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MAGNETIC BEHAVIOR OF SOME BIOTITE SAMPLES FROM WEST THRACE, N.E. GREECE

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Abstract—The magnetic behavior of some biotite samples, from volcanic rocks of W. Thrace area, N.E. Greece, was studied in the temperature range from 85 to 270°K and compared with the chemical composition. The magnetization of the samples depends linearly on the applied field, and the magnetic susceptibility obeys the Curie law, showing a typical paramagnetic behavior which is due to Fe^{2+}, Fe^{3+} and Mn^{2+} The effective magnetic moment was calculated from the structural formulas of the samples and deviation from the experimental values is discussed.

INTRODUCTION

THE INVESTIGATION of the magnetic behavior of biotite is part of a general laboratory program dealing with the study of the magnetic properties of minerals and soils in Greece.

The volcanic rocks of the West Thrace area, N.E. Greece, form a whole series of differentiated products ranging from basaltic andesites to rhyolites, including dacites and rhyodacites. Among some intermediate rocks, biotite and hornblende are the only ferromagnesian minerals. The chemistry and geochemistry of these two minerals have been already discussed in detail by Sideris (1972) and a X-ray study of them has been made by Profi *et al.* (1973). For the present work, five fresh samples of intermediate composition from dacites to rhyodacites were chosen in order to separate the coexisting biotite and hornblende, and to study their magnetic behavior in comparison with their chemical composition.

Biotite is a trioctahedral mica rich in iron and has the general formula

$$X_2\, Y''_{6-4}\, Y'''_{0-2}\, Z_8O_{20}(OH,F)_4$$

X is mainly K^+ but Ca^{2+}, Ba^{2+}, Rb^+, Cs^+ and especially Na^+ are among the most common substitutions. Y'' corresponds to Mg^{2+}, Fe^{2+}, or Mn^{2+}, and Y''' to Fe^{3+}, Al^{3+}, and Ti^{4+}. Z corresponds to $Si_{6-5}Al_{2-3}$.

The structure of biotite can be described by a composite sandwich-type layer in which a sheet of octahedrally co-ordinated Y cations is placed between two sheets of linked $(Si,Al)O_4$ tetrahedra. Every such layer is separated by planes of twelve fold co-ordinated X ions (Deer *et al.*, 1967).

EXPERIMENTAL PROCEDURES

Mineral separation

The volcanic rocks were first crushed to 100 mesh by the use of a C. W. Cook & Sons crushing machine. Extreme care was taken to avoid contamination of the biotite grains from the cylinders of the crushing machine. Dust was eliminated by stirring the powdered minerals in water. Magnetite was removed by the use of a hand magnet. The powder was then enriched in magnetic minerals by passing it several times through a C. W. Cook & Sons magnetic separator. The extracted part, which contained a mixture of biotite, hornblende and magnetic feldspar grains, was centrifuged in adjusted solutions of tetrabromo–ethane in water in order to separate biotite and hornblende from the feldspars. The separation between the two ferromagnesian minerals, biotite and hornblende, was obtained by centrifugation in adjusted solution of methylene–iodide in acetone. Final purification of biotite grains was achieved with the aid of the magnetic separator. The biotite grains were then cleaned with acetone and thoroughly washed with boiling distilled water in order to eliminate any remaining methylene–iodide. The obtained purity of biotite was better than 99 per cent.

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Chemical analysis

The chemical analysis of separated biotite samples was based on the system of Washington (1930). SiO_2, 'R_2O_3', and CaO were determined gravimetrically as oxides, and Mg as pyrophosphate. The total iron in the form of Fe_2O_3 and the FeO were determined by titration with ceric sulphate and potassium permanganate respectively. TiO_2 and MnO were determined colorimetrically by the use of an EEL absorptiometer. The value for Al_2O_3 was obtained by subtracting the sum 'Total iron as Fe_2O_3 + TiO_2 + manganese as Mn_3O_4' from 'Total R_2O_3'.

Alkali metals were determined by the use of an EEL flame photometer by comparing the observed results with those of standard solutions. Total water was determined by the Penfield Tube method, and fluorine by the method of Huang and Johns (1967).

Magnetic measurements

Measurements of the specific magnetization (magnetic moment per gram) vs magnetic field were made on the five powder samples of biotite in a temperature range 85–262°K. The measurements were carried out with the use of a Princeton Applied Research—Model 155 vibrating sample magnetometer, equipped with a Janis—Model 153 variable temperature cryostat filled with liquid nitrogen. Different temperatures were obtained by adjusting the amount of heat added to the vapor stream of nitrogen flowing through the sample compartment of the cryostat. Two copper vs constantan thermocouples were provided in the cryostat, one for temperature monitoring and the other for the measurement of the sample temperature. The applied magnetic field ranged from 70 to 10200 Oe.

RESULTS AND DISCUSSION

Table 1 presents the chemical analysis obtained for five different biotite samples. The corresponding structural formulas and formula weights, computed on the basis of 24 (O, OH, F), are listed in Table 2.

The behavior of the specific magnetization σ as a function of the ratio of the applied magnetic field H over the temperature T, for samples A, B, C and D is shown in Fig. 1. Figure 2 shows the dependence of σ on the applied field for sample E at different temperatures.

We note that although σ varies linearly with the field for samples A, B, C and D, the sample E presents a non linear behavior at relatively low fields. This can be attributed to the presence of a small quantity of ferro- or ferrimagnetic material characterized by an easily saturable magnetization. Assuming that the measured magnetization of the sample E results from the superposition of an easily saturable component σ_1 and a linear one σ_2, we have calculated by extrapolation, using a least square fit method, the saturation values of σ_1 for different temperatures. The results are listed in Table 3. These values can be explained by the presence of 0·02 per cent magnetite with a saturation magnetization at room temperature equal to 93 emu g^{-1} (Smit *et al.*, 1959).

Such a low concentration of magnetite is far beneath the total impurity content of our samples and indiscernible by X-ray Debye–Scherrer patterns (Profi *et al.*, 1973).

The molar magnetic susceptibility χ_m of each biotite sample was calculated with the aid of the relation

$$\chi_m = W\sigma/H \qquad (1)$$

Table 1. Chemical analysis of biotite samples

Sample	*A* L52Bi*	*B* F55Bi*	*C* F20Bi*	*D* F25Bi*	*E* L71Bi*
SiO_2	38·91	37·69	37·84	37·76	37·75
TiO_2	3·41	3·45	3·57	3·51	3·41
Al_2O_3	15·30	15·74	15·35	15·54	15·33
Fe_2O_3	4·13	3·53	5·09	4·31	4·72
FeO	9·42	10·52	9·74	10·13	10·40
MnO	0·18	0·11	0·25	0·18	0·23
MgO	15·79	15·97	15·31	15·64	14·53
CaO	0·82	0·38	0·32	0·35	0·62
Na_2O	0·72	0·82	0·71	0·76	0·76
K_2O	7·44	8·29	8·37	8·33	7·98
OH_2^+	3·85	3·30	3·31	3·30	3·77
OH_2^-	0·06	0·06	0·00	0·03	0·14
F_2	0·15	0·23	0·27	0·25	0·16
	100·12	100·03	100·13	100·06	99·66
$O \equiv F$	0·06	0·09	0·11	0·10	0·06
Total	100·06	99·94	100·02	99·96	99·60

* Sample notation corresponding to Sideris (1972) and Profi *et al.* (1973).

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Table 2. Structural formulas and molecular weight (W) of biotite samples recalculated to 24 (OH, O, F)

Sample	A	B	C	D	E
Si	5·652	5·558	5·595	5·579	5·574
Al	2·348	2·442	2·405	2·421	2·426
Al	0·272	0·288	0·259	0·280	0·236
Ti	0·366	0·381	0·390	0·382	0·372
Fe^{3+}	0·436	0·390	0·550	0·462	0·514
Fe^{2}	1·144	1·294	1·199	1·252	1·278
Mn	0·017	0·008	0·026	0·017	0·026
Mg	3·415	3·510	3·366	3·438	3·195
Ca	0·122	0·053	0·044	0·053	0·097
Na	0·192	0·230	0·195	0·213	0·213
K	1·362	1·560	1·563	1·563	1·491
O	20·210	20·650	20·626	20·643	20·220
OH	3·721	3·244	3·250	3·251	3·709
F	0·069	0·106	0·124	0·106	0·071
Z	8·000	8·000	8·000	8·000	8·000
Y	5·650	5·871	5·781	5·831	5·621
X	1·676	1·841	1·802	1·829	1·801
OH + F	3·790	3·350	3·374	3·357	3·780
W	879·486	893·680	883·499	884·690	880·334

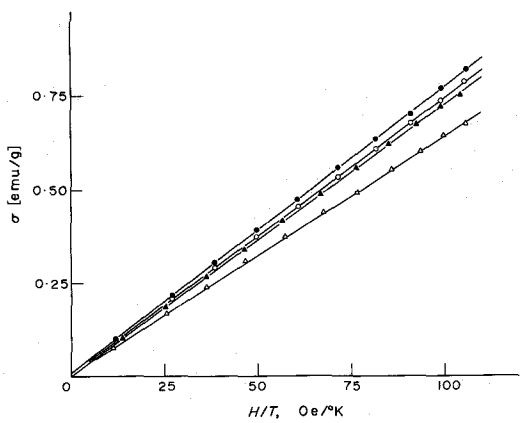


Fig. 1. Specific magnetization σ of the biotite samples as a function of H/T. Full curves are obtained by a least square fit method. △ Sample A; ● sample B; ▲ sample C; ○ sample D.

where W is the molecular weight of the sample taken from Table 2. The quantity $1/\chi_m$ is plotted against temperature in Fig. 3. It appears that the magnetic susceptibility of all the samples follows quite well the Curie–Weiss law

$$\chi_m = \frac{C_m}{T - \theta} \qquad (2)$$

where C_m is the molar Curie constant and θ the Weiss temperature.

The values of the experimentally determined C_m and θ are listed in Table 4. We note that θ values lie very close to zero implying the absence of any considerable exchange interaction between the paramagnetic ions. This typically paramagnetic behavior of biotite is due to the presence of Fe^{2+}, Fe^{3+}, and Mn^{2+} ions found in the chemical analysis. According to Butler (1967), Ti

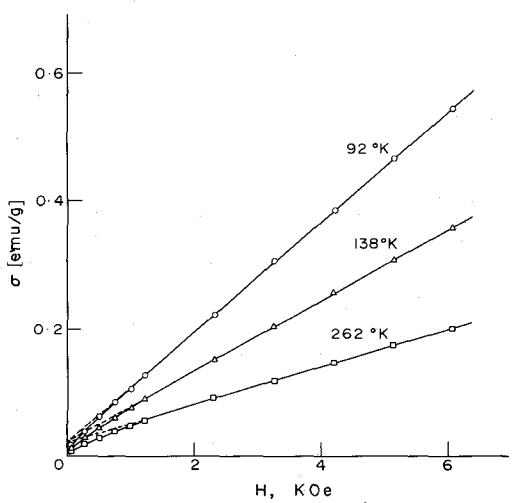


Fig. 2. Specific magnetization σ as a function of the applied magnetic field H for sample E at different temperatures.

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Table 3. Extrapolated saturation values of the easily saturable magnetization component σ_1 of sample E at different temperatures

Temperature (°K)	Saturation magnetization (emu/g)
92	0·0284
138	0·0279
188	0·0265
240	0·0242
262	0·0226

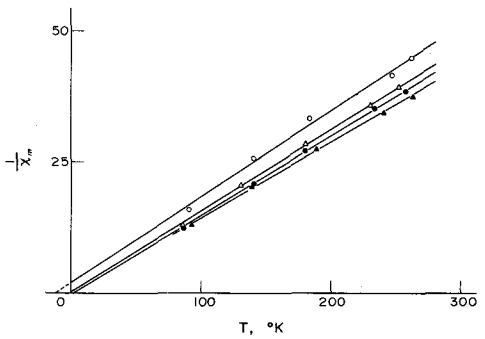


Fig. 3. Reciprocal molar magnetic susceptibility $1/\chi_m$ of the biotite samples as a function of the temperature. Full curves are calculated according to equation (2) with C_m and θ taken from Table 4. ○ Sample A; ● sample B; △ sample D; ▲ sample E.

Table 4. The molar Curie constant and the Weiss temperature θ, for the biotite samples as determined from the experimentally obtained values of $1/\chi_m$ at different temperatures by a least square fit method

Sample	C_m	θ (°K)
A	6·0 ± 0·2	−11 ± 5
B	6·49 ± 0·04	+4 ± 1
C	6·54 ± 0·07	−4 ± 2
D	6·40 ± 0·06	−1 ± 1
E	7·05 ± 0·08	−4 ± 2

ions are tetravalent and offer no contribution to the total magnetic susceptibility. We can therefore assume that Fe^{2+}, Fe^{3+} and Mn^{2+} ions are dispersed in a diamagnetic medium and behave magnetically as "free" ions. Under these conditions the total paramagnetic susceptibility of each sample is equal to the sum of the partial susceptibilities of its paramagnetic components. We may therefore write that the effective magnetic moment, μ_{eff}, per mole of biotite is given by

$$\mu_{eff}^2 = n_1 \mu_1^2 + n_2 \mu_2^2 + n_3 \mu_3^2 \qquad (3)$$

Table 5. Effective magnetic moment per mole of biotite for different temperatures

Sample	Temperature (°K)	μ_{eff} (in Bohr magnetons)
	90	7·08
	140	6·82
A	183	6·81
	246	7·01
	261	6·88
	85	7·24
	140	7·21
B	180	7·17
	233	7·21
	257	7·22
	91	7·30
	141	7·19
C	188	7·20
	237	7·25
	260	7·24
	85	7·20
	130	7·10
D	180	7·09
	230	7·17
	252	7·15
	92	7·62
	138	7·42
E	188	7·48
	240	7·52
	262	7·51

where μ_1, μ_2, μ_3 are the effective magnetic moments and n_1, n_2, n_3 the number of the Fe^{2+}, Fe^{3+} and Mn^{2+} ions in one mole of biotite, respectively.

μ_{eff} Is calculated from the experimental values of χ_m and θ according to the formula

$$\mu_{eff} = \left[\frac{3k}{N\beta^2}\chi_m(T-\theta)\right]^{1/2} \qquad (4)$$

where N is the Loschmidt number, β the Bohr magneton, and k the Boltzmann constant. Table 5 presents the μ_{eff} values for each of the five biotite samples. We have then determined for each sample the most suitable set of μ_1, μ_2 and μ_3 values which satisfy relation (3). We first note from Table 2 that the concentration of Mn^{2+} ions in all five samples is so small compared to the concentration of Fe^{2+} and Fe^{3+} ions, that the influence of any deflection of μ_3 from the theoretical "spin-only" moment given by $\mu_{s-o} = 2\sqrt{S(S+1)} = 5{\cdot}92$ is practically undiscernible. Therefore, we can put $\mu_3 = 5{\cdot}92$ and limit ourselves to the estimation of a suitable combination of μ_1, and μ_2 in order to satisfy relation (3). Using the spin-only value $\mu_1 = 4{\cdot}90$ for Fe^{2+} we find μ_2 values for Fe^{3+} which are 10–23 per cent greater than the theoretical spin-only value for

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Table 6. Calculated effective magnetic moment per Fe^{3+} ion from the relation (3) (see text) assuming $\mu_1 = 4{\cdot}90$ and $\mu_3 = 5{\cdot}92$. The experimental values commonly found in the literature lie in the range 5·70–6·00 (König, 1966)

Sample	Temperature (°K)	μ_2 (in Bohr magnetons)
	90	7·11
	140	6·50
A	183	6·48
	246	6·95
	261	6·65
	85	7·35
	140	7·27
B	180	7·17
	233	7·27
	257	7·30
	91	6·55
	141	6·32
C	188	6·34
	237	6·45
	260	6·43
	85	6·77
	130	6·54
D	180	6·52
	230	6·70
	252	6·66
	92	7·18
	138	6·76
E	188	6·88
	240	6·97
	262	6·95

Table 7. Calculated effective magnetic moment per Fe^{2+} ion from the relation (3) assuming μ_2 and $\mu_3 = 5{\cdot}92$ (see text). The experimental values commonly found in the literature lie in the range 5·10–5·70 (König, 1966).

Sample	Temperature (°K)	μ_1 (in Bohr magnetons)
	90	5·47
	140	5·17
A	183	5·16
	246	5·39
	261	5·24
	85	5·45
	140	5·42
B	180	5·38
	233	5·42
	257	5·43
	91	5·25
	141	5·13
C	188	5·14
	237	5·20
	260	5·18
	85	5·29
	130	5·18
D	180	5·17
	230	5·26
	252	5·24
	92	5·53
	138	5·32
E	188	5·38
	240	5·43
	262	5·42

this ion (Table 6), i.e. much too important even in comparison with the experimental values commonly found in the literature (König, 1966). On the contrary, inserting the spin-only value $\mu_2 = 5{\cdot}92$ for Fe^{3+} we get μ_1 values only about 5–10 per cent greater than the spin-only value for Fe^{2+} (Table 7) which can be accepted for the following reason: the effective magnetic moment of the Fe^{2+} ion can be superior to its spin only value, because Fe^{2+} ions have six $3d$ electrons, and are, therefore, in ^5D states with $L = 2$ and $S = 2$. The presence of an octahedral crystal field splits the D state into E and T_2 terms, the latter giving rise to appreciable orbital contribution. But even an E term of a weak field d^6 configuration in the presence of spin-orbit coupling increases the effective moment above its spin-only value (König, 1966). On the contrary, Mn^{2+}, and Fe^{3+} ions have five $3d$ electrons which half fill the $3d$ shell so that the resultant orbital momentum is equal to zero, and consequently, their effective magnetic moment lies very closely to the spin-only value (Martin, 1967).

We therefore conclude that the set of μ_1, μ_2 and μ_3 values of Table 7 is consistent with the fundamental assumption of structurally allocating the three paramagnetic ions to the octahedral layer of biotite. Furthermore, the absence of any considerable exchange interaction between these ions supports the hypothesis of a dispersion rather than a clustering of the paramagnetic ions in the biotite matrix.

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Résumé—Le comportement magnétique d'échantillons de biotite provenant de roches volcaniques de l'ouest de la Thrace, au N.E. de la Grèce, a été étudié dans un domaine de températures allant de 85 à 270°K, et comparé à la composition chimique. La magnétisation des échantillons dépend linéairement du champ appliqué, et la susceptibilité magnétique suit la loi de Curie en montrant un comportement paramagnétique typique dû à Fe^{2+}, Fe^{3+} et Mn^{2+}. Le moment magnétique efficace est calculé à partir des formules structurales des échantillons et on discute de l'écart qu'il manifeste avec les valeurs expérimentales.

Kurzeferat—Das magnetische Verhalten einiger Biotitproben aus vulkanischem Gestein von Westthrazien in Nordostgriechenland wurde im Temperaturbereich von 85°K bis 270°K untersucht und zur chemischen Zusammensetzung in Beziehung gesetzt. Die Magnetisierung der Proben hängt linear vom angelegten Feld ab. Die magnetische Suszeptibilität gehorcht dem Curie–Gesetz und zeigt ein typisches paramagnetisches Verhalten, das auf Fe^{2+}, Fe^{3+} und Mn^{2+} zurückzuführen ist. Das effektive magnetische Moment wurde aus der Strukturformel der Probe berechnet und die Abweichung von den experimentellen Werten diskutiert.

Резюме — Образцы изверженного вулканического биотита из Западной Фракии в Северо-восточной Греции исследовались при температуре от 85°K до 270°K и анализировался их химический состав. Намагниченность образцов линейно зависит от приложенного поля, и их магнитная чувствительность подчиняется закону Кюри, проявляя типовое парамагнитное поведение, зависящее от Fe^{2+}, Fe^{3+} и Mn^{2+}. Эффективный магнитный момент высчитывался по структурной формуле образцов и обсуждались отклонения от экспериментального значения.

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