

rocks in order to see whether in some parts the magnetization points to the right and in others to the left?

P. M. S. BLACKETT: I do not think this would be possible with the natural magnetization of a rock as this is too weak.

E. W. GORTER: 1. Several ferrimagnetics show P-type behaviour in low fields (like 3500 Oe), but ordinary P type in saturating field of e.g. 30000 Oe is due to large anisotropy at low temperatures. Since P type develops at $M_A/M_B < 1 + \beta$, and β is small, the sublattice magnetizations must be almost equal. Verhoogen has given reason why this will probably not occur when only Fe^{3+} , Ti^{4+} and Fe^{2+} are present.

2. All saturation magnetization data on rocks are given in arbitrary units. It would be very important to be able to determine real saturation magnetization e.g. by selective chemical dissolution.

3. You showed a micrograph of titanomagnetite with exsolved ilmenite. The latter could not play a rôle in the reversal because the ilmenite is non-magnetic. If the two-phase reversal mechanism plays a rôle, is it possible that a ferrimagnetic ilmenite may have caused reversal, and have later undergone chemical change to give non-magnetic ilmenite?

S. AKIMOTO: We have also found the P-type-like thermomagnetic curve in the synthetic magnetite-ulvöspinel system ($x\text{Fe}_2\text{TiO}_4 \cdot (1-x)\text{Fe}_3\text{O}_4$) around $x=0.6$.

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Magnetic Properties of $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ System as a Basis of Rock Magnetism

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Magnetic properties of the ferromagnetic oxide minerals in rocks can generally be well interpreted as characteristic of the $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ ternary system, in which there exist the three fundamental solid solution series with different crystal structure, i.e., spinel, rhombohedral and orthorhombic phases. Changes of the Curie temperature, saturation moment and the cell dimension with the composition were examined in detail with respect to the spinel phase minerals in the ternary system including not only ideal titanomagnetite ($\text{Fe}_2\text{TiO}_4\text{-Fe}_3\text{O}_4$ series) but also titanomaghemite with varying vacancy in the metal ion site of the crystal structure.

Magnetic properties of rocks are principally attributable to those of the ferromagnetic minerals scattered with a very small proportion among the practically non-magnetic silicate minerals. The chemical analyses made hitherto reveal that the majority of the ferromagnetic mineral contained in rocks are the metallic oxides which are composed mainly of FeO , Fe_2O_3 and TiO_2 involving small quantities of MnO , MgO , Al_2O_3 and

V_2O_5 as minor components. Consequently, the magnetic properties of the ferromagnetic oxide minerals can generally be well interpreted as characteristic of the $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ ternary system, in which almost all the simple oxide minerals of interest in rock magnetism, viz. wüstite (FeO), magnetite (Fe_3O_4), maghemite ($\gamma\text{-Fe}_2\text{O}_3$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), ilmenite (FeTiO_3), ulvöspinel (Fe_2TiO_4) and pseudobrookite (Fe_2TiO_5) are included.

It is now established from recent synthetic experiments that there exist the following three fundamental solid solution series in the FeO-Fe₂O₃-TiO₂ ternary system which are marked in Fig. 1 by the solid straight lines^{1,2)}.

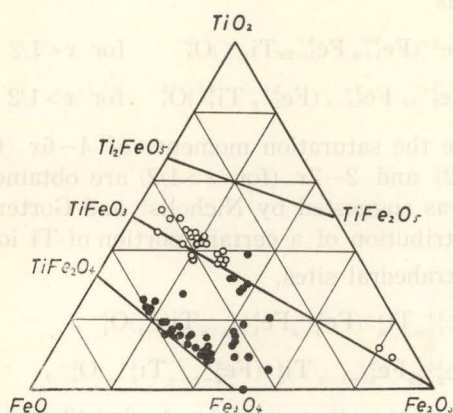


Fig. 1. Chemical composition of natural ferromagnetic oxide minerals represented on FeO-Fe₂O₃-TiO₂ diagram in mol percent.

- : Titanomagnetites and titanomaghemites
- : Ilmenite-hematite series minerals

I. Fe²⁺Fe₂³⁺O₄-Fe₂³⁺Ti⁴⁺O₄ of spinel structure (titanomagnetite series)

II. Fe₂³⁺O₃-Fe²⁺Ti⁴⁺O₃ of rhombohedral structure (ilmenite-hematite series)

III. Fe₂³⁺Ti⁴⁺O₅-Fe²⁺Ti₂⁴⁺O₅ of orthorhombic structure (pseudobrookite series)

In addition to these three fundamental series, occurrence of the homogeneous spinel phase, of which the chemical composition enters into a compositional field between the Fe₃O₄-Fe₂TiO₄ series and the Fe₂O₃-FeTiO₃ series in the ternary system, is also ascertained from a systematic oxidation experiment of the Fe₃O₄-Fe₂TiO₄ solid solution series³⁾. The concept of generalized titanomagnetite, progressively changing to titanomaghemite, i.e. the spinel phase in the FeO-Fe₂O₃-TiO₂ system with varying vacancy in the metal ion site of the crystal structure, is applicable to the interpretation of the magnetochemical properties of these abnormal spinel phases.

Titanomagnetites and Titanomaghemites

Principal ferromagnetic oxide minerals in rocks are, in almost all cases, the spinel phases including both titanomagnetite and

titanomaghemite. The chemical composition of the natural spinel phase minerals, which were chiefly separated from a large number of Japanese igneous rocks and of which homogeneity was carefully confirmed by x-ray analysis, is represented by full circles in Fig. 1⁴⁾. As will be seen in the figure, the chemical composition of the natural spinel phase minerals does not always accord with the ideal titanomagnetite line (Fe₂TiO₄-Fe₃O₄ line), but in most cases deviates from this line towards the FeTiO₃-Fe₂O₃ join. Furthermore, it is also ascertained that the spinel structure still remains unchanged even in the specimens near the FeTiO₃-Fe₂O₃ line.

Variations in the cell dimensions in the ideal titanomagnetite series (Fe₂TiO₄-Fe₃O₄ series) is shown in Fig. 2, where an almost linear increase of cell dimensions with an increase of Fe₂TiO₄ molecular percent, from about 8.39 Å of Fe₃O₄ to 8.53 Å of Fe₂TiO₄,

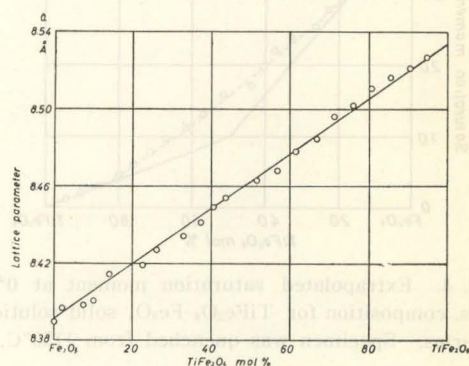


Fig. 2. Relation between cell dimension and chemical composition in TiFe₂O₄-Fe₃O₄ solid solution series.

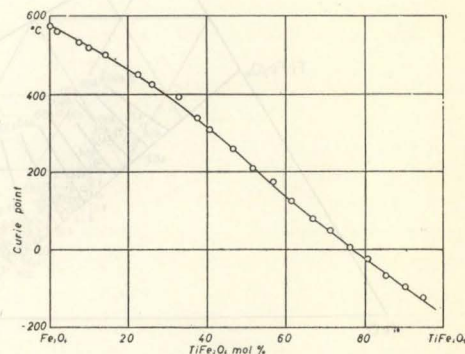


Fig. 3. Relation between the Curie temperature and chemical composition in TiFe₂O₄-Fe₃O₄ solid solution series.

is clearly seen. The Curie temperature decreases continuously from 578°C of Fe_3O_4 with an increasing content of Fe_2TiO_4 , reaching room temperature for $0.8 \text{ Fe}_2\text{TiO}_4 \cdot 0.2 \text{ Fe}_3\text{O}_4$. The variation in the Curie temperature is shown in Fig. 3. From the figure the extrapolated Curie temperature of the pure Fe_2TiO_4 is about 120°K. The actual situation where Fe_2TiO_4 becomes ferrimagnetic below 120°K may suggest that ideal antiferromagnetic coupling between tetrahedral and octahedral sites is somewhat disturbed in the prepared specimen. The dependence of the saturation moment at 0°K upon the composition of the Fe_3O_4 – Fe_2TiO_4 series is shown in Fig. 4 where the magnetization decreases gradually with the increase in the Fe_2TiO_4

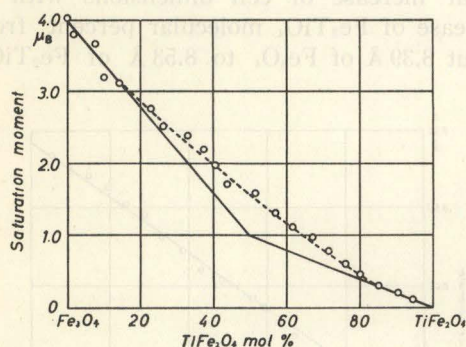


Fig. 4. Extrapolated saturation moment at 0°K vs. composition for TiFe_2O_4 – Fe_3O_4 solid solution series. Specimen was quenched from 1150°C.

molecular percent. It is also found in the figure that the experimental values are always larger than the theoretical values, which were postulated by Néel⁵⁾ and Chevallier, Bolfa and Mathieu⁶⁾ by taking into consideration Verwey's empirical law concerning the location of cations in the spinel structure, that is

$$\text{Fe}^{3+}(\text{Fe}_{1+x}^{2+} \text{Fe}_{1-2x}^{3+} \text{Ti}_x^{4+})\text{O}_4^{2-} \quad \text{for } x < 1/2,$$

$$\text{Fe}_{2-2x}^{3+} \text{Fe}_{2x-1}^{2+} (\text{Fe}_{2-2x}^{2+} \text{Ti}_x^{4+})\text{O}_4^{2-} \quad \text{for } x > 1/2,$$

where the saturation moments of $4-6x$ (for $x < 1/2$) and $2-2x$ (for $x > 1/2$) are obtained. As was suggested by Nicholls⁷⁾ and Gorter⁸⁾, a distribution of a certain portion of Ti ions in tetrahedral sites,

$$\text{Fe}_{1-a}^{3+} \text{Ti}_a^{4+} (\text{Fe}_{1+x}^{2+} \text{Fe}_{1-2x+a}^{3+} \text{Ti}_{x-a}^{4+})\text{O}_4^{2-},$$

$$\text{or } \text{Fe}_{2-2x}^{3+} \text{Fe}_{2x-1-a}^{2+} \text{Ti}_a^{4+} (\text{Fe}_{2-2x+a}^{2+} \text{Ti}_{x-a}^{4+})\text{O}_4^{2-},$$

with a saturation moment $4-6x+10a$ or $2-2x+8a$ respectively, may explain the slight increase in the saturation moment above the theoretically expected value for a given chemical composition.

It is also established based on the oxidation experiments of the Fe_2TiO_4 – Fe_3O_4 series that the cell dimension becomes smaller and the Curie temperature becomes higher in accordance with the procedure of oxidation and further the saturation moment of the specimen with lower content of TiFe_2O_4 decreases according as the oxidation proceeds,

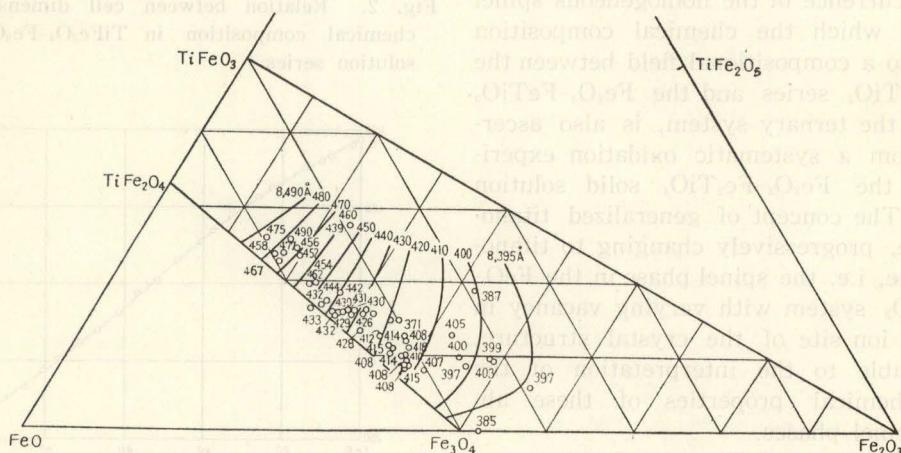


Fig. 5. Relation between cell dimension and chemical composition of titaniferous magnetite in volcanic rocks. The equal cell dimension diagram of the spinel region obtained from the synthetic titanomagnetites is also indicated in the figure.

while that of the higher content of TiFe_2O_4 increases³⁾.

The accumulation of reliable data on the chemical, crystallographic and magnetic properties of the synthetic Ti-bearing spinel specimens enables us to draw the contour line, on which the cell dimensions, Curie temperature and the saturation moment conserve a constant value on the spinel region in the $\text{FeO-Fe}_2\text{O}_3\text{-TiO}_2$ system. The interrelation among the crystal parameter, magnetic properties and the chemical composition of the natural spinel phase minerals can be well indicated by the equal lattice para-

meter diagram, the equal Curie temperature diagram and the equal saturation moment diagram, shown in Figs. 5, 6 and 7.

Ilmenite-Hematite Series^{9,10,11,12)}

Magnetic properties of the ilmenite-hematite series minerals $x\text{FeTiO}_3 \cdot (1-x)\text{Fe}_2\text{O}_3$ can be classified into the following three parts according to their composition: i) the antiferromagnetism of pure ilmenite ($x=1.0$) ii) the ferrimagnetism of the compositional range of $1 > x \geq 0.45$ and iii) antiferromagnetism, on which parasitic ferromagnetism is superimposed, of a compositional range of $0.5 \geq x \geq 0$. It has been established from x-ray analysis

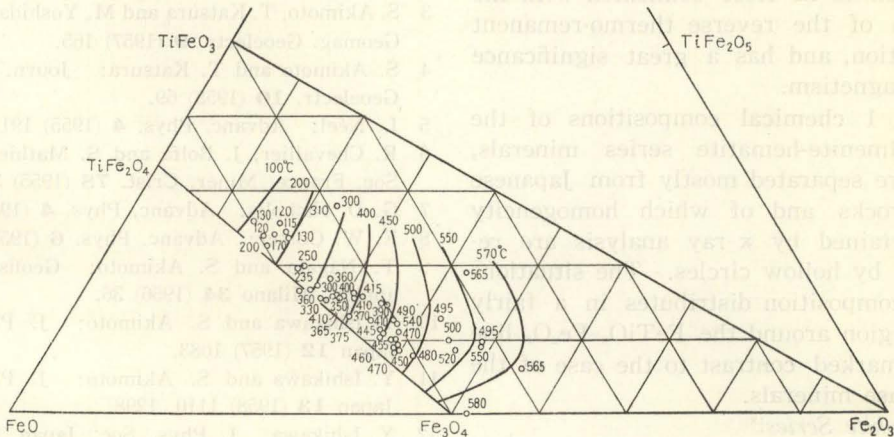


Fig. 6. Relation between Curie temperature and chemical composition of titaniferous magnetites in volcanic rocks. The equal Curie temperature diagram of the spinel region obtained from the synthetic titanomagnetites is also indicated in the figure.

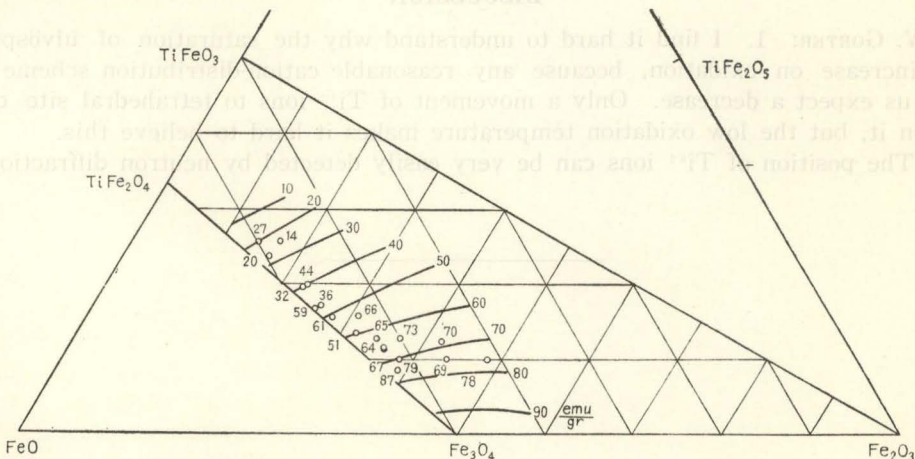


Fig. 7. Relation between saturation moment at room temperature and chemical composition of titaniferous magnetites in volcanic rocks. The equal saturation moment diagram of the spinel region obtained from the synthetic titanomagnetites is also indicated in the figure.

of a single crystal and the neutron analysis that the ferrimagnetism and the antiferromagnetism of this series correspond entirely to the crystal symmetry $R\bar{3}$ and $R\bar{3}c$ respectively. One of the most interesting character of the magnetic properties of the ilmenite-hematite series is that the specimens around $x=0.5$ are very sensitive to the heat treatment, the transformation from ferrimagnetic state to the antiferromagnetic one taking place cooperatively at a critical transition temperature. This was interpreted as the order-disorder transformation phenomenon of the atomic arrangement of Ti and Fe ions. This order-disorder transformation phenomenon is in close connexion with the production of the reverse thermo-remanent magnetization, and has a great significance in rock magnetism.

In Fig. 1 chemical compositions of the natural ilmenite-hematite series minerals, which were separated mostly from Japanese igneous rocks and of which homogeneity was ascertained by x-ray analysis are represented by hollow circles. The situations that the composition distributes in a fairly narrow region around the FeTiO_3 - Fe_2O_3 line are the marked contrast to the case of the spinel phase minerals.

Pseudobrookite Series⁽¹³⁾

A complete solid solution series between Fe_2TiO_5 and FeTi_2O_5 has been prepared by quenching from 1150°C. The Fe_2TiO_5 - FeTi_2O_5

series has an orthorhombic crystal structure and shows a paramagnetic behaviour at temperatures higher than the liquid nitrogen temperature. Consequently the orthorhombic pseudobrookite series is not so important in rock magnetism in comparison with the above two phases, i.e. spinel and rhombohedral phases. The pseudobrookite series minerals in nature are believed to be produced by the ultimate oxidation of the titanomagnetite or the ilmenite-hematite series minerals.

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DISCUSSION

E. W. GORTER: 1. I find it hard to understand why the saturation of ulvöspinel may increase on oxidation, because any reasonable cation-distribution scheme will make us expect a decrease. Only a movement of Ti^{4+} ions to tetrahedral site could explain it, but the low oxidation temperature makes it hard to believe this.

2. The position of Ti^{4+} ions can be very easily detected by neutron diffraction.