Bol'shesayansk, USSR. Rass (1970).
5. Syenite. Vishenevyye, USSR. Ganzeyev et al. (1966).
6. Alkalisyenite. Kola, USSR. Lyakhovich & Barinskii (1961).
7. Alkaline rock. Khibina, Kola, USSR. Denisov et al. (1961).
8. Carbonatite. Iron Hill, USA. Nash (1972).
9. Carbonatite. Sokli, Finland. Pers. comm. H. Vartiainen.
10. Carbonatite. Sokli, Finland. Pers. comm. H. Vartiainen.
11. Fenitized gneiss-migmatite. Vishenevyye, USSR. Ganzeyev et al. (1966).
12. Fenite. Vishenevyye, USSR. Ganzeyev et al. (1966).
13. Ultrabasic alkali rock. Vuorijärvi, USSR. Vlasov (1966, p. 227).
14. Nefeline-syenite. Lovozero, USSR. Vlasov (1966, p. 233).
15. Nefeline-syenite. USSR. Vlasov (1966, p. 245).
16. Fenite. Lovozero, USSR. Vlasov (1966, p. 251).

8	9	10	11	12	13	14	15	16
0.1-0.9	0.45-0.67	2.28-2.96						
0.05-0.18	tr.	tr.						
1.5-3.3	2.52-2.53	3.19-4.06						
0.01-0.06	tr.	tr.						
	0.22-0.25	0.25-1.30						
	0.26-0.27	0.14-0.84						
	tr.	tr.						
		0.04						
	tr.	tr.-0.10						
0.52-0.89	0.26-0.31	0.21-0.44	0.02-0.07	0.17-1.11				
0.01-0.06		tr.-0.14						
0.86-1.88	0.60-0.74	tr.-0.78	0.29-0.82	2.1-3.3	1.0	6.8	2.86	
Ce 14-25			Ce 13-43	Ce 48-55	Ce 43	Ce 42	Ce 52	Ce 53
La 8-17			Nd 10-24	La 19-27	Nd 24	La 29	La 31	La 25
Nd 12-17			Sm 7-13					
Dy 8-18			La 2-11	Nd 12-18	La 20	Nd 19	Nd 12	Nd 16
Y 7-13			Gd 5-16					
Σ Ce 50-70			Dy 2-17		Y 0	Y 0	Y 0	Y 0
			Er 1-14					
			Σ Ce 35-90 ¹⁾	Σ Ce 96-100 ¹⁾	Σ Ce 97	Σ Ce 97	Σ Ce 100	Σ Ce 99

¹⁾ Yttrium not included.

TABLE 5. CHEMICAL ANALYSES OF APATITE FROM SEDIMENTARY IRON ORE AND PHOSPHORITE. WEIGHT PER CENT.

	1	2	3	4	5	6	7	8	9	10	11	12
CO ₂	1.98						1.03-1.67	1.14	2.2			
SO ₃								0.85	1.8			
F	2.80			2.95	2.20	0.85	3.2-3.4	3.55	3.1			
Cl				0.12	0.17	2.10			0.0-0.02			
H ₂ O+	0.66						1.02-1.08	1.02	2.20			
Na ₂ O							0.10-0.52	0.36	0.6			
MgO	tr.						0.16-0.31	0.10	0.3			
Al ₂ O ₃	tr.						0.58-1.10	0.63	1.7			
K ₂ O							0.12-0.13	0.06	0.5			
MnO							0.04-0.37					
SrO	0.13											
BaO												
(REM) ₂ O ₃											0.01-0.1	0.059
Rare earth		Y 39-63	Y 36-45							Ce 33	Ce 14-45	La 26
oxides, per		Yb 3-13	Ce 16-19							La 16	La 12-34	Ce 21
cent		Er 6-10	Nd 14-17							Nd 24	Nd 15-30	Y 19
		Dy 1-11	Gd 7							Y n.d.	Y n.d.	Nd 12
		Ce 6-11	Dy 5-7							Σ Ce 85 ¹⁾	Σ Ce 76-92 ¹⁾	Σ Ce 68
		Nd 2-8	La 4-7									
		Σ Ce 8-17	Σ Ce 37-48									

¹⁾ Yttrium not included

1. Oolitic ironstone. Yorkshire, England. Deer et al. (1962).
2. Meta-sediments. Krivoi Rog, USSR. Tugarinov et al. (1969).
3. Meta-sediments. Singbhum, India. Tugarinov et al. (1969).
4. Iron formation. Broken Hill, Australia. Richards (1966).
5. Iron formation. Broken Hill, Australia. Richards (1966).
6. Iron formation. Broken Hill, Australia. Richards (1966).

7. Phosphorite. Georgina Basin, Australia. Cook (1972).
8. Phosphorite. Duchess, Australia. Russel & Trueman (1971).
9. Phosphorite. Phosphoria formation, USA. Gulbrandsen (1966).
10. Phosphorite. Different places and ages. Vlasov (1966, p. 262).
11. Phosphorite. Different places and ages. Bliskovskiy et al. (1969).
12. Phosphorite. Florida, USA. Altschuler et al. (1967).

Sedimentary rocks

In the exogenic cycle phosphorus is precipitated as phosphate in the hydrolysates. Further, phosphorus occurs in oxidates (e.g. limonite and oolitic iron ores) also as phosphate, but is here bound partly to other elements such as aluminium and iron. The sedimentary phosphates have either a biogenetic or an inorganic origin. In the first case they are remains of bones, guano etc. The abiotic type is the important one and forms phosphorite deposits of great economic value. The phosphate is here formed by an inorganic precipitation of phosphate from sea water. According to most authors (e.g. Altschuler et al. 1953, Goldschmidt 1954, Roberson 1966, Gulbrandsen 1969, Smirnov 1970, Cook 1972) the mineral of marine phosphorites is fluorine-apatite with a varying but fairly considerable content of carbonate (Table 5). It can rise to several per cent equivalent CO_2 . The substitution with hydroxyl ions is common and sometimes relatively high, the content of crystal water often exceeding one per cent. As already pointed out chlorine-apatite is not formed in seawater, which depends on the more stable structure of fluorine- and hydroxy-apatite. Most authors now believe that fluorine-apatite is the stable calcium phosphate of seawater, and hydroxy-apatite which was considered by Sillén (1961) the stable phosphate of seawater, is converted to fluorine-apatite even in environments low in fluorine (Roberson 1966).

According to Gulbrandsen (*ibid.*) there is also in the apatite of the phosphorites a paired substitution of sodium and sulfate for calcium and phosphate in about the same magnitude as the carbonate substitution. Lesser substitutions are strontium, rare earth metals, uranium and thorium for calcium.

The apatite replacement of carbonates is the most probable mode of formation of the the large marine phosphate deposits. The precipitation of apatite occurs in cold water saturated with respect to apatite. The water to which the phosphate is added is warmer, of higher pH and higher salinity than normal sea water (Gulbrandsen *ibid.*).

Iron ores of the Kiruna type

The formerly published analyses of the apatite in the iron ores of the Kiruna type are shown in Table 6. All these determinations show that this ore type contains a fluorine-apatite. The earliest analyses, published by Lundbohm (1890, 1982) are from the Vålkomman Claim at the Malmberget mine in Northern Sweden (analyses Nos 1–2, Table 6). The apatite is, however, not occurring directly in the ore but in later pegmatites, which according to Geijer (1930) have had a strong resorbing action on the older surrounding rocks. The pegmatites thus carry a great amount of ore minerals and apatite. It is not known if the latter has been affected by any chemical changes in composition during the resorption. In any case one of the analyses shows a fluorine-do-

TABLE 6. CHEMICAL ANALYSES OF APATITE FROM IRON ORES OF THE KIRUNA TYPE. WEIGHT PER CENT.

	1	2	3	4	5	6	7	8
P ₂ O ₅	40.63	41.81	41.51	39.8				40.86
CO ₂								0.05
SO ₃				0.20				0.37
F		3.67		4.0	2.78-3.85	2.72-3.70	3.12	3.54
Cl	0.22	0.19	0.22	<0.01				0.41
H ₂ O + H ₂ O-								0.01
Na ₂ O				0.07				0.23
MgO				0.56				
Al ₂ O ₃				0.26				
SiO ₂				2.2				0.34
K ₂ O				0.04				0.01
CaO		55.20	55.00	53.2				54.13
TiO ₂				0.05				
MnO				0.05				0.01
FeO	{ 0.07	0.24	0.22	0.3				
Fe ₂ O ₃				1.0				
SrO								0.07
BaO								
(REM) ₂ O ₃								1.43
Rare earth metals, per cent								Ce 34 La 31 Nd 15 Y 5 Σ Ce 89

1. Malmberget, Sweden. Lundbohm (1890).
2. Malmberget, Sweden. Lundbohm (1892).
3. Kiirunavaara, Sweden. Lundbohm (1892).
4. Grängesberg, Sweden. Pers.comm. K.-A. Björkstедt.
5. Grängesberg, Sweden. Ekström (1972).
6. Malmberget, Sweden. Ekström (1972).
7. Kiirunavaara, Sweden. Ekström (1972).
8. Cerro de Mercado, Mexico. Young et al. (1968).

minance. The analysis from Kiirunavaara published by Lundbohm (1892) is from the Direktören claim and shows 0.22 per cent chlorine, the fluorine content not determined. Other analyses of apatite in ores of Kiruna type in Northern Sweden are taken from the work of Ekström (1972) who analyzed the fluorine content in the apatite by means of a microprobe. Other elements were not determined. The fluorine content in the Malmberget apatite is 2.72-3.70 per cent (8 samples) and in the Kiirunavaara apatite 3.12 per cent (1 sample). In addition there are 8 analyses of the fluorine content in the apatite from the Grängesberg ore, Central Sweden, which deposit, in spite of the relatively

high degree of metamorphism, shows similarities with the above mentioned deposits. The Grängesberg apatite contains 2.78–3.85 per cent fluorine. According to a personal communication by Mr. K.-A. Björkstедt the apatite concentrate from Grängesberg contains 4.0 per cent fluorine and less than 0.01 per cent chlorine (analysis No. 4, Table 6). In a recent work Parák (1973) showed that the apatites from the iron ores of the Kiruna type in Northern Sweden contain 2.4–3.4 per cent fluorine and mostly less than 0.1 per cent chlorine.

Outside Sweden iron ores of the Kiruna type in *senso strictu* are rare. The deposit Cerro de Mercado at Durango in Mexico seems to be a member of this type (Geijer 1931b). New data on the magmatic origin of many of the apatite-bearing magnetite-hematite iron ores found along the eastern border of the Pacific Ocean is given by Park (1972). There is evidence that these deposits are the result of a mobilization of iron in various rocks below, and that the process is connected to the mobile belt along the continental margins. Paulick & Newesly (1968) have investigated the composition of 15 apatites from the Durango deposit and found that the composition is $\text{Ca}_5 [\text{F}_{0.92} \text{OH}_{0.07} \text{Cl}_{0.01} (\text{PO}_4)_3]$, i.e. a pronounced fluorine-apatite. Further there occur as trace elements La, Y, Ce, Mg, Na, Sr and Ba.

Sedimentary iron ores

Gross (1965, 1966, 1970) has divided the iron formations of the world into four main types with respect to mineralogical and chemical composition and depositional environment. The early Precambrian Algoma type and the middle or late Precambrian Superior type are in most cases rather low in phosphorus, less than 0.05 per cent. The early Paleozoic Clinton type and the Mesozoic Minette type differ chemically from the latter by a relatively high content of aluminium and phosphorus. Mostly the content of phosphorus exceeds 0.4 per cent. According to Lepp & Goldich (1964) the Precambrian iron formations in the Canadian shield have an average content of 0.11 per cent phosphorus compared to the post-Precambrian iron formations which have an average of 0.37 per cent phosphorus.

Geijer (1962) points out that during the Precambrian time the only possible source of phosphorus in non-detrital sediments was an abiotic precipitation and that the conditions concerning this type of precipitation during the Phanerozoic time must have been similar to those in Precambrian time. The great change in the phosphorus content of sedimentary iron ores took place at the boundary between the Precambrian and the Lower Paleozoic and, according to Geijer, this change, like the first appearance of phosphorite, coincides with the first development of phosphatic animal shells. The biogenic source is the main factor behind the increase of the phosphorus content in these Phanerozoic ores.

Even if the phosphorus content of the Precambrian iron formations is mostly low there are some exceptions. According to Dutton & Zimmer (1968) the iron formations at the Crystall Falls and Iron River areas of the Menominee district, are relatively rich in phosphorus and aluminium. The phosphorus content is on an average 0.21 per cent. The minerals containing these two elements have not been identified but some apatite has been recognized. In the Cuyuna range the iron ores contain on an average 0.13 per cent phosphorus (Lepp & Goldich 1964). Other Precambrian iron formations rather rich in phosphorus are found in Australia. In Broken Hill there is a banded garnet-magnetite-apatite-quartz iron formation with a mean content of 1.0 per cent phosphorus (Richards 1966). In the iron formations in the Hamersley group there occurs apatite and the phosphorus content varies between 0.008 and 0.38 per cent (Trendall & Blockley 1969). In the Pretoria Series in the Transvaal System in southern Africa there are found oolitic iron ores the age of which is about 2000 m.y. (Davidson 1963). The phosphorus content reaches in places 0.5 per cent and at least a part is occurring as apatite (Geijer 1962). Further a relatively high content of phosphorus, varying between 0.17 and 1.78 per cent, is found in the iron formation of the Porkonen-Pahtavaara area in Northern Finland (Paakkola 1971). The age of the formation is older than 2200 m.y. The phosphorus is mostly bound in apatite but Kaitaro (1949) described small amounts of barrandite (an aluminium-iron-phosphate) and the existence of a mineral of the variscite-barrandite series was later confirmed by Paakkola (*ibid.*). The occurrence of aluminium-iron-phosphates in this unweathered iron formation, is somewhat astonishing as these minerals otherwise are only found in iron formations which have been affected by supergene processes under tropical to subtropical conditions. During the leaching of the iron formation phosphorus is enriched in the upper parts, being fixated to aluminium or to some degree to iron (Dorr 1964, Eichler 1966).

These relatively high phosphorus contents in some of the Precambrian iron formations are certainly due to primary features and there must have prevailed special conditions during the precipitation of these iron formations compared to most iron formations which are low in phosphorus. If the richness in phosphorus can be attributed to a certain type of magmatic activity giving the iron or to special pH conditions in the sedimentary basin, is not known.

Even if it is almost certain that the relatively high amount of phosphorus found in some of the Precambrian iron formations is made up by apatite, there is unfortunately scarcely any information about the chemical composition of it. The only analytical data are of the apatite from Broken Hill (analyses Nos 4-6, Table 5). Two of the apatites are clearly fluorine-dominated with minor amounts of chlorine. Further there is one analysis of a chlorine-dominated apatite with subordinate amounts of fluorine. No information about this irregularity can be obtained from the literature (Richards 1966). The only

available analysis (No. 1, Table 5) of an apatite in a Post-Precambrian (Paleozoic) sedimentary iron ores shows a similarity with the apatite in the phosphorites. In both the content of fluorine, carbonate and hydroxyl is relatively high.

The formation of chlorine-apatite

As has been mentioned earlier chlorine-rich apatites are seldom found in nature. This is most likely due to the fact that the chlorine-apatite is unstable under normal conditions and is transformed to a hydroxy- or fluorine-apatite. The chlorine-apatite is only formed in the magmatic affiliation and the sedimentary phosphorites are devoid of chlorine. According to Taborszky (1972) the chlorine-apatite is probably formed under special conditions with rather high temperature and pressure. According to Walters & Luth (1969) ionic size and structural relations imply that a continuous solution fluorine-chlorine may exist at higher temperatures, while crystalline solubility may be limited at lower temperatures.

The highest chlorine content found in apatite has been reported from the Ödegården gabbro, Bamble, Southern Norway. It contains according to Taborszky (*ibid.*) 5.70 per cent chlorine, 0.18 per cent fluorine and 0.14 per cent hydroxyl (analysis No. 8, Table 2). A high chlorine value has been given by Harada (1938), quoted from Deer et al. (1962): in an apatite which occurs in a quartz-diorite at Kurokura in Japan, the contents are 3.75 per cent chlorine, 1.15 per cent fluorine and 0.11 per cent hydroxyl. High chlorine contents are further recorded from phlogopite deposits in Aldan in the USSR. Vasileva (1957) gives an analysis with 3.50 per cent chlorine, the others contain between 0.81 and 2.10 per cent chlorine (analyses Nos 9–12, Table 7). Apatites relatively rich in chlorine have also been described by Vasileva & Kudrayaschova (1958) from the trap rock formation in Siberia. The chlorine content varies between 0.65 and 1.95 per cent (analyses Nos 5–8, Table 7), but dominating is fluorine with 1.20–2.60 per cent. Further there is an apatite with 2 per cent chlorine occurring in a schist intruded by ultramafic rocks at Norilsk in Siberia (analysis No. 4, Table 7).

The question is now why chlorine is an essential component in the above mentioned apatites (*cf.* Fig. 10) as the content of this element in most cases is rather low (*cf.* Fig. 9). As mentioned before the chlorine-apatite has a less stable structure than the fluorine- and hydroxyl-apatite. There must thus have been special circumstances to form the apatites rich in chlorine. It is here suggested that the formation occurred at a relatively high temperature and with a high chlorine concentration in the process giving the apatite. In many cases there is clear evidence that the formation of the chlorine-apatite has been connected with a strong metasomatic activity in which chlorine played

TABLE 7. CHEMICAL ANALYSES OF APATITE FROM DIFFERENT CONTACTMETAMORPHIC ORES AND ROCKS. WEIGHT PER CENT.

	1	2	3	4	5	6	7	8	9	10	11	12
CO ₂								0.82			1.05	
SO ₃				0.54					0.53	0.22	2.58	0.36
F	2.82	3.30	3.57	2.20	1.20	2.35	2.60	2.24	2.56	1.50	0.10	1.80
Cl	0.31	0.07	0.20	2.02	1.67	1.95	0.65	0.71	0.81	1.40	3.50	2.10
H ₂ O +				0.15	0.61	0.36	0.35	0.43	0.28	0.69	0.79	0.39
Na ₂ O				0.14	0.53		0.20		0.35	0.29	0.98	0.16
MgO	0.21	0.31	0.44	0.31								0.18
Al ₂ O ₃	0.76	1.37	0.20	0.17	0.31	0.13	0.15					
K ₂ O				0.01	0.05							
MnO				tr.	0.07		0.12					0.02
SrO				0.12	0.10					0.09	0.20	0.02
BaO												
(ReM) ₂ O ₃	0.84	1.23	1.31	1.59	2.13	0.10	0.90		2.05	0.89	tr.	1.29

1. Magnetite. Gora Blagodat, USSR. Sumin (1957).
2. Magnetite. Garinsk, USSR. Sumin (1957).
3. Magnetite. Scheregesch, Gornaja Schorija, USSR. Sumin (1957).
4. Schist. Norilsk. Gontscharov (1965).
5. Diabase. Siberian trap, USSR. Vasileva & Kudrayaschova (1958).
6. Diabase. Siberian trap, USSR. Vasileva & Kudrayaschova (1958).
7. Diorite-pegmatite. Siberian trap, USSR. Vasileva & Kudrayaschova (1958).
8. Magnetite ore. Siberian trap, USSR. Vasileva & Kudrayaschova (1958).
9. Phlogopite deposit. Leglier, Aldan, USSR. Vasileva (1957).
10. Phlogopite deposit. Snezhnoe, Aldan, USSR. Vasileva (1957).
11. Phlogopite deposit. Nadezhnoe, Aldan, USSR. Vasileva (1957).
12. Phlogopite deposit. Emeraldjak, Aldan, USSR. Vasileva (1957).

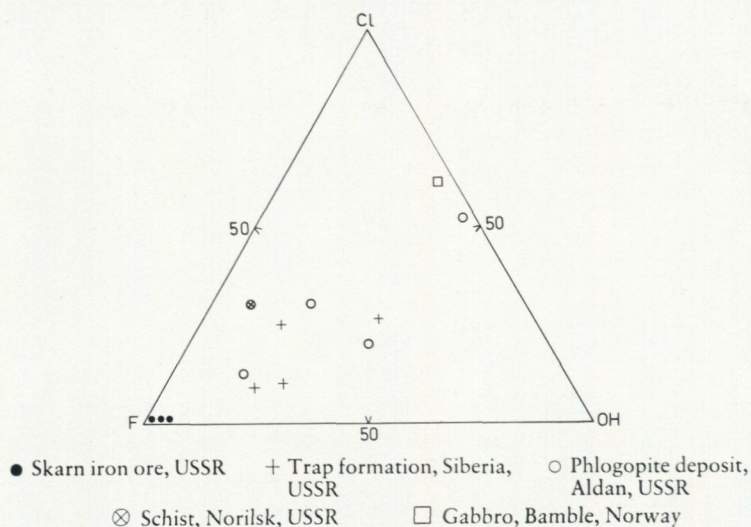


Fig. 10. Distribution of fluorine, chlorine and hydroxyl in apatite from different contact metasomatic rocks and iron ores.

an important role. This is valid for the the high-chlorine apatite from Bamble in Norway. The gabbro or "hyperite" of the area has been strongly altered giving rise to scapolite-hornblende-rich rocks, the so-called "ödegårdites" after Ödegården in Bamble (Brögger 1934). The scapolite contains up to 3.5 per cent chlorine. Connected with the scapolitization is the formation of the apatite. In many places the apatite dikes in the hyperite are followed by a scapolite-hornblende rock. According to Frodesen (1968) who investigated basic intrusions from the area, the gabbro is heavily scapolitized. The content of chlorine in the gabbro is 0.2–1.5 per cent. In the "ödegårdite" the hornblende contains 0.52–0.86 per cent chlorine and the scapolite 2.3–2.8 per cent chlorine.

A similar occurrence with a chlorine-dominated apatite in a scapolitized gabbro occurs at Dundret, Northern Sweden. The apatite, which in fact was found by looking for similar alterations as in the Bamble occurrence, contains 2.32 per cent chlorine and 0.10 per cent SO_3 , other components not being determined (Geijer 1919). The gabbro is, in the apatite-bearing parts, strongly scapolitized and contains also small amounts of tourmaline.

Further indications of a relationship between a chlorine-apatite and chlorine-bearing scapolite is given by Vasileva (1957) from the Aldan phlogopite deposits which possibly have been formed by metasomatic processes.

The fluorine-chlorine apatites in the Siberian trap rocks described by Vasileva & Kudrayaschova (1958) seem also to be related to metasomatic processes. The apatites occur in different rocks of the trap formation, namely diabase, diorite-pegmatite vein and magnetite ore. The ore deposits, in which the magnetite contains a high amount magnesium, are localized in the Siberian platform mantle series where the trap magmatism and evaporites in the lower part of the stratigraphic sequence occur together (Sokolov 1970). The magnetite is formed simultaneously with the intrusions of the trap rock which form volcanic pipes and diatremes in the overlying Paleozoic sediments. The iron mineralization occurs only in those areas where the trap rock intrudes salt and evaporate layers. Through the intrusion there occurred a thermal activity and metasomatic alteration of the enclosing rocks. When the trap rock entered the salt-bearing strata high temperature metasomatic iron ore deposits were generated. The iron is partly thought to have formed fluorides or chlorides, this being confirmed by laboratory results (Pavlov 1958, Pavlov et al. 1966). In consequence it is therefore very plausible that the high activity of halogens was responsible for the formation of the fluorine-chlorine-apatite in this case.

The high chlorine content in all these above mentioned apatites is therefore most probably connected with a high chlorine concentration in the metasomatic activity giving rise to the apatite. These apatites differ from those formed in normal contact metasomatic (skarn) deposits which are fluorine-dominated and contain only quite small amounts of chlorine (cf. analysis Nos 1–3, Table 7 and Fig. 10).

As seen from Fig. 10 the apatites rich in chlorine have also a relatively high content of hydroxyl, at least those apatites which are chlorine-dominated. The increase of hydroxyl concomitant with the chlorine in these apatites depends probably on a higher hydroxyl concentration brought about by the same high-temperature, metasomatic activity giving the chlorine.

The content of rare earth metals and their distribution in apatite

Igneous rocks

There is a clear difference in the content of rare earth elements (lanthanides and the related yttrium metal) in apatite depending on the different mode of formation of the rock or ore in which the apatite occurs. Thus the content of rare earths in magmatic apatite increases with acidity of the igneous rock (Kind 1939, Vasileva 1957). This is due to the relatively large radius of the ions (0.85–1.14 Å) and their trivalent charge which prevents the rare earths replacing the major (divalent) elements during the magmatic crystallization, and the rare earths are consequently found in the late fractions. In igneous apatites the mean content of rare earths, expressed as oxides, is 0.69 per cent (Lyakhovic & Balanova 1971). The apatite from granites contains about two times as much rare earths as apatite from basic rocks (Lyakhovic & Barinskii 1961). The highest contents are without doubt found in the apatite from the alkaline intrusions. The content of rare earths in apatite from these rocks is, according to Lyakhovic & Barinskii (*ibid.*), three times as high as in apatite from granites. From Tables 2–4 it is seen that the content of rare earth oxides in apatites from ultrabasic and basic rocks is mostly less than 0.5 per cent and in apatites from granites and alkaline intrusives higher than this value, in many cases exceeding 1 per cent. A similar high amount is also found in the apatites formed by metasomatic processes (Table 7). The highest content of rare earths in apatite ever noted is from magnetite ores in the Mineville district, New York. The ores occur in highly metamorphic rocks which possibly are mixtures between igneous intrusives and the Grenville sedimentary rocks. According to McKeown & Klemic (1956) the apatite is a fluorine-apatite with an anomalously high content of rare earths (4.7–32.4 per cent metal), thorium (0.01–0.33 per cent Th) and uranium (0.009–0.11 per cent U). To the paragenesis belong also monazite and bastnaesite.

From the close similarity between the rare earth metals and yttrium in chemical respect it follows that in magmatic processes, and especially in sedimentary processes, there is a relatively small separation of the different elements. In the most cases there is, however, a dominance of the cerium earths in comparison to the yttrium earths. According to Taylor (1972) there is in

fractional crystallization a preferential entry of the "heavier" elements with smaller cations (Gd^{3+} 0.97 Å– Lu^{3+} 0.85 Å) into Ca^{2+} – positions and the "lighter" elements with larger ions (La^{3+} 1.14 Å– Eu^{3+} 0.98 Å) are thus enriched in the later stages of the crystallization. The La-Eu-association is collectively called the cerium group. The ionization potential and electronegativity values are rather similar for all rare earth metals and cannot be used to predict the entry of the different elements during the crystallization. Yttrium which has a small radius (Y^{3+} 0.92 Å) accompanies the "heavier" elements with the smaller cations and this association is thus called the yttrium group. Among the yttrium earths the content of yttrium is usually three times the content of the lanthanides (Vlasov 1966). Following crystal chemical rules there would thus in a magmatic differentiation be an earlier incorporation of the yttrium earths compared to the cerium earths. According to some authors (e.g. Goldschmidt 1954, Rass 1970) the distribution of rare earth elements depends on the difference in basicity of the elements and their complexing capacity, and variations in the distribution reflect a changing alkalinity in the mineral-forming processes. The oxides of the cerium earths are fairly strong bases, approximating to calcium in basicity, whereas the yttrium earth oxides are more similar to magnesium. The enrichment of the cerium-lanthanides in later phases of a fractional crystallization is due to the lower melting point of the cerium silicates compared to the yttrium silicates.

The analyses of apatite from different magmatic rocks show, however, that the rare earths do not follow any simple rules for the partition in different phases. There are a lot of contradictory observations, meaning that the distribution is not only regulated by crystal chemical laws.

According to Tugarinov et al. (1969) there is a relative enrichment of yttrium earths in apatite from ultramafic and mafic rocks compared to apatites in acid rocks. There is thus a preferential enrichment of the cerium earths in the apatite from granites. Vlasov (1966) reported a trend of concentration of cerium in later members in a magma. The apatite in a gabbro-norite from Rai-Iz in the Urals is richer in yttrium and poorer in cerium earths (analysis No. 9, Table 2) than the apatite in a later granodiorite (analysis No. 11, Table 3). In late hydrothermally formed apatites the cerium earths are enriched compared to apatites in granites (Lyakhovic & Barinskii 1961). In apatites from alkaline intrusives there is a dominance of cerium earths compared with apatites in acid igneous rocks (Borodin 1960, Lyakhovic & Barinskii 1961). This very conspicuous feature is clearly elucidated in Table 4. In almost every analysis the cerium earths make up more than 90 per cent of the total amount of rare earths.

In all these apatites dominated by cerium earths compared to yttrium earths (yttrium not included), the cerium earths make up about 70–100 per cent of the total amount of rare earths. The distribution between the different

cerium earths is always the same. Cerium dominates and is roughly 40–50 per cent of the total amount of rare earths. It is succeeded in amount by neodym and lanthanum, the order between these being alternate. The content of these two elements is about 30–40 per cent. In consequence the amount of the other lanthanides is mostly less than 10–20 per cent.

On the other hand Sumin (1957) and Lyakhovic & Barinskii (1961) stated that yttrium earths in apatite become more important during the later stage of the magmatic evolution and are relatively enriched in apatites from granites and pegmatites. This is thus opposed to what has been said earlier about the preferential concentration of yttrium earths in the early stages of a fractional crystallization. The same statement is made by Cruft (1966): in apatite from pegmatites the ratio of yttrium to cerium and lanthanum is higher, and the total content of cerium, lanthanum and yttrium is lower than in apatite from regional metamorphic and plutonic environments. This is due to the selective incorporation of the cerium earths in potassium feldspars and monazite during the crystallisation of granites and the enrichment of yttrium earths in the residual solutions. Analyses Nos 10 and 12, Table 3, taken from Vlasov (1966), support the statement that yttrium earths are enriched in apatites from pegmatites. According to the same author an yttrium concentration is characteristic, of the last differentiates rich in silicon, alkalis and fluorine. Yttrium pegmatites are generally formed later than cerium pegmatites.

In addition it has to be pointed out that some of the apatites in mafic intrusions are enriched in cerium earths compared to yttrium earths (analyses Nos 1 and 5, Table 2).

From the above stands it is clear that a generalization of the distribution of the rare earth elements in apatite from different milieus of formation in the magmatic affiliation is not possible. The contradictions found are in most cases certainly dependent on the internal differences in the crystallization of each magmatic rock. The statements on the rare earth distribution made by different authors are also somewhat confusing as the yttrium earths according to some authors comprise only the heavier lanthanides, and to others the heavier lanthanides plus yttrium.

Sedimentary rocks

According to Taylor (1972) the outstanding feature of the behaviour of rare earths in sedimentary processes is the uniformity in the abundance patterns observed for different rock types. This indicates that only a minor fractionation takes place and that the dominant process is one of remixing of the diverse patterns produced by the fractionation in igneous processes. There are, however, some signs of a fractionation of the rare earths in the apatites from sedimentary rocks. Tugarinov et al. (1969) showed that a selective

accumulation of yttrium earths occurred in the phosphate rocks in the oldest sediments, as compared with phosphates of younger sedimentary rocks. There is for example a predominance of yttrium earths in apatite from the Lower Proterozoic meta-sediments at Krivoi Rog, USSR and Singbhum, India. This is especially notable with the apatite from Krivoi Rog where the Ce-earths are less than 20 per cent of the total amount (analysis No. 2, Table 5). Tugarinov et al. (*ibid.*) explain this feature as due to the fact that the sediments were derived from a predominantly basic source (amphibolites, graywackes). In such rocks there is an enrichment in the yttrium earths compared to acid igneous rocks which are predominantly enriched in the cerium-earths.

The same tendency for a relative concentration of yttrium earths occurs, however, also in the younger, Paleozoic phosphate deposits. In the phosphorites from the European part of the Soviet Union the rare earths consist essentially of yttrium. Contents of approximately 0.01 per cent Y_2O_3 are reported (Vlasov 1966). On the other hand according to the same author the content of the lanthanides in phosphorites varies between 0.03 and 0.36 per cent (expressed as oxides). There is a clear dominance of cerium and neodym over the other lanthanides.

The investigation by Bliskovskiy et al. (1969) showed similar results. Phosphorites of different ages and from different places in the Soviet Union roughly contain 0.01 to 0.1 per cent rare earth oxides, yttrium not included. In these there is a clear predominance for the lighter cerium earths, making up 76–92 per cent of the total lanthanides. In apatites from other phosphorite deposits in the world the content of rare earth oxides reaches 0.05–0.2 per cent; here, however, yttrium is included.

Altschuler et al. (1967) found also in the Florida phosphorite a relatively high amount of yttrium, the cerium earths reaching 68 per cent of the total sum of lanthanides and yttrium (of. analysis No. 12, Table 5).

Thus there seems to be a somewhat greater tendency for yttrium to become enriched in the sedimentary phosphates compared to most of the igneous apatites.

The iron ores of the Kiruna type

Data concerning the content of rare earths in the apatite from iron ores of the Kiruna type in Northern and Central Sweden are shown in Table 8. It is obvious that the content of rare earths is astonishingly uniform, being roughly around 0.5 per cent rare earth metals (as oxides). Further it is evident that most of the apatites from the ores in Northern Sweden are rich in cerium earths compared to yttrium earths, the percentage of the first being 68–85 per cent of the total amount of rare earths. A notable exception is the apatite in the Blötberget and Risberget deposits in Central Sweden which is relatively rich in yttrium, being even higher than cerium which is usually not the case. Unfortunately the

TABLE 8. THE CONTENT OF RARE EARTHS IN APATITE FROM IRON ORES OF THE KIRUNA TYPE IN SWEDEN.

		p.p.m.					
		% (REM) ₂ O ₃	Y	La	Ce	Nd	Σ Ce ¹)
Central Sweden							
No.	1. Blötberget	0.47	1360	400	1060	540	
	2. Grängesberg	0.67	1870	470	1440	1000	
	3. Idkerberget	0.66					
	4. Risbergsfältet	0.51	1270	420	1340	980	
Northern Sweden							
	5. Tuolluvaara	0.37	880	200	870	690	
	6. Malmberget	0.55	1190	550	1950	760	65
	7. Kiirunavaara	0.59	680	740	1640	980	76
	8. Rektorn	0.55	890	570	1280	750	65
	9. Henry	0.47	650	460	1160	750	70
	10. Nukutus	0.45	450	520	1300	750	78
	11. Kiirunavaara	0.71					} 80- 85
	12. Rektorn	0.64					
	13. Henry	0.62					
	14. Nukutus	0.50					

Source: Nos 1-5 from Anderson (1972), Nos 6-10 from unpublished analyses, Luossavaara-Kiirunavaara Aktiebolag and Nos 11-14 from Parák (1971).

¹) Calculated as $\frac{\Sigma(\text{La}-\text{Eu})}{\Sigma(\text{La}-\text{Lu}) + \text{Y}} \cdot 100$

percentage of the cerium earths to the total amount of rare earths cannot be calculated, as in these analyses (taken from Anderson 1972) only the four elements Y, La, Ce, and Nd are determined. Parák (1973) showed that in the apatite from the iron ores of the Kiruna type in Northern Sweden the elements Ce, La and Nd dominate, Y is subordinate and the other rare earths are insignificant.

The only available analysis of rare earths in apatite in other iron ores of the Kiruna type is from Durango, Mexico given by Young et al. (1968). The content of rare earths is here 1.43 per cent (as oxides) which is high compared to the Swedish apatites. The cerium earths are dominating, making up 90 per cent of the total amount of rare earths. The yttrium content is 760 p.p.m. Y which is the same amount as in the apatites from the iron ores of the Kiruna type in Northern Sweden.

The composition of apatite in iron ores and rocks in Northern Sweden

The chemical variations which in the present investigation are found to occur in the apatites from different types of iron ore and rocks in Northern Sweden will now be discussed. The analytical data, presented in Table 1, are, however,

in many respects incomplete, and this restricts the value of the investigation as only some aspects of the compositional variations in the apatites can be dealt with.

Iron ores of the Kiruna type

The present investigation shows that the apatite from the iron ores of the Kiruna type in Northern Sweden is fluorine-dominated with, in most cases, only small amounts of chlorine and hydroxyl (Fig. 11). The content of SO_3

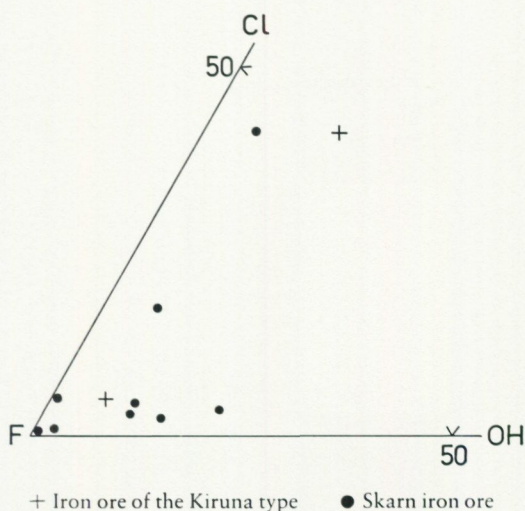


Fig. 11. Distribution of fluorine, chlorine and hydroxyl in apatite from iron ores in Northern Sweden.

seems also to be low (Table 1). The fluorine dominance is very pronounced in the high-phosphorus ores (average higher than 2 per cent P). The fluorine content is here greater than 3 per cent and the chlorine content lower than 0.2 per cent, except for one sample from the Pattok deposit which contains 0.3 per cent chlorine. The fluorine/chlorine-ratio (calculated as atomic equivalents) in these apatites is thus always greater than 25 (Table 9). The apatite in the ores with a "normal" content of phosphorus (average less than 2 per cent P) contains on the other hand in most cases more than 0.2 per cent chlorine. Only the apatites from Painirova and one apatite from Ekströmsberg have a fluorine/chlorine-ratio of 25 or higher. In the other deposits the higher chlorine content in the apatite gives fluorine/chlorine-ratios between 1 and 9. An exceptionally high chlorine content is found in the samples from Leveäniemi (0.9–2.2 per cent) and Tjårrojåkka (0.7 per cent). It is interesting

TABLE 9. THE F/CL-RATIO (ATOMIC EQUIVALENTS) IN APATITES FROM DIFFERENT ORES AND ROCKS IN NORTHERN SWEDEN.

IRON ORES OF THE KIRUNA TYPE

"Normal" type, <2 % P

Sample No.	Locality	
1828	Ekströmsberg	>32.0
1829	Ekströmsberg	8.8
1845	Leveäniemi	1.3
1846	Leveäniemi	4.9
1847	Leveäniemi	1.7
1806	Painirova	24.5
1807	Painirova	26.4
1800	Tjärrojäkka	6.4
1801	Tjärrojäkka	6.0

High-phosphorus type, >2 % P

1808	Hauki	>32.0
1809	Hauki	>33.8
1813	Henry	>25.4
1814	Henry	>31.0
1810	Nukutus	>27.2
1811	Nukutus	>30.0
1812	Nukutus	>31.0
1802	Pattok	17.5
1803	Pattok	>19.7
1815	Rektorn	>33.0
1816	Rektorn	>31.0

SKARN IRON ORES

1824	Rakkurijoki	2.1
1825	Rakkurijoki	3.0
1826	S. Sautusvaara	>25.4
1827	N. Sautusvaara	4.5
1830	Tjavelk	1.7
1831	Tjavelk	1.1
1832	Vieto	18.2
1833	Vieto	5.7

METASOMATIC IRON ORE

1805	Nautanen	>29.2
1823	Kartovaara	>32.0
1820	Vattuvaara	>33.0

GABBRO

1839	Saarikoski	6.4
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APATITE-RICH META-SEDIMENT

1848	Päläng	>17.8
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to note that in the Leveäniemi deposit the apatite is chlorine-rich both in the main ore and in the magnetite-dikes which intersect the ore and the wall rock. In Fig. 11 the chlorine-rich apatites from Leveäniemi are clearly separated from the other apatites in the ores of the Kiruna type.

As pointed out earlier most of chlorine-apatites seem to have been formed in connection with metasomatic processes rich in chlorine. It is debatable whether or not such processes have been active in the formation of the chlorine-rich apatites from the Leveäniemi and Tjärrojåkka iron ores. It should, however, be pointed out that both deposits are heavily affected by a secondary scapolitization, the effects of which are most intense in the wall rock (Frietsch 1966, 1973). The scapolite in the Svappavaara area, in which the Leveäniemi deposit occurs, is like the scapolite from other areas in Norrbotten, a dipyre with a chlorine content which exceeds 1 per cent. The formation of scapolite in Norrbotten is believed to be related to the late Archean Lina granite (Geijer 1931a). According to Geijer (1931b) there are, however, some indications (in the Mertainen deposit) that the scapolite in the iron ores of the Kiruna type, is related to the ore formation and thus much older. It cannot be said if there is any "primary" scapolite in the Leveäniemi and Tjärrojåkka deposits. It is clear, however, that in the other deposits of the Kiruna type investigated in this paper, where a scapolitization process has not been active, (at least not on a major scale,) the apatite contains only small amounts of chlorine. As the scapolitization in Leveäniemi and Tjärrojåkka most likely is later than the ore and in consequence is also later than the apatite, this would necessitate a metasomatic alteration of the earlier formed apatite by the chlorine-rich solutions forming the scapolite. The chlorine concentration must have been high enough to bring about a substitution of the fluorine by chlorine in the apatite. The larger size of the chlorine ions prevents their entry into the apatite lattice, and chlorine-apatites do not seem to form in low chlorine concentrations (and at low temperatures, viz. in seawater a fluorine-apatite is formed). On the other hand it cannot be ruled out that the high chlorine content in the apatite in Leveäniemi and Tjärrojåkka is primary, meaning that the magmatic activity giving rise to the deposits must have been especially rich in chlorine compared to the other deposits of the Kiruna type. The coincidence between a high chlorine-content both in the apatite and the scapolite in these two deposits is, on the basis of what has been stated earlier about the formation of the chlorine-rich apatites, too remarkable to be ignored.

In a recent paper by Ekström (1973) support is given for the notion of a metasomatic alteration of the apatite in the Leveäniemi ore. Ten apatite samples have been analyzed and most are rich in chlorine. The analyses show 40–92 (mole) per cent fluorine, 0–33 per cent chlorine and 5–31 per cent hydroxyl. In apatites from other deposits of the Kiruna type (Malmberget and Grängesberg) the content of chlorine and hydroxyl is considerably less. The apatite from Grängesberg contains almost exclusively fluorine. According to Ekström the amount of chlorine in apatite is mainly controlled by temperature, pH and activity of the chlorine ion in the fluidal phase. With increasing temperature and chlorine-concentration in the solutions the chlorine-content in apatite

increases. In the Leveäniemi apatite the original fluorine has been substituted by chlorine in connection with the later scapolitization. The relatively high content of hydroxyl is due to an increase in pH or partial pressure of water during the scapolitization.

Otherwise the analyses in Table 1 show that there are no special chemical features connected with the apatites from the iron ores of the Kiruna type. The apatite from the Pattok high-phosphorus deposit is relatively high in magnesium (0.2 per cent Mg) which most probably is sited in the apatite lattice, as no magnesium minerals are found in the samples. An interesting feature concerning all the phosphorus-rich ores of the Kiruna type, is that they are relatively enriched in yttrium compared to the ores with a "normal" phosphorus content. In the high-phosphorus ores the content is 0.06–0.09 per cent Y and in the "normal" ores 0.03–0.06 per cent Y. In the other apatites investigated in this paper the yttrium content does not exceed 0.05 per cent, the apatites in the high-phosphorus iron ores of the Kiruna type have thus a pronounced dominance of yttrium. If there is any other difference with respect to the rare earth elements between the apatite in the high-phosphorus and "normal" phosphorus ores of the Kiruna type cannot be decided on the basis of the results in Table 1. There seems to be a slight tendency for the apatites in the high-phosphorus ores to be somewhat richer in La and Nd than the apatites in the "normal" ores. The dominance of the yttrium content in the apatite from the high-phosphorus ores is, however, rather obvious and corresponds well with the hypothesis that these ores are a later phase in the same magmatic activity that give rise to the main mass of the iron ores of the Kiruna type with a "normal" content of phosphorus. Yttrium has as in some other intrusives (cf. p. 36) been enriched in a late phase of the magmatism.

Skarn iron ores

As seen from Tables 1 and 9 the apatite from the skarn iron ores in Northern Sweden is a fluorine-apatite with a rather high content of chlorine. The fluorine/chlorine-ratio is in most cases lower than 5. In some samples chlorine is even dominating. The content of other main components such as water, SO_3 and CO_2 , is low according to the few analyses available. The distribution of the fluorine, chlorine and hydroxyl ion in two analyses is shown in Fig. 11.

The common high chlorine in these apatites is remarkable. The highest content is found in the Tjavelk deposit, where the apatite contains 2.3 per cent chlorine and 1.3 per cent fluorine. As has been stated earlier in this paper the apatite in the skarn iron ores is most presumably syngenetic with the iron. This would mean that in those deposits where noteworthy amounts of apatite have been formed, the magmatic activity giving rise to these chemical precipitations, was not only rich in iron, silicon and carbonate, but also in halogens.

The halogen content of the skarn minerals accompanying the apatite is not known, but from other deposits of the skarn iron ores in Northern Sweden the content found in the silicates is rather low. The fluorine content dominates, reaching 0.5 per cent or somewhat more. Chlorine is very low, about 0.01 per cent (Geijer 1961, Frietsch 1966). Many of the skarn ore deposits are affected by a scapolitization similar to that described above from the Leveäniemi and Tjårrojåkka iron ores of the Kiruna type. The intensity of this metasomatic alteration in each of the skarn iron ores investigated here is, however, not closely known. In none of the samples with apatite is scapolite found. If the scapolitization is responsible for the chlorine content in the apatite it would mean, as with the apatite in the Leveäniemi and Tjårrojåkka ores, a chlorine substitution for fluorine in an earlier formed apatite.

Other special chemical features have not been discerned in the apatites from the skarn iron ores in Northern Sweden. As pointed out in the beginning of this paper there are two samples (from N. Sautusvaara and Tjavelk) which are relatively rich in magnesium (0.5 per cent Mg). This can be due to impurities of calcium-magnesium- or magnesium-rich minerals, but as the content of silicon in the analyses is rather low, the magnesium can be sited in the apatite lattice. Small amounts of magnesium are also found in apatites from basic rocks (Table 2) and in contact-metasomatic rocks (Table 7).

Metasomatic iron ores

The apatite in the metasomatic iron ores investigated from Northern Sweden is fluorine-dominated, the chlorine content being less than 0.2 per cent. The fluorine/chlorine-ratio is greater than 30 (Table 9). In Nautanen the iron ores are considered to have been formed by a metasomatic activity which i.a. give rise to the formation of scapolite. In this case there is no support for a high chlorine concentration resulting in a chlorine-rich apatite. The titanium content (0.05 per cent Ti) in the apatite from this deposit is higher than in all the other apatites analyzed. In the Narken iron ores, which are of a metasomatic origin and of late formation, later than the Archean Lina granite which otherwise is considered as the youngest Precambrian rock in Northern Sweden, the apatite is fluorine-dominated with only small amounts of chlorine.

Gabbro

The content of fluorine and chlorine in the apatite from the gabbro at Saarikoski is rather similar to apatites from other basic igneous rocks (Table 2). The fluorine/chlorine-ratio is about 6.

Apatite-rich meta-sediment

The apatite from the apatite-rich meta-sediment at Påläng is dominated by fluorine, chlorine occurring only in small amounts. The sum of the halogen

content is very low making it questionable if a pure apatite phase has been analyzed. The contents of magnesium and aluminium are also unusually high, which confirms the suspicion that other minerals are present.

Conclusions

Apatite shows a relatively wide range of chemical variations depending on the environment in which it is formed. In the magmatic affiliation apatite occurs mainly in the ultrabasic-basic intrusions, acid intrusions (mostly pegmatites) and alkaline ultrabasites, in part in the carbonatites associated with the latter. In the magmatic iron ores of the Kiruna type apatite is a common mineral. In the sedimentary rocks apatite is mainly found in the phosphorites, but occurs in many Phanerozoic iron ores giving them a relatively high phosphorus content. Further, some of the Precambrian iron formations contain small amounts of apatite. On the basis of the present investigation and by comparative studies of the literature the following conclusions concerning the chemical variations in apatite can be drawn:

1. Elements or chemical radicals which are of importance for characterizing apatite of different genesis, are fluorine, chlorine, water (hydroxyl), carbonate, manganese, strontium, barium and the rare earth elements. The fluorine-apatite is without doubt the most common variety and is found in every type of rock. Chlorine and hydroxyl ions occur as common constituents, but apatites rich in chlorine are seldom found. This fact is elucidated in Fig. 12 where the F-Cl-OH-distribution previously shown in Figures 9-11 is compiled. Also in Fig. 12 is shown the area that is covered by the phosphorites according to the analyses given by Gulbrandsen (1966), Russel & Trueman (1971) and Cook (1972). Even in (low-temperature) chlorine-rich milieus, such as seawater, a fluorine-hydroxy-apatite and not a chlorine-apatite is formed. This depends on the restriction of the large chlorine ion to enter the apatite lattice. Chlorine-rich apatites seem to form only under special magmatic conditions, where high-temperature, metasomatic solutions rich in chlorine have been active. There is no tendency, as stated earlier in the literature, that the chlorine content of apatite increases with the basicity of igneous rocks.

2. In apatite from ultrabasic-basic igneous rocks there is a lower content of fluorine than in apatites from acid igneous rocks and most of the alkaline intrusions. The chlorine content in apatites from the ultrabasic-basic rocks is mostly the same as in the other magmatic apatites, but they are decidedly richer in the hydroxyl ion than the apatites from the acid igneous intrusions, and most of the apatite in the alkaline intrusions. In ultrabasic-basic rocks the apatite shows slight tendency to be enriched in magnesium.

3. Apatite in acid igneous intrusions (mostly pegmatites and to a lesser

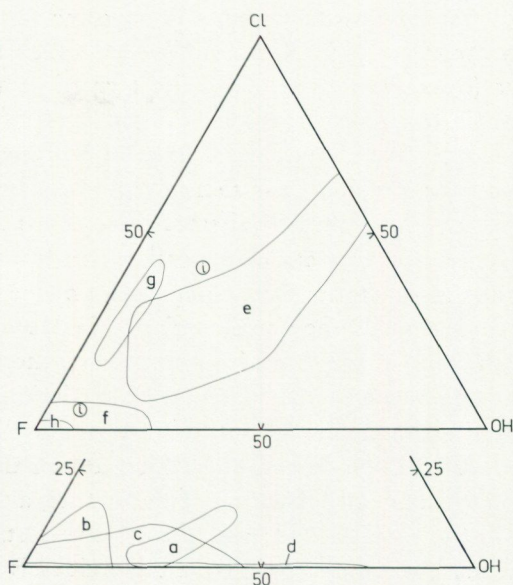


Fig. 12. Distribution of fluorine, chlorine and hydroxyl in apatite from different rocks and ores.

a. Ultrabasic-basic intrusives. b. Acid intrusives. c. Alkaline intrusives. d. Phosphorites. e. Contact-metasomatic rocks and ores formed by high chlorine activity. f. Iron ores of the Kiruna type, Northern Sweden. g. Iron ore of the Kiruna type, Leveäniemi. h. Skarn iron ores, USSR. i. Skarn iron ores, Northern Sweden.

amount granites) is an almost pure fluorine-apatite with only small amounts of hydroxyl. The chlorine ion is almost totally missing. The apatite is relatively enriched in manganese.

4. The apatite from alkaline intrusions is a fluorine-apatite with varying amounts of hydroxyl, and is in some cases relatively rich in carbonate, especially when occurring in carbonatites. The content of rare earth elements is always relatively high. Further there is a tendency towards concentration of strontium and barium in the apatite.

5. In contact-metasomatic rocks where the apatite is formed by high-temperature, metasomatic solutions with a high concentration of chlorine, an apatite rich in chlorine is formed. The content of the hydroxyl ion in the apatite is partly relatively high. In normal contact-metasomatic skarn ores there are no chlorine and hydroxyl ions present in the apatite, the fluorine ion is quite dominating.

6. Apatite in the sedimentary environment occurs mostly in the Phanerozoic phosphorites. These are characterized by a fluorine-apatite with relatively high amounts of carbonate and hydroxyl ions.

7. The apatite in the magmatic iron ores of the Kiruna type is in most cases

a fluorine-apatite with only small amounts of chlorine and hydroxyl. This concerns especially the deposits in Northern Sweden which have a high content of phosphorus (over 2 per cent P) and are formed at a somewhat later stage of the magmatic fractionation than the main mass of the ores of this type. In the deposits Leveäniemi and Tjärrojåkka in Northern Sweden which have a normal P-content, the apatite is rich in chlorine, but this fact can be assigned to a late scapolitization which affected these deposits.

8. Some Precambrian iron formations are rather rich in phosphorus which element is mostly bound to apatite. The composition of the apatite is imperfectly known, but there seems to be a wide variation between the fluorine and chlorine contents. In some of the skarn iron ores in Northern Sweden, which are interpreted as metamorphosed sediments, this variation in the halogens can be assigned to the above mentioned scapolitization.

9. The rare earth metals, which substitute for Ca^{2+} in the apatite lattice, show, depending on the mode of formation of the apatite, a rather wide range of variation both in the total amount and the relative distribution between the different elements. The content of rare earth oxides is in apatites from ultrabasic-basic rocks mostly below 0.5 per cent. In apatite from acid igneous rocks it is somewhat higher and reaches the highest value in apatites from alkaline intrusion and carbonatites. The content exceeds here mostly 1 per cent. Similar high values are also found in the apatites from the contact-metamorphic rocks and iron ores. The magmatic iron ores of the Kiruna type contain about 0.5 per cent. The sedimentary apatites show low values, the content being below 0.1 per cent.

The different elements of the rare earths show, in spite of their similar chemical character, rather large differences in relative abundance depending on the environment of formation of the apatite. There seem to be several irregularities and exceptions in the distribution. In apatites from igneous rocks the partition of the rare earths does not always follow crystal chemical laws, and there seem to be variations from intrusion to intrusion. According to the ionic size there would be, in a fractional crystallization, a preferential entry of yttrium earths compared to cerium earths.

In apatite from the ultrabasic-basic igneous rocks there is mostly an enrichment of the cerium earths compared to the yttrium earths, but in some cases the latter are dominating. In apatite from acid igneous rocks there are cerium earths enriched, but in others there is a concentration of yttrium earths. In the alkaline intrusives there is a clear tendency for the cerium earths to become concentrated, yttrium earth being almost missing.

The apatite from the iron ores of the Kiruna type shows a dominance of the cerium earths, but in some deposits there is a relatively high content of yttrium earths.

The sedimentary apatites are partly relatively enriched in yttrium.

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