A detailed magnetic and mineralogical study of self-reversed dacitic pumices from the 1991 Pinatubo eruption (Philippines)


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SUMMARY
39 dacitic pumice and lithic samples from the 1991 eruption of Mount Pinatubo were investigated through both magnetic and mineralogical means. As in a previous study, natural remanent magnetization (NRM) is found to be reversed for most of the samples, with respect to the direction of the actual geomagnetic field direction. A few samples, amongst them ancient lithics transported by pyroclastic flows, show scattered NRM directions. From thermal demagnetization of these particular samples it is concluded that their orientation changed after emplacement. The emplacement temperature is estimated to be more than 460 °C from thermal demagnetization of lithic samples.

Two magnetic minerals with large grain sizes are observed under the optical microscope: titanomagnetite (TM) and haemo-ilmenite (hem–ilm). Microprobe analyses yield \( x \approx 0.10 \) for TM and \( y \approx 0.52 \) and \( y \approx 0.54 \) for two hem–ilm phases, in agreement with the observed Curie temperatures (~480 °C for TM and ~250 °C for hem–ilm). The hem–ilm particles display chemical zonation, which seems to be correlated with a change of the domain structure: typically, a ferrimagnetic (FM) phase with slightly higher titanium content is observed in the central part whilst the crystal margin, which is weakly ferromagnetic (WF, due to spin-canted antiferromagnetism) is slightly poorer in titanium. Two different mechanisms for the origin and formation of the two observed phases are discussed: (1) chemical zonation of hem–ilm crystals due to a change in conditions in the magma chamber shortly before eruption; (2) similar to the micro-structures observed from synthetic samples, this zonation in the large natural hem–ilm could be the result of migration of the WF phase towards the grain boundary during residence below the order–disorder transition temperature in the magmatic chamber. The room temperature hysteresis loop, which seems to be dominated by TM, provides multidomain (MD)-like parameters: \( J_{r}/J_s = 0.01 \) and \( H_{cr}/H_{c} = 20 \). The large coercivity of remanence (40–40 mT), which is attributed to hem–ilm, may be intrinsic or due to interactions between WF and FM phases. The field dependence of the magnitude of the thermoremanent magnetization (TRM) is not linear: it increases first, reaches a maximum (negative) value for an applied field \( H \) close to 0.5 mT, then decreases steadily. By extrapolation, it is estimated that the TRM should be zero for a field of about 12 mT and become positive beyond. This total TRM is in fact the sum of several components. AF demagnetization of TRMs acquired in different fields shows the presence of at least three components: a self-reversed (SR) component that contains both hard and moderately hard components and a soft normal component. Independently of the value of \( H \), the median destructive field of the SR component is of the order of
The magnetic properties of natural and synthetic haemo-ilmenite (hem–ilm) solid solutions \( y\FeTiO_3(1 - y)Fe_2O_3 \) have been intensively studied in order to understand the mechanism of self-reversal of TRM. According to the data obtained on synthetic samples, only minerals with \( 0.45 < y < 0.70 \) are ferrimagnetic at room temperature (Uyeda 1958). The lower values of \( y \) (\(< 0.45\)) basically correspond to spin-canted antiferromagnetic (weak ferromagnetic, WF) material, and higher values (\( > 0.70 \)) to phases which are paramagnetic at room temperature (\( T_0 \)). Another property of the ferrimagnetic hem–ilm phases, observed by Uyeda (1958) from pumices and by Ishikawa & Syono (1963) from synthetic minerals, is the dependence of their magnetic properties upon laboratory heat treatments. For a given \( y \), the cation distribution is disordered above a critical temperature, \( T_{cr} \), whilst it can be ordered at lower temperatures. During reheating, a disordered distribution evolves towards a partially ordered state. According to Hoffmann (1975, 1992), the kinetics of cation ordering result from nucleation, growth and development of cation-ordered regions.

The first self-reversed rock discovered was the Mount Haruna dacite from Japan (Nagata et al. 1951). Two magnetic minerals were found: iron-rich titanomagnetite (TM) and hem–ilm, with the NRM mainly carried by the hem–ilm phase (Nagata et al. 1953; Uyeda 1958). This self-reversal was first attributed to interaction occurring either between TM and hem–ilm (Nagata et al. 1952) or between two intergrown hem–ilm phases with different \( y \) (Uyeda 1958). Finally, Ishikawa & Syono (1962) proposed that the reverse TRM was the result of antiparallel coupling (through superexchange interaction) between an ordered matrix and a disordered boundary where antiphase regions richer in iron are found (the enigmatic \( x \) phase). They suggested that these boundaries have a higher Curie temperature and magnetize first during cooling in a magnetic field. When the Curie temperature of the ordered phase is reached, this phase acquires a reversed TRM by negative exchange interaction with the disordered phase. Transmission electron microscopy (TEM) observations on synthetic samples quenched from above the transition order–disorder temperature, \( T_{cr} \), basically confirmed this view (Lawson et al. 1981 and Nord & Lawson 1989). These authors succeeded in observing two kinds of regions: ‘twin domains’ (TD) (or ‘antiphase domains’, APD) separated by ‘twin-domain boundaries’ (TDB) (or ‘antiphase domain boundaries’, APB). Annealing of such samples at temperatures below the order–disorder transition gives rise to the coarsening of APD, which reduces the density of TDB (Nord & Lawson 1992; Hoffman 1975, 1992). According to these authors, this has important consequences in terms of magnetic properties: TRM can even turn to become normal.

This model was used to explain the self-reversed TRMs of the Mount Natib dacite in the Philippines (Kennedy & Osborne 1987) and Mount Shasta in California (Lawson et al. 1987). In the latter case, Lawson et al. (1987) showed through magnetic considerations (Lowrie–Fuller test) and mineralogical observations (dark-field TEM) that in spite of their large size (100 \( \mu \)m), the hem–ilm crystals behave as SD or PSD grains because of their subdivision into 0.01–0.02 \( \mu \)m cation-ordered domains.

In contrast to the above model, Haag et al. (1993) suggested that the self-reversal of the pyroclastics from Nevado del Ruiz in Colombia (Heller et al. 1986) was due to negative exchange interaction between two chemically and mineralogically distinct hem–ilm phases in close contact with TM, which can be identified using magnetic force and an optical microscope and electron microprobe.

The major 1991 eruption of Mt Pinatubo (Philippines) produced several cubic kilometres of hot pyroclastic flow deposits containing pumice fragments whose NRM was found to be self-reversed by Ozima et al. (1992). Hoffmann & Fehr (1996) carried out domain and microchemical observations on several samples from Ozima’s collection. They found that the large hem–ilm crystals show clear evidence for the coexistence of two magnetic phases within single hem–ilm crystals. According to their description, the crystal core is a ferrimagnetically ordered (with respect to cations) phase slightly depleted in haematite, whereas the crystal margin is a WF disordered phase slightly enriched in haematite. They suggested that self-reversal is due to exchange coupling between these two phases, both of them having a true multidomain structure. Previous studies of the Pinatubo pumices were either palaeomagnetic or mineralogical. This paper contains some palaeomagnetic data but is mainly focused on magnetic properties.

Key words: domain pattern observations, emplacement temperature, exchange/ magnetostatic interactions, ilmenite–haematite, microchemical analysis, self-reversed TRM.

1 INTRODUCTION

The magnetic properties of natural and synthetic haemo-ilmenite (hem–ilm) solid solutions \( y\FeTiO_3(1 - y)Fe_2O_3 \) have been intensively studied in order to understand the mechanism of self-reversal of TRM. According to the data obtained on synthetic samples, only minerals with \( 0.45 < y < 0.70 \) are ferrimagnetic at room temperature (Uyeda 1958). The lower values of \( y \) (\(< 0.45\)) basically correspond to spin-canted antiferromagnetic (weak ferromagnetic, WF) material, and higher values (\( > 0.70 \)) to phases which are paramagnetic at room temperature (\( T_0 \)). Another property of the ferrimagnetic hem–ilm phases, observed by Uyeda (1958) from pumices and by Ishikawa & Syono (1963) from synthetic minerals, is the dependence of their magnetic properties upon laboratory heat treatments. For a given \( y \), the cation distribution is disordered above a critical temperature, \( T_{cr} \), whilst it can be ordered at lower temperatures. During reheating, a disordered distribution evolves towards a partially ordered state. According to Hoffmann (1975, 1992), the kinetics of cation ordering result from nucleation, growth and development of cation-ordered regions.

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2 GEOLOGICAL SETTING, SAMPLING AND PETROLOGY

Mount Pinatubo is one of the calc-alkaline stratovolcanoes that dominate the western part of North Luzon. Although voluminous pyroclastic deposits were known to have been erupted 400–600, 2300–3000 and 4400–5100 yr BP (Pinatubo Volcano Observatory Team 1991), Pinatubo was not included amongst active volcanoes before it ‘awakened’ on 2 April 1991 with small phreatic explosions. Both seismic and volcanic activity steadily increased during the next two months and culminated in a series of major explosive eruptions on 12–15 June that produced some 3 km$^3$ of tephra fall and 7 km$^3$ of pyroclastic flows (ignimbrite), corresponding to about 5 km$^3$ of dacitic magma or dense rock equivalent. Plinian columns reached 30–40 km in height and pyroclastic flows travelled as far as 16 km from the summit, filling canyons as deep as 200 m, mainly on the N, NW, SW and E flanks of the volcano. These events resulted in the formation of a new 2.5-km-diameter caldera from which ash was vented almost continuously until the end of July. Explosive activity ceased on 2nd September 1991 and a lake due to rainfall soon appeared at the bottom of the caldera. A further phase consisted of the slow and moderate extrusion of a small lava dome within the crater lake during the second half of 1992.

The huge quantity of hot pyroclastic flows considerably altered the hydrographic network. For years, heavy rainfall, especially during the monsoon season (June–October), triggered extensive lahars, secondary phreatic explosions and even secondary pyroclastic flows. Some of these (e.g. 15–21 September 1992) produced ash clouds of 18 km in height. The ignimbrite field, which in the beginning resembled a nearly featureless, barren plain, was deeply incised by gullies. A large amount of ignimbrite material was reworked and transported through the lahars. This reworking of primary material was a source of problems in sampling pumice pebbles for palaeomagnetic studies.

Although probably triggered by the injection of a new basaltic magma within a dacitic chamber (Pallister et al. 1992), the 1991 eruptions mainly produced two types of juvenile dacite clasts: white crystal-rich pumice (about 45 per cent crystals) and grey to tan pumice which is relatively poor in crystals (15–20 per cent). The two pumice types have similar bulk rock compositions (64 per cent SiO$_2$ and 1.5 per cent K$_2$O) and similar phenocryst assemblages dominated by plagioclase and hornblende with minor quartz (<2 per cent). Both types contain primary anhydrite (CaSO$_4$), showing that the Pinatubo magma is also rich in sulphur (Bernard et al. 1991). Fe-Ti oxides make up to 2 per cent of the rock as microphenocrysts. They consist of titanomagnetite and hematite-ilmenite series, a detailed description of which is given in the following section. Very rare pyrohitite is present as tiny inclusions in the silicate phenocrysts. Experimental results (Rutherford 1993) have shown that in the pre-eruptive conditions the dacitic magma contained about 5.5 per cent H$_2$O under a pressure range of 150–350 MPa at 790 °C. Its oxygen fugacity was close to 10$^{-12}$, about 1.5 log units above the Ni–NiO buffer.

Some uncommon material consists of lithic blocks of older lavas which are scattered within the ignimbrite, together with the juvenile pumice. Such lithics are usually darker in colour and consist of andesite. They have been sampled for NRM studies but not investigated for magnetic mineralogy, since they exhibit a normally directed magnetization.

39 samples of large size weighing 0.2–1 kg were collected from five sites situated in three locations in the north and northwestern parts of the volcanic edifice (Fig. 1). Because of the poor consistency of the pumice or rock pieces within the ash flow, sampling was carried out using the plaster method (Thellier 1966).

3 PALAEOMAGNETIC ANALYSIS

3.1 NRM directions

All the samples were subjected to the viscosity test (Prévot 1981), followed by NRM measurement using a laboratory-made rotating inductometer (Le Goff 1975). Table 1 shows the NRM and several magnetic parameters such as susceptibility, viscosity index (the ratio of two weeks’ viscosity to the NRM), medium destructive field (MDF) and Koenigsberger $Q$ ratio. (Note that, as we show below, NRM is carried by hem-ilmenite, whereas susceptibility is almost entirely due to TM. The $Q$ ratio of the hem-ilmenite phase is discussed in Section 9.) About 80 per cent of the samples have a reversed NRM before treatment (Fig. 2). No normal NRM was observed in pumices. Two lithic samples give a normal direction close to the actual geomagnetic field direction. However, 20 per cent of the samples reveal intermediate directions, more or less far from those of the actual field or its reversed direction. The laboratory TRM (for procedure see Section 6.1) of the few pumice samples showing directions deviating substantially from that of the present field exhibits self-reversal, except for sample PN9528, which will be studied in detail below. According to the low viscosity index, the scattered directions cannot be due to magnetic viscosity. Scattered directions were also observed on the distal part of a pyroclastic flow by Ozima et al. (1992), who suggested that the emplacement temperature at this site might have been lower than the Curie point of hem-ilmenite. Our sites were located closer to the crater. We observed that the samples that gave anomalous directions were collected from the same sites, sometimes only a few metres apart from each other. Also, from field sketches and photographs we found that, except for PN9528, these samples were taken from pyroclastic flow units from which no sample with the correct direction was found.

Both thermal and AF demagnetization of the samples with anomalous directions showed that their directions are as stable as those of the other samples upon heating (Fig. 3). If the rock piece had cooled in air whilst it was moving, the direction of NRM should change progressively as soon as the unblocking temperature becomes higher than the emplacement temperature. Thus, a more plausible hypothesis is a post-emplacement slumping or rotation, due either to phreatic explosions (more frequent just after eruption and less frequent later) or to the topping over or collapsing of large units due to instability caused by nearby lahars or torrents. Such phenomena can happen for several years until the soil is stabilized, for example by vegetation. Some unexplained unusual directions observed from historical or geological pumice eruptions (e.g. Kennedy 1981) may also have their origin in such post-emplacement orientation changes.© 1999 RAS, GJI 138, 159–178
Figure 1. Map of Mount Pinatubo and location of the sampling sites. The large ash deposit area is shown by the shaded zone.

3.2 Magnetic cleaning

AF treatment was used to check for the presence of secondary magnetizations such as viscous remanent magnetization (VRM) or isothermal remanent magnetization (IRM) produced by lightning. The MDF of pumices ranges from 40 to 70 mT (Fig. 4 and Table 1). However, one sample (PN9528) was almost entirely demagnetized by about 20–30 mT. Most of the directions did not change significantly up to about 100 mT or in some cases 150 mT, although the initial moment can be reduced by 90 per cent (Figs 4 and 5).

The susceptibility of the samples was measured after each heat treatment. Very small changes were observed after heating, particularly below 500 °C. In general, the change in susceptibility is less than a few per cent. In most cases, there is a tendency for small increase in susceptibility up to about 400 °C and then a decrease. The susceptibility of the lithic samples shows a systematic decrease with temperature, steeper beyond 400–500 °C, but still remaining in the same range as for pumice samples.

During thermal demagnetization in air almost all pumice samples show a stable (and reversed) NRM direction, even or isothermal remanent magnetization (IRM) produced by lightning. The MDF of pumices ranges from 40 to 70 mT when the intensity is reduced to 5 per cent or less, and at temperatures as high as 500 or 600 °C (Figs 5 and 6). How do we explain such behaviour when we know that the hem–ilm phase has a Curie temperature of about 260 °C (see below)? It cannot be due to titanomagnetite because of its very low coercivity (see below) and because its TRM is not self-reversed, reduced by 90 per cent (Figs 4 and 5).
I scattered at higher temperatures. Lithic sample PN9561 changes continuously during thermal demagnetization with samples (see text for definition).

Table 1. NRM intensity (10–6 Am2 kg–1), direction, susceptibility (10–6 m3 kg–1), Q ratio (for H = 0.04 mT), MDF (mT) and viscosity rate of samples (see text for definition).

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<th>I</th>
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The Q ratio is only given for lithic samples since NRM is almost entirely due to hem–ilm, whereas k is almost entirely due to TM. For real Q ratio of pumices see text.

The NRM direction of lithic sample PN9527 (D = 30°, I = −19°) is stable up to 460 °C (Fig. 7) and then becomes scattered at higher temperatures. Lithic sample PN9561 shows two directions: up to 340 °C the direction is D = 1° and I = 26°, near the present field, then from 340–600 °C the values are close to D = 15° and I = 70° (Fig. 8). It is possible that this sample has been subjected to a local phreatic explosion after partial cooling. The lithic sample PN9524 gives several directions during thermal demagnetization. The first two directions are close to the actual field and are obtained by heating to 160 °C (D = 3°, I = 15° and D = 9°, I = 1°); the others are then found by heating to higher temperatures. This sample seems also to have been subjected to several small orientation changes, with the present field as its last direction.

Sample PN9528 is the only pumice sample for which the NRM direction was very unstable upon thermal and AF demagnetization. Specimens from the same block show different NRM directions. The direction of magnetization changes continuously during thermal demagnetization with an almost reversed component (D = 180°, I = −20°) between 340 and 650 °C (Fig. 9). The laboratory TRM (450 °C–room temperature, Tm, H = 0.2 mT) was normal, but became reversed when treated by AF close to 30 mT and did not change in intensity for higher AFs (Fig. 10). In this sample the normal remanence from TM with low coercivity may dominate NRM at Tm.

The emplacement temperature can only be estimated from thermal demagnetization of the lithic samples since the pumice samples have a lower Curie point than the emplacement temperature, at least at the present sampling sites. As discussed above, lithic sample PN9527 has a stable direction, different from that of the present field, up to 460 °C (Fig. 7), which is
Figure 2. NRM directions of pumice (circles) and lithic (squares) samples before AF and heating treatments; negative inclinations are indicated by open symbols and the actual field direction is shown by a star. Several intermediate directions can be seen for lithic and pumice samples.

Figure 3. Example of the directional change during stepwise heating to 650 °C of NRM of a sample showing an intermediate direction. The stable direction suggests that the orientation of the rock sample was changed after cooling.

Figure 4. Intensity changes during stepwise AF demagnetization of the NRM shown in Fig. 5.

Figure 5. Directional change during AF (to 150 mT) and thermal (20–650 °C) demagnetization of NRM of sample PN0532 were reported for the 1883 Krakatau subaqueous pyroclastic flows (Mandeville et al. 1994) and for the Shirahama Group submarine deposits from Japan (Tamura et al. 1991).

4 IDENTIFICATION OF MAGNETIC MINERALS

4.1 Mineralogical investigations

Optical microscope observations (Zeiss-Axioplan in reflected light) indicate that the magnetic oxides are large crystals, typically several 10 to >100 μm in size. No microscopic exsolution or other fine structures could be detected either optically or in backscattered SEM pictures. Two distinct magnetic minerals were found: titanomagnetite (which is dominant and represents two-thirds of the total) and hem–ilm. Both minerals seem to be chemically homogeneous. The chemical
For the hem-ilm solid solution, the bulk molecular fraction of ilmenite is $y = 0.537 \pm 0.005$. This bulk $y$-value is an average including both between-crystal and within-crystal variations. The value of $y$ is significantly lower than the maximum value of $y = 0.75$ found, according to Lawson et al. (1981), for synthetic minerals to exhibit self-reversal. According to the review of Nord & Lawson (1989), a $y$-value equal to 0.54 would correspond to a Curie point, $T_c$, close to 280°C in synthetic hem-ilm. The expected $T_c$ should be somewhat lower if the presence of non-magnetic cations that substitute for iron reduces the Curie point.

Two slightly different chemical phases of hem-ilm were observed depending on whether the magnetic structure is FM or WF (Section 5). We measured the chemical composition along several profiles across both magnetic phases (Figs 11f–h and 12) and within one phase (Fig. 11g) by using a Camebax SX50 ( Cameca comp.) system. Further explanation about the analysis of data is given by Hoemann & Fehr (1996). In all cases, in agreement with Hoemann & Fehr (1996), we found that the WF phase is slightly depleted in ilmenite compared to the FM phase, with average values of 0.526 ± 0.004 for the WF phase and 0.538 ± 0.003 for the FM phase. Note that we observed some fluctuations of $y$ from one crystal to another, which are given for different profiles in Table 2. Interestingly, the differences found in the present study are smaller than those reported by Hoffmann & Fehr (1996). Thus, the chemical contrast between the two magnetic phases varies from crystal to crystal. However, in all cases, regardless of their relative position within the crystal, the diffusion zone WF phase was found to be poorer in ilmenite than the FM phase.

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Figure 8. Two directions related to the orientation change during cooling, observed from thermal demagnetization of the NRM in lithic sample PN9561: 600–380 °C and 340–20 °C (near the actual direction). Local phreatic explosion is suggested to be the origin of this orientation change (see text).

Figure 9. Directional change of NRM during stepwise heating for sample PN9528 (showing several different components).

Generally speaking, the magnetic properties of the Pinatubo dacite are similar to that reported for other volcanic rocks exhibiting self-reversal (Uyeda 1958; Kennedy & Osborne 1987; Lawson et al. 1987; Haag et al. 1990a,b, 1993).

4.2 Thermomagnetic data

The high-field (0.5 T) \( J_s-T \) curve up to 700 °C in argon obtained on the sample used for electron microprobe analyses (PN933) is shown in Fig. 13. Surprisingly, only one single phase was found, with a Curie point close to 530 °C from the heating curve, which changes to about 480 °C on the cooling curve. This phase is probably a Ti-poor titanomagnetite. No
Table 2. Microprobe analyses of titanomagnetite (stoichiometric) and bulk haematite–ilmenite. Average Y-values of WF and MF phases are given for different profiles.

|        | TiO$_2$ | Fe$_2$O$_3$ | FeO | MnO | MgO | Cr$_2$O$_3$ | Al$_2$O$_3$ | Mn$_2$O$_3$ | TiO | Cr$_3$O$_4$ | Mn$_3$O$_4$ | CrO | Cr$_3$O$_4$ | MnO | Mn$_3$O$_4$ | Al$_2$O$_3$ | FeO | Cr$_3$O$_4$ | Mn$_3$O$_4$ | TiO | Cr$_3$O$_4$ | Mn$_3$O$_4$ | Al$_2$O$_3$ | FeO | Cr$_3$O$_4$ | Mn$_3$O$_4$ | TiO | Cr$_3$O$_4$ | Mn$_3$O$_4$ |
|--------|---------|------------|-----|-----|-----|-------------|-------------|-------------|-----|------------|-------------|-----|-------------|-----|-------------|-------------|-----|------------|-------------|-----|------------|-------------|-----|------------|-------------|-----|------------|-------------|-----|------------|-------------|-----|------------|-------------|-----|
| Profiles |        | n | average Y (WF phase) | n | average Y (MF phase) | n | average Y (FM phase) | n | average Y (FM phase) | n | average Y (FM phase) | n | average Y (FM phase) | n | average Y (FM phase) | n | average Y (FM phase) | n | average Y (FM phase) | n | average Y (FM phase) | n | average Y (FM phase) | n | average Y (FM phase) | n | average Y (FM phase) | n | average Y (FM phase) | n | average Y (FM phase) |
| PIN1    |        | 24 | 0.542 ± 0.0085 | 26 | 0.552 ± 0.0069 | 21 | 0.572 ± 0.0077 | 21 | 0.572 ± 0.0077 | 21 | 0.572 ± 0.0077 | 21 | 0.572 ± 0.0077 | 21 | 0.572 ± 0.0077 | 21 | 0.572 ± 0.0077 | 21 | 0.572 ± 0.0077 | 21 | 0.572 ± 0.0077 | 21 | 0.572 ± 0.0077 | 21 | 0.572 ± 0.0077 | 21 | 0.572 ± 0.0077 | 21 | 0.572 ± 0.0077 |
| PIN2    |        | 25 | 0.554 ± 0.0098 | 26 | 0.576 ± 0.0082 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 |
| PIN3    |        | 17 | 0.529 ± 0.0004 | 26 | 0.572 ± 0.0089 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 | 21 | 0.532 ± 0.0098 |

5 MAGNETIC MICROSTRUCTURE OF OXIDES

Microscopic observations using an optical microscope as well as domain structure observations using Bitter and ICC (interference colloid contrast) techniques were performed in order to see and study the remanence carriers directly. In this way, information can be obtained regarding (1) the domain state of the magnetic phases, (2) the type and style of magnetic domain patterns and (3) the magnetic structure of the magnetic phases.

The photomicrographs in Fig. 11 show particles which are typical of the remanence carriers in the dacitic pumice samples from Mount Pinatubo. Bright-field and polarized light revealed brownish particles with cubic anisotropy and light grey particles with uniaxial anisotropy. The grain sizes of the cubic phase vary from submicron to more than 100 μm diameters. The uniaxial grains, however, show a more restricted distribution in size; grains smaller than several tens of microns were never detected, and many of them are larger than 100 μm. Very few (∼1 per cent) pyrrhotite particles were observed.

The results of the experiments indicate that the cubic as well as the uniaxial grains show well-defined magnetic domain structures. The cubic grains reveal typical patterns of iron-rich titanomagnetite with a total number of non-magnetic cations higher than 0.3 (Soffel et al. 1982). This is in agreement with the results of the electron microprobe analyses reported in Table 1 (N$_{Fe}$ + N$_{Mg}$ + N$_{Mn}$ + N$_{Al}$ ≈ 0.3).
Figure 11. Domain observations using the Bitter technique. (a) Titanomagnetite grain revealing the typical domain structure of low-Ti TM. (b), (d) Hem–ilm grains: the FM phase is completely surrounded by the WF phase (a so-called closed structure). (c) Hem–ilm grain showing the domain patterns of a WF and a ferrimagnetic phase (FM) (a so-called open structure). (e) Hem–ilm grain consisting only of a WF phase; microstructures are typical of haematite. (f), (g) Hem–ilm particles revealing two phases. Electron microprobe analyses were performed across the indicated profiles (see Fig. 12). (h) Hem–ilm particles showing the opposite situation: a ferrimagnetic rim and WF core phase. An electron microprobe analyses was performed across the indicated profile (see Fig. 12).
Figure 12. Variations of the ilmenite content ($y$) across rim–core–rim profiles (a), (b) across the particle shown in Fig. 11(f) (profiles 1–1 and 1–2), (c), (d) across the particle shown in Fig. 11(g) (profiles 2–1 and 2–2) and (e) across the particle shown in Fig. 11(h) (profile A_2). (f) Variations of the Mg, Al and Mn contents along profile 1–1. (g) Statistics of the ilmenite content along the rim of profile A_2 of the particle shown in Fig. 11(h) (FM phase). (h) Statistics of the content in the WF phase of the particle shown in Fig. 11(h). The vertical lines indicate the boundary between WF and FM phases.

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In agreement with previous studies (Hoffmann & Fehr 1996), the optically uniaxial grains exhibit two different types of magnetic domain patterns. Very few single-phase grains show the typical domain patterns of a WF phase such as haematite (Hoffmann 1996). The domain patterns are characterized by wavy walls and very irregular shapes (Fig. 11e). These features are typical of antiferromagnetic domain patterns. The domain structures are quite resistant to external magnetic fields, which again is typical of weak ferromagnets.

However, some hem–ilm particles display two types of domain patterns within a single particle. In reflected polarized light these particles are anisotropic and seem to be a homogenous hem–ilm phase. No indication for intracrystalline grain or other phase boundaries could be detected under the optical microscope. In Fig. 11, the magnetic domain structures are made visible using the Bitter- and ICC methods. Once covered by ferrofluid, the single crystal shows two distinct zones with well-defined but extremely different domain patterns. Consequently, both phases are ferro- or ferrimagnetic and are potential remanence carriers. The boundary between the two magnetic structures is very sharp and is sometimes accompanied by a wall-like stray field structure. Both phases seem to be in a true MD state. No two-phase grains were observed amongst grains smaller than 50 μm.

The WF hem–ilm phase can be interpreted as disordered with respect to the cations. This basically antiferromagnetic phase exhibits WF with very low saturation magnetization due to spin-canting. The magnetic moments are thus oriented parallel to the c-plane, like in haematite.

The second phase reveals a magnetic uniaxial structure which is typical of ferro(i)magnets with a positive magnetocrystalline anisotropy constant. Similar domain structures are known for cobalt or magnetoplumbite (e.g. Träuble et al. 1965). This second hem–ilm phase can be interpreted as an FM phase partially ordered with respect to the cations Fe$^{2+}$, Fe$^{3+}$ and Ti$^{4+}$, which results in a high spontaneous magnetization. The transition zone between the two magnetic phases should be an antiphase boundary (Hoffmann 1992; Haag et al. 1993; Putnis 1992); it is not a crystallite boundary due to exsolution or unmixing.

The geometric relationship between these two phases is very different from one crystal to another. Sometimes, as shown in Fig. 11(b), the FM phase is surrounded by the WF phase. Such a situation is analogous to that described by Hoffmann & Fehr (1996); we call it a closed structure. In other magnetically heterogeneous crystals, we found that the FM and WF phases are simply adjacent (a so-called 'open' structure, Fig. 11c). Obviously, the magnetic behaviour of the ferrimagnetic hem–ilm phase would be very different in these two distinct environments. In 'open' structures like the ones shown in Fig. 11(c), the walls within the FM phase can be moved easily and continuously when the field is changed, without being affected by jumps or pinning effects. This situation may be an artefact due to removal of the upper WF phase by polishing, since AF demagnetization showed that fields as high as 30–40 mT are not able to modify the remanence (obviously carried by the core). We did not observe single FM crystals. Fig. 11(h) shows a rare two-phase hem–ilm particle displaying the opposite situation. The FM phase constitutes the crystal rim and the WF phase the core. Fig. 12(e) clearly demonstrates the relation between chemical composition and domain
structure of the particle in Fig. 11(h). In Section 9 we discuss a model explaining such a situation.

6 PROPERTIES OF TRM

6.1 Polarity

The unblocking spectrum of the TRM (680 °C–T₀, 0.2 mT) was obtained by stepwise thermal demagnetization in air and measurement at T₀. Most unblocking temperatures ranged from 250 to 400 °C (Fig. 16). Thus, almost the entire reversed TRM is unblocked below 400 °C. In order to limit the changes in intrinsic magnetic properties due to heating, and also the TRM due to TM, the experiments reported in this and the following section refer to partial thermoremanent magnetizations (PTRM) induced by cooling in air from about 400 °C.

All pumice samples but one acquired a reversed PTRM, whilst lithic samples acquired a normal TRM. Only the pumice sample PN9528 acquired a normal PTRM in fields of 0.1 and 0.2 mT, despite the strong hem–ilm signal seen on its k–T curve. However, as described above (Section 3), the remanence reversed beyond approximately 20 mT of AF treatment. The normal component is thus probably carried by TM. As for the other pumice samples, the negative component could not be entirely demagnetized even using 220 mT AF (Fig. 10).

6.2 Field dependence and AF demagnetization

Fig. 17 shows that the reversed PTRM initially increased in absolute intensity when the field H was increased to about 0.5 mT and then decreased beyond that (curve AF = 0 in Fig. 18). The field at which the PTRM becomes zero is called by several authors the ‘suppressing field’, Hₛ. In our experiments, the PTRM remained negative for the maximum H applied (6 mT). Hₛ can vary with the thermal history of the sample and differs for different pumices. In the Haruna pumices (Uyeda 1958) the maximum remanence intensity was found at an alternating field of H = 0.15 mT and TRM became normal beyond 0.35 mT. For the Nevado del Ruiz andesite, Haag et al. (1990a) reported corresponding values of 0.5 and 1.2 mT. In these rocks, TRM is in fact the combination of several opposing components probably acquired by different mechanisms and with different AF stabilities, as can be seen in Fig. 17; this is discussed in the following sections. For synthetic hem–ilm solid-solution series, Uyeda (1958) obtained reversed TRM even in inducing fields as high as 1.6 T. The variation of TRM with H was suggested to depend also on the size of the magnetic grains (Westcott-Lewis & Parry 1971). According to these authors, for y = 0.68 the grains with d < 5 μm always carry a normal TRM, whilst a reversed TRM is observed in larger grains.

According to Fig. 18, the hardest fraction (Hₑₑ > 30 mT) of the SR-PTRM component was almost saturated at inducing fields H larger than 0.5 mT. In contrast, the normal component with smaller unblocking fields seems to be roughly proportional to H over the entire range of fields investigated. The quite different behaviour of these two remanences suggests that the carriers of the SR and the normal magnetization components are different. Thus, for rocks Hₛ is not an intrinsic characteristic of SR TRM. The normal component with low coercivity is probably carried by titanomagnetite.
changes induced by the second, third and subsequent heatings. The stabilized sample was used for further investigations with this equipment.

Fig. 20 shows that the maximum intensity for both the normal and reversed components is in the blocking temperature range of 280–250 °C. This is also in reasonable agreement with the average Curie temperature of the hem–ilm of about 250 °C that is obtained from the k–T curves (Fig. 14). We attribute this Curie point to the ferrimagnetic hem–ilm phase because the susceptibility of the WF phase is much weaker than that of the FM phase. It is more surprising that PTRMs acquired within higher temperature ranges (reaching 350 °C) are still self-reversed by cooling to $T_0$ in zero field. This seems to indicate that the blocking range largely exceeds the average $T_c$. One reason might be dispersion of the Curie points of individual crystals around the average value because of the variations in chemistry observed between crystals (Section 3). More importantly, however, one must realize that because of the interaction with the WF phase, the FM phase can acquire a magnetization at a temperature well below the temperature range in which the laboratory field is applied during cooling (see below).

If we turn to unblocking temperatures, Fig. 19 (first heating curve) shows that the decrease of the SR component is dominant up to 300 °C whilst the decrease of the normal component (due to the WF phase) dominates beyond (up to about 400 °C). The fact that the reversed component unblocks at lower temperatures than the normal component is in agreement with the self-reversal models, which all require the Curie temperature of the normal component to be higher than that of the reversed one. Fig. 19 also suggests that the maximum unblocking temperature of the normally magnetized hem–ilm as measured during the first heating is close to 380 °C. Thus, this phase can have Curie points reaching at least 380 °C. The chemical analyses reported in Section 4 suggest that the average Curie point of the WF is slightly above that of the FM phase. This discrepancy can be accounted for by two distinct hypotheses. The first one is that there is a large dispersion of the $T_c$s of individual

6.3 Thermal demagnetization

Continuous thermal demagnetization of NRM and three successive total TRMs acquired after heating to 650 °C were carried out in air using a vibrating sample thermomagnetometer (Orion VTM) which measures remanence at $T$. As commonly observed for hem–ilm, the PTRM characteristics depend significantly on the thermal history of the sample. Fig. 19 shows that the first heating resulted in a decrease of the unblocking temperatures by almost 100 °C. Apparently, this single heating was sufficient to stabilize the sample (chemical alteration? cation diffusion?), as shown by the absence of

![Figure 19](https://example.com/fig19.png)

**Figure 19.** Continuous thermal demagnetization of NRM and several TRMs. A noticeable change in unblocking temperature occurs by the second heating and seems to stabilize the sample.

![Figure 20](https://example.com/fig20.png)

**Figure 20.** Continuous thermal demagnetization of several indicated PTRMs.
crystals. This does not seem to be in agreement with the rather narrow range of chemical variations observed from microprobe analyses, except if microstructures finer than 1–2 μm are present. The second hypothesis is that mineralogical changes occur during heating, resulting in an increase in Tₐ. This explanation seems in contradiction with Fig. 19, which shows that the unblocking temperatures of both the SR and the normal magnetizations decrease (rather than increase) after the first heating. Possibly successive heating decreases the main unblocking temperature of both phases, but also produces a minute quantity of the WF phase, the composition of which extends to haematite. The very weak normal remanence acquired by this quantity would produce, by exchange interaction, a reversed component in the FM phase when temperature decreases below the Curie temperature of this phase (∼280 °C). The magnetic signal due to the minute quantity of WFs cannot be detected by measurements at high temperatures because of its weakness and the reducing effect of thermal fluctuations. Finally, we wish to point out that the remanence which might be attributed to TM is negligible (Fig. 19).

Another set of experiments was carried out in order to evaluate independently the effects of thermal unblocking of remanence and thermal decay of spontaneous magnetization. A PTRM was first imparted from 300 °C to T₀ in H = 0.1 mT, then the sample was thermally stepwise demagnetized and the remanence measured for each temperature step T, at both T and T₀ (Fig. 21). The PTRM measured at T₀ (curve b) shows no decrease at all up to about 250 °C. This is an interesting situation: in this temperature range, curve (a) of Fig. 21 (measurements at T) is simply proportional to the change in spontaneous magnetization, which is quite large but could not be documented through high-field thermomagnetic measurements because of the overwhelming effect of TM (Fig. 13). The thermal decrease of the SR remanence (measured at T₀) reaches a maximum between 250 and 300 °C. However, almost one-third of the initial intensity remains after 300 °C, the maximum temperature of the blocking range. Heating to more than 400 °C is necessary to remove the PTRM completely. Thus, the unblocking temperature range of the SR PTRM largely exceeds its blocking temperature range, reaching the maximum Curie point of the WF phase. Similar behaviour was also observed for synthetic samples. Hoffman (1975) suggested that WF–FM superexchange interactions constrain the Fe spins of FM along the interface region to maintain an ordered arrangement (Hoffman 1992) beyond the Tₑ of the FM phase. This model may not explain the rather strong SR intensity of PTRM above the maximum Tₑ. For any ferro- or ferrimagnetic single phase, the exchange links between atomic moments are broken above Tₑ. In our case, at best the FM region coupled to the WF would be restricted to one atomic layer and cannot carry any significant remanence.

The following alternative explanation can be proposed. As for any MD particle (Bol’shakov & Shcherbakova 1979), the unblocking temperatures of a PTRM acquired by the WF phase exceed the blocking temperatures so that any PTRM is not entirely destroyed until the Curie point is reached. For heating temperatures between 250 and 400 °C, the FM phase is effectively demagnetized during heating. But, due to the WF/FM interaction, the FM phase is magnetized again during cooling, even though the external field is zero in that temperature range. This mechanism, together with the chemical alteration discussed above, also explains the resistance of NRM to thermal cleaning (Section 3) for which a rather strong reversed component remains after stepwise thermal demagnetization of NRM up to 650 °C (Figs 3 and 5).

7 HYSTERESIS CHARACTERISTICS

Hysteresis parameters were first measured at T₀ using a laboratory-made automatic translating magnetometer in fields reaching 1.6 T. Five parameters were measured or calculated: saturation magnetization (Jₛ); saturation remanent magnetization (Jₑ); high-field para/diamagnetic susceptibility (kₑ); coercive force free from para/diamagnetism (Hₑ); remanent coercive force (Hₑₑ) (Table 3). Note that saturation magnetization is not reached in the case of hem–ilm even though an apparent saturation is reached due to the dominant contribution of soft TM. Laboratory heating affects all these parameters. For sample PN9532, we observed an increase in Jₛ (~15 per cent), Jₑ (~75 per cent) and Hₑ (~70 per cent) after the heat treatments were carried out for NRM progressive demagnetization. These changes may be partly due to the oxidation of titanomagnetite and also to changes in the intrinsic properties of hem–ilm. The changes in the magnetic properties of hem–ilm by heating were observed for all studied samples (see Section 6), and previously reported by several authors (Uyeda 1958; Warner et al. 1972).

The main characteristics of hysteresis in our rocks are high Jₛ and Hₑₑ and very low Jₑₑ and Hₑₑ. For several specimens studied, the ratios of Jₑₑ/Jₛ and Hₑₑ/Hₑₑ are similar to those of large MD or a mixture of MD and SD grains with Jₑₑ/Jₑₑ close to 0.01 and Hₑₑ/Hₑₑ reaching 20 (Table 3). These ratios are difficult to interpret because of the presence of three mineralogical and magnetic phases (excluding very rare pyrrhotite). As seen above, TM dominates the high-field induced magnetization. In contrast, hem–ilm dominates low-field thermoremanences, and can also play the most important role regarding high-field remanences. Thus, the anomalously high Hₑₑ value (Table 3) may be due to hem–ilm. However, the fact that the applied fields are much too low to saturate the WF phase makes any interpretation difficult.
Table 3. Hysteresis parameters of several samples before and after different heat treatments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before heating</th>
<th>After heating</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J_\alpha$ ($10^{-3}$ Am² kg⁻¹)</td>
<td>$J_\alpha$ ($10^{-3}$ Am² kg⁻¹)</td>
<td>$H_{\alpha}$ (mT)</td>
</tr>
<tr>
<td>PN933a</td>
<td>960</td>
<td>1030</td>
<td>0.01</td>
</tr>
<tr>
<td>PN933B</td>
<td>1001</td>
<td>1293</td>
<td>0.01</td>
</tr>
<tr>
<td>PN933c</td>
<td>741</td>
<td>798</td>
<td>0.02</td>
</tr>
<tr>
<td>PN9524</td>
<td>1214</td>
<td>794</td>
<td>0.04</td>
</tr>
<tr>
<td>PN9527</td>
<td>1834</td>
<td>1821</td>
<td>0.15</td>
</tr>
<tr>
<td>PN9532</td>
<td>580</td>
<td>1114</td>
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<td>0.03</td>
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<tr>
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<td>534</td>
<td>791</td>
<td>0.05</td>
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</tbody>
</table>

8 EXCHANGE ANISOTROPY EXPERIMENTS

Characteristic features of exchange coupling as given by Meiklejohn (1962) are as follows.

(a) Asymmetric major hysteresis loops displaced towards positive or negative field values (depending on the sign of coupling on the interface boundary) due to displacement with respect to the magnetization axis.

(b) A sin $\theta$ torque component on the torque curve (in a rotating magnetic field, high enough for saturation), which indicates unidirectional exchange anisotropy, in contrast to the uniaxial anisotropy, which is bidirectional and therefore represented by a $\sin^2 \theta$ torque function.

(c) A non-vanishing rotational hysteresis loss in high fields. In contrast, a single ferro(i)magnetic phase with uniaxial anisotropy would exhibit rotational hysteresis losses only in fields $H$ between 0.5 $H_K$ and $H_K$ (where $H_K = 2K/J_\alpha$ is the anisotropy field). Thus, losses are zero for $H > H_K$. The existence of non-vanishing rotational hysteresis in $H > H_K$ can indicate an exchange interaction between an antiferromagnetic or WF phase and a ferro(i)magnetic phase.

(a) and (b) can be observed when the sample is cooled in an external field below the magnetic ordering temperature of the antiferromagnetic/WF phase in order to produce an additional preferred direction (anisotropy). According to Meiklejohn (1962), these are just two different expressions of the same property and (c) should be observed in any case. However, a non-vanishing rotational hysteresis is believed to be intrinsic to the symmetry of the anisotropy expected in haematite (Owens 1981), and thus presumably in WF hem–ilm.

8.1 Shift of hysteresis loop

Meiklejohn & Carter (1960) observed a 35 mT shift in the major hysteresis loop of synthetic hem–ilm subsequent to the acquisition of total TRM in a 1 T field. In contrast to experiments on synthetic materials, the induced magnetization carried by low-coercive titanomagnetite (TM) dominates the hysteresis loop in natural rocks with self-reversed TRM. This makes it difficult to observe a possible shift. Haag et al. (1990b) observed a shifted hysteresis loop for the pumice from Nevado del Ruiz using a maximum field of only 50 mT. They interpreted the temperature dependence of the shift, from 10 K to $T_C$, as indicative of exchange interactions. However, only a displacement of the major hysteresis loops (corresponding to near-saturation maximum magnetic fields) may be considered as indicating exchange interaction. For sample PN933, a 0.5 mT shift is found using a maximum field of 25 mT subsequent to the acquisition of a 0.2 mT TRM. When this experiment was repeated using a maximum field of 0.18 T, the shift was reduced to 0.2 mT. In $H_{max} = 0.5$ or 1 T the shift was no longer significant and remained on the order of experimental errors.

The failure of the high-field tests does not demonstrate that exchange coupling is not present. The first reason for this is that TM plays an almost exclusive role in high-field experiments (e.g. Fig. 13), making it very difficult to see any effect due to hem–ilm. The second and more fundamental reason is that a SR TRM acquired in a 0.2 mT field is partly destroyed by a 0.2 T field and is perhaps largely destroyed by a 0.5 or 1 T dc field (see Fig. 17). A much larger TRM-inducing field, possibly as high as 1 T, as used by Meiklejohn & Carter (1960) in their study of synthetic hem–ilm, might be required to observe a possible shift in natural hem–ilm separated grains.

8.2 Sin $\theta$ function and losses from high-field torque curves

The measurements were performed on a laboratory-built system. Torque curves were measured in rotating magnetic fields up to 1.5 T at room temperature on sample PN933. The sample with cylindrical shape carried a laboratory TRM in $H = 0.5$ mT perpendicular to its axis. Magnetic fields were applied perpendicular to the cylinder axis and making a complete rotation. From Fourier analysis, Fig. 22 shows the sin $\theta$, sin$^2 \theta$ and sin$^4 \theta$ components of the torque curves as a function of the applied field. No influence of the laboratory TRM direction was detected. Similar curves were found on samples with and without a TRM. The dominating sin$^2 \theta$ component (uniaxial anisotropy) could be due to the presence of a uniaxial ferromagnet (WF hem–ilm). Furthermore, a sin$^4 \theta$ component would possibly result from the TM phase. The sin $\theta$ component was found to be very weak and not very significant (Fig. 22). A model exhibiting a sin $\theta$ torque function also shows a hysteresis shift (Meiklejohn 1962). The failure to observe a noticeable sin $\theta$ points to the same explanations as given above for the absence of a clear shift of major hysteresis loops.

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The loss at high magnetic field is probably a more general characteristic of exchange anisotropy than is a shifted hysteresis loop (Meiklejohn 1962). Integration of the torque moment for a complete 360° rotation of the external field provides a rotational hysteresis loss \( W_{\text{RH}} = \int T \, dh \), where \( T \) is the torque and \( \theta \) the rotation angle. Fig. 23 shows \( W_{\text{RH}} \) as a function of the field. The sharp peak at about 0.2 T results from the TM phase. The curve (b) shows the high-field part of the curve (a) as a function of \( 1/H \) and extrapolated to infinite fields. This figure shows that there is no clear evidence for non-vanishing rotational hysteresis losses, and exchange anisotropy is not detected as for synthetic samples. Fig. 24 shows \( W_{\text{RH}} \) as a function of the external field for sample PN933 (carrying a laboratory TRM) and two synthetic hem–ilm samples with \( y = 0.5 \) and \( y = 0.6 \) (after Ponat 1975). Measurements on pure haematite (Owens 1981; Keller & Schmidbauer 1996) revealed a behaviour qualitatively and quantitatively similar to that observed here for sample PN933, which was attributed to the very high anisotropy of haematite. A similarly high magnetocrystalline anisotropy can be expected for hem–ilm with a haematite-like magnetic structure (WF phase).

**Figure 22.** Torque function components versus applied fields as obtained from Fourier analysis.

**Figure 23.** (a) Rotational hysteresis loss as a function of the field and (b) versus \( 1/H \) with extrapolation to infinite field for sample PN933 [the peak at low fields in curve (a) is due to TM].

**Figure 24.** Rotational hysteresis loss as a function of the field for sample PN933 (Fig. 23) and for two synthetic hem–ilm samples with \( y = 0.5 \) and \( y = 0.6 \) (after Ponat 1975).

**9 DISCUSSION**

### 9.1 Chemical and magnetic microstructures

In contrast to most previous models of self-reversal, Hoffmann & Fehr’s (1996) model assumes that the WF and FM magnetic phases correspond to the large-MD crystals. This model was based on their observation of a single hem–ilm crystal from Pinatubo in which a chemical zonation related to the micro-magnetic structure occurs. The crystal margin was found to be about 10 per cent Fe-enriched and exhibited a WF structure, whilst the centre of the crystal was ferrimagnetic (FM). The present study confirms their conclusion that the two distinct magnetic microstructures correspond to two distinct chemical compositions. However, chemical profiles can present a much lower contrast than reported by Hoffmann & Fehr (1996) between the FM and WF phases. We also observed that the FM phase does not always occur in the crystal centre. Several crystals were observed having a marginal FM.

Two different mechanisms are proposed to explain the presence of a ferrimagnetic core surrounded by a WF Fe-rich margin. (1) This association can be viewed as a chemical zonation resulting in a magnetic zonation due to the difference in Fe content between the two zones. The chemical zonation within crystals is commonly interpreted as the result of physico-chemical changes of the magmatic melt after intrusion of the juvenile basaltic magma that triggered the eruption. In this mechanism the rim phase represents the reaction zone according to the new conditions in the magma chamber. Keeping the new conditions for a longer period of time after magma mixing would cause a penetration of the diffusion zone through the core, altering it completely. (2) A more sophisticated mechanism can be proposed assuming the presence of very small-scale antiphase domains (or alternatively twin-related domains) separated by disordered boundaries (Nord & Lawson 1989). These authors showed that in quenched synthetic hem–ilm, the size of the ordered domains coarsens progressively when
the sample is annealed for a long period of time at a temperature close to but below the transition temperature \( T_C \). Building on a suggestion from Hoffman (1992), we can assume that this coarsening results in part from the migration of the disordered boundaries towards the grain edge (possibly under strains caused by the cell volume difference between the two phases). This mechanism might explain the formation of a disordered Fe-rich margin by accumulation (through migration) and growth (through coalescence). In this migration model, the chemical zonation is not related to the change in magmatic conditions. It seems difficult to apply this model to the present case because chemical zonations are also observed in other kinds of minerals from Pinatubo dacite (e.g. Hattori & Sato 1996).

Are these two phases perfectly homogeneous? Lawson et al. (1987) reported that the hem–ilm crystals from Mt Shasta, which seem similar to those from Pinatubo, reveal a heterogeneous fine microstructure with ordered crystallographic domains up to 10–20 nm in size separated by disordered boundaries. We have not carried out transmission electron microscopy (TEM) on the Pinatubo hem–ilm but there are several lines of indirect magnetic evidence for the existence of ultrafine structures in the hem–ilm crystals. First, there is a striking similarity between the resistance to AF of the natural TRM of the Pinatubo dacite (Fig. 4) and that of the Mount Shasta sample (Lawson et al. 1987). Another indication regarding the effective magnetic grain size is the Koenigsberger ratio \( Q_n \), which is quite large \( Q_n = 140 \) from \( J_{\text{rem}} \) and the susceptibility decrease observed near 260°C (Fig. 14). This \( Q_n \) is an SD value, not an MD value. Similarly, the initial plateau of the AF demagnetization is SD-like (Dunlop & Argyle 1991). Thus the magnetic evidence seems to favour the presence of fine microstructures in the Pinatubo hem–ilm. TEM would be desirable to verify this possibility.

### 9.2 Self-reversal process and interactions

It is commonly believed that SR TRM/NRM in hem–ilm of intermediate compositions is produced during the cooling of two interacting phases with slightly different compositions, and therefore different Curie temperatures (Ishikawa 1958; Ishikawa & Syono 1962; Hoffman 1975, 1992; Heller et al. 1986; Nord & Lawson 1989). However, the exact mechanism of spin alignments between the two interacting phases is not well understood. The WF haematite-like spin-canted and disordered phase is first magnetized when the temperature decreases through its Curie point. As both canted spins are in the c-plane, the resultant moment \( J_{\text{c}} \) is also in the c-plane, although it is almost normal to spins and oriented in a direction between the projection of the external field and the easy direction. By further cooling through the Curie temperature of the ferrimagnetic ilmenite-rich partially ordered phase, the antiferromagnetic exchange coupling between WF spins and FM spins would give rise to the FM phase, a magnetic ordering which is not opposite but almost perpendicular to the projection of the external field. This problem was discussed by Hoffman (1992), who proposed a model of exchange interactions allowing some spin tilting near the boundary when the temperature decreases below the Curie point of the FM phase. In addition, the random distribution of the symmetry axis of individual crystals may also favour the exact alignment of magnetic moments of both phases with the external field and opposite to it.

The resistance to AF of the SR TRM of the Pinatubo dacite is large but not as great as that for synthetic samples (Uyeda 1958). This suggests that exchange interaction due to the WF phase affects only a fraction of the volume of the FM phase. The dynamic domain observations described here show that large FM cores are less resistant to the external field than small FM cores. As exchange anisotropy is an interfacial property (Meiklejohn 1962), exchange interaction in our samples can act only along the interface between the two phases. Thus exchange interaction should lock only the spins of FM which are the closest to the WF/FM boundary. The small cores (Fig. 11d) may not be affected by AF as most of the FM volume can be locked by negative superexchange coupling with the WF phase. Fig. 18 shows that the magnitude of the hardest TRM fraction (unblocking AF greater than 120 mT) is independent of the magnitude of the applied dc field. This confirms that this part of the TRM is locked by exchange interaction.

The fact that exchange coupling could not be positively identified using magnetic means might be due to the large grain size of hem–ilm in the Pinatubo dacite. To date, all investigations of exchange coupling through hysteresis/torque experiments have been performed on synthetic minerals with very small crystals, presumably of SD or PSD structure. In our case, only a very small volume close to the WF/FM transition zone (boundary) would be the source of the expected magnetic effects of exchange interaction. In contrast, magneto-static interactions, even weak, may act in all the grain volume, and the SR TRM component due to this interaction would have much lower coercivity (Fig. 17). Magnetostatic interactions were suggested to be the main cause of SR TRM in the pyrrhotite/magnetite system (Bina & Daly 1994). In this case, the normal remanence carried by magnetite could be isolated through AF demagnetization (Fig. 25). In the present case, this normal magnetization was identified through continuous thermal demagnetization (Figs 19 and 20), but it was not apparent on the AF demagnetization curves, probably because the unblocking fields of the WF hem–ilm phase exceeded the AF range available. High unblocking fields are typical of fine-grained haematite and are not uncommon in large MD natural crystals due to wall pinning (Dunlop 1971).

### 10 CONCLUSIONS

(1) The magnetic properties and magnetic mineralogy of dacitic pumices from Pinatubo resemble those already reported for the few other volcanics exhibiting self-reversals. Two magnetic minerals control the magnetic properties of these rocks: Fe-rich titanomagnetite and hem–ilm of intermediate composition (two phases). Both have compositions similar to those found for other pyroclastic rocks showing self-reversals, easy direction. By further cooling through the Curie temperature of the ferrimagnetic ilmenite-rich partially ordered phase, those found for other pyroclastic rocks showing self-reversal, easy direction. Those compositions (two phases). Both have compositions similar to those found for other pyroclastic rocks showing self-reversals, easy direction. Those compositions (two phases). Both have compositions similar to those found for other pyroclastic rocks showing self-reversals, easy direction. Those compositions (two phases). Both have compositions similar to those found for other pyroclastic rocks showing self-reversals, easy direction. Those compositions (two phases). Both have compositions similar to those found for other pyroclastic rocks showing self-reversals, easy direction. Those compositions (two phases). Both have compositions similar to those found for other pyroclastic rocks showing self-reversals, easy direction. Those compositions (two phases). Both have compositions similar to those found for other pyroclastic rocks showing self-reversals, easy direction. Those compositions (two phases). Both have compositions similar to those found for other pyroclastic rocks showing self-reversals, easy direction. Those compositions (two phases). Both have compositions similar to those found for other pyroclastic rocks showing self-reversals, easy direction.
ilmenite/haematite content which would be the origin of the difference in Curie temperatures and magnetic properties.

Except for sample PN9528, with very soft and multidirectional NRM and TRM including a normal component larger than the SR TRM, no normal total TRM was found for the pumice samples. The anomalous NRM direction found for a few samples is due to the post-emplacement orientation changes, and the laboratory TRMs of pumices were all reversed. The lithic samples are normally magnetized. Thermal demagnetization of these samples suggests that the emplacement temperature of these volcanic deposits was between 460 and 500 °C at the studied site.

(2) The total TRM of the Pinatubo dacite acquired in weak to moderate laboratory fields (0.05–6 mT) consists of three or possibly four components.

(i) A small normal component which is approximately proportional to the applied field and is characterized by AF unblocking fields typically less than 40–50 mT. The main magnetic carriers of this component are large (up to a few hundred μm in size) Fe-rich titanomagnetite (χ = 0.10) crystals.

(ii) A (dominant) self-reversed component with moderate MDF (60–80 mT) and unblocking temperatures (as measured at T) mostly below 300 °C. This SR TRM component increases with the inducing field H up to 0.5 mT and then becomes saturated. This magnetization seems to reside in the (generally central) ferrimagnetic zone of large (a few hundred μm) hem–ilm crystals with γ ≈ 0.54. The hardest fraction of this remanence (which remains unchanged in high AF fields) is probably due to superexchange coupling along the interface of the FM phase to the (generally marginal) WF phase in the same hem–ilm crystals (γ ≈ 0.52).

(iii) A quite small normal magnetization with unblocking temperatures slightly higher than (maximum 400 °C) those of SR TRM can be seen on continuous thermal demagnetization curves of total TRM. This component is not detected by AF treatment, probably because it is unaffected by the AF used (less than 220 mT). This component is probably carried by the WF zone of hem–ilm crystals.

(iv) We cannot rule out the possibility that some ferrimagnetic zones of hem–ilm crystals that are not included within a WF zone (‘open’ ferrimagnetic zones) become normally magnetized under the direct influence of the applied field.

(3) The fact that a SR-PTRM can be produced at much higher temperatures than the average Curie point (250 °C) suggests that this temperature is that of the ferrimagnetic phase, whilst the WF phase, particularly in heated samples, may have a large spectrum of Curie points, with a maximum density just above Tc of the ferrimagnetic phase, but the upper limit reaching the Curie temperature of haematite.

(4) The arrangement and the intergrowth geometry of the two magnetic hem–ilm phases as found from Bitter pattern observations are in general agreement with the models proposed by Neé (1955) and Ishikawa & Syono (1962), in which self-reversed TRM results from exchange anisotropy between a WF (canted antiferromagnetic) and an FM phase. However, exchange anisotropy can act only at the FM/WF interface. This corresponds to a quite small volume fraction of the FM phase and can explain some SD-like magnetic properties of the Pinatubo hem–ilm. Several experiments involving things such as a shift in the hysteresis loop and rotational hysteresis, considered as indicators of exchange coupling, were performed. The results, however, were not positive, in contrast to most of the observations for synthetic hem–ilm minerals (Fig 24) or thin-film Co–CoO systems. In addition to the difference in microstructure, the Pinatubo hem–ilm minerals also contain noticeable amounts of Mg, Mn and Al cations, which necessarily affect their magnetic properties. AF demagnetization shows that most of the SR TRM is removed by fields which do not seem to affect the WF phase. This suggests that in addition to the short-range exchange interaction acting along the interface between the two phases, part of the SR TRM (at least for large FM cores and ‘open’ structures) could be due to magnetostatic interaction, which is weaker but is able to act over a larger volume. The resistance of this component to AF of medium intensity may be due to wall pinning by fine microstructures acting as defects in the FM phase, similar to those observed in the Mt Shasta hem–ilm (Lawson et al. 1987).


