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Original Investigations

Partial Self-Reversal of Natural Remanent Magnetization of an Historical Lava Flow of Mt. Etna (Sicily)*

F. Heller[1], H. Markert[2], and E. Schmidbauer[3]

[1] Institut für Geophysik, ETH Zürich, CH-8093 Zürich, Switzerland
[2] Physikalisches Institut, Universität Bayreuth, D-8580 Bayreuth, Federal Republic of Germany
[3] Institut für Allgemeine und Angewandte Geophysik, Universität München, D-8000 München 2, Federal Republic of Germany

Abstract. Three historical lava flows of Mt. Etna (Sicily) have been sampled. Various rock magnetic parameters as well as microchemical and Mössbauer characteristics have been investigated. The natural remanent magnetization (NRM) of one lava flow shows partial self-reversal upon heat treatment. As two different magnetic phases have been identified in this flow, it is suggested that negative magnetostatic interaction causes the observed self-reversal of NRM.

Key words: Rock magnetism – Continental basalts – NRM – Self-reversal.

1. Introduction

The discovery of reversed polarity of natural remanent magnetization (NRM) of rocks was one of the early findings in palaeomagnetism. Reversals of the geomagnetic field or self-reversal mechanisms such as those suggested by Néel (1955) may cause the reversed polarities of NRM observed in the course of many palaeomagnetic investigations. Nowadays field reversals are generally accepted to be responsible for the vast majority of reversed NRM directions. Nevertheless some examples of self-reversal of NRM have been reported: for instance the self-reversing Haruna dacite (Nagata et al., 1952), certain oceanic basalts studied by Ozima and Ozima (1967) and Sasajima and Nishida (1974) and more recently a fragment of continental basalt investigated by Schult (1976). Furthermore it has been shown by several authors (Havard and Lewis, 1965; Creer et al., 1970; Creer and Petersen, 1969) investigating continental basalts which contain titanium-rich homogeneous titanomagnetites that an artificial thermoremanent magnetization (TRM) produced during moderate heat treatment in the laboratory can acquire self-reversal or at least partial self-reversal characteristics at room temperature.

* Institut für Geophysik, ETH Zürich, Contribution no. 240

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Self-reversals can be classified into three categories according to different physical mechanisms: (1) A one-constituent model in which the direction of spontaneous magnetization J_s changes sign at a certain temperature. This behaviour is found in Néel's *P*- or *N*-type ferrimagnets because of the different temperature dependence of the antiparallel sublattice magnetizations. (2) A two-constituent model in which exchange interaction across the boundary of two magnetic phases plays the essential role. This is thought to be the mechanism in the self-reversing compositional range of the ilmenite-haematite solid solution series (Hoffmann, 1975). (3) A two-constituent model in which magnetostatic interaction between two phases leads to complete or partial self-reversal of remanence. This mechanism has been invoked for the TRM reversal found by Creer et al. (1970).

There is also a type of apparent partial self-reversal which was detected in experiments on oxidized titanomagnetite by Petherbridge et al. (1974) and Rahman and Parry (1975). This type has been interpreted theoretically by Stephenson (1975) in terms of screening of the magnetization of a high Curie point phase by a surrounding host material with lower Curie temperature.

This paper deals with observations on partial self-reversal of natural remanent magnetization found in recent lavas of Mt. Etna. Continuous thermal demagnetization of NRM, field dependence of TRM and IRM, $J_s(T)$ behaviour, microprobe analysis and Mössbauer studies together with routine palaeomagnetic investigations have been carried out in order to investigate the reversal mechanism of these basalts.

2. Sampling Sites, Ore Microscopic Observations and Fundamental Rockmagnetic Data

Three historical lava flows of Mt. Etna originating from the eruptions in 1329, 1669, and 1971 have been sampled. The lava flow of 1329 was drilled near Stazzo (geogr. coord.: Lat. 37°35′ N, Long. 15°11′ E) where the flow now dips into the Mediterranean sea. Samples were taken along a vertical profile of 2 m depth from the top surface of the flow. The samples of the 1669 eruption were drilled in a quarry about 1 km to the west of Nicolosi (geogr. coord.: Lat. 37°36′ N, Long. 15°00′ E). This quarry is situated closely to the former eruption point of the flow. Two profiles A and B on either side of the quarry were drilled, profile A reaching a depth of about 3 m from the top of the lava surface. The specimens of the 1971 lava were obtained from two roughly oriented hand samples taken along the road about 1 km to the north of Fornazzo (geogr. coord.: Lat. 37°44′ N, Long. 15°05′ E).

Microscopic observation reveals a fairly uniform magnetic ore mineralogy throughout the three lavas. The only highly reflecting mineral to be found is titanomagnetite of various grain sizes. The titanomagnetites of the 1329 and 1971 lavas are optically homogeneous (oxidation class I according to Ade-Hall et al., 1968) showing only in very rare cases oxidation features along cracks in the larger grains; a few grains appear to be strongly oxidized and may be titanohaematite. The visible grain size distribution is different in both lavas. The 1971 lava contains two fractions: a very high percentage of the grains consist of euhedral to subeuhedral, sharply edged small grains whose size reaches up to 5 μm. A smaller fraction of larger grains usually covers a size distribution between 250 μm and 500 μm. They are rounded or even corroded. The smaller grains of the 1329 lava have a size frequency maximum around 20 μm and very small grains below 5 μm diameter are very seldom. In the 1669 lava homogeneous titanomagnetites also prevail, but about 5 percent of the ore grains have a bluish-grey tint which is seen in high magnification observation to be caused by granulation of the surface. This indicates partial oxidation to titanomaghemite and perhaps further to Ti-poor magnetite (see Sect. 4.2). The grain size distribution has a frequency maximum between 20 μm and 50 μm. Larger grains are also observed with size and appearance like in the other two flows.

Some fundamental rock magnetic data of the 1329 and 1669 lavas, such as initial susceptibility and the direction and intensity of NRM before and after AF-cleaning, are given in Fig. 1 and Table 1. The variation of these parameters with depth along the drilled sections has been plotted in Fig. 1 together

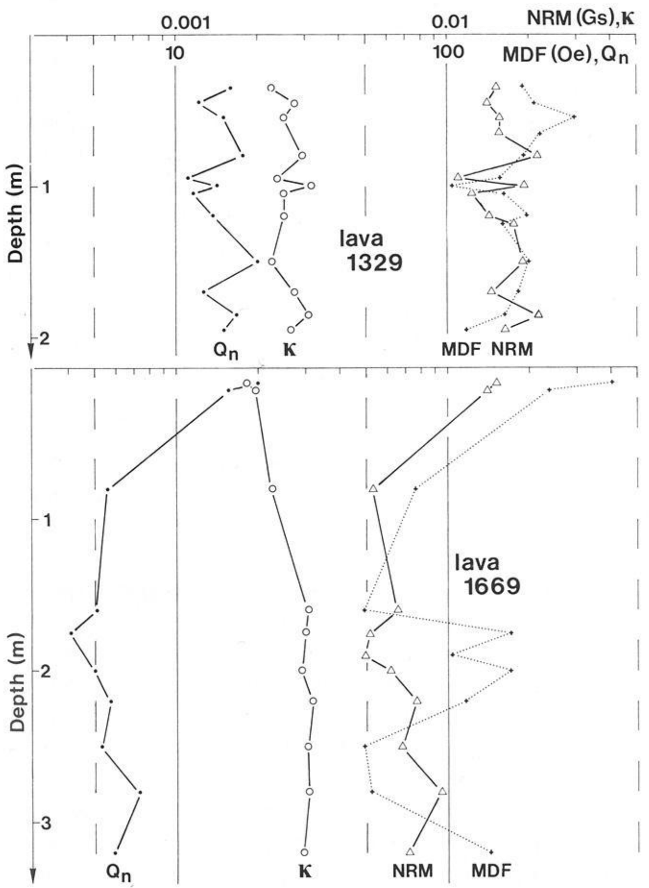


Fig. 1. Semilogarithmic plot of NRM before cleaning, initial susceptibility κ, median destructive field MDF and Koenigsberger ratio Q_n as a function of distance from the top surface of the lavas 1329 and 1669

Table 1. NRM mean directions and intensities before (D_o, I_o, NRM$_o$) and after optimum AF cleaning (D_{opt}, I_{opt}) with intensity standard deviation (σ) and 95% circle of confidence (α_{95}) of the lava flows 1329 and 1669. n = number of samples, κ = mean initial susceptibility, Q_n = Koenigsberger factor mean

Lava flow	n	NRM$_o$ (Gs)	σ (%)	D_o	I_o	α_{95}	D_{opt}	I_{opt}	α_{95}	κ (emu)	σ (%)	Q_n
1329	15	1.66E-02	±28	106.3	76.5	9.5	2.2	64.5	2.5	2.59E-03	±14	15.2
1669	16	7.48E-03	±42	12.9	29.9	25.0	359.4	57.7	4.2	2.68E-03	±17	6.6

with the variation of the Koenigsberger ratio Q_n and the median destructive field MDF which denotes the AF peak amplitude necessary to reduce the NRM intensity to 50% of its initial value.

In contrast to the findings of Tanguy (1970) the distribution of NRM directions before AF cleaning is appreciably scattered (Fig. 2). This is especially true for the lava flow 1669 which according to Tanguy should display extremely low NRM scatter. The different NRM scatter results possibly from a difference in the technique of sample extraction. Tanguy took oriented hand samples without any drilling and cutting. He measured his rock fragments using Thellier's (1967) big sample spinner magnetometer. Our samples always were drilled and cut into cylindrical specimen shape. Although we have used different equipment (electrical and gasoline powered machines) for that purpose, nearly all specimens possess secondary magnetization components. Magnetic stray fields eventually originating from electrical apparatus have been measured. They are smaller than the Earth's magnetic field and probably do not produce the observed secondary magnetization. Perhaps mechanical forces applied during the drilling and cutting procedure may change the magnetostrictive strain energy of the samples in the presence of the geomagnetic field. Thus a soft secondary magnetization having an arbitrary direction with respect to the present Earth's field may have been acquired.

The secondary magnetization components can be erased by AF-cleaning (optimum fields vary between 120 Oe and 240 Oe) so that well grouped NRM mean directions are obtained in the lava flows (Table 1). Nevertheless the cleaned NRM directions of the lava 1669 still show a systematic scatter (cf. Fig. 2). Samples taken from profile *A* differ significantly in inclination from samples taken from profile *B* at the other side of the quarry. Mechanically unstable tuffs and ashes underly the flow and may be responsible for later attitude changes and post-magnetization displacement of certain parts of the outcrop. Our mean directions of 1329 and 1669 (Table 1) differ slightly from Tanguy's (1970) values. They fit only marginally to the secular variation curves for Sicily published so far (Chevallier, 1925; Tanguy, 1970) which however are based on uncleaned NRM results.

The within site scatter of NRM intensity, initial susceptibility κ, Koenigsberger ratio and MDF values, as demonstrated in Table 1 and Fig. 1, is small for the lava originating from 1329. On the other hand these parameters clearly show a strong dependence on the position within the section in the 1669 basalt flow. Here the two uppermost samples have high initial NRM intensity (com-

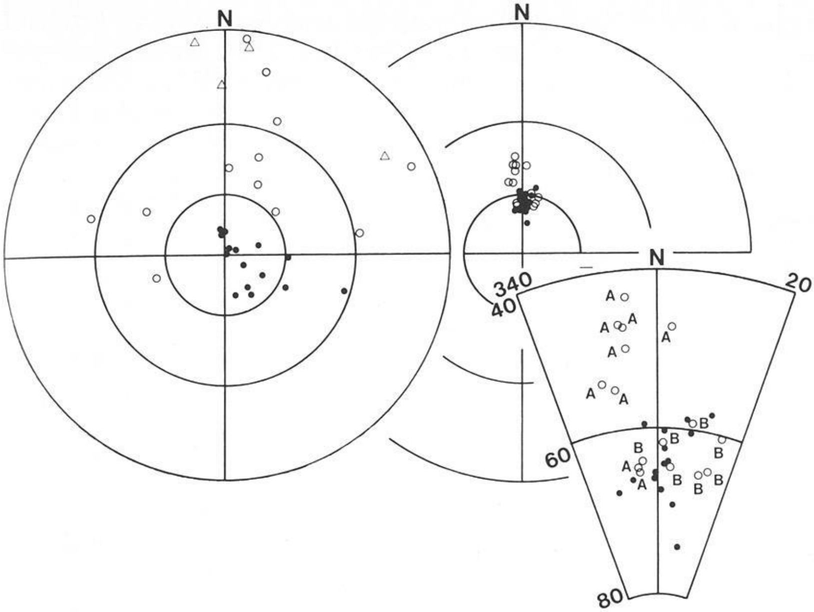


Fig. 2. Equal area projection of NRM directions before (*left side*) and after optimum AF cleaning (*right side*). *Triangles* indicate projection on upper hemisphere, *circles* and *dots* indicate projection on lower hemisphere. *Open symbols* refer to NRM directions of lava 1669, *dots* represent NRM directions of lava 1329. Circles plotted on the enlarged section and denoted with *A* or *B* refer to samples collected from the flow 1669 along profile *A* or *B* respectively

pared to the rest of the section), high MDF values (up to 400 Oe) and slightly reduced susceptibility. This is probably due to oxidation occurring in the uppermost, very porous part of the lava. The main difference between the two sections 1329 and 1669 is given by the lower NRM intensity of the 1669 lava. As susceptibility and visible ore grain size distribution in both profiles are very similar, the NRM difference seems to be quite remarkable and may be caused by partial self-reversal of NRM found in the 1669 basalt (see Sect. 3.1).

3. Thermomagnetic Measurements

3.1. Continuous Thermal Demagnetization of NRM

Heiniger and Heller (1976) developed a magnetometer system which allows spinner magnetometer measurements to be performed throughout a wide temperature range between $-200°$ C and 700° C. The NRM vector can be measured continuously in zero field as a function of temperature down to intensities of about 1×10^{-6} Gs. The continuous thermal demagnetization of Mt. Etna basalts yielded the following results.

At first the original uncleaned NRM of some representative samples taken from the three lavas was investigated (Fig. 3). The resulting vector plots indicate

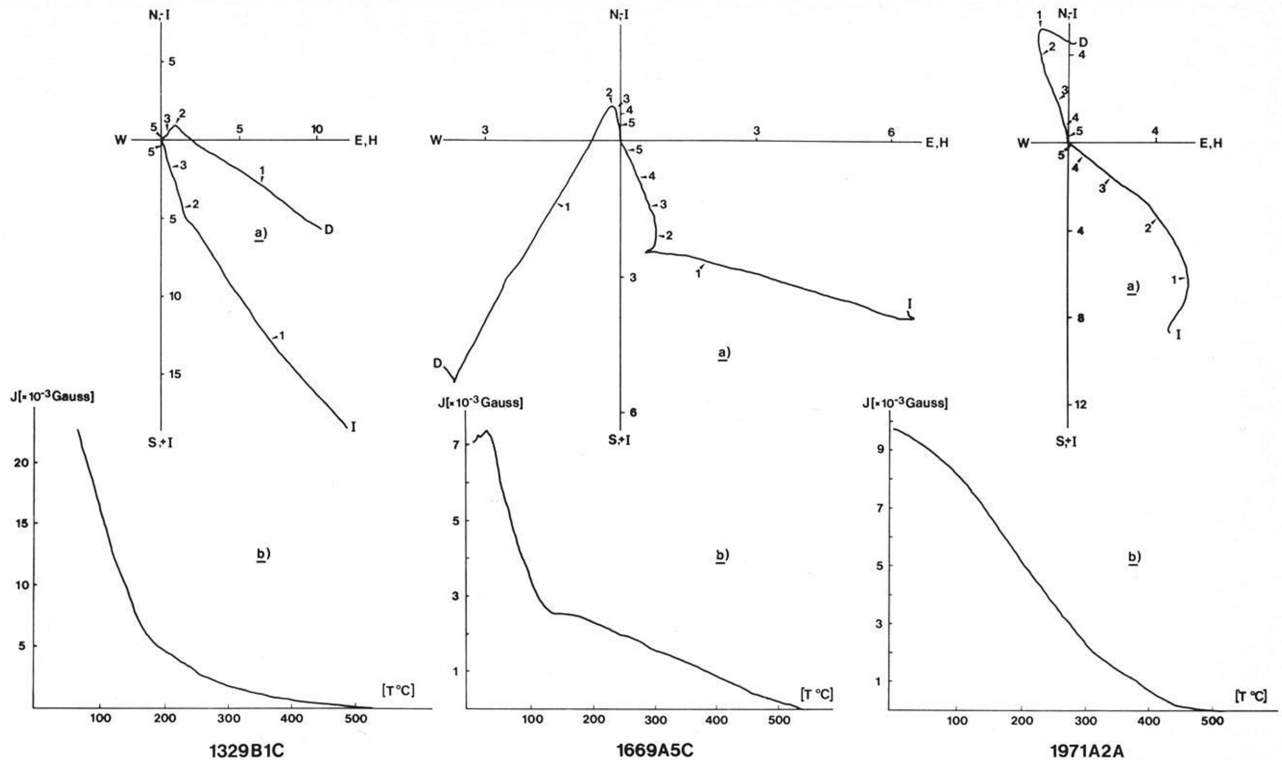


Fig. 3. Continuous thermal demagnetization of NRM of three samples taken from the 1329, 1669, 1971 lavas respectively. The vector diagrams (scale unit: 1 mG) show declination and inclination as function of temperature. The numbers 1–5 along each curve indicate the temperature $T/100°$ C. Heating rate in all experiments: 10° C/min. Thermal demagnetization always done in zero field and under normal air pressure

the presence of rather strong unstable secondary NRM components which are removed between 200° C and 300° C, whereas stable components remain up to temperatures around 500° C. The stable components are aligned parallel to the expected direction of the historical geomagnetic field. They possess northerly declinations and relatively steep inclinations (cf. Fig. 3). The unstable components are up to four times as strong as the stable components residing in phases with high Curie points.

The curves which represent the change of NRM intensity with increasing temperature [($J(T)$-curves], generally show a regular intensity decay. This applies especially to samples originating from the 1329 and 1971 lavas. A conspicuous qualitative difference is observed in the $J(T)$ curves of the 1669 lava, namely the development of a level of constant intensity and even a very slight intensity increase between temperatures of 140° C and 180° C. Secondly the uppermost blocking temperatures of the 1669 samples are distinctly higher (around 550° C) than those of the other two flows (ca. 500° C).

As the secondary NRM components present in our samples obscure the behaviour of the stable components during thermal demagnetization below 200° C to 300° C, some samples from all three basalts were subjected to partial AF demagnetization. The maximum field amplitude (between 60 Oe and 90 Oe) was chosen so that the secondary components just had been removed. After this cleaning procedure the samples were continuously demagnetized by heating in air. Fig. 4 demonstrates the resulting demagnetization plots.

Since any directional changes during heating are absent in all three vector plots, we conclude that secondary components have been successfully removed by the preceding AF cleaning. The NRM intensity curves of 1329 and 1971 samples decrease monotonously with increasing temperature and remanent magnetism with normal polarity, i.e., parallel to the present earth's field disappears at maximum blocking temperatures around 500° C. Up to 200° C the intensity of the 1329 sample is much more rapidly reduced than that of the 1971 sample. The NRM intensity of the 1669 sample shows up to 200° C very unusual behaviour: at first up to about 140° C there is only very little change in intensity, then up to 180° C a sharp intensity increase by ca. 11% which is followed by a continuous intensity loss with increasing temperature. From the corresponding vector plot it can be seen that the intensity increase is caused apparently by a magnetization component which is antiparallel or reversed with respect to the normal magnetization direction at temperatures above 180° C. The highest blocking temperatures are reached at around 550° C.

The 1669 sample appears to be partially self-reversed with a dominant high Curie point magnetization of normal polarity. This partial self-reversal is an intrinsic property of all 1669 samples and can be reestablished by thermal cycling of NRM above and below 200° C in zero field. Prior to the process of thermal cycling, another 1669 sample was cleaned by AC fields to remove secondary NRM components. As can be seen from Fig. 5, the first cooling and reheating cycle in zero field develops a stronger reversed component than the original NRM showed at first. When the original NRM had been acquired, the geomagnetic field was present during the whole cooling process thus acting against the reversal mechanism below 200° C. Also, as we will see later, some chemical

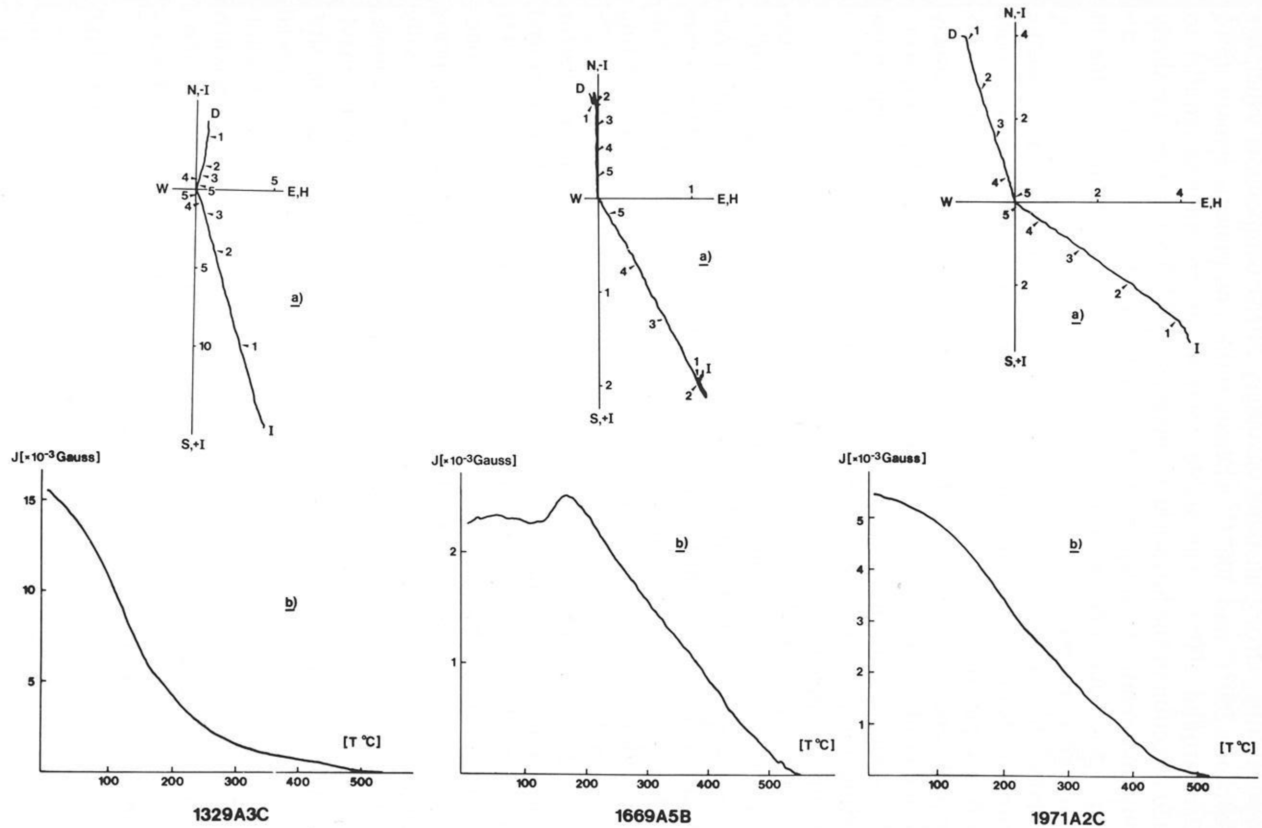


Fig. 4. Continuous thermal demagnetization of *AF* cleaned NRM, the *AC* field amplitude just high enough to remove secondary magnetization components. Scale units and signatures as in Fig. 3

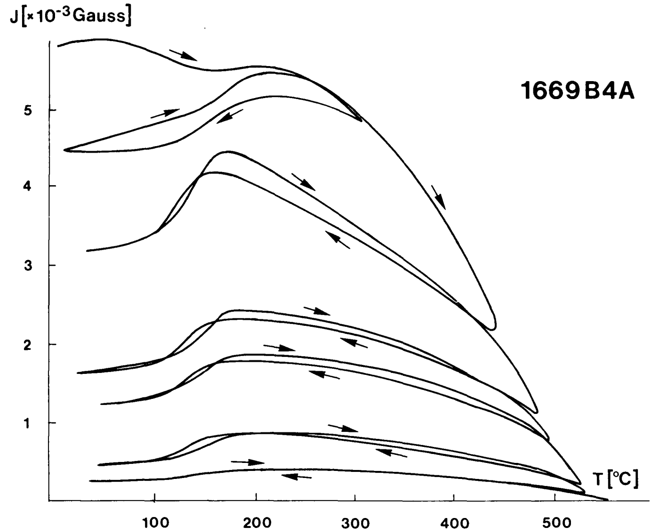


Fig. 5. Repeated heating and cooling cycles (*thermal cycling*) of *AF* cleaned NRM of a 1669 sample which shows partial self-reversal. During each cycle the maximum temperature has been progressively increased

changes may take place during re-heating. They may affect especially any titano-maghemite phases present. Extrapolating the intensity of the higher Curie point component down to room temperature in the second cooling cycle it can be estimated that the intensity of the apparently reversed component comes roughly to one third of the normal component at room temperature. Repeated cycling with progressively increased maximum temperature lowers the absolute intensities of both magnetization components thus suggesting that the reversed component is closely connected to the intensity (and hence the field) of the normal component. An apparent decrease of the lower Curie point by as much as 80° C is also observed. The onset of the reversal gets much more distinct in the second and later cycles where the temperature had been raised above 400° C. Assuming no alteration of the high Curie temperature phase during thermal cycling, it is evident from Fig. 5 that about three quarters of the stable normal NRM are blocked in the temperature interval ranging from 450° C to 550° C.

3.2. Saturation Magnetization

In order to determine type and compositional range of the magnetic phases present in the three lavas, saturation magnetization has been measured as a function of temperature. An automatically recording translation balance has been used. The results obtained by measuring pulverized samples in air (size fraction: 1 mm ∅) with an applied field $H = 1.7$ kOe have been plotted in Fig. 6.

The magnetization of the 1971 lava is nearly reversible upon heating and cooling and a distinct Curie point is indicated around $T_c = 240°$ C. A component

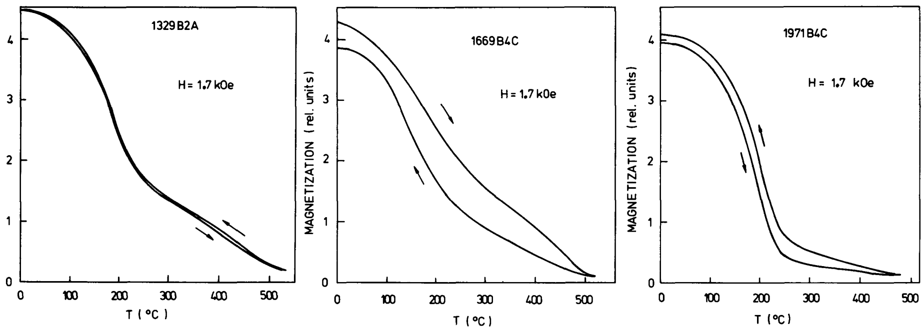


Fig. 6. $J_s(T)$ curves of three basalt samples of Mt. Etna. Applied field $H = 1.7$ kOe. Grain size fraction: ca. 1 mm

of minor importance with a higher Curie temperature is faintly seen during heating. It is more strongly pronounced during the cooling cycle. The slightly higher intensity of magnetization upon cooling is probably due to oxidation and production of a Ti-poor magnetite phase with a Curie temperature around $T_c = 500°$ C during heat treatment. The $J_s(T)$ curve seems to contradict the monotonic decay of NRM during continuous thermal demagnetization up to $T = 500°$ C (Fig. 4). The different behaviour is possibly due to different heating times, since the oxidation process is time dependent.

The $J_s(T)$ curve of the 1329 lava is reversible during heat treatment. Two distinct Curie points can be recognized: the higher one at $T_c = 530°$ C and the lower around $T_c = 220°$ C. This is in agreement with the decay of NRM during thermal treatment where the major portion of NRM is lost below 200° C (Fig. 4).

The 1669 lava shows a distinct Curie temperature just above 500° C. Upon heating the $J_s(T)$ curve seems to indicate a broad range of lower Curie temperatures between 200° C and 300° C. $J_s(T)$ is not reversible upon cooling – probably due to oxidation of the Ti-richer phases (Ti-maghemite?) –, but the lower Curie temperature range gets more restricted and a second Curie point may be defined around 225° C.

3.3 Low Temperature Susceptibility

According to Syono (1965) the zero-transition temperature ($T_{K=0}$) of the magneto-crystalline anisotropy constant K_1 of stoichiometric titanomagnetites of general composition $x\mathrm{Fe_2TiO_4} \cdot (1-x)\mathrm{Fe_3O_4}$ depends strongly on the titanium concentration x. This is illustrated in Fig. 7 which also shows the relationship between Curie temperature T_c and ulvospinel content for a wide range of titanomagnetites.

At the temperature $T_{K=0}$ the magneto-crystalline anisotropy energy of a multidomain titanomagnetite grain of given Ti- concentration x becomes minimum. The domain wall energy of the grain becomes minimum, too. Thus the domain wall mobility passes through a maximum at $T_{K=0}$ leading to a susceptibility maximum at that temperature.

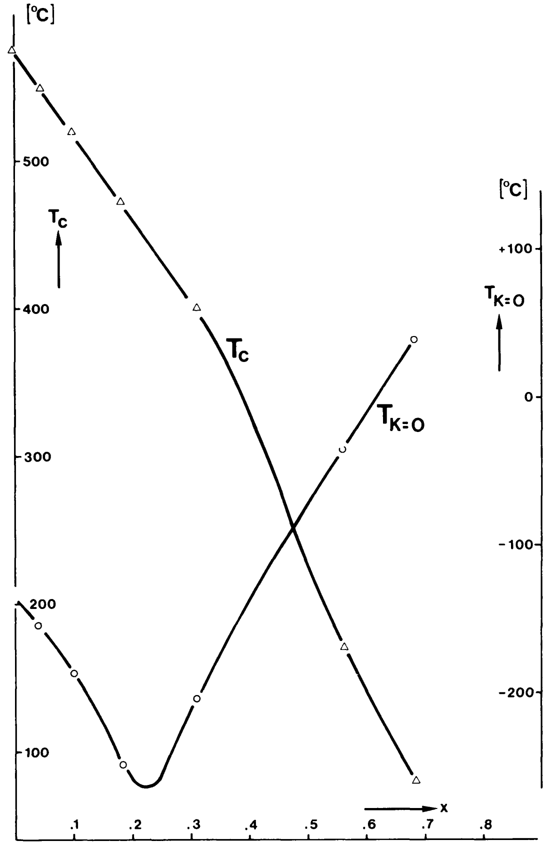


Fig. 7. Curie temperature (T_c) and zero transition temperature ($T_{K=0}$) of the magneto-crystalline anisotropy constant K_1 as a function of composition in the magnetite-ulvospinel solid solution series according to Syono (1965)

If for instance the Ti-content equals $x = 0.5$, it follows from Fig. 7 that the Curie temperature amounts to about 225° C, while the anisotropy constant K_1 changes sign at about $-83°$ C. At this temperature the susceptibility passes through a maximum. Therefore throughout a wide compositional range the low temperature dependence of susceptibility can be used to estimate the Ti-content of titanomagnetites. These measurements avoid the danger of oxidation of the material which is always involved in the usual Curie point determination. Figure 7 also shows some practical limitations of the method: (1.) Unambiguous estimates of x can only be obtained for $x > 0.4$ since $T_{K=0}$ passes through a minimum at $x = 0.22$. (2.) Temperatures below $-196°$ C (liquid nitrogen) can be gained only with special low temperature devices. Thus $T_{K=0}$ of titanomagnetites with composition $0.12 \leqq x \leqq 0.32$ usually cannot be detected.

The $\chi(T)$ measurements below room temperature have been carried out using the Fraunberger resonance bridge described by Markert et al. (1974). At the same time the high frequency losses $\alpha(T)$ which show the same temperature dependence as $\chi(T)$ have been measured. The results for the three lavas are shown in Fig. 8. The overall increase of $\chi(T)$ and $\alpha(T)$ is mainly caused by instrumental drift. The sharpness of the susceptibility and high frequency loss maxima which are superposed in all curves, is conspicuously different for the

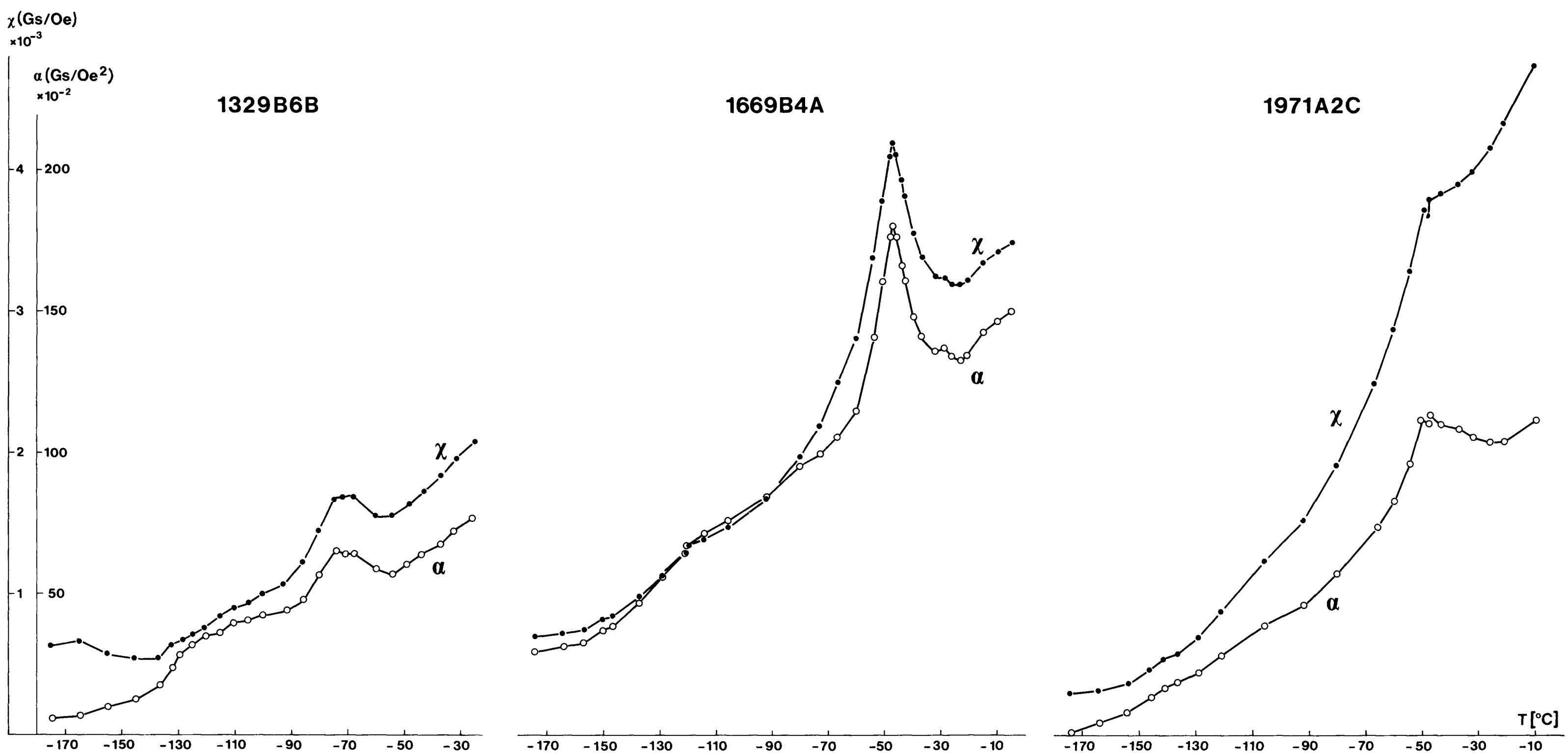


Fig. 8. Low temperature dependence of susceptibility (χ) and high frequency loss (α) in samples taken from the three lava flows

three samples. Only the 1669 sample shows very clear peaks at $T = -45°$ C which may correspond to a very well defined titanomagnetite phase having a Ti-content $x = 0.55$. The samples 1329 and 1971 behave as if the titanium concentrations of their Ti-rich magnetite phases are smeared out to some extent. Nevertheless some fairly pronounced peaks can be recognized at $T = -70°$ C corresponding to a composition $x = 0.51$ (sample 1329 B6B) and $T = -50°$ C corresponding to $x = 0.54$ (sample 1971 A2C). The $\chi(T)$ curves of the lavas originating from 1329 and 1669 have a second, less well developed maximum at lower temperatures. These maxima which are not found in the 1971 lava, indicate the presence of another titanomagnetite phase. The second peak is clearly seen in the 1669 lava around $T = -120°$ C and corresponds to a titanomagnetite with $x = 0.43$. The 1329 basalt has a very vaguely indicated second maximum at about $T = -165°$ C which may reflect a phase either with $x = 0.36$ or with $x = 0.07$.

3.4. *Significance of Thermomagnetic Measurements*

Out of the three lava flows from Mt. Etna the 1669 lava clearly shows partial self-reversal. The reversed component of NRM is increased by thermal cycling at moderately elevated temperature so that the reversed component makes up to nearly 50% of the normal component. Similar results have been obtained by Creer and Petersen (1969) on laboratory produced TRM of a Rauher Kulm basalt sample. In contrast to the findings of these authors, however, the reversed component of the historical Etna basalt disappears by heating above 200° C and the normal component is held by a phase with a high Curie point around 550° C.

Table 2 summarizes the results of low temperature behaviour of susceptibility and $J_s(T)$ curves including the composition parameter x of stoichiometric titanomagnetites derived by the two methods. Two titanomagnetite phases consistently indicated by both methods are contained in the 1329 lava: the compositions are given with $x = 0.51$ and $x = 0.07$. For the 1669 basalt the susceptibility curves indicate two phases with $x = 0.55$ and $x = 0.43$ which may reflect the smeared Curie temperature distributions between 200° C and 300° C in the $J_s(T)$ curves. The higher Curie temperature at $T_c = 510°$ C is attributed to a titanomagnetite with $x = 0.12$. This phase could not be proved in the $\chi(T)$ curves, since $T_{K=0}$ is below $-170°$ C the lowest temperature which could be achieved during low

Table 2. In the three lavas observed susceptibility maxima ($T_{K=0}$) with corresponding Curie temperature (T_{cs}) and composition parameter x_{cs} according to Syono (1965) and directly measured Curie temperatures (T_{cm}) with corresponding composition parameter x_{cm}

Lava flow	$T_{K=0}$ (° C)	Corresp. x_{cs}	T_{cs} (° C)	T_{cm} (° C)	Corresp. x_{cm}
1329	−70, −165	0.51, 0.36 or 0.07	215, 530	220, 530	0.51, 0.07
1669	−45, −120	0.55, 0.43	185, 305	200–300, 510	0.4–0.5, 0.12
1971	−55	0.52	200	240	0.48

temperature measurements. The composition of the titanomagnetite in the 1971 lava is equally well determined by both methods and gives a mean value of $x = 0.50$.

When comparing the results of $J_s(T)$ and $\chi(T)$ measurements it is found that the $\chi(T)$ method, although certainly limited for the determination of titanomagnetite compositions, in many cases may work as an important tool for the rock magnetist. As demonstrated by the 1669 sample the method may be especially helpful when dealing with $J_s(T)$ curves which indicate Curie temperatures apparently not sharply defined.

The different phases in the 1329 and 1669 lavas must be caused by oxidation and exsolution before laboratory heating. Prolonged heat treatment during continuous thermal demagnetization therefore alters only the unoxidized titanomagnetite of the 1971 lava, and maximum blocking temperatures are reached around 500° C although the original Curie temperature was found around 240° C. The macroscopically high porosity of this flow also may favour rapid oxidation during thermal demagnetization. The magnetic phases in the 1329 and 1669 basalts are more stable against heating due to low rock porosity and previous oxidation, thus allowing thermal cycling without major chemical changes. Only the 1669 titanomaghemite phase gets oxidized so that the partial self-reversal becomes more pronounced and shifted to lower temperatures during heat treatment. Petersen and Bleil (1973) have shown that self-reversal in synthetic titanomagnetite occurs at a critical state of oxidation caused by heating in air. This oxidation state seems to have been achieved naturally by the 1669 lava.

4. Microchemical and Mössbauer Analysis

4.1. Microprobe Analysis

Three optically homogeneous titanomagnetite grains of variable size from each lava have been analyzed. Readings were taken along profiles across the polished surface of the grains and analyzed for Fe, Ti, Al, Mg, and Cr. Some of the profiles have been plotted in Fig. 9.

Table 3 contains the average weight percentage of cations analyzed in each grain with the respective standard deviation. Using Gidskehaug's (1975) program the composition parameter x has been calculated assuming stoichiometric titanomagnetite together with the equivalent Curie point T_{cx}. Following Richards et al. (1973) the influence of the 'impurity' cations Al and Mg on depressing the Curie temperature has been taken into account. This Curie point is denoted with $T_{c\delta}$. Also the oxidation parameter z has been evaluated following the method proposed by the latter authors. For the grains which show two measurable Curie points, this has been done by assuming that the chemical analysis reflects the composition of the lower Curie point phase rather than that of the high Curie point phase.

A relatively high 'impurity' content of Al and Mg is recognized in all grains. Thus the estimated Curie point $T_{c\delta}$ of the substituted stoichiometric

Table 3. Microprobe analysis of three titanomagnetite grains of each lava sampled. Elements analyzed: Ti,Fe,Cr,Al,Mg. x = resulting composition parameter in the magnetite-ulvospinel solid solution series. T_{cx} = Curie temperature resulting from x. T_c = Curie temperature depressed by Al and Mg according to Richards et al. (1973). z = oxidation parameter calculated following Richards et al. (1973). n = number of observation points

Flow year	Grain	Size (μm)	n	Ti (wt %)	Fe (wt %)	Cr (wt %)	Al (wt %)	Mg (wt %)	Sum (wt %)	x	T_{cx} (° C)	$T_{c\delta}$ (° C)	z
1329	A3BA	90	10	9.47 ± 0.06	55.71 ± 0.30	0.33 ± 0.06	2.13 ± 0.06	2.42 ± 0.11	70.07 ± 0.33	0.43	264	143	0.4
	A3BB	140	8	9.45 ± 0.30	55.64 ± 0.32	0.36 ± 0.18	2.07 ± 0.16	2.12 ± 0.31	69.64 ± 0.31	0.43	261	147	0.4
	A3BC	150	8	9.01 ± 0.17	56.00 ± 0.10	0.02 ± 0.03	2.39 ± 0.15	2.48 ± 0.20	69.90 ± 0.26	0.41	279	146	0.4
1669	B4BA	600	7	7.62 ± 0.69	56.45 ± 0.47	0.11 ± 0.02	3.27 ± 0.20	2.84 ± 0.54	70.29 ± 0.28	0.34	331	156	0.0, 0.9
	B4BB	200	11	8.04 ± 0.92	56.65 ± 0.48	0.38 ± 0.08	3.08 ± 0.34	1.83 ± 0.21	69.99 ± 0.39	0.37	311	155	0.0, 0.9
	B4BC	120	7	8.77 ± 0.43	56.23 ± 0.28	0.36 ± 0.03	2.91 ± 0.21	1.75 ± 0.11	70.02 ± 0.30	0.40	286	140	0.0, 0.9
1971	A3AA	240	7	7.37 ± 0.35	56.02 ± 0.46	0.06 ± 0.01	3.06 ± 0.13	3.45 ± 0.30	69.95 ± 0.23	0.33	339	166	0.0
	A3AB	100	6	6.70 ± 0.11	56.55 ± 0.18	0.06 ± 0.01	3.18 ± 0.09	3.25 ± 0.12	69.73 ± 0.23	0.30	360	184	0.0
	A3AC	90	7	6.56 ± 0.10	56.45 ± 0.19	0.07 ± 0.03	3.28 ± 0.06	3.27 ± 0.16	69.65 ± 0.25	0.29	364	184	0.0

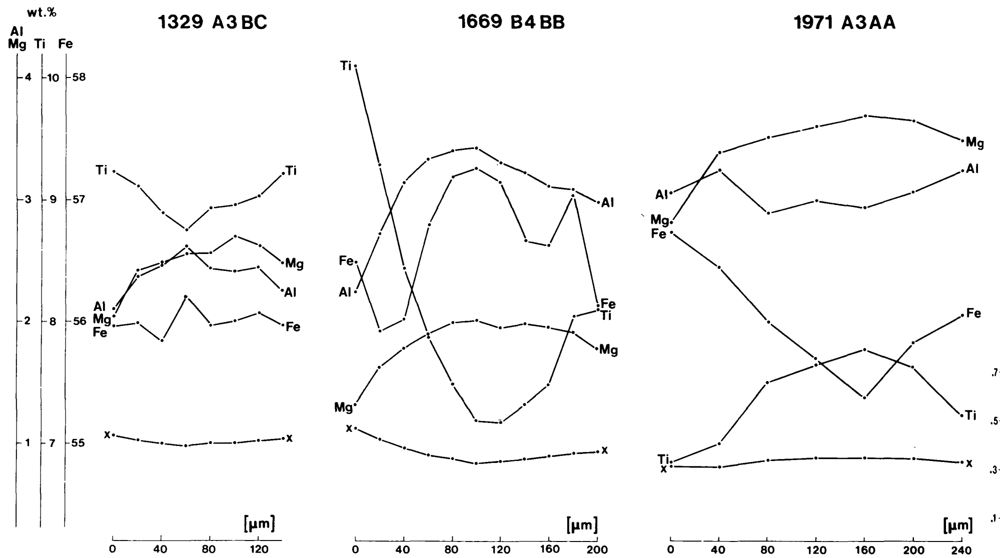


Fig. 9. Microchemical analysis of Fe, Ti, Mg, Al concentration and corresponding x value of the series $x \cdot Fe_2TiO_4(1\text{-}x)Fe_3O_4$ as a function of distance in grains selected from the three lavas. All profiles cross the grains from one margin to the other

titanomagnetite $Fe_{3-x-\delta}$ (Al, Mg) $_{\delta}Ti_xO_4$ is depressed by up to 180° C compared to T_{cx} of pure titanomagnetite, since δ averages 0.22 for each of both impurity elements. The measured Curie temperatures T_{cm} which range between 200° and 300° C, as well as the Curie temperatures T_{cs} which according to Fig. 7 can be derived from low temperature susceptibility measurements, always fall in between the values which have been calculated for substituted and pure stoichiometric titanomagnetite.

The 1971 lava shows the lowest degree of oxidation (z-parameter$\cong$0.0) which is indicated by only one measured Curie point and a small difference between $T_{c\delta}$ and T_{cm}. The Ti- content is low and therefore the calculated x value is at $x=0.3$ only; Al and Mg show the highest concentrations of all three lavas. The 1329 lava is fairly oxidized. We have measured two distinct Curie points (Fig. 6) and the oxidation parameter equals $z \cong 0.4$. Most complicated is the situation for the 1669 basalt. The homogeneity of cation distribution of the two mayor elements Ti and Fe as indicated by the standard deviation is definitely less uniform than in the other lavas. The Curie points as measured in the $J_s(T)$ curves seem to be smeared out between 200° C and 300° C. Taking the T_{cs} values as representative for the lower Curie point phases one is forced to conclude that one of these phases is strongly oxidized ($z \cong 0.9$ for $T_{cs}=305°$ C) and the other phase not ($z \cong 0.0$ for $T_{cs}=185°$ C). The high Curie point phase obviously cannot be resolved by microchemical analysis perhaps due to very fine grain size or intergrowth with the titanomaghemite phase.

The inhomogeneous cation distribution in the 1669 titanomagnetite grains is more clearly observed in Fig. 9 and depends on the position in the grains.

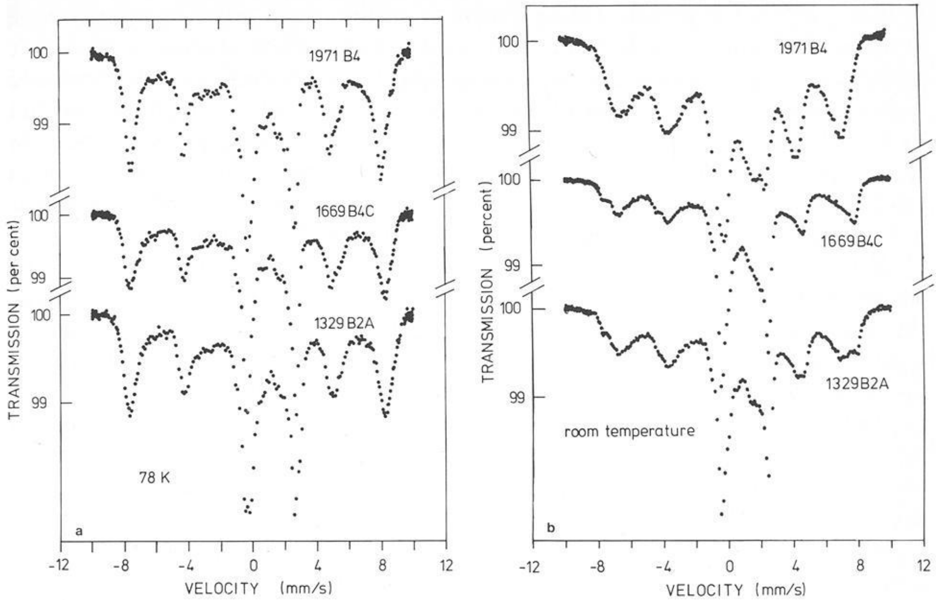


Fig. 10a and b. Mössbauer absorption spectra on Fe^{57} of magnetic ore grains extracted from three basalt samples. **a** Temperature: 78 K. **b** Room temperature

Thus the Ti-content of the 1669 grains increases by about 50% towards the grain margin, whereas Al and Mg increase towards the grain centre where their concentration is about 50% higher than at the margins. For iron the concentration-distance relationship is not so well developed. Looking at the grains of the 1329 lava we find the same relations for the cations analyzed, but not as pronounced as in the former case. The grain which is representative for the 1971 titanomagnetites, shows the opposite concentration-distance relations for Ti and Al, whereas Mg again is enriched towards the grain centre. In general we see that the changes in cation concentration are most pronounced in the 1669 samples.

4.2. Mössbauer Absorption Spectra

Mössbauer absorption spectra on Fe^{57} have been taken at room temperature and −195° C on ore grains extracted from pulverized samples by a bar magnet. A description of the Mössbauer instrumentation will be given elsewhere.

The spectra from the three basalts are presented in Fig. 10. Any information about the ferrimagnetic ore can be deduced merely from the outer parts of the spectra in the positive and negative velocity ranges, as in the centre of the spectra the dominant contribution arises from diamagnetic and/or paramagnetic mineral phases of the rock matrix due to a non complete separation of the ore minerals.

At $-195°$ C, a six-line sub-spectrum is visible from Fig. 10a in all three samples. The inner two lines of each six-line field are contained in the rock matrix contribution of the centre of the spectra. Line broadening and asymmetric lines indicate a superposition of two six-line patterns which might be created by two distinct phases. From the spectra the internal magnetic hyperfine field H_{int} at the site of a Fe nucleus can be derived. The spectra are not well enough resolved to allow a reliable determination of the isomer shift IS and the quadrupole splitting QS [by least squares computer fit (Wertheim, 1964)].

Room temperature absorption spectra (Fig. 10b) reveal more clearly the existence of two overlapping subspectra for the 1669 and 1329 samples, although the lines appear to be broad. The outermost lines of the respective spectra consist of two lines in the negative and positive velocity ranges, whereas in the case of the 1971 sample one broad peak is observed.

$J_s(T)$ curves have shown that the ore grains of 1669 and 1329 exhibit at least two Curie points each, whereas the 1971 sample has one Curie point and, hence one ferrimagnetic phase. These findings are in accordance with the Mössbauer data. We assign the patterns with the larger internal magnetic hyperfine field H_{int} to phases with the higher Curie temperatures. The broad lines reflect the fact that there is a certain range of Curie points. Our assignment accounts also correctly for the intensity relations. $J_s(T)$ and NRM continuous thermal demagnetization curves for 1329 samples show the phase with the lower Curie temperature to be dominant, whereas the phase with the higher Curie temperature seems to prevail in the 1669 basalt.

A ferrimagnetic titanomagnetite phase with a Curie point $T_c > 500°$ C gives, similar to Fe_3O_4, at room temperature a Mössbauer absorption spectrum with the outermost line in the negative velocity range clearly split into two distinct lines. The latter arise from Fe ions on tetrahedral (A) and octahedral (B) sites. Thus two values of H_{int} can be deduced, the lower one arising from the mixture of Fe^{2+} and Fe^{3+} on B-sites of the spinel lattice. This situation appears to exist for the 1669 sample concerning the dominating phase. From the asymmetry of the outermost lines a second phase with a smaller H_{int} can be suggested.

The values of H_{int} taken from the spectra of all samples are listed in Table 4.

Table 4. Magnetic hyperfine field H_{int} deduced from the Mössbauer absorption spectra at 20° C and $-195°$ C; also Curie temperatures T_{cm} given as derived from $J_s(T)$ measurements

Sample	T (°C)	$H_{int} \pm 10$ (kOe)				Remarks
		Phase I	T_{cm} (°C)	Phase II	T_{cm} (°C)	
1971 B4	20	431	240	–	–	one phase
	−195	489		–		
1669 B4C	20	< 450	200–300	454(A)[a], 476(B)[a]	510	more than one phase; dominating phase with higher T_c
	−195	< 490		496		
1329 B2A	20	432	220	485	530	more than one phase; dominating phase with low T_c
	−195	495		495		

[a] A and B indicate A sites and B sites of the spinel lattice

5. Discussion

The three Mt. Etna lava flows sampled show very different magnetic properties. $J_s(T)$ curves, Mössbauer spectra and microchemical analysis indicate the presence of several ferromagnetic phases. The 1971 lava contains a single unoxidized titanomagnetite phase with a low Curie point around $T_c=240°$ C. This titanomagnetite is homogeneous according to microprobe data. Nevertheless maximum blocking temperatures of 500° C have been obtained upon heating of NRM. This indicates a rapid oxidation and production of remanent magnetization above 240° C which directionally is controlled by the magnetization of the original Ti-magnetite. No partial self-reversal has been found in this flow.

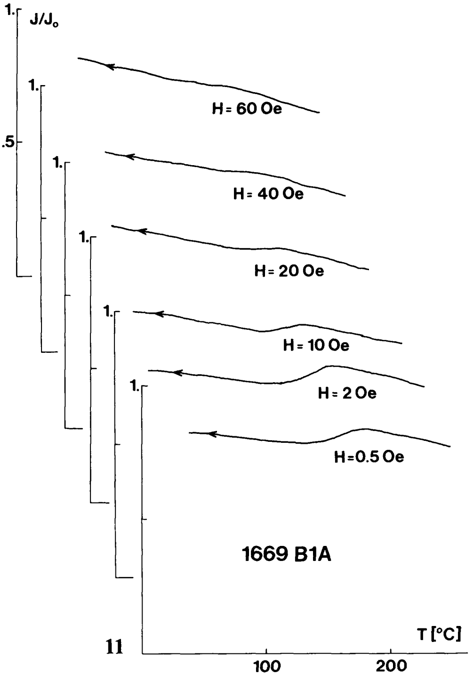
Two distinct Ti-magnetite phases have been detected in the 1329 lava using $J_s(T)$ and Mössbauer techniques. A slightly oxidized intermediate titanomagnetite seems to control the magnetic behaviour of the 1329 samples. A higher Curie point titanomagnetite may be concentrated towards the centre of the ore grains where the Ti-content shows a vaguely defined minimum (Fig. 9). Therefore interaction between the two phases which effects the remanence properties cannot be ruled out. In fact some 1329 samples have been found which show anomalous thermal demagnetization curves of NRM (cf. Heiniger and Heller, 1976), but not to the same extent as all the 1669 samples.

Most difficult is the identification of the ferromagnetic material present in the 1669 lava. The asymmetry of the outermost Mössbauer lines suggests more than one titanomagnetite phase to be present. The $J_s(T)$ curves show a titanomagnetite with $T_c=510°$ C and a smeared range of Curie temperatures between 200–300° C which may be caused by the two phases with $T_c=305°$ C and $T_c=185°$ C indicated by low temperature measurement of $\chi(T)$. After heating the strongly oxidized Ti-maghemite with $T_c=305°$ C disappears in the $J_s(T)$ curve. This may be one of the reasons why the apparent partial self-reversal gets more pronounced after the first heating cycle and the onset of the reversal is shiftet to lower temperatures (Fig. 5).

The partial self-reversal seems to be bound to some kind of interaction between the (unoxidized) titanomagnetite with $T_c=185°$ C and the Ti-poor magnetite with $T_c=510°$ C. These two phases occur within one grain – at least in grain sizes which allow microprobe analysis. In these grains the Ti-poor material which carries the normal NRM component is concentrated towards the grain centre (Fig. 9) and surrounded by a Ti-richer phase. We could not prove, if the geometry of this structure is closed or open. There is some microprobe evidence that the Ti-rich outer shell is not fully closed, at least its thickness varies considerably (cf. Fig. 9).

As mentioned in the introduction, there are several theoretical models to explain the observed reversal in the 1669 lava. We exclude single phase models like Néel's P-type, because firstly $J_s(T)$ curves do not indicate this (Fig. 6) and secondly we have Mössbauer and microchemical evidence for two magnetic phases. The two-phase models can be divided into three categories: (1) exchange interaction across phase boundaries, (2) magnetic screening and (3) magnetostatic interaction.

The field and temperature dependence of artificial TRM is one possibility to test which two-phase model might apply to the 1669 lava. Figure 11 shows



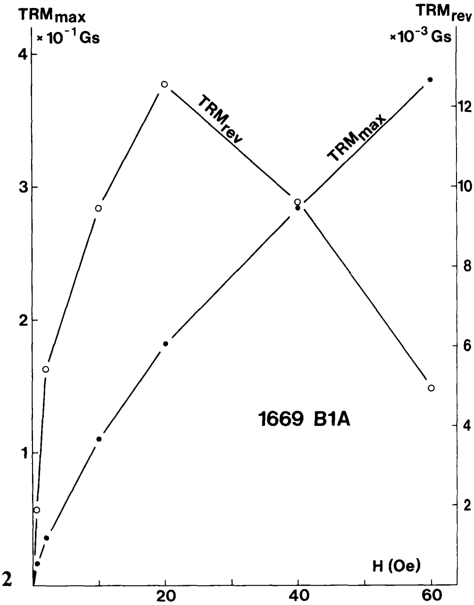


Fig. 11. Cooling cycles of total TRM acquired in dc fields ranging from $H=0.46$ Oe to $H=60$ Oe. TRM has been measured after the sample had been reheated to about 250° C in zero field

Fig. 12. Absolute intensities of total TRM at room temperature (TRM_{max}) and of the reversed TRM component (TRM_{rev}) as a function of the applied field

the resulting assemblage of TRM cooling cycles after the sample had been heated to 600° C and was allowed to cool down to room temperature in various *dc*-fields. The field had been increased step by step after each measuring cycle up to the maximum temperatures (ca. 250° C) indicated in Fig. 11. Clearly the reversal effect becomes reduced with increasing *dc*-field amplitude. Figure 12 indicates the absolute intensities of total TRM after each heating cycle in the applied field together with the absolute amount of the reversed component detected during cooling in zero field. The reversed component increases up to $H_{dc}=20$ Oe and decreases with further increments of the external field so that by extrapolation it would disappear well below 100 Oe.

This field dependency is not to be expected for the exchange interaction model, since the coupling is due to Weiss-Heisenberg forces which result in extremely high interaction fields. Uyeda (1958) found by experiment for the intermediate members of the ilmenite-haematite series interaction fields greater than 500 Oe.

In the model of magnetic screening the magnetization of a high Curie point phase encircled more or less completely by a lower Curie point phase can be shielded magnetically as soon as the lower Curie point is reached upon cooling. Stephen-

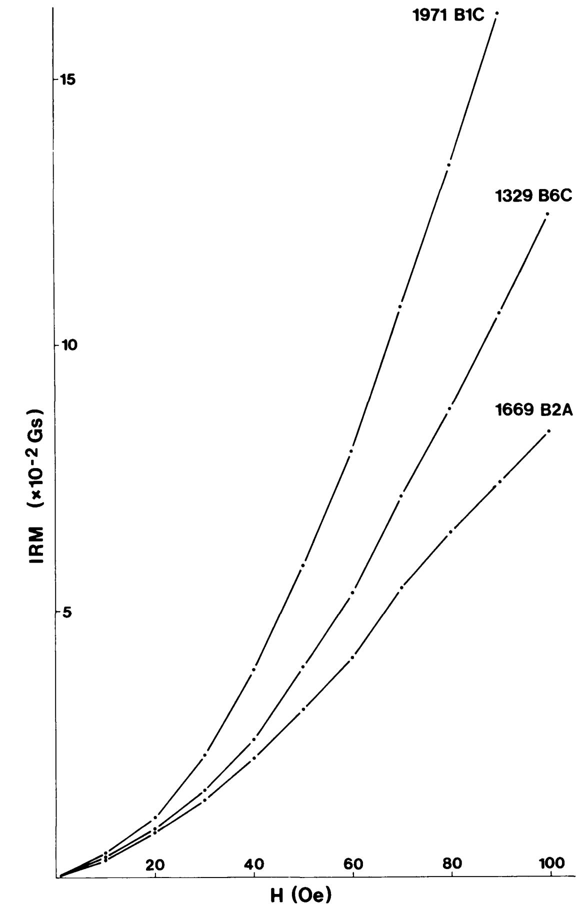


Fig. 13. Isothermal remanence (IRM) acquisition curves of the three lavas of Mt. Etna. Only the 1669 sample shows a distinct inflexion at $H = 70$ Oe

son (1975) derived that the screening factor depends only on the relative permeabilities and the demagnetization factors of the two phases. His theory has been backed up experimentally by Rahman and Parry (1975) who found for certain titanomagnetite material a largely field independent screening up to $H_{ex} =$ 135 Oe. Our result is different from their finding and this model does not apply to the 1669 lava, since our partial self-reversal is suppressed certainly below 100 Oe external field.

Therefore magnetostatic interaction remains to explain the partial self-reversal of NRM and laboratory produced TRM in the 1669 Mt. Etna lava. Obviously the negative magnetostatic interaction field reaches a maximum at $H_{ex} = 20$ Oe and certainly below 100 Oe the external field overwhelms the negative interaction during TRM acquisition. Negative interaction is also observed during acquisition of isothermal remanence (Fig. 13). The IRM of the 1669 lava sample shows a small inflexion at $H_{ex} = 70$ Oe which indicates that this field amplitude is sufficient to suppress the interaction mechanisms.

Certain geometric relations are necessary for the model of negative magnetostatic interaction (for details see Uyeda, 1958, p. 50 ff.). These relations must hold for the majority of ferromagnetic grains in the 1669 lava. We don't know yet the cause for this kind of alignment, but it may be connected to the flow structure or to the asymmetric exsolution of these titanomagnetites indicated by microprobe analysis. Since the 1669 sampling site is very near to the former eruption point, the lava may have cooled down very slowly and some alignment of the ore grains due to viscous flow combined with asymmetric high temperature oxidation may have led to the geometrical conditions necessary for negative magnetostatic interaction. Thus the high Curie point phase developed at temperatures above 500° C and was magnetized parallel to the earth field at the time, whereas the lower Curie point phase(s) at least partly interacted in a negative way with the high Curie point titanomagnetite.

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