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Rare earth elements in apatite-rich iron deposits and associated rocks of the Avnik (Bingöl) region, Turkey

by *Cahit Helvaci*[1]

Abstract

In the Avnik region, Paleozoic basic to felsic metavolcanics are interbedded with massive and banded apatite-rich iron deposits, and are intruded by granitoids. These rocks are unconformably overlain by micaschists and marbles, which were folded and metamorphosed during the Alpine orogeny.

Neutron activation analyses for rare earth elements have been carried out on a suite of iron ores, separated apatites, and associated metavolcanic rocks and granitoid intrusions from the Avnik metamorphic terrain. The major-element geochemistry of metavolcanics is that of an igneous suite of generally calc-alkaline character. Similarities with modern calc-alkaline volcanic rocks extend to REE patterns. The apatite-rich iron ores and associated metavolcanic rocks have similar REE patterns, which implies close genetic relationships between them.

All the separated apatites, iron ores, and the host metavolcanic rocks show a marked negative Eu anomaly. The REE patterns of granitoid are fundamentally different from those of the metavolcanic rocks and the associated iron ores.

REE data on coexisting apatite and magnetite and on the associated metavolcanic rocks suggest that the ores formed from immiscible liquids which separated from magmas that underwent strong fractionation.

REE patterns have not been affected by the metamorphism, later retrogression, and recrystallization of the rocks and the ores.

Keywords: Iron deposite, apatite, rare earth elements, geochemistry, Avnik region, Turkey.

1. Introduction

The Bitlis Massif is a large area of metamorphic rocks of Paleozoic age, lying in the interior of the Eastern Taurus fold-belt of Southeast Turkey. The Avnik (Bingöl) area is situated in the western part of the massif. The study was done on rocks collected from an area approximately 30 km southwest of Bingöl city and 20 km west of the town of Genç (Fig. 1).

The Bitlis Massif includes an extensive tract of greenschist to amphibolite facies metamorphic rocks. Geological and paleontological evidence (ALTINLI, 1966) and radiometric dating (YILMAZ, 1971, HELVACI and GRIFFIN, 1985) suggest that these rocks were deposited, deformed, and metamorphosed in Paleozoic time. The southern edge of the Bitlis Massif marks the boundary between the Anatolian and the Arabian plates along the SE-Anatolian thrust fault. The metamorphic rocks of the Bitlis Massif are thrust southward over sedimentary rocks of the Arabian foreland (e.g. ALTINLI, 1966; KETIN, 1966; YILMAZ, 1971; HALL and MASON, 1972; AYKULU and EVANS, 1974; HALL 1976; GENÇ, 1977; ERDOĞAN et al., 1981; HELVACI and GRIFFIN, 1983, 1985).

An extensive exploratory trenching and drilling programme in the iron deposits of the Bitlis Massif was undertaken by the Mineral Research and Exploration Institute of Turkey (M.T.A.) from 1976 to 1981.

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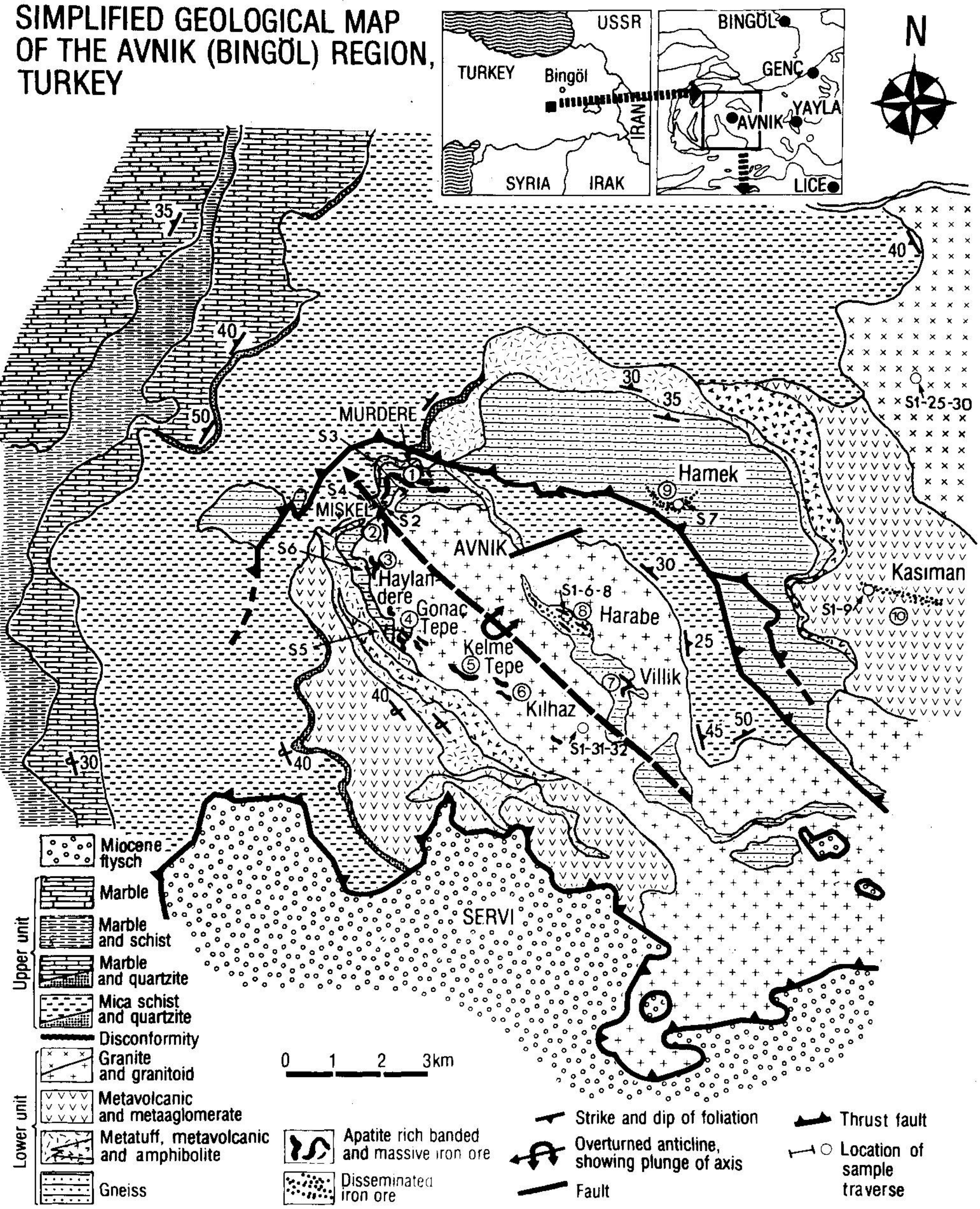

Fig. 1 Simplified geological map of the Avnik region, based on the work of Erdoğan et al. (1981).

REE elements, owing to their coherent geochemical behavior, their wide usage for evaluation of rocks genesis, resistance to alteration and metamorphism, and the high precision with which they can be analyzed, will form the backbone of the following discussion. This paper is intended to present REE analyses and distribution of the metavolcanic rocks, granitoids, and apatite-rich iron deposits, and attempts to define both the relationships between these rocks, and the nature of the apatite-rich iron deposits.

2. Geological setting

In the Avnik area, rocks are subdivided into lower and upper units (ERDOĞAN et al., 1981). The lower unit rocks are a series of basic to felsic calc-alcaline metavolcanic rocks (ca. 450 M.a.) (HELVACI and GRIFFIN, 1985), interbedded with banded and massive apatite-rich iron deposits, and intruded by the Avnik granitoid and the Yayla granite (ca. 350 M.a.) (HELVACI and GRIFFIN, 1985). The upper unit rocks include micaschist, marbles (with Permian fossils), marble-schist intercalations, and white marbles.

On the basis of field relations (ERDOĞAN et al., 1981) and petrography (HELVACI and GRIFFIN, 1983), the lower unit rocks can be divided into four formational groups: quartz-feldspar gneiss (strongly foliated felsic metavolcanics), amphibolites, metavolcanics / metatuffs, and metavolcanic / metaagglomerates. The quartz-feldspar gneisses often alternate with amphibole-rich gneisses and amphibolites and are migmatized along the contact with the granitoid.

The apatite-rich iron deposits are massive, banded, disseminated, and stockwork bodies of magnetite, apatite, and actinolite within the calc-alkaline metavolcanic rocks. Apatite and actinolite occur in large amounts as gangue minerals.

The lower unit is intruded by the heterogeneous and strongly albitized Avnik granitoid, which has intrusive and gradational contacts with the supracrustals, and by the homogeneous Yayla granite with sharp intrusive contacts (Fig. 1).

In the Avnik region, the upper unit consists of the following succession grading upwards: garnet-biotite micaschist, grey marble (with Permian fossils), marble-schist intercalations, and white marble. The garnet-biotite micaschists of the upper unit rest with angular disconformity on the metavolcanic rocks, the iron deposits, the Avnik granitoid, and the Yayla granite. Lensoidal quartz-marble intercalations locally intervene between the micaschist and both the metavolcanic rocks, the associated iron ores and the granitoids of the lower unit (Fig. 1). These quartzites, the lower parts of which are mainly metaconglomerates, contain pebbles of the lower unit rocks, and are interpreted as a basal conglomerate.

Petrographic studies and chemical analyses show that the metavolcanic rocks and the granitoids of the lower unit have been subjected to extensive feldspathization and silicification (HELVACI and GRIFFIN, 1983). Rb–Sr analyses suggest that this metasomatic event occurred ca. 90 M.a. ago, long after the intrusion of the granitoids into the volcanic pile (HELVACI and GRIFFIN, 1985).

In the Avnik area, the metamorphic rocks of the Bitlis Massif form a regional scale anticline overturned to the south (Fig. 1). The lower and upper units have been affected by several stages of deformation. Several imbricated thrust planes occur within the massif. After Miocene time the Bitlis Massif, in the Avnik region, was carried tectonically to the south over the Miocene flysch along nearly horizontal planes (ERDOĞAN et al., 1981) (Fig. 1).

The rocks and the associated apatite-rich iron deposits in the Avnik region have been affected by several stages of alteration and metamorphism. A regional deformation and metamorphism, probably in the amphibolite facies (?), has affected the lower unit before or during the intrusion of the granitoids. The intrusive event was followed by uplift, folding, and faulting that has not affected the upper unit. The lower unit then underwent a second metamorphism which also affected the upper unit, and subsequently overprinted the previous metamorphic assemblages with greenschist-facies assemblages (up to the epidote-amphibolite facies at some places). The isotopic data (HELVACI and GRIFFIN, 1985) together with the field and petrographic observations (HELVACI and GRIFFIN, 1983), therefore suggest three possible metamorphic stages:

1. Folding and (at least) contact metamorphism of the volcanic rocks before and during intrusions of the granitoids, before deposition of the overlying micaschists.
2. Folding and metamorphism in Eoalpine time, affecting both lower and upper units.
3. Late Alpine retrograde metamorphism.

3. Analytical methods

In all cases the collected samples weighed approximately 2 kg, of which half was prepared for chemical analysis. Major elements were determined by microprobe analysis of fused rock powders. The major element analyses, and the methods used, were presented by HELVACI and GRIFFIN, 1983.

REE were analysed by instrumental neutron-activation techniques, essentially as described by GORDON et al. (1968) and BRUNFELT and STEINNES (1969). The USGS reference sample BCR-1 was used as the standard for calibration. The rock and magnetite ore samples were irradiated (in the JEEP-11 reactor, Kjeller, Norway) in duplicate and analysed in replicate relative to BCR-1, using the assigned values for elements given by BRUNFELT and STEINNES (1978). The precision estimated from the replicate values is in the order of ±2% (2σ) for La, Ce, Nd, Sm and Eu; ±5% (2σ) for Tb and Yb; and ±8% (2σ) for Lu. Accuracy was checked by repeatedly analysing another reference sample (G-2).

Mineral fractions were purified by means of heavy liquids and a magnetic separator. For apatite, REE were determined nondestructively by Ge (Li) and LEPD γ-ray spectometry with thermal neutrons using a 2-minute irradiation, as described by BRUNFELT and REOLANDTS (1974). The Ödegaarden and Durango apatites were used as the standards. The precision estimated from replicate measurements is in the order of ±2% (2σ) for La, Sm, Eu, Tb, Dy, Ho, Yb, Lu and ±10% (2σ) for Ce, Nd, Gd, Er, Tm, within the range of concentrations studied here.

4. Results

The REE distributions in metavolcanic rocks, granitoids, micaschists, separated apatites, amphiboles and magnetites from the iron ores, the massive-banded iron ores, and the stockwork iron ores are presented in Figs. 2 to 10. All concentrations were normalized against a set of chondritic values given by HASKIN et al. (1968).

4.1. METAVOLCANICS

Major-element analyses of the metavolcanic rocks are summarized in Table 1. Whole-rock compositions of the metavolcanic show basic to intermediate composition in the lower parts, while the upper parts are dominated by felsic volcanics. Volcanic layers between ore horizons are enriched in Fe, Ca and P, reflecting the presence of disseminated magnetite and apatite.

The metavolcanic rocks are similar in *overall* composition to the Proterozoic leptite series of Scandinavia (LÖFGREN, 1979), and to the modern calc-alcaline volcanics of New Zealand (CHALLIS, 1971).

REE analyses for the metavolcanic rocks are given in Table 2. REE patterns for the Avnik metavolcanic rocks show high ΣREE, essentially flat HREE, and an enrichment in the LREE (Fig. 2). The regularity of the REE patterns, and the lack of any correlation between ΣREE and SiO_2, suggests that the REE were not disturbed by secondary feldspathization (HELVACI and GRIFFIN, 1983). All samples have negative Eu anomalies; the anomaly increases with increasing ΣREE. This effect is typical of

Tab. 1 Whole rock analyses from metavolcanic rocks, granitoids and micaschist from Avnik region.

	Metavolcanics									Granitoids							Micaschist
	S2-8	S2-12	S2-13	S2-14	S2-15	S2-16	S2-17	S2-18	S2-19	S2-2	S2-3	S2-4	S2-5	S3-1	S3-2	S3-3	S2-20
SiO_2	49.22	34.43	51.21	72.82	67.63	65.89	68.35	60.60	56.68	69.94	72.46	72.19	72.69	70.20	71.14	68.59	60.06
TiO_2	2.72	2.18	2.81	0.77	0.47	0.82	0.81	1.48	1.26	0.50	0.59	0.09	0.51	0.61	0.37	0.54	0.69
Al_2O_3	16.19	13.70	16.18	11.14	15.10	12.55	13.55	15.66	19.19	14.87	16.68	16.81	16.64	16.02	15.93	15.74	22.64
Fe_2O_3	8.72	27.16	7.31	4.20	6.51	8.43	5.41	8.98	6.97	3.92	0.21	1.18	0.44	0.56	0.39	2.05	3.09
FeO	5.82	2.23	4.67	0.57	0.50	0.50	0.86	1.65	5.17	0.72	0.29	0.36	0.43	0.43	0.65	1.29	3.66
MnO	0.04	0.08	0.12	0.03	0.13	0.02	0.04	0.04	0.07	0.04	0.06	0.02	0.01	0.02	0.03	0.03	0.02
MgO	8.24	9.79	9.11	0.07	0.14	0.06	1.63	2.23	5.52	1.08	0.36	0.80	0.49	1.11	1.16	1.03	3.30
CaO	2.23	5.14	2.11	0.10	0.12	0.35	0.56	0.56	0.40	0.86	0.16	0.12	0.11	2.14	1.57	0.83	0.34
Na_2O	5.44	1.01	5.29	0.50	3.72	1.22	2.90	3.04	2.15	4.54	6.75	7.48	7.30	7.69	8.32	3.74	2.68
K_2O	0.28	0.25	0.21	9.45	5.09	9.86	4.09	6.68	2.75	3.12	0.96	0.33	1.23	0.34	0.12	5.46	4.85
P_2O_5	0.53	1.73	0.58	0.04	0.05	0.23	0.21	0.35	0.18	0.12	0.03	0.03	0.03	0.08	0.13	0.13	0.19
Total	99.43	97.70	99.60	99.69	99.46	99.93	98.41	101.27	100.34	99.71	98.55	99.41	99.88	99.20	99.81	99.43	101.52

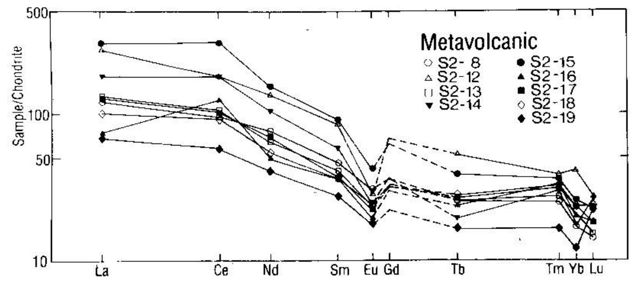

Fig. 2 Chondrite-normalized REE patterns of the Avnik metavolcanic rocks. All samples are from Section 2 on Fig. 1. Gd is interpolated from the Sm and Tb values in this and subsequent figures.

a magmatic-differentiation series in which plagioclase fractionation has been important and is consistent with the presence of plagioclase phenocrysts in many of the metavolcanics. Sample S2-12 has a large apatite content, and thus a large ΣREE; for the other samples no such correlation is observed.

These REE patterns are similar to those of many modern calc-alkaline volcanic series, for example that of the Andes (DOSTAL et al., 1977). The negative Eu anomalies of even the least-REE-rich rock suggest equilibration with plagioclase. These rocks may have been derived either by extreme fractional crystallization of more basic, more plagioclase-rich magmas, or from anatexis of a feldspathic rock where plagioclase was an important part of the anatectic residue. Unfortunately the Sr-isotope systems of these rocks are so disturbed that they can not be used to distinguish between these alternatives (HELVACI and GRIFFIN, 1985).

4.2. GRANITOIDS

The chemical composition of the Avnik granitoids is given in Table 1. The granitoids show large variations in K/Na ratios which reflect the secondary albitization of many samples (HELVACI and GRIFFIN, 1983). Several samples from the center of the body, at some distance from the metavolcanic rocks, have K/Na ratios and K concentrations of typical granites. These may be close to the composition of the original magmatic rocks. The K/Na ratios are severely disturbed, but the SiO_2 content of the granitoid may have remained essentially constant during the albitization (HELVACI and GRIFFIN, 1983).

REE patterns of the Avnik granitoids show HREE contents similar to those of the metavolcanics, but smaller LREE contents and larger negative Eu anomalies (Fig. 3). There is no correlation of ΣREE with K/Na ratio, which suggests that albitization has not disturbed the REE patterns. The Eu anomaly remains essentially constant through a large (5x) increase in ΣREE, suggesting that feldspar fractionation was not the prime cause of variation in ΣREE. The source rock of these granitic magmas apparently retained plagioclase, but not garnet or amphibole, in the anatectic residue. This inference suggests an origin involving crustal anatexis, which is consistent with the available Sr isotope data (HELVACI and GRIFFIN, 1985).

4.3. MICASCHISTS

The REE distribution pattern for the micaschist sample shows flat HREE, and an enrichment in the LREE (Fig. 4). The pattern is characterized by a marked negative Eu anomaly and a negative Yb anomaly. The REE pattern for the micaschist is very similar to that the uppermost metavolcanic sample (S2-19), which is within 1 metre of the micaschist. This observation may suggest that the micaschists were most likely derived from the underlying metavolcanic rocks, or that mutual contaminations occurred during metamorphism.

4.4. APATITES

Fluorapatite samples were separated from the recrystallized banded-massive iron ores

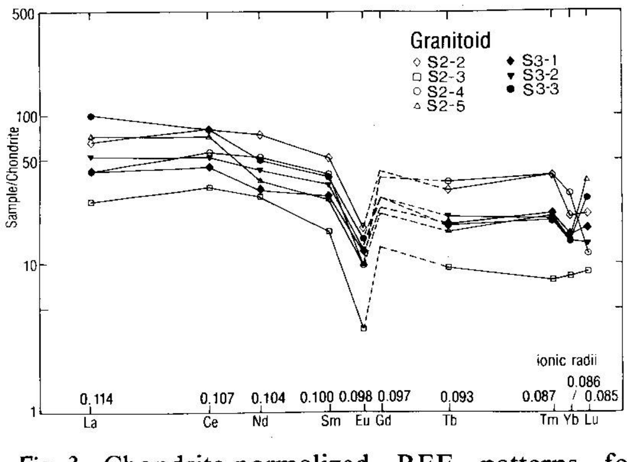

Fig. 3 Chondrite-normalized REE patterns for Avnik granitoids. Samples are from Section 2 and 3 on Fig. 1.

Tab. 2 REE abundances (ppm) in granitoids, metavolcanic rocks and micaschist from Avnik region. Data obtained on the standard rock G-2 are also shown.

Sample No.	La	Ce	Nd	Sm	Eu	Tb	Tm	Yb	Lu
Granitoids:									
S2-2	24	64	22	4.91	0.68	0.77	0.63	3.01	1.20
S2-3	14	50	32	7.40	0.65	1.69	1.18	6.20	0.42
S2-4	8.6	29	17	3.00	0.25	0.44	0.23	1.69	0.30
S2-5	22	71	45	9.44	1.18	1.48	1.18	4.29	0.73
S3-1	14	40	19	5.15	0.82	0.87	0.65	3.17	0.59
S3-2	17	45	26	6.18	0.87	0.98	0.61	2.99	0.47
S3-3	33	71	30	6.98	1.01	0.85	0.58	2.93	0.92
Metavolcanics:									
S2-8	40	86	47	8.47	2.10	1.19	0.75	3.56	0.49
S2-1	92	159	83	15.5	2.68	2.43	1.16	8.66	0.93
S2-13	44	95	40	7.49	1.64	1.20	0.82	4.40	0.70
S2-14	62	161	63	10.6	1.67	0.93	0.90	3.68	0.89
S2-15	101	276	93	16.4	2.88	1.82	1.08	5.39	0.78
S2-16	25	113	30	6.54	1.34	1.12	1.01	4.25	0.81
S2-17	43	93	42	7.80	1.54	1.24	0.92	4.86	0.63
S2-18	34	82	34	7.67	1.68	1.28	1.00	4.90	0.81
S2-19	23	52	25	5.03	1.22	0.78	0.50	2.52	0.77
Micaschist:									
S2-20	28	55	29	5.58	1.03	0.69	0.49	2.37	0.73
Granite:									
G-2	78	152	49	7.08	1.43	0.48	0.31	0.77	0.11

and the stockwork iron ores. The REE results from the apatites are listed in Table 3.

In the apatite of the Avnik ore LREE dominate and HREE are mostly subordinate, a feature similar to those found for many magmatic apatites. The REE patterns for the Avnik apatites are totally different than those of apatites from marine origin, for example the apatites from the Väyrylänkylä deposits, Finland, studied by LAAJOK (1975).

The REE patterns of the Avnik apatites show large REE and very similar patterns within the Murdere-Mişkel and Harabe deposits respectively (Fig. 5). All of the samples have larger negative Eu anomalies than do the associated metavolcanics (see Fig. 2). In general the

Tab. 3 REE abundances (ppm) in apatites and amphiboles from Avnik (Bingöl) region.

Sample No.	La	Ce	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Avnik apatites:													
S3-5	340	796	374	97	5.1	136	16.3	88	20.8	79	-	45	8.0
S3-15	691	1620	792	199	8.8	123	24.3	128	30.0	51	-	63	10.9
S1-2	435	722	418	110	5.9	240	19.1	104	27.0	101	-	63	11.0
S1-3	631	1190	752	152	7.9	110	24.9	128	29.4	68	-	72	14.0
S1-4	514	936	338	107	5.9	193	15.7	84	20.7	82	-	50	6.5
S1-6	134	469	718	343	13.3	447	66	365	85.7	297	-	144	21.4
S1-7	69	312	433	271	10.2	669	62	350	85.0	303	-	150	20.7
S1-8	157	555	721	296	10.5	576	58	323	82.6	284	-	154	21.0
Durango apatite:													
	2900	4519	1190	133	13.6	120	18.0	69	9.5	29	-	31	4.4
Avnik amphiboles:													
S1-2	11	35	9	1.1	0.4	-	0.51	-	-	-	0.27	2.83	0.11
S1-4	59	108	27	5.8	0.4	-	0.54	-	-	-	0.19	1.59	0.32
S1-6	263	730	547	155.8	4.2	-	13.64	-	-	-	5.64	47.62	0.05

Murdere-Mişkel apatites show greater LREE contents than do the Harabe apatites. The Harabe apatites are depleted in LREE owing to the presence of coexisting allanite and sphene, which is believed to have taken up most of the LREE.

The Avnik apatites do not show negative Ce anomalies, which if present, might indicate sedimentary deposition (equilibration with sea water). The similarity of the REE in the apatites from the iron ores to the REE patterns of the volcanic rocks suggests a magmatic origin.

The Durango apatite (YOUNG et al., 1969) resembles the Murdere and Mişkel apatites, but its ΣREE is much greater than that of the Avnik apatites (Fig. 5). The REE patterns of the Mişkel and Murdere apatites also resemble those of the apatites from the Kiruna magnetite deposits, Northern Sweden (PARÁK, 1973).

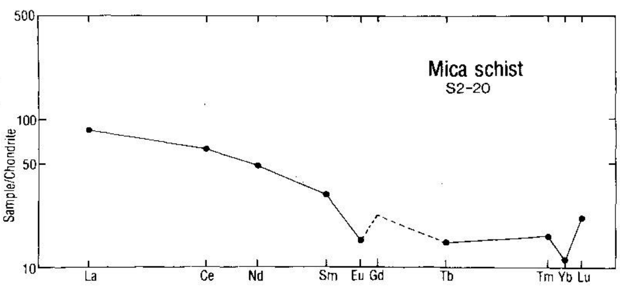

Fig. 4 Chondrite-normalized REE pattern for micaschist. Sample is from Section 2 on Fig. 1.

4.5. AMPHIBOLES

Amphibole samples were separated from the stockwork iron ores, and are represented dominately by actinolite. The REE results of the amphiboles are also listed in Table 3.

S1-2 and S1-4 samples are collected from the Mişkel deposit and S1-6 is from the Harabe deposit, as indicated on Fig. 6. The REE patterns of the amphiboles show dominant LREE and subordinate HREE. In general, the Harabe amphibole has higher ΣREE than the Mişkel amphiboles. All of the samples have nega-

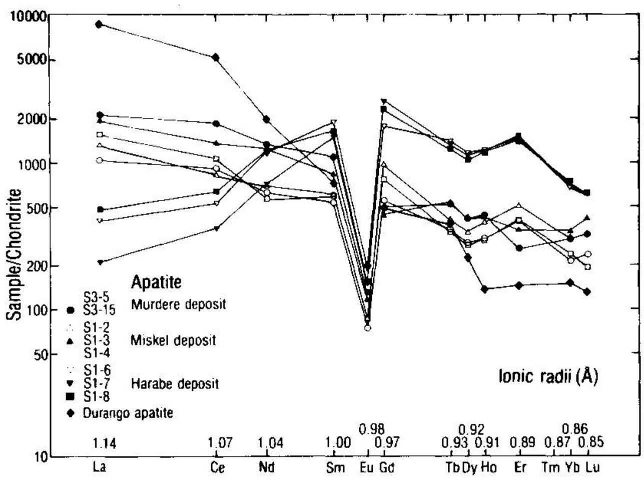

Fig. 5 Chondrite-normalized REE patterns of the Avnik apatites. Numbers in the figure correspond to those in Table 3 and they are shown on Fig. 1.

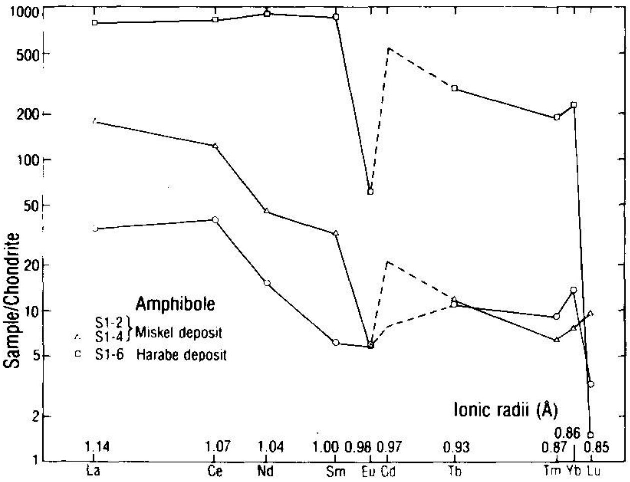

Fig. 6 Chondrite-normalized REE paterns of the Avnik amphiboles. Numbers in the figure correspond to those in Table 3 and they are shown on Fig. 1.

tive Eu anomalies, except the S1–2 sample, which shows lower ΣREE and has no negative Eu anomaly. All samples appear to be depleted in the HREE concentrations, especially in Lu concentrations (Fig. 6).

4.6. MASSIVE AND BANDED ORES – WHOLE ROCK REE

REE analyses for the massive and banded ores are given in Table 4. The REE patterns of the massive-banded ores are mainly controlled by apatite and the absolute REE concentrations in the ores are largely related to the proportion of apatite.

REE patterns for some massive-banded ores show very large contents of REE owing to large concentrations of apatite. They also show a greater enrichment in the LREE, and large negative Eu anomalies (Fig. 7). Their REE patterns are thus similar to those of the associated metavolcanic rocks, which in turn are similar to those of many modern calc-alkaline volcanic series (DOSTAL et al., 1977). Some of the ores show smaller ΣREE and the most impoverished one has a positive Eu anomaly.

4.7. STOCKWORK ORES – WHOLE ROCK REE

REE analyses of the stockwork iron ores are also given in Table 4. They all show identical REE proportions and reflect a variation in ΣREE related to apatite concentration within the ores, with an enrichment in the LREE, and a depletion in the HREE (Fig. 8). Remobilization and recrystallization of the stockwork ores during the granitoid intrusion and the metamorphism has not disturbed the REE patterns, with the exception of Eu anomalies, as there are no other obvious differences between the patterns of the massive-banded and the stockwork ores. This observation may also suggest that the REE analyses can be considered as representative of the original rocks. The negative

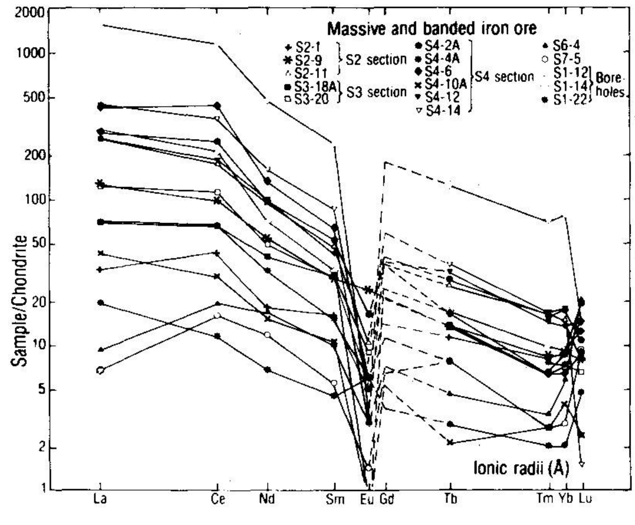

Fig. 7 Chondrite-normalized REE patterns of the massive and banded iron ones. Numbers in the figure correspond to those in Table 4, and they are shown on Fig. 1.

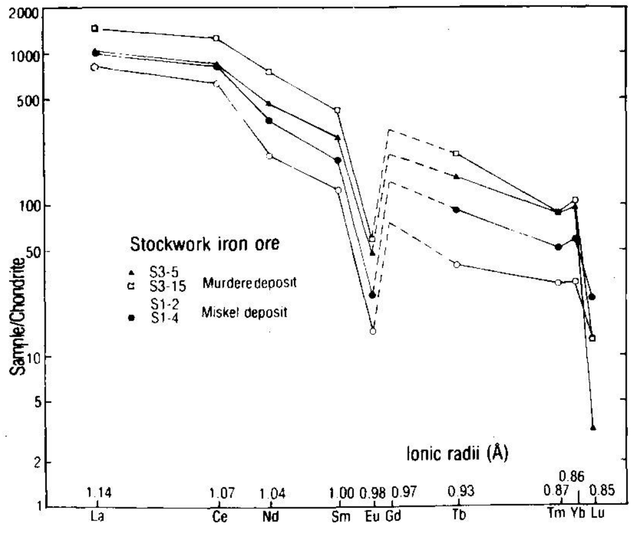

Fig. 8 Chondrite-normalized REE patterns of the stockwork iron ores. Numbers in the figure correspond to those in Table 4, and they are shown on Fig. 1.

Tab. 4 REE abundances (ppm) in massive-banded iron ores, stockwork iron ores and separated magnetites from Avnik (Bingöl) region.

Sample No.	La	Ce	Nd	Sm	Eu	Tb	Tm	Yb	Lu
Massive and banded iron ores:									
S2-1	10.0	38	11	2.9	0.4	0.53	0.24	1.78	0.49
S2-9	41	86	32	5.1	1.7	0.63	0.25	1.83	0.27
S2-11	84	153	56	8.5	0.7	1.18	0.49	3.12	0.27
S3-18A	21	58	24	5.4	0.4	0.62	0.19	1.84	0.65
S3-20	40	89	29	5.3	0.6	0.63	0.19	1.48	0.22
S4-2A	93	217	57	9.5	1.1	1.31	0.47	3.61	0.36
S4-4A	6.3	10	4	0.8	0.4	0.13	0.06	0.41	0.16
S4-6	141	383	78	11.4	0.2	0.76	0.19	1.34	0.30
S4-10A	14.1	26	9	1.9	-	0.10	0.08	0.81	0.08
S4-12	89	162	59	7.6	1.1	1.48	0.43	2.84	0.49
S4-14	143	313	95	15.5	0.4	1.67	0.50	3.70	0.05
S6-4	3.0	17	10	1.8	0.2	0.21	0.10	1.19	0.70
S7-5	2.2	14	7	1.0	0.1	0.36	0.08	0.60	0.32
S1-12	505	982	281	43	2.7	5.79	2.15	16.3	0.49
S1-14	99	188	42	5.9	-	0.79	0.29	1.94	0.43
S1-22	23	58	19	2.7	0.4	0.35	0.23	1.53	0.27
Stockwork iron ores:									
S3-5	334	741	280	51	3.2	7.12	2.57	19.9	0.11
S3-15	489	1090	451	75	4.1	10.2	2.63	22.4	0.43
S1-2	271	558	126	22	1.0	2.32	0.88	6.40	0.43
S1-4	330	728	212	35	1.7	4.24	1.58	12.4	0.81
Separated magnetites:									
S1-2	137	299	67	10.0	1.3	1.13	0.35	2.19	0.11
S1-3	101	256	52	7.7	0.8	0.76	0.27	1.50	0.76
S1-4	11	54	8	1.5	0.2	0.33	0.09	1.05	0.22
S1-5	8	19	11	1.7	0.6	0.12	0.08	0.53	0.22
S3-5	66	189	62	10.1	0.4	0.97	0.37	2.42	0.38
S3-15	58	143	47	7.2	0.6	0.79	0.28	2.35	0.05
S7-5	1.9	8	5	0.9	0.1	0.31	0.09	0.49	0.32

Eu anomaly of the stockwork ores is not as large as in the massive and banded ores, which might suggest that remobilization occurred in an oxidizing environment.

4.8. SEPARATED MAGNETITES

Magnetites were separated from the massive-banded iron ores (S7-5), the disseminated iron ores (S1-5) and the stockwork iron ores (S1-2, S1-3, S1-4, S3-5 and S3-15). S7-5 and S1-5 samples are from the Hamek deposit, and all the other samples were collected from the Murdere-Mişkel deposits. REE results of the separated magnetites are also listed in Table 4.

Separated magnetites reflect a variation in REE concentrations with an enrichment in the LREE, and a depletion in the HREE (Fig. 9). REE concentrations of the separated magnetites are not as high as in the massive-banded, disseminated and stockwork iron ores, and they show negative Eu anomalies, except the S1-5 sample, which is from the disseminated iron ores.

In general, the magnetites from the stockwork iron ores show larger ΣREE contents than the magnetites of the massive-banded and disseminated iron ores. The REE patterns of the magnetites resemble the massive-banded and stockwork iron ores, but their ΣREE are much smaller than that of the massive-banded and stockwork iron ores (Fig. 7, 8 and 9).

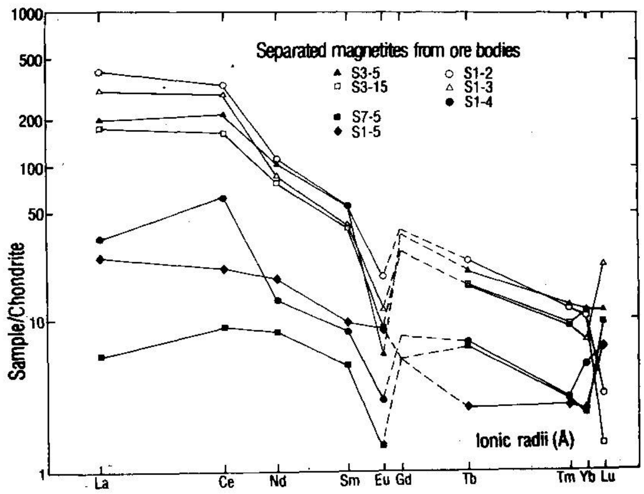

Fig. 9 Chondrite-normalized REE patterns of the separated magnetites from stockwork iron ore bodies. Numbers in the figure correspond to those in Table 4, and they are shown on Fig. 1.

5. Discussion

As with all sophisticated analytical approaches to geological problems, the possibilities of interpretation of the results are highly dependent on basic geological data. Many of the conclusions in the following discussion therefore depend heavily on observations drawn from a more comprehensive study of the petrologic and geochemical features of the Avnik area (e.g. ERDOĞAN et al., 1981; HELVACI and GRIFFIN, 1983; HELVACI, 1984; HELVACI and GRIFFIN, 1985).

As shown above, the REE patterns and general bulk compositions of the Avnik metavolcanic rocks are comparable to those of modern calc-alkaline volcanic suites, for example those of the Andes or of New Zealand (CHALLIS, 1971; DOSTAL et al., 1977). Similar metavolcanic rocks, less affected by albitization, occur in the Cacas area of the Bitlis Massif, and these are calc-alkaline, with normal K/Na ratios (YILMAZ et al., 1981). It is suggested that the original compositions of the Avnik metavolcanic rocks were calc-alkaline, and that the present extreme variations in K-Na-Si ratios (HELVACI and GRIFFIN, 1983) are the result of post-depositional processes.

A major question arising from field relations is the genetic relationship, if any, between the Avnik granitoids and the overlying metavolcanics (HELVACI and GRIFFIN, 1983). REE patterns, combined with major-element compositions, suggest that there is no genetic relation between the granitoids and the metavolcanic rocks. In terms of major- and minor-element chemistry, the granitoids are the more *evolved* of the two groups, but their REE patterns are *less* differentiated. It is therefore difficult to envision a differentiation scheme that would produce the metavolcanic rocks from the granitoids, or vice versa, by fractional crystallization.

To interpret the field, petrographic, and REE data on the apatite-rich magnetite ore deposits from the Avnik area, it must be stressed that magnetite-apatite ores occur in a series of basic to felsic calc-alkaline metavolcanic rocks (HELVACI, 1984). The volcanic rocks occur as lavas and tuffs, and there is no evidence of volcanic material having been redeposited or reworked in water. The ores are essentially stratiform within the volcanic pile which later has been deformed.

The apatite, massive-banded ores, stockwork ores and the associated metavolcanic rocks show similar REE patterns, which are very different from those of deposits in sedimentary environments (LAAJOKI, 1975) and suggest a genetic relation between ores and volcanics. A similar observation was made for the Damberg deposits, Central Sweden (ARVANITIDIS and RICKARD, 1981). The large Eu anomaly of the apatites and the coexisting iron ores is indicative of a relationship with the host volcanic series. Each shows a marked negative Eu anomaly and no Ce depletion; both features are consistent with extreme fractional crystallization of felsic magmas.

Negative Ce anomalies are good evidence of REE derivation from sea water. Metalliferous sediments on the East Pacific Rise and modern sea floor deposits show such large negative Ce anomalies and small negative Eu anomalies (GRAF, 1978; FRYER, 1977a, b).

In the Avnik deposits the iron ores and the associated volcanics REE patterns do not show negative Ce anomalies which also suggest that the ores and the volcanic have not been influenced by sea water and thus are not chemical sediments or even volcanic exhalative-sedimentary ores (HELVACI, 1984).

The only apatite-rich iron ores that do show sea-water REE patterns are the Precambrian iron formations in Väyrylänkylä deposites in Northern Finland (LAAJOKI, 1975). They have large negative Ce anomalies which indicate sedimentary deposition and essentially no Eu anomalies. The REE patterns for the Avnik apatites are totally different from those of apatites of marine origin, such as apatite from the Väyrylänkylä deposits, Finland (LAAJOKI, 1975). LAAJOKI (1975) also indicates that an apatite-rich iron ore is very resistant to metamorphic disturbance of the REE patterns; this conclusion seems reasonable, and suggests that the REE analyses of the Avnik apatites and iron ores can indicate a genetic relationship with their host rocks.

The formation of remarkably pure apatite and iron-rich deposits from a felsic magma requires that separation of the iron fraction occurred during magma intrusion and crystallization. The most attractive mechanism is one of liquid immiscibility, which is a common phenomenon within alkaline and phosphorus-rich magmas provided there are large concentrations of Fe, P, and volatile components. WATSON (1976) and WATSON and GREEN (1981) show that when such a melt separates into immiscible basic and felsic liquids, the REE and P are concentrated in the basic melt by factors of 4 and 10 respectively. With further fractionation, the basic melt could then separate an immiscible apatite/magnetite melt as proposed by PHILPOTTS (1967).

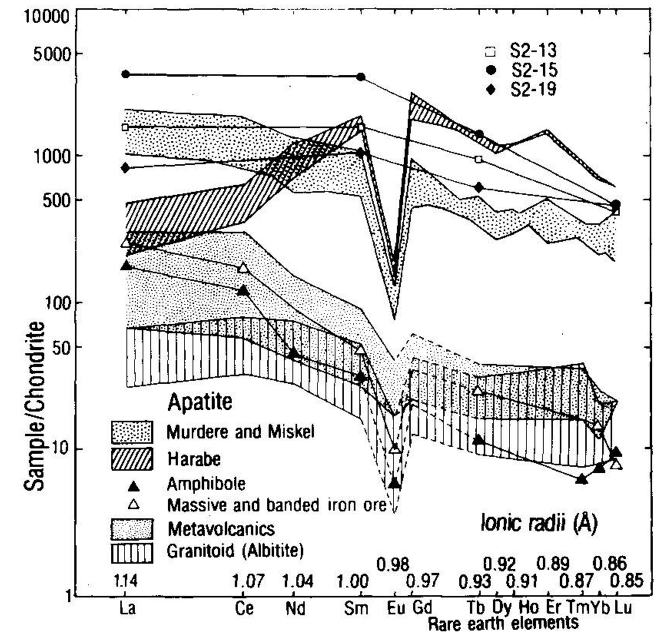

Fig. 10 Chondrite-normalized REE patterns of the Avnik metavolcanics, granitoids, ores, amphibole and apatites combined with the calculated apatites (S2-13, S2-15, S2-19) from hypothetical immiscible basic liquid coexisting with rhyolitic magmas in the Avnik deposits.

On the basis of this model, it is possible to calculate the REE pattern of apatite that would crystallize from an immiscibel basic liquid coexisting with the Avnik rhyolitic magma (HELVACI, 1984). The calculated REE patterns are parallel to those of apatites from the ore, which is consistent with the hypothesis that the Avnik apatite-rich massive and banded ores were formed by separation of immiscible apatite/magnetite liquid from basic melts which were cogenetic with the felsic volcanics (Fig. 10).

The massive and banded magnetite-apatite ores have been remobilized to form stockwork ores by the intrusion of granitoids. The $^{87}Sr/^{86}Sr$ values (ca. 0.712) of the separated apatites from the stockwork deposits are close to those estimated for the initial ratio (ca. 0.708 to ca. 0.718) of the Avnik granitoids (HELVACI and GRIFFIN, 1985). This observation is consistent with the stockwork iron ores being remobilized by fluids from the Avnik granitoid when it intruded (HELVACI, 1984).

6. Conclusions

Field, textural, and REE data suggests that the apatite-rich massive, banded, and disseminated iron ores of the Avnik region were initially formed in a volcanic environment and were separated from the coexisting basic to felsic calc-alkaline magma as immiscible liquids, aided by a large volatile and alkali-element content. The stockwork iron ores were formed during the emplacement of the Avnik granitoid by remobilization of the massive-banded and disseminated iron ores. The following conclusions regarding the formation of the ores and associated rocks of the Avnik area can be drawn from the present REE study:

1. The REE patterns and general bulk composition of the Avnik metavolcanic rocks are comparable to those of modern calc-alkaline volcanic suites.

2. REE patterns, combined with major-element composition, suggest that there is no genetic relation between the metavolcanic rocks and the granitoids.

3. The REE distribution pattern in the iron ore is similar to that in the metavolcanic rocks and has no similarity to that in the granitoids. The REE distribution patterns in both magnetite-apatite iron ores and metavolcanic rocks are relatively similar, which suggests a cogenetic relation between the ores and the metavolcanic rocks.

4. The massive-banded and disseminated iron ores are a product of extreme fractionation from an unusually P- and Fe-rich magma, followed by the immiscible separation of a liquid rich in magnetite and apatite.

5. The volatile and apatite contents of the iron-rich melt enabled it to exist in a volcanic environment close to or on the surface.

6. The comparatively large REE contents, large negative Eu anomalies, and lack of negative Ce anomalies of the apatites, the iron ores, and the associated volcanic rocks strongly suggest that the Avnik ores and the host rocks have not equilibrated with sea water, and thus are not chemical sediments or even volcanic exhalative-sedimentary ones.

7. The stockwork ores are a result of remobilization of the massive-banded and disseminated ores during the granitoid intrusion, followed by recrystallization during the metamorphism.

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