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Laboratory Synthesis of Aluminium-Substituted Titanomaghemites and Their Characteristic Properties

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Abstract. Sintered polycrystalline specimens of titanomagnetite containing aluminium, of composition $Fe_{2.6-\delta}\ Ti_{0.4}\ Al_\delta\ O_4$ and $Fe_{2.4-\delta}\ Ti_{0.6}\ Al_\delta$ ($\delta=0$, 0.1, and 0.2) were prepared by the method of partial self buffering. X-ray and magnetic analysis confirm that the synthesized materials are single phase spinels. The synthesized material was ball-milled in a high purity methanol slurry to produce submicron particle sizes and the fine grain material oxidized in air at temperatures below about 350° C. The titanomaghemites so produced are single phase spinels over almost the entire oxidation range. Characteristic properties of the samples such as Curie temperature and unit cell edge were determined as an aid in the identification of titanomaghemites in basalts.

Key words: Titanomaghemites – Oxidation – Gravimetry – Curie temperatures – Mineral identification – Deep sea basalts

Introduction

A large part of the established picture of the history of the Earth's crust has come from the information stored in the magnetic minerals of the crust. The continuing evolution of the crust has been traced out in the latest phase of such investigations, the *Deep Sea Drilling Project* (DSDP). The fine grain magnetic minerals produced in quenched submarine basalts should carry a faithful record of the geomagnetic field. However, submarine weathering appears to rapidly alter the magnetic minerals and the consequent modification in their magnetic properties may obscure the palaeomagnetic record.

The remanence carriers in almost all igneous rocks are the titanomagnetites ($Fe_{3-x}\ Ti_x\ O_4$, $0<x<1$) and their derivatives. Naturally occurring titanomagnetites often contain 'impurity' cations. According to the electron microprobe analysis of titanomagnetites from subaerial basalts, typical impurities are aluminium and magnesium up to 4% by weight (Creer and Ibbetson 1970). Other cation species such as manganese, chromium, nickel and zinc are also often present. Analysis of titanomagnetites in pillow basalts from the FAMOUS Rift Valley indicates that the weight percentage of the aluminium is about 1.5% and that this is the most abundant minor cation species (Lecaille and Prevot, in press 1980).

The single phase spinel oxidation products of titanomagnetites are known as titanomaghemites, $Fe_{(3-x)R}\ Ti_{xR}\square_{3(1-R)}\ O_4$, $R=8/\{8+z(1+x)\}$ and $z(0<z<1)$ is the degree of oxidation). R may be considered as simply a parameter of convenience or may be called the 'spinel stoichiometry parameter' It is equal to the ratio of the oxygen in the stoichiometric composition to that in the nonstoichiometric case. For oxidation $1<R<8/(9+x)$. In the compositional formula R shows the number of cations per spinel formula unit reducing as they are spread throughout the crystal, physically enlarged when oxidation takes place by addition of oxygen. The oxidation process, which is generally referred to as "maghemitization", appears to be especially favoured by the submarine environment.

The laboratory simulation of the maghemitization of titanomagnetites will provide us with a better understanding of the magnetic properties of naturally occurring material in the oceanic crust. Ozima and Sakamoto (1971), Readman and O'Reilly (1972), and O'Donovan and O'Reilly (1977) studied the magnetic properties of the cation-deficient products of titanomagnetites which were oxidized in air. Joshima (1975) presents a brief report of studies on the effect of aluminium contamination in titanomagnetites and titanomaghemites. More recently Ryall and Hall (1979) have heated submarine basalts in water in the laboratory in order to study the variation of magnetic properties with oxidation. In some studies only a limited range of oxidation maintaining the spinel structure could be achieved.

The purpose of the present study is to prepare synthetic analogues of naturally occurring titanomagnetite and titanomaghemites substituted by aluminium, this being the most abundant species of cation, other than iron or titanium, in oceanic rocks. The characteristic properties of the synthetic analogues, such as lattice parameter and Curie temperature, may then be used for identification of the magnetic minerals in submarine basalts. An understanding of the alteration process and its magnetic consequences are necessary for the interpretation of the palaeomagnetic record and of the anomalies in the geomagnetic field, observed over the ocean basins, due to the remanence of the basement rocks. Conversely, magnetic studies of the rocks may be used to trace out the thermal and chemical evolution of the basement material.

Experimental Method

The results of the previous investigations of maghemitization – the characteristic properties of the titanomaghemites produced and the range of non-stoichiometry attainable – are not in good agreement. The successful preparation of single phase well-characterized homogeneous materials is crucial to such investigations.

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The synthesis and characterization procedures adopted in the present investigation are therefore described in some detail.

Synthesis of Titanomagnetites

Polycrystalline specimens of six compositions in the systems $Fe_{2.4-\delta}Al_{\delta}Ti_{0.6}O_4$ ($x=0.6$, the ATM60 series) and $Fe_{2.6-\delta}Al_{\delta}Ti_{0.4}O_4$ ($x=0.4$ the ATM40 series) ($\delta=0$, 0.1 and 0.2 in both cases) were synthesized by the method of partial self buffering.

The starting materials Fe, TiO_2, Al_2O_3 and Fe_2O_3 were pre-treated before firing. The iron powder was heated in pure dry hydrogen at 350° C to remove any surface oxide layer The Fe_2O_3 was heated in a stream of dry oxygen at 625° C to oxidize any Fe^{2+} ions to Fe^{3+} Al_2O_3 and TiO_2 were heated in air for 23 h at 620° C and 30 h at 320° C, respectively, to remove adsorbed moisture. The stoichiometric mixtures of the powders were pressed into pellets and placed in a mullite tube which was evacuated and flushed with argon at a pressure of 200 torr. The tube was heated at 1,350° C for six hours then the pellets allowed to cool down to room temperature in 25 h in the furnace. Finally the material was re-crushed and pelleted and fired at 1,350° C in the mullite tube, this time containing a mixture of 90 vol.% argon and 10 vol.% CO_2–CO, in a proportion slightly reducing with respect to the mixture corresponding to stoichiometry at the firing temperature.

After each of the two firings the X-ray cell edges were determined from Debye-Scherrer powder photographs and the Curie temperatures found from the temperature dependence of initial volume-susceptibility (Özdemir and O'Reilly 1978). The cell-edges for the composition $\delta=0.10$ and 0.2, decreased by a considerable amount after the second firing. This may be because aluminium diffusion through the crystalline lattice was only completed after the second firing and the stoichiometry was improved. The synthesized materials were single phase spinels.

Curie temperature is very sensitive to the degree of high temperature non-stoichiometry and cell edge rather less sensitive. Increasing non-stoichiometry results in a higher Curie temperature and decreased cell edge. The method of partial self-buffering and two firings used in the present study produces more highly stoichiometric material than single firings or total self-buffering. This may account for differences between the present data and that of Readman and O'Reilly (1972) and Richards et al. (1973). The degree of non stoichiometry for the TM60 material can be estimated using the Hauptman (1974) formula. This gives $z=0.028$.

Preparation of Fine Grain Titanomagnetites

To prepare the fine particle titanomagnetites, the twice-fired materials were ground for 16 h in a high purity methanol slurry in a tungsten carbide ball mill. Then the slurry was gently dried under an infra-red lamp for half an hour The Curie temperature and cell-edge parameters were remeasured after ball-milling. The results are given in Table 1 The Curie temperatures of the finely ground samples were found to be slightly higher than the twice-fired coarse grain samples. This is a result of the oxidation which invariably takes place during the grinding process. This was confirmed by wet-chemical analysis. Values of the oxidation parameter, z, obtained from the chemical analysis are given in Table 1.

Electron Microscope Observations of Fine Grain Material

Grain size measurements were made using the transmission electron microscope. The particle size distribution was determined from separate grains on the high magnification electron micrographs. The low magnification micrographs showed that the particles tended to flocculate, due to magnetostatic interactions between grains, into agglomerates in the size range 0.1–0.4 μm. However the observations at higher magnification (Fig. 1) show the presence of separate grains which, together with the small agglomerates within which separate grains could be distinguished, allowed an attempt to determine the grain size distribution. Because of the tendency to flocculate, only 103 separated grains were measured from four micrographs, projected through a photographic enlarger. The grain size distribution is shown as a histogram in Fig 2a. The grain size was found to be about 300 ± 70 Å. However, this value can only be approximate when the small number of grains counted is taken into account. Readman and O'Reilly (1970) produced fine grain material by a similar technique and the mean crystal size from X-ray line broadening appeared to be about 400 Å.

The shape of grains was not equidimensional as expected. Apparently the ball milling produces irregular shapes although the particles are rounded. An attempt has been made to determine the ratio of the smallest (d_B) to the largest diameter (d_A) on the grains counted. The results are shown in the histogram of Fig. 2b. The mean value of the distribution was found to be 0.66 ∓ 0.11.

Table 1. Cell edge, Curie temperature and initial oxidation parameters for finely ground samples of the ATM40 and ATM60 series

	Composition	Chemical analysis			Curie[a] temperature T_c (°C)	Cell edge[b] a (Å)	X-ray densities (gm/cm^3)
		Fe^{2+}% (Stoichiometric, theoretical)	Fe^{2+}% (Experimental)	z			
$Fe_{2.6-\delta}Al_{\delta}Ti_{0.4}O_4$	0	34.48	29.49 ± 0.04	0.14 ± 0.03	363	8.459 ± 0.005	4.925
	0.10	34.92	28.75 ± 0.04	0.18 ± 0.03	325	8.448 ± 0.007	4.982
	0.20	35.38	30.06 ± 0.04	0.15 ± 0.03	270	8.435 ± 0.006	5.080
$Fe_{2.4-\delta}Al_{\delta}Ti_{0.6}O_4$	0	39.40	34.13 ± 0.04	0.13 ± 0.04	206	8.486 ± 0.006	4.839
	0.10	39.91	33.89 ± 0.04	0.15 ± 0.03	148	8.473 ± 0.006	4.908
	0.20	40.43	34.14 ± 0.08	0.16 ± 0.07	102	8.462 ± 0.006	4.981

[a] The samples were heated in sealed evacuated silica capsules for T_c measurements to prevent oxidation
[b] The cell parameters were derived from Guinier de Wolff powder pictures

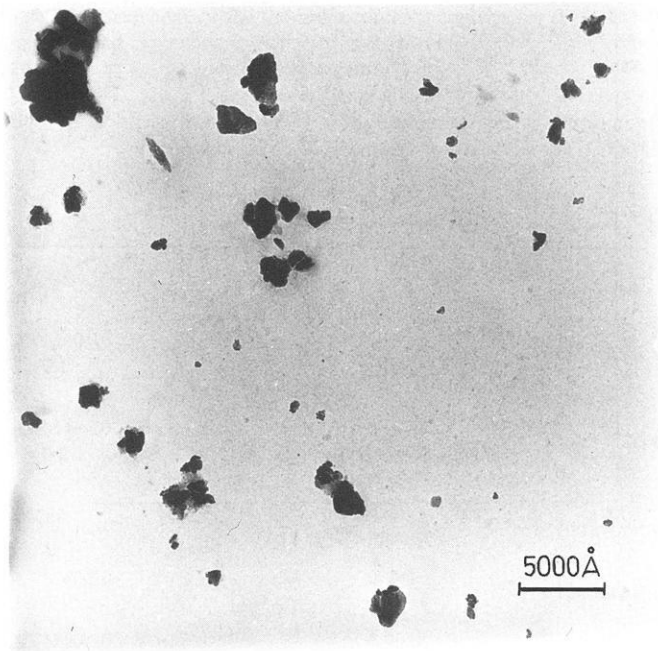

Fig. 1. Electron micrograph of a fine grain titanomagnetite sample showing isolated grains and small agglomerates

Preparation of Titanomaghemites

The same technique was used to prepare the titanomaghemites as described by Readman and O'Reilly (1970) for unsubstituted titanomaghemite and O'Donovan and O'Reilly (1977) for magnesium substituted compositions. Samples of the finely ground titanomagnetite were oxidized by heating in air in a Stanton Massflow thermobalance. The instrument consists of a precision air-damped analytical balance with electric weight loading. The standard tube furnace is counterbalanced by its own low voltage transformer and may be raised or lowered over the charge. A chart recorder provides simultaneous recording of weight change and temperature.

The oxidation experiments were carried out in two stages: (i) First, straight runs were made in which specimens (1 gm) were heated at a constant rate to about 900° C. The derivatives of such weight-temperature curves are DTG curves. The DTG curves for the ATM60 series are given Fig. 3. The curves of all samples show two peaks or can at least be fitted by two independent peaks. The lower temperature peak, which is centered at about 250° C, is the higher. The second, less definite, peak occurs at about 350° C. This has been attributed to the limited availability for oxidation of Fe^{2+} in the tetrahedral sites of the structure (O'Donovan and O'Reilly 1977). The various parameters (onset of weight gain, position and height of peaks, end of weight gain, relative areas under the inferred peaks) of the curves change systematically with composition within each of the two series. The parameters of the DTG curves are listed in Table 2.

X-ray powder pictures of the products of the straight DTG runs were made using a Guinier de Wolff camera for the ATM40 samples. The samples heated to high temperatures (say 900° C) show mixed phases, consisting of a rhombohedral (haematite) and a Ti-rich phase (pseudobrookite). The samples of ATM40 ($\delta=0.1$) heated between temperatures 100°–550° C show spinel and rhombohedral phases. The cell edge of the spinel phase is 8.348 ± 0.009 Å. Heating above 550° C results in a titanium-rich phase together with haematite.

(ii) Secondly, isothermal runs were made at temperatures below about 350° C to produce single-phase homogeneous titanomaghemites of the required composition.

Differential thermogravimetric analysis indicates that the oxidation of the fine grain titanomagnetite takes place readily between 100°–350° C. Heating above this temperature is expected to result in multiphase products.

A starting weight of 1 gm was used in each oxidation experiment. The titanomaghemite samples were prepared by heating at isotherms between 100° and 350° C in air in the thermobalance for times of the order of 10 h.

In some of the most highly oxidized compositions very faint lines due to non-spinel phases were just visible. Because of the sensitivity of the Guinier de Wolff system the concentration of the non-spinel phases is considered to be low enough (~a few percent) that the error in the estimated composition of the spinel phase is negligible and that the observed magnetic properties are those of the spinel phase only.

The oxidation parameter, z, is defined as the fraction of the Fe^{2+} ions in the stoichiometric composition oxidized to Fe^{3+}.

$$Fe^{2+}+\tfrac{1}{2}zO\rightarrow zFe^{3+}+(1-z)Fe^{2+}+\tfrac{1}{2}zO^{2-}.$$

When the desired weight increase was obtained, the sample was quenched to room temperature by raising the furnace. No weight increase was found to have taken place during the cooling period. Before quenching to room temperature the sample was allowed to come into 'equilibrium', i.e., the rate of weight increase became

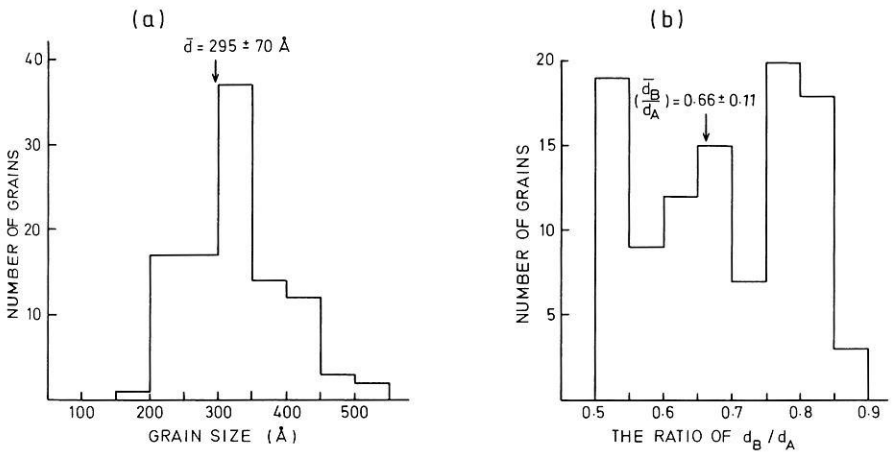

Fig. 2. Histograms of the grain size distribution and the ratio of the longest to smallest dimension (d_B/d_A) for the fine grain sample of $Fe_{2.2}\ Ti_{0.6}\ Al_{0.2}\ O_4$ determined from electron micrographs such as Fig. 1

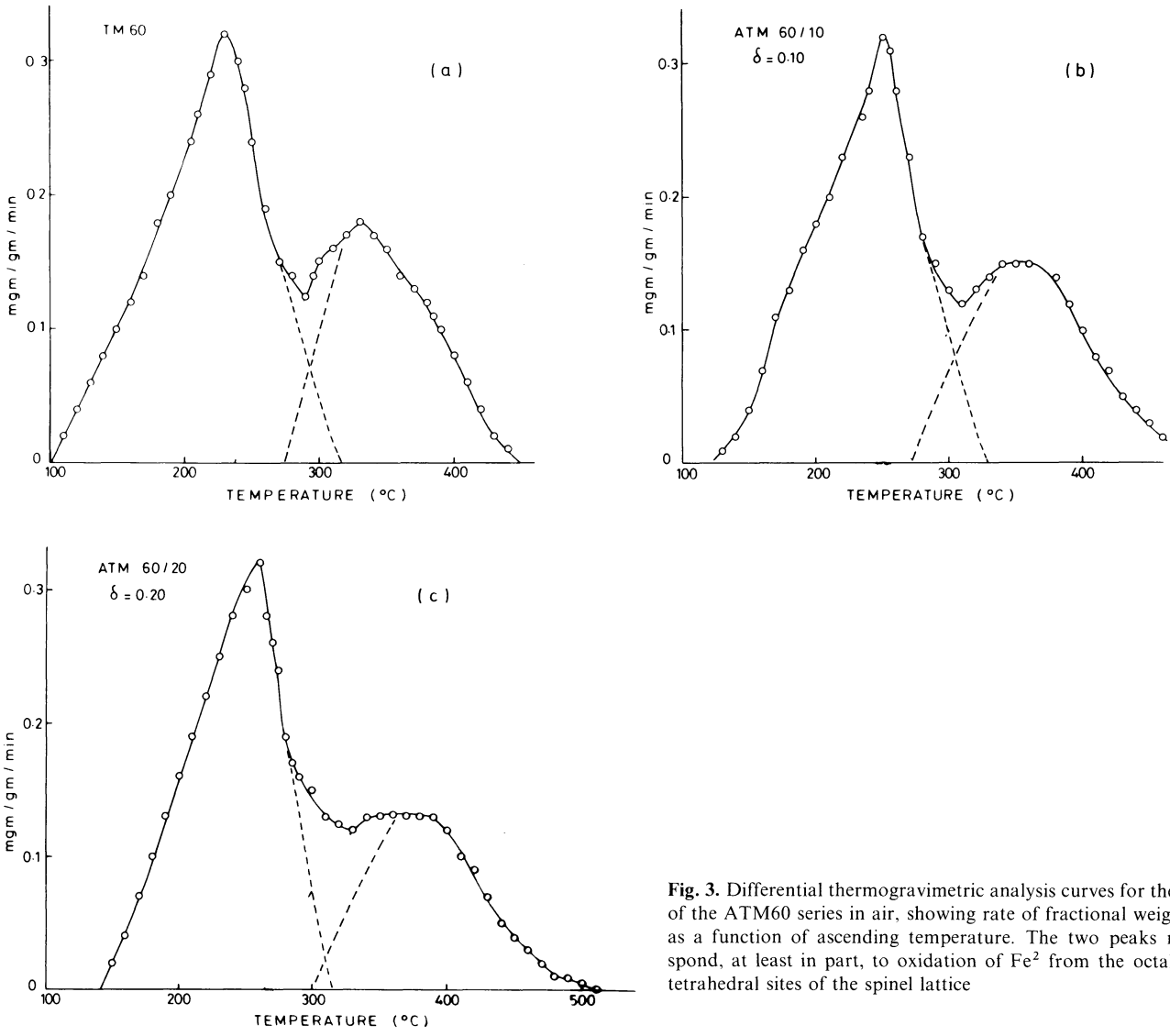

Fig. 3. Differential thermogravimetric analysis curves for the oxidation of the ATM60 series in air, showing rate of fractional weight increase as a function of ascending temperature. The two peaks may correspond, at least in part, to oxidation of Fe^2 from the octahedral and tetrahedral sites of the spinel lattice

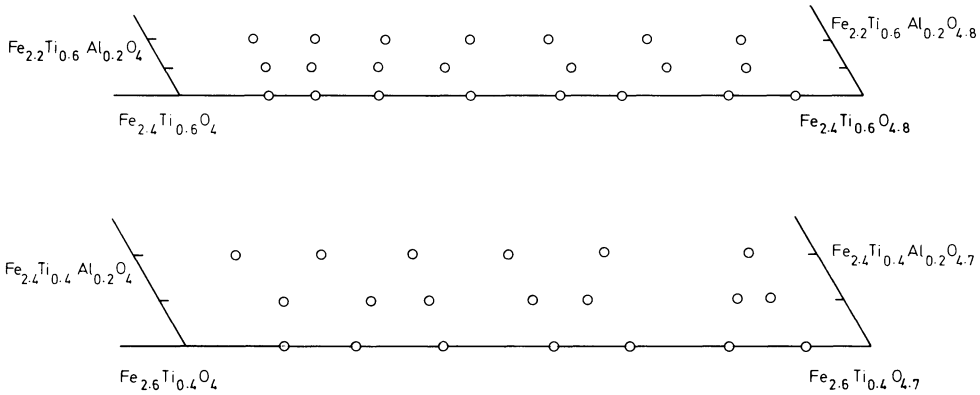

Fig. 4. Location of the synthesized titanomaghemites in the relevant quadrilaterals of the Al_2O_3–FeO–TiO_2–Fe_2O_3 quaternary tetrahedron

undetectably small. This gave a definite final weight and also promoted homogeneity in the specimen by annealing at the isotherm.

The oxidation parameter z was calculated from the observed weight increase during the oxidation by $z=(\Delta m \cdot M)/\{8 \cdot m(1+x)\}$ where Δm is the observed weight increase, m is the constant starting weight (taken after the adsorbed water or other volatiles were driven off), M and x are the molecular weight and composition parameter respectively.

The initial z parameter for the samples produced by ball-milling

Table 2. Parameters of the thermogravimetric analysis for the ATM40 and ATM60 series

Sample	Onset of weight gain			Positions of the peaks			
	weight loss (mgm)	constant weight (gm)	Position of the DTG curve	Low temperature		High temperature	
				Maximum weight change (mgm/gm/min)	Relative area	Maximum weight change (mgm/gm/min)	Relative area
TM40	2.2 (20°–120° C)	0.9981 (120°–125° C)	130°–430° C	0.32 at 250° C	0.68	0.12 at 350° C	0.23
ATM40/10 $\delta=0.1$	4.1 (20°–120° C)	0.9965 (120°–130° C)	130°–450° C	0.3 at 245° C	0.73	0.12 at 330° C	0.33
ATM40/20 $\delta=0.2$	3.5 (20°–120° C)	0.9967 (120°–130° C)	130°–460° C	0.32 at 250° C	0.75	0.14 at 340° C 0.08 at 400° C	0.33
TM60	2.8 (20°–95° C)	0.9982 (95°–105° C)	100°–450° C	0.32 at 230° C	0.65	0.18 at 330° C	0.37
ATM60/10 $\delta=0.1$	3.2 (20°–130° C)	0.997 (130° C)	120°–470° C	0.32 at 250° C	0.63	0.15 at 350° C	0.35
ATM60/20 $\delta=0.2$	3.8 (20°–130° C)	0.9964 (130° C)	140°–500° C	0.32 at 260° C	0.60	0.13 at 370° C	0.32

Table 3. X-ray cell edge and Curie and inversion temperatures of the oxidized ATM60 series. An asterisk indicates faint haematite lines in the X-ray powder picture estimated at a few percent

	z Oxidation degree	Cell edge (Å) G-de-W camera	T_c (°C) (Titano-maghemite)	T_I (°C) (Inversion temperature)	T_c (heating) (°C) (First stage inversion product)	T_c (cooling) (°C) (Second stage inversion product)
$\delta=0$	0.13	8.486	206	–	–	–
	0.20	8.472	299	323	567	463
	0.29	8.464	320	333	560	513
	0.43	8.452	360	370	554	531
	0.56	8.436	367	377	568	562
	0.65	8.408	375	381	582	561
	0.8	8.380*	423	437	598	578
	0.9	8.351*	438	458	595	580
$\delta=0.1$	0.15	8.473	147	–	–	–
	0.22	8.476	236	290	520	393
	0.32	8.465	271	293	539	463
	0.41	8.459	304	325	571	464
	0.59	8.417	317	360	555	536
	0.74	8.376*	368	434	573	558
	0.85	8.356*	384	464	562	544
$\delta=0.2$	0.16	8.462	102	–	–	–
	0.25	8.459	198	253	532	397
	0.35	8.455	242	268	573	459
	0.47	8.446	261	299	557	467
	0.59	8.394	275	360	570	521
	0.73	8.352*	326	442	580	512
	0.87	8.330*	373	367	464	521

was determined by wet-chemical analysis. The wet chemically determined initial values are adopted and gravimetry used to monitor changes in degree of oxidation. Therefore the quoted z values of Tables 3 and 4 are determined by a combination of thermogravimetric and wet-chemical analysis.

The location of the fine grain aluminium-substituted titanomaghemites (oxidized ATM40 and ATM60 series) in the relevant quadrilaterals of the Al_2O_3–FeO–TiO_2–Fe_2O_3 quaternary tetrahedron are shown in Fig. 4.

Thermomagnetic Properties – Curie Temperatures and Inversion

The metastable non-stoichiometric titanomaghemites 'invert' without change in bulk chemical composition when heated above

Table 4. X-ray cell edge and Curie and inversion temperatures of the oxidized ATM40 series. An asterisk indicates faint haematite lines in the X-ray powder picture estimated at a few percent

	z Oxidation degree	Cell edge (Å) G-de-W camera	T_c (°C) Titano-maghemite	T_I (°C) (Inversion temperature)	T_c (cooling) (Final inversion product)	M_F/M_I
	0.14	8.459	363	–	–	–
	0.25	8.437	410	250	410	1.08
	0.37	8.413	440	250	424	1.11
$\delta=0$	0.54	8.385	450	290	435	1.28
	0.65	8.376	470	300	453	1.43
	0.79	8.362*	475	300	455	1.58
	0.90	8.339*	–	–	–	–
	0.18	8.448	325	–	–	–
	0.31	8.418	402	250	400	1.16
	0.39	8.409	404	280	392	1.12
$\delta=0.1$	0.054	8.389	420	260	410	1.36
	0.62	8.382	424	290	402	1.77
	0.84	8.349*	440	280	420	1.82
	0.89	8.339*	460	260	450	2.11
	0.15	8.435	270	–	–	–
	0.28	8.418	359	300	348	1.45
$\delta=0.2$	0.41	8.412	380	300	326	1.19
	0.55	8.369	395	300	334	1.17
	0.67	8.345	420	300	350	1.67
	0.90	8.325*	430, 580	280, 320	308, 610	1.8

about 350° C (or at lower temperatures under increased pressure). The simplest case is the inversion of maghemite to haematite. The inversion products of titanomaghemites are generally multiphase, one phase being a near stoichiometric Fe^{2+}-containing spinel (except for $z=1$). The high-field thermomagnetic curve of a titanomaghemite therefore shows a rise in magnetization at temperatures of about 350° C. This may be obscured if the Curie point of the titanomaghemite lies above this temperature. Continuation of the thermomagnetic run to higher temperatures reveals the Curie temperature of the first-formed magnetic inversion product. Inversion seems to be a two-stage process, however, and the Curie point of the (final) inversion product found on the cooling run is often lower than that of the first formed magnetic phase. The saturation magnetization of the final assemblage is generally higher than that of the starting titanomaghemite.

In the present investigation the temperature dependence of magnetic properties was studied using three instruments – a susceptibility bridge, a magnetic balance and a *vibrating sample magnetometer* (VSM). The first instrument measures initial susceptibility. This property is not necessarily easily related to the concentration of a magnetic phase but usually shows a sharp peak just below the Curie temperature. Difficulties also arise if inversion starts before the Curie temperature of the titanomaghemite is reached. The second instrument measures high field magnetization. This property is simply related to the concentration of a magnetic phase. The transition at the Curie point is less sharply defined in this case and a convention has to be adopted for defining the Curie point. However, a 'virtual' Curie point, lying above or near the inversion temperature can be estimated by extrapolation. The inversion is also unambiguously revealed by the rise (or fall in the case of small x and high z values) in magnetization. The third instrument (VSM) can also be used to measure high field magnetization usually during the process of recording hysteresis loops as a function of temperature. A high temperature VSM run would therefore normally require a much slower rate of temperature increase than runs on a bridge or a balance, and the sample would spend a longer time at each temperature.

The Curie temperatures of the ATM60 series, being generally below about 400° C, could be determined from runs on the susceptibility bridge. The Curie temperatures, so determined, of the ATM60 series are listed in Table 3 together with the Curie temperatures of the first-formed and final inversion products and the inversion temperatures. However these latter are believed to be overestimated perhaps because the susceptibility is not a good indicator of inversion.

The susceptibility bridge is unsuitable for metastable samples with Curie points above about 350° C, such as the ATM40 series, and these were run on the magnetic balance. The Curie temperatures, inversion temperatures and Curie temperatures of the final inversion product are given in Table 4. Also given in the table are the ratios (M_F/M_I) of the magnetization of the inverted material after completing the run to that of the starting titanomaghemite.

Some of the ATM60 samples were run on the high temperature VSM. The titanomaghemite Curie temperatures obtained in this way are similar to those from the susceptibility bridge. The inversion temperatures were however lower, in the range 300°–350° C

Identification of Naturally Occurring Titanomaghemites

It is a tradition to plot the Curie temperature, unit cell edge and saturation magnetization as contours on the FeO–Fe_2O_3 TiO_2 ternary diagram since the pioneering work of Akimoto et al. (1957). Ozima and Sakamoto (1971), Readman and O'Reilly (1972), and O'Donovan and O'Reilly (1977) have presented characteristic properties for cation-deficient spinels in the titanomaghemite quadrilateral or subsystems containing magnesium. The cell edge and Curie temperature data for the aluminium-substituted

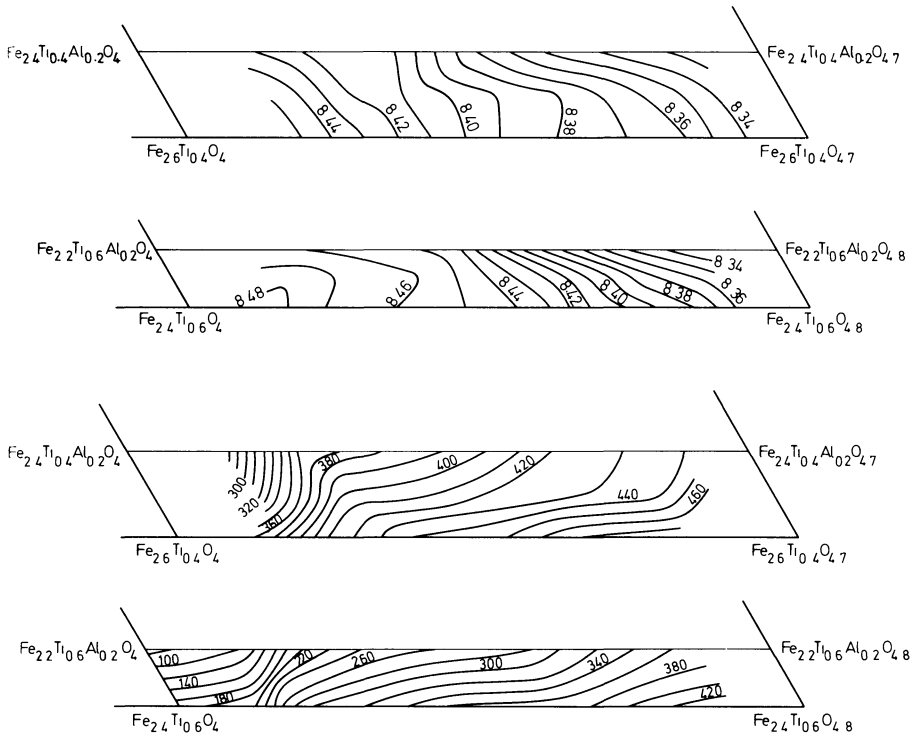

Fig. 5. Contours of constant unit cell edge (determined using a Guinier de Wolff camera) for the synthesized titanomaghemites

Fig. 6. Contours of constant Curie temperature for the synthesized titanomaghemites

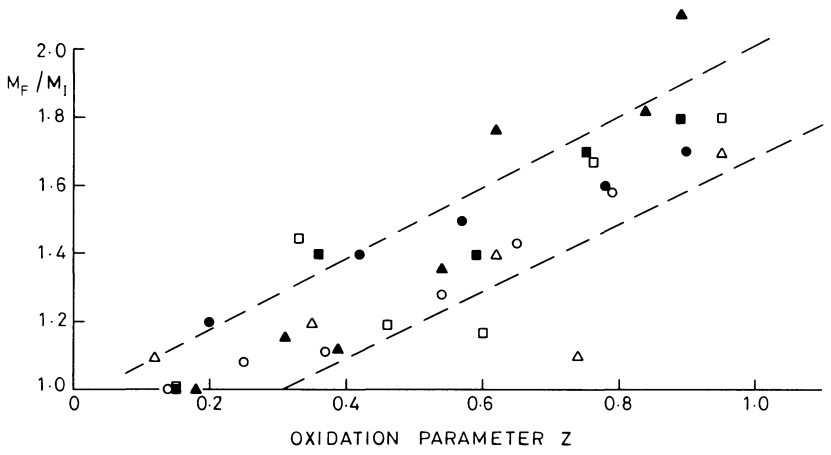

Fig. 7. The ratios (M_F/M_I) of the magnetization of inverted titanomaghemites (of different x values and substituted cations) after heating to about 700° C in a magnetic balance (in times of the order of 1 h) to the magnetization of the initial titanomaghemites, plotted against degree of maghemitization, z. The data are from Table 4 and from O'Donovan and O'Reilly (1977). (Composition parameters: *open circles, triangles,* and *squares* correspond to $x=0.4$; $x=0.6$, $\delta(\mathrm{Mg})=0.25$; $x=0.4$, $\delta(\mathrm{Al})=0.2$ respectively; *Solid circles, triangles,* and *squares* correspond to $x=0.6$, $\delta(\mathrm{Mg})=0.15$; $x=0.4$, $\delta(\mathrm{Al})=0.1$, $x=0.6$, $\delta(\mathrm{Mg})=0.05$ respectively)

synthetic titanomaghemites of the present investigation are shown in contour form in Figs. 5 and 6.

The use of any single technique (e.g., the measurement of Curie temperature) does not unambiguously identify a magnetic mineral. At least two methods are needed to narrow down the compositional field, within which a mineral may lie, to a useful range. The intersection of Curie temperature and cell edge contours serves this function but the latter property may be difficult to measure, requiring extraction of the magnetic phase. In the case of the fine grain titanomaghemites in DSDP basalts the prolonged pulverization needed to achieve an adequate degree of refinement may indeed lead to alteration in the minerals themselves. The inversion of titanomaghemites qualitatively indicates their presence and may also provide a quantitative measure of the degree of non-stoichiometry. A single thermomagnetic run may therefore contain enough information to provide at least a first approximation to the composition of a titanomaghemite. Such a run will provide (i) the Curie temperature of the univerted titanomaghemite, (ii) the Curie temperature of the inversion product, and (iii) the ratio (M_F/M_I) of the magnetization of the inversion product to that of titanomaghemite. All three are functions of the composition coordinates (x,z) of the titanomaghemite. However the inversion process would have to be better understood before it could be put to such a use. The M_F/M_I ratios of Table 4 and data from O'Donovan and O'Reilly (1977) who studied Mg substituted titanomaghemites are plotted against oxidation parameter, z, in Fig. 7. Although there is some scatter in the data the general trend is clear. The reason for the scatter may lie in the different heating rates which might be employed in runs on a magnetic balance, for example, although an hour might be a typical heating time. It may be that inversion proceeds in a different way or is incomplete depending on the time available. Indeed M_F/M_I ratios as high as about 5 were found for some samples of the TM60 series run in the high temperature VSM (for the order of a day). For this reason we have not combined the data of Table 4 with Fig. 4 to produce contours of M_F/M_I,

and the Curie temperature of the inversion product. A standard inversion procedure would have to be worked out before the inversion phenomenon could be used for quantitative determination of titanomaghemite composition.

Conclusions

The magnetic properties of basalts recovered from the submarine basement provide an important means of investigating both the history of the geomagnetic field and the evolution of the Earth's crust. The determination of the physical and chemical state of the remanence-carrying magnetic minerals is a necessity in either case. The present study provides characteristic data on synthetic analogues of the magnetic minerals believed to occur in submarine basalts. Such data should be useful in tracing out the petrological history of the basement rocks.

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