The iron–titanium oxides of some Dunedin (New Zealand) lavas, in relation to their palaeomagnetic and thermomagnetic character (with an appendix on associated chromiferous spinel)

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Summary. Earlier palaeomagnetic studies on the Dunedin volcano showed that a portion of the sequence is reversely or anomalously magnetized. Some of the rocks used for palaeomagnetic study were subsequently classified into groups according to their thermomagnetic behaviour (unpublished work).

Cell dimensions and Curie-point curves have been measured for oxides separated from representative rocks of each group. The oxides are mostly homogeneous titanomagnetites containing between 40 and 55 mol. % of ulvöspinel, with a generally small degree of late low-temperature alteration. X-ray and thermomagnetic data also suggest that there was some early oxidation to titanomaghemite, probably during cooling.

The thermomagnetic behaviour of rocks classified in the different groups is attributed to variable oxidation of the titanomagnetite during thermomagnetic treatment. The high Curie points of rocks used for palaeomagnetic studies may often be due merely to oxidation of titaniferous magnetite and not to nearly pure primary Fe_3O_4. Since there is insufficient oxidation in the lavas examined for any currently accepted self-reversal process to have been operative, the reversely magnetized part of the Dunedin sequence was probably erupted during a reversed polarity epoch, possibly between about 13 and 11 million years ago.

The basanitic lavas contain minor amounts of chromiferous spinel, as inclusions in silicate phenocrysts and as cores to separate microphyric titanomagnetite; its significance is briefly discussed.

COOMBS and Hatherton (1959) established that the magnetic polarity of a suite of basanites, olivine basalts, trachyandesites, and phonolites from the Mio-Pliocene Dunedin volcano varied with respect to their position in the eruptive sequence:

Third eruptive phase		*Normal magnetization*
Second eruptive phase	(Upper)	*Reversed and anomalous magnetization*
	(Middle)	
Second eruptive phase	(Lower)	*Normal magnetization*
First eruptive phase		
(Initial eruptive phase not tested)		

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No correlation between character of magnetization and petrographic type was observed. Subsequently Hatherton (personal communication) determined thermomagnetic curves for some of the samples used in the palaeomagnetic study. The curves could be classified into six groups which are reproduced in fig. 1 (solid lines). The groups show little correlation between time, polarity, and petrographic type (table I).

TABLE I

Flow no.		Curie point curve group	Magnetic intensity*	Magnetic polarity†	Age‡
19	Olivine basalt; Grants Braes	1	M	N	L2
32	Basic trachyandesite; Shiel Hill		L	A–S	M2
21	Trachyandesite; Burns Pt.		L	N	1
17	Basanite; Hautai Hill area		H	S	U2
3	Dolerite; Roslyn		H	R	U2
S6	Ankaramitic basalt; Swampy Hil		H	A	U2
23	Basanite	2	H	S	U2
22	,, Hautai Hill area		M	R	U2
24	,,		H	A–S	U2
29	Doleritic basalt; Little Papanui Cone		M	N	1
10	Olivine basalt; N. Head		M–H	N	1
35	Phonolitic trachyandesite, Robin Hood Quarry	3	L	S–N	U2
33	Phonolite; Logan Pt.		L	N	L2
13	Trachyandesite; Pilots Beach		M	N	1
16	Basanite; Hautai Hill	4	H	A–S	U2
38	Mugearite; Saddle Hill		H	S	
18	Basanite; St. Clair	5	M	N	1/L2
26	Atlantite Little Papanui Cone		H	S	U2
27	,,		H	S–N	U2
5	Trachyandesite; Bullock Track	6	L	R	U2
15	Atlantite; Tairoa Head		L	S	M2
51	Basanite; Buccleugh St.		M	R	U2
50A	,, ,,		L	S	U2
47	Basanite; Hautai Hill area		L	S	U2
S3	Olivine basalt; Swampy Hill		L	A	U2

* L = low intensity
M = medium intensity
H = high intensity

† N = normal magnetization
R = reverse magnetization
A = anomalous magnetization
S = scattered magnetization

‡ 1 = first eruptive phase
2 = second eruptive phase
U = upper
M = middle
L = lower

For this study the magnetic oxides were separated from specimens representing each of Hatherton's groups, taken from the same sites and in most cases from the same blocks as those collected by Coombs and Hatherton. Although only relatively few specimens were examined in this way, the results are sufficiently interesting to warrant recording, particularly as further work is likely to be indefinitely delayed.

The *basanitic rocks* are olivine- and titanaugite-phyric, with plagio-

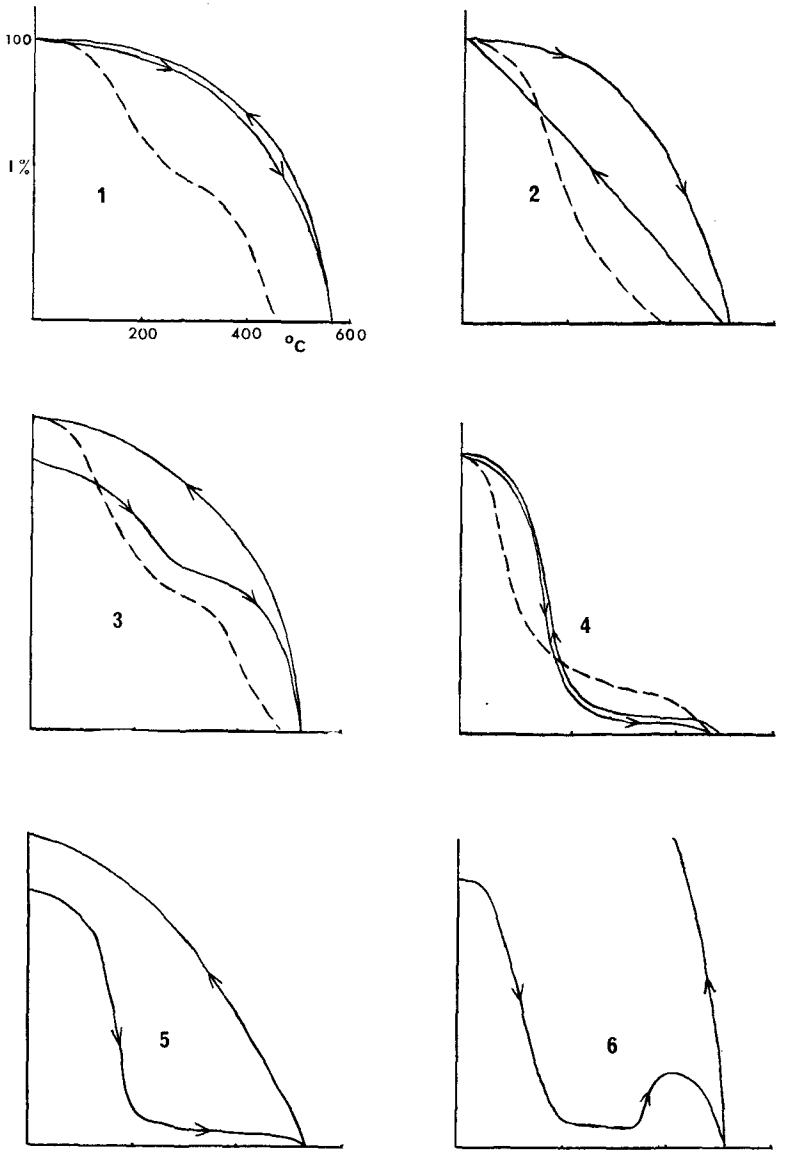


FIG. 1. Generalized thermomagnetic curves for whole rock samples (solid lines) and separated oxides (dashed lines) in Hatherton's groups. Ordinate and abscissa scales as for top left diagram throughout

clase confined to the groundmass except in one rock (specimen 16A/1). Titanaugite occasionally has very pale green cores and olivine is generally fresh. Biotite flakes and chlorite patches are scattered through the groundmass of some rocks, and two contain interstitial glass (specimens 18A, 47/3). Oxide microphenocrysts are 0·1–0·3 mm in diameter and very abundant groundmass cubes range down to less than 0·001 mm (1 μ), except in specimen 47/3, where they are usually not less than 0·01 mm and less plentiful, as in the trachyandesites.

The *trachyandesites* contain phyric andesine/labradorite, olivine pseudomorphs, and titanaugite, some with pale green cores. Alkali feldspar is mainly confined to the groundmass, although rare calcic anorthoclase (?) phenocrysts were seen in specimen 13, in which there is considerable phenocryst corrosion, suggesting a degree of disequilibrium during cooling. Oxide microphenocrysts are 0·1–0·5 mm in diameter, while groundmass granules are usually not much less than 0·01 mm (10 μ) and are not as abundant as in most basanites.

Titanomagnetite. The magnetic oxides were separated mainly by a combination of wet-magnetic and heavy-liquid techniques, generally similar to those described by Schreiter and Vollstädt (1964). Sufficient concentration for thermomagnetic and X-ray measurements was achieved and no additional phases were recorded on the X-ray diffractograms from which the cell dimensions were calculated. Broad diffractometer peaks obtained with some samples are attributed to compositional variation (see below). Thermomagnetic curves were determined on small quantities of some samples sealed in evacuated pyrex ampoules, by A. E. Leopard of Geophysics Division, D.S.I.R., Wellington. Only the heating curves are shown (fig. 1, dashed lines) because there is good evidence that some reduction took place during thermomagnetic treatment, so that the cooling curves gave anomalously low Curie points. The reduction is attributed mainly to olivine and pyroxene impurities with high FeO/Fe_2O_3 ratios, and to rare small shreds of metallic iron in two of the samples. Other relevant data for the samples examined in detail are summarized in table II.

Chromiferous spinel. All the basanitic rocks examined contain small amounts of early-crystallized spinel, grey and with low reflectivity relative to the iron–titanium oxides. It is described more fully in the Appendix.

Small *sulphide* globules, usually pyrite but possibly chalcopyrite also, are sometimes trapped within microphenocryst oxide.

Compositional variation in the titanomagnetites. Cell-edge values and

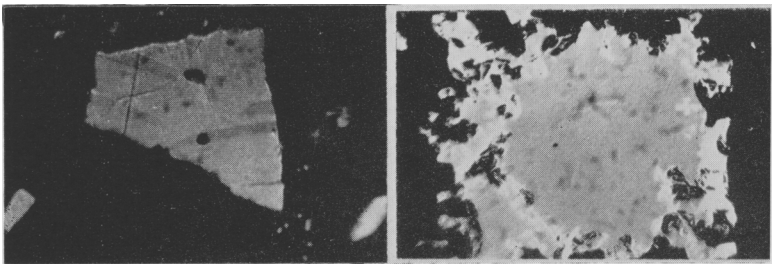
TABLE II

Group	Specimen no.*	Rock type	Eruptive phase†	Type of magnetization†	Cell edge of oxide	Approximate compositions using curves of Akimoto *et al.* (1957)	Remarks
1.	32A/1	Trachyandesite	M2	A–S	8·467 ±0·002 Å, with indications of spread down to weak subsidiary peaks appropriate to 8·42 Å	$Mt_{43}Usp_{55}$	Homogeneous titanomagnetite, rare streaky white maghemitization.
2.	23A/3	Basanite	U2	S	8·447 ±0·001 Å	$Mt_{60}Usp_{40}$	Mainly homogeneous titanomagnetite, some streaky white maghemitization.
	24A/1	Basanite	U2	A–S	8·445 ±0·002 Å	$Mt_{60}Usp_{40}$	Mainly homogeneous titanomagnetite, some streaky white maghemitization, very rare ilmenite lamellae (fig. 2).
3.	13	Basic trachyandesite	1	N	8·457 ±0·007 Å (Broad peaks)	$Mt_{50}Usp_{50}$	Homogeneous titanomagnetite, rare streaky white maghemitization.
4.	16A/1	Basanitic olivine basalt	U2	A–S	8·465 ±0·003 Å, with indications of very weak peaks appropriate to 8·42 Å	$Mt_{45}Usp_{55}$	All gradations from homogeneous titanomagnetite to homogeneous titanomaghemite (fig. 3). Patchy oxidation, some parts of a polished section may be unaffected, in others every grain is oxidized. Weak peaks at 8·42 Å attributed to titanomaghemite.
5.	18A	Basanite	1/L2	N	8·447 ±0·003 Å	$Mt_{60}Usp_{40}$	Homogeneous titanomagnetite.
6.	47/3	Basanite	U2	S	8·443 ±0·002 Å	$Mt_{60}Usp_{40}$	Homogeneous titanomagnetite, rare streaky white maghemitization.

* Initial numbers refer to flows as in table I, subsequent letters and numbers to blocks from which cubes were cut for palaeomagnetic study. For localities, see table I.

† Key to abbreviations as for table I.

thermomagnetic curves of the separated oxides suggest a fairly narrow compositional spread for titanomagnetites in the basanites (Groups 1, 2, and 4 to 6). What variation there is can be attributed mainly to differences in Ti content both within microphenocrysts and between microphenocrysts and groundmass (cf. Meitzner, 1963; Babkine, 1965). For the trachyandesite samples (Groups 1 and 3), however, the much longer thermomagnetic slopes and greater range of cell dimensions[1] can be attributed partly to variations in Ti content and partly to some development of titanomaghemite, perhaps during later stages of cooling, sufficient to extend the Curie point range but not enough to be obvious under the microscope (cf. Wilkinson, 1965). The patchy formation of



FIGS. 2 and 3: FIG. 2 (left). Ilmenite-rich lamellae in specimen 24A/1 (Group 2) This is non-typical, only a few grains contain separate ilmenite and most of these have even fewer lamellae. ×330. FIG. 3 (right). Titanomagnetite partly oxidized to white titanomaghemite in specimen 16A/1 (Group 4). Homogeneous grains of both kinds are also found in this rock. ×330

white titanomaghemite, best developed in the basanite specimen 16/A1 but visible to some degree in most of the rocks examined, is considered more likely to have resulted from later more intensive oxidation at low temperatures.

Whole-rock Curie points. The pattern of whole-rock thermomagnetic behaviour in Hatherton's groups is attributable to different degrees of additional oxidation in each rock during thermomagnetic treatment. Experiments by Meitzner (1963) and Babkine (1965) showed that the titanomagnetite in lava samples can become oxidized on heating in air even at quite low temperatures and for short periods. The extent of such oxidation will depend mainly on the amount of volatiles in the rock and results either in maghemitization or, with increased P_{O_2}, in separation

[1] Titanomagnetite separated from a Group 1 basanite could be expected to resemble those in other basanites, especially Group 2.

TABLE III

Sample no.	Rock type	Locality	Eruptive phase*	Type of magnetization*	Remarks
23A/4	Basanite	Harrington Pt.	U2	A	Cf. 23A/3 (Group 2). Homogeneous titanomagnetite, also patchy development of white titanomaghemite and some pink ilmenite-rich lamellae.
41	Basanite	Tanner Road	3	S–N	Homogeneous titanomagnetite.
46/1	Basanite	Hautai Hill	U2	A–S	Homogeneous titanomagnetite.
51/4	Basanite	Buccleigh St.	U2	R	(Group 6.) Gradation from homogeneous titanomagnetite to white titanomaghemite.
67	Kaiweckite	North Head	1	N	Homogeneous titanomagnetite.
80/5	Feldsparphyric olivine basalt	North Head	M2	A	Over-all brownish coloration in hand specimen. Much development of white titanomaghemite and pink ilmenite-rich lamellae.

* Key to abbreviations as for table I, with addition: 3 = third eruptive phase.

of a Ti-rich rhombohedral phase, either of which will increase the magnetic intensity and Curie point (Akimoto *et al.*, 1957; Wright and Lovering, 1965).

For Groups 1 to 3 oxidation was evidently progressive during thermomagnetic treatment and kept pace with heating, while delayed oxidation characterized Groups 4 to 6—although in Group 4 it was hardly significant. Indeed, the patchy titanomaghemite seen in specimen 16A/1 is sufficient to account for the high-temperature part of the curve in fig. 1, without additional oxidation. The low Curie point of around 200° C in Groups 5 and 6 is evidently that of the titanomagnetite, which then underwent sudden high-temperature oxidation with concomitant sharp increases of both magnetic intensity and Curie point. It may be significant that the representatives of these groups contain interstitial glass.

A suite of rocks may thus yield a wide range of whole-rock Curie points which could easily be interpreted as due to magnetites of widely differing compositions, when in fact they are all fundamentally similar in composition and differ only in the degree of oxidation. In particular, double Curie points should not be attributed to two separate primary magnetic phases without verification by other means; nor should high Curie points necessarily be inferred to signify nearly pure primary magnetite.

Palaeomagnetic implications. Some extrapolation to other samples used in the original palaeomagnetic work is permissible, given two reasonable assumptions: first, that since all of Hatherton's groups are represented, a fair cross-section of oxide compositions has probably been covered. Secondly, that as the specimens used for palaeomagnetic study were selected for maximum freshness, the degree of oxidation in the remaining samples is probably not excessive. The second assumption gains support from results of microscopic examination of some additional specimens taken at random from the palaeomagnetic suite (table III).

A high degree of oxidation, with extensive development of titanhematite, would be necessary in the reversed and anomalous rocks before it could be suggested that they might have undergone self-reversal (e.g. Ade-Hall, 1964; O'Reilly and Banerjee, 1966). Only one of the Dunedin rocks examined remotely approaches this condition (80/5, table III) and even in that the rhombohedral phase is rich in ilmenite rather than hematite.

While it is possible that low-temperature maghemitization could be responsible for some of the anomalous polarities (cf. Powell, 1963), the

available evidence is consistent with a reversed polarity episode during eruption of the Middle and Upper Second Phase rocks, as concluded by Coombs and Hatherton (1959), who placed it close to the Mio-Pliocene boundary. Recent age determinations (reported in Coombs, 1965) bear this out and place the reversed episode somewhere between about 13 and 11 million years ago (further work on the ages of these rocks is in progress). The place of the reversal in a global context has been discussed previously by Coombs *et al.* (1960); see also Wright, 1967.

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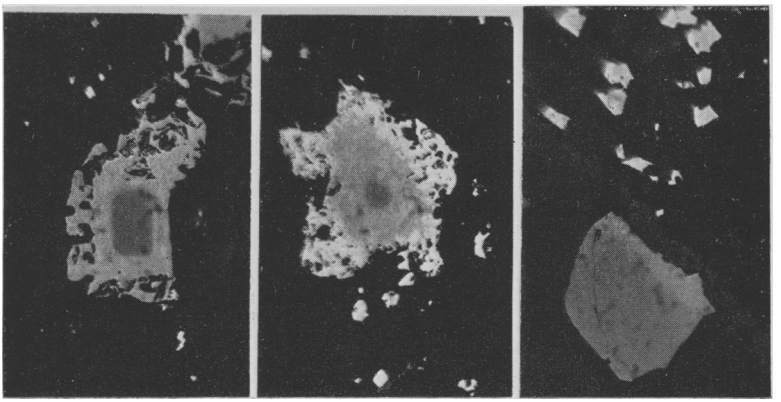
Appendix

In three of the samples (23A/3, 24A/1, and 18A—Groups 2 and 5) chromiferous spinel is found only as microphenocryst inclusions within silicate phenocrysts, probably both olivine and titanaugite. The inclusions vary in habit from euhedral



FIGS. 4, 5, 6: FIG. 4 (left). Grey chrome-spinel core to pink titanomagnetite in specimen 16A/1. Note irregular sieve-structured outer margin of titanomagnetite. × 330. FIG. 5 (middle). Three-tiered grain of grey chrome-spinel, pink titanomagnetite and white titanomaghemite in specimen 16A/1. ×330. FIG. 6 (right). Pink titanomagnetite overgrowth on chrome-spinel coinciding with pink Ti-enriched margin of titanaugite phenocryst, specimen 47/3. Note patchily maghemitized groundmass cubes. ×330

to amoeboid, and are generally outnumbered by titanomagnetite inclusions. In the other two basic rocks (16A/1 and 47/3—Groups 4 and 6), it occurs both as inclusions in silicate phenocrysts and as cores to microphyric titanomagnetite (fig. 4). The relative size of core and rim in the latter varies considerably and boundaries between the two phases can be very diffuse. Marginal maghemitization of composite crystals

in specimen 16A/1 has given rise to striking three-tiered grains (fig. 5). In very thin sections of this rock, the spinel can sometimes be seen as very dark green translucent parts of opaque microphenocryst inclusions in phyric feldspar. It was never seen even in very thin sections of the other rocks, which contain no phenocryst feldspar.

In specimen 47/3 the spinel is commonly found in titaniferous augite, with which it has an interesting compositional relationship: wherever spinel cubes are situated on the margins of pyroxene crystals they have diffuse boundaries to pink titanomagnetite borders, the latter coinciding with the outermost pinker and presumably more titaniferous zones of the augite, which probably formed at the same time (fig. 6).

Babkine *et al.* (1965) have described and figured almost identical relationships in basanites from the Loire Valley. The main difference is that the latter contain only olivine phenocrysts, which are therefore the only hosts for spinel inclusions, but this has not prevented development of titanomagnetite overgrowths on the latter at phenocryst margins (cf. fig. 6).

Microprobe analyses showed the grey spinel to be chrome-rich magnesian picotite (Babkine *et al.*, 1965) although there are compositional differences between the phenocryst inclusions and the cores of microphyric titanomagnetite. There is little doubt that the spinels in these Dunedin rocks will prove to be similar when more detailed examinations are made, although there may well be additional composition variables—for example, between the spinel inclusions in phenocryst feldspar, which are the only ones visible under transmitted light, and those in the mafic phenocrysts, which are opaque. The situation could also be complicated by the presence of additional spinel crystals derived from disaggregation of ultrabasic inclusions (cf. Babkine *et al.*, 1965).

Both spinel and titaniferous magnetite commenced crystallizing in the intratelluric stage, for both are found as inclusions in silicate phenocrysts. Spinel crystallization ceased before eruption but the ragged outline of titanomagnetite microphenocrysts (figs. 4, 5) suggests that they continued growing during crystallization of the groundmass.

Re-solution of early crystallized aluminous spinel in basaltic melts is predicted by well-established phase equilibrium data (Osborn and Tait, 1952), and Babkine *et al.* (1965) have concluded that the titanomagnetite overgrowths result in part from replacement of the spinel. Early chrome-rich spinels are well known as accumulations near the base of major intrusions such as the Bushveld, but their occurrence in basic rocks of alkaline affinities does not seem to have been widely reported.

Addendum. Aoki has recently (1966) shown that homogeneous chromium-free titanomagnetite phenocrysts in Iki Island trachyandesite contain 15 to 24 % of spinel plus hercynite in solid solution. The presence of kaersutite and calcic augite in the trachyandesite suggest comparatively low temperatures and high P_{H_2O} (Aoki, 1966), conditions under which aluminous spinels might be more stable, for signs of resorption are not recorded.

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