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A Mössbauer spectroscopic study of the cooling history of hypersthenes from selected members of the Taupo Pumice formation, New Zealand

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SUMMARY. ^{57}Fe Mössbauer spectroscopy has been used to determine the Mg^{2+}-Fe^{2+} distribution between the two crystallographically inequivalent cation sites in hypersthenes from a stratigraphic tephra sequence of the Taupo Pumice formation, North Island, New Zealand. From these distributions and X-ray fluorescence analytical data, cooling histories were constructed using previously determined Mg^{2+}-Fe^{2+} equilibrium isotherms for orthopyroxenes. The results showed that this cooling history geothermometer could be used to enable airfall and airflow tephra to be distinguished. In addition, they showed that the cooling rate of the above deposits correlated better with the deposit thickness, than with the distance of the deposit from the source.

IN recent years ^{57}Fe Mössbauer spectroscopic studies have shown that the ordering of the Fe^{2+} and Mg^{2+} ions between the $M(1)$ and $M(2)$ crystallographically inequivalent cation sites in orthopyroxenes is temperature-dependent, and may be used as a geothermometer to study the cooling histories of such minerals (Hafner and Virgo, 1969; Virgo and Hafner, 1969, 1970; Hafner *et al.*, 1971; Bancroft, 1973).

In these studies, both synthetic and a selection of natural orthopyroxenes from various volcanic and metamorphic rocks from a variety of locations were used to investigate initially the theoretical and practical feasibility of this geothermometer. Following this, only a small number of natural orthopyroxenes have been investigated. In general, these show that orthopyroxenes from volcanic rocks yield significantly higher temperatures (more rapidly quenched) than those from intrusive and metamorphic rocks (Ghose and Hafner, 1967; Virgo and Hafner, 1970).

In this paper we report the results of a similar Mössbauer spectroscopic study of the cooling history of hypersthene orthopyroxenes from the stratigraphic volcanic tephra sequence of the Taupo Pumice formation, North Island, New Zealand. The sequence was selected as it has been characterized by previous stratigraphic studies. It comprises recent volcanic tephra, the members of which erupted within a hundred years of each other and are all less than 2100 ± 100 years old. The members in order youngest to oldest are: Upper Taupo Pumice, Rhyolite Block, Taupo Lapilli, Rotongaio Ash, Putty Ash, and Hatepe Lapilli (Ewart, 1963; Healy, 1964; Poole, 1974). In addition, it was possible to sample this sequence in a number of different locations, to see if such a geothermometric Mössbauer spectroscopic study could be used to elucidate any intermember and/or intramember correlations between their respective cooling histories.

Geothermometric considerations

Hypersthene composition and structure. Hypersthene is a member of the orthopyroxene series in the composition range $Mg_{0.7}Fe_{0.3}SiO_3$-$Mg_{0.5}Fe_{0.5}SiO_3$ (Deer *et al.*, 1970). In the pyroxene structure the M_1 octahedral cation site is regular and contains principally Mg^{2+} while the M_2 is more distorted and occupied principally by Fe^{2+} together with small amounts of Ca^{2+} and Mn^{2+} (Ghose, 1965; Deer *et al.*, 1970).

Mg^{2+}-Fe^{2+} distribution (order-disorder phenomenon). In general, cations exhibit degrees of differential preference among such non-equivalent octahedrally coordinated sites. In orthopyroxenes with $Fe/(Fe+Mg) < 0.6$ the process of ordering or disordering is considered as an ideal temperature-dependent interchange reaction involving the partitioning of ferrous and magnesium ions between M_1 and M_2 (Virgo and Hafner, 1969). It is formulated by the simple relationship

$$Mg(M_1) + Fe(M_2) \rightleftharpoons Fe(M_1) + Mg(M_2)$$

and the equilibrium constant for the above reaction at a certain P and T is given by

$$K = \frac{X_{\mathrm{Fe}}^{M_1}(1 - X_{\mathrm{Fe}}^{M_2}) f_{\mathrm{Fe}}^{M_1} f_{\mathrm{Mg}}^{M_2}}{(1 - X_{\mathrm{Fe}}^{M_1}) X_{\mathrm{Fe}}^{M_2} f_{\mathrm{Mg}}^{M_1} f_{\mathrm{Fe}}^{M_2}}$$

where $X_{\mathrm{Fe}}^{M_1}$, $X_{\mathrm{Fe}}^{M_2}$ are site-occupancy factors or the atomic ratio $\mathrm{Fe}^{2+}/(\mathrm{Fe}^{2+} + \mathrm{Mg}^{2+})$ for the M_1, M_2 sites respectively. Similarly, $f_{\mathrm{Fe}}^{M_1}$,M_2 is the respective partial activity coefficient for M_1 or M_2. K is mainly a function of T. P has little influence (Saxena, 1973). The low activation energies for ordering and disordering ($Ea_o = 63$ kJ mol^{-1} and $Ea_d = 83$ kJ mol^{-1} respectively) indicate that the rates of Mg^{2+}-Fe^{2+} diffusion in orthopyroxenes are relatively rapid in contrast to the sluggish rates of atomic order-disorder transitions in many silicate minerals (Hafner and Virgo, 1969). It is considered that this cation ordering takes place in two steps. The first from 1000° to approximately 600° is rapid (short-range diffusion) and the second step from about 600° to 480° is very slow (long-range diffusion), and could require times of a geological scale. Temperatures thus obtained in this latter range, from the quenched metastable cation distributions, may be used as a geologic thermometer to study the cooling histories of the respective orthopyroxene minerals (Hafner and Virgo, 1969; Virgo and Hafner, 1969, 1970; Bancroft, 1973). The measurement of such cation distribution may readily be obtained by the use of ^{57}Fe Mössbauer spectroscopy and associated computer-based curve-fitting procedures.

Experimental

Representative samples (approximately 600 g) of the Upper Taupo Pumice, Taupo Lapilli, Rotongaio Ash, Putty Ash, and Hatepe Lapilli members were collected from four sites near Lake Taupo, North Island, New Zealand (see figs. 1 and 2, Table I). The Rhyolite Block member was observable at only one site and as it was strongly weathered, no sample was collected. The Upper Taupo Pumice, Taupo Lapilli, and Hatepe Lapilli samples were lightly crushed and the hypersthene fraction, which constituted less than 0.6 wt%, separated magnetically. Dust particles and other surface contaminants were removed by ultrasonification, and the resulting hypersthene fraction further purified by density separation methods. The purity of the final hypersthene separates was checked by optical and X-ray diffraction methods. Because of the extremely fine-grained nature of the ash samples, no attempt was made to separate the hypersthene from these.

The hypersthene compositions were determined by X-ray fluorescence analysis, using the glass

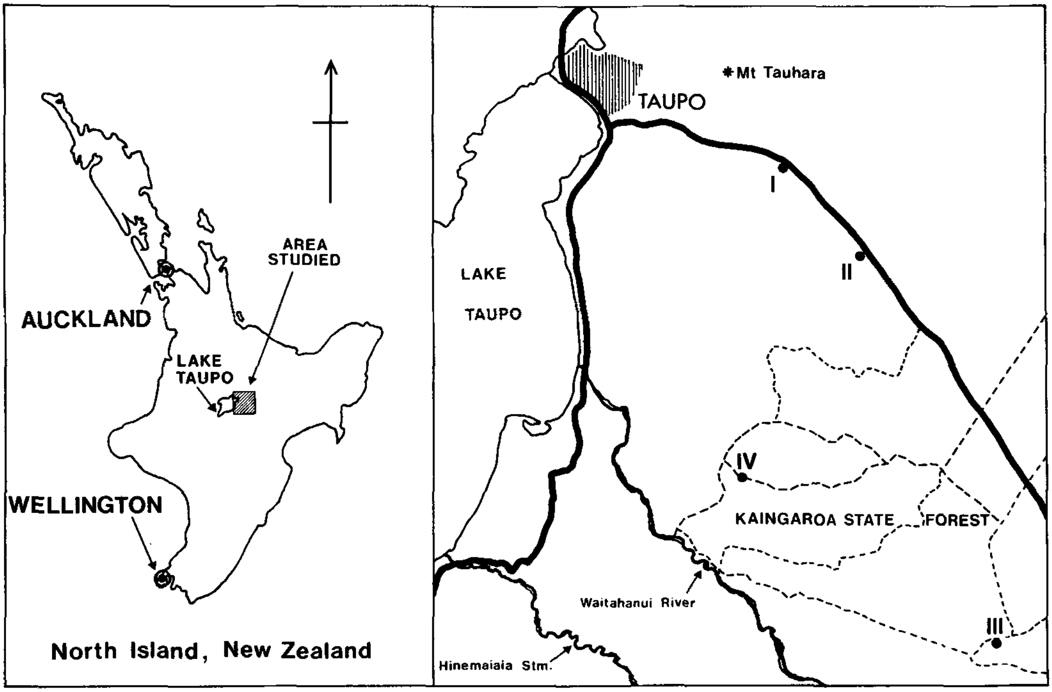

FIG. 1. The sampling area and sites. Sampling sites numbered. State Highway bold, forest roads pecked.

TABLE I. *Sample location*

Site	Map reference	Sample no.	Member
I	NZMS 1	1	Upper Taupo Pumice
	N94/631699	2	Taupo Lapilli
		3	Rotongaio Ash
		4	Putty Ash
		5	Hatepe Lapilli
II	NZMS 1	6	Upper Taupo Pumice
	N94/665302	7	Taupo Lapilli
		8	Rotongaio Ash
		9	Putty Ash
		10	Hatepe Lapilli
III	NZMS 1	11	Rotongaio Ash
	N103/719138	12	Hatepe Lapilli
IV	NZMS 1	13	Upper Taupo Pumice
	N103/614208	14	Taupo Lapilli
		15	Rotongaio Ash
		16	Putty Ash
		17	Hatepe Lapilli

fusion method of Norrish and Hutton (1969). A selection of the results are shown in Table II. These show the samples do in fact lie within the hypersthene composition range.

^{57}Fe Mössbauer spectra, using a ^{57}Co source in a copper matrix, were obtained at room temperature for all samples using a 400-channel constant-acceleration Mössbauer spectrometer (Johnston and Nixon, 1971). Counts were accumulated for each spectrum until peak absorptions (peak heights) approaching 10^6 counts were obtained. To avoid line-broadening effects due to excessive sample thickness, all samples contained 8 mg Fe per cm^2 of sample area (Bancroft, 1973).

Four Lorentzian peaks (two ferrous doublets) were computer-fitted to each experimental spectrum using a modified version of the χ^2 non-linear regression minimization procedure of Stone (1967). The resulting χ^2 values and residual deviations plots showed that the fits were all statistically acceptable (Johnston, 1977). The δ and Δ values for each spectrum are shown in Table III, and the respective peak area ratio data (required for subsequent calculations) in Table IV.

TABLE II. *Typical hypersthene compositions as determined by X-ray fluorescence analysis. The results tabulated are the number of respective atoms per six oxygen atoms*

Sample no.	Tetrahedral framework		M_1,M_2 octahedral sites					
	Si^{4+}	Al^{3+}	Fe^{2+}	Mg^{2+}	Ca^{2+}	Mn^{2+}	K^+	Na^+
2	1.930	0.070	1.031	0.857	0.049	0.046	0.012	0.005
7	1.907	0.093	1.045	0.850	0.050	0.046	0.009	—
10	1.936	0.064	1.024	0.867	0.051	0.046	0.008	0.003
12	1.929	0.071	1.024	0.868	0.050	0.047	0.008	0.003
13	1.931	0.069	1.039	0.855	0.051	0.046	0.009	—
17	1.927	0.073	1.056	0.837	0.050	0.043	0.011	0.003

Previously Virgo and Hafner (1968, 1969, 1970) have suggested it is necessary to record the orthopyroxene Mössbauer spectra at liquid nitrogen temperature (80 °K), in order to resolve the component overlapping peaks sufficiently and obtain precise site-occupancy data. Such low-temperature facilities were not available in this laboratory. However, the computer-based curve-fitting procedure used here enabled these component peaks to be resolved with sufficient accuracy in the room-temperature spectra, negating the necessity for liquid nitrogen facilities. Also in this work a single spectrum spanned 400 channels thus providing greater resolution than that of Virgo and Hafner (1968, 1969, 1970) whose spectra spanned only 200 channels. To verify the fitting procedure the experimental spectra of samples 6 and 12 were each subjected to a number of computer-fitting attempts, with significantly varied initial estimates

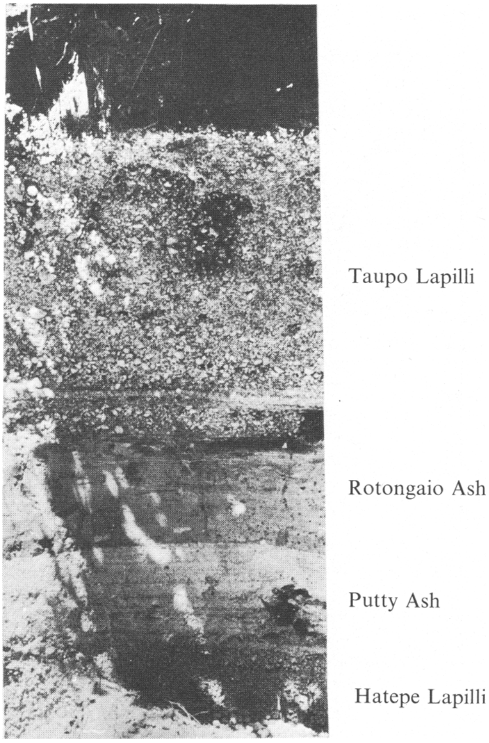

FIG. 2. The section at site I showing the respective Lapilli and Ash members.

for the peak position, width, and particularly the area parameters. For each spectrum these attempts either diverged, or converged, yielding identical fitted parameters respectively. This shows that the fit obtained and hence the resulting site-occupancy parameters for each orthopyroxene sample are in fact unique. Thus meaningful geothermometric data may be obtained from such room-temperature Mössbauer spectra.

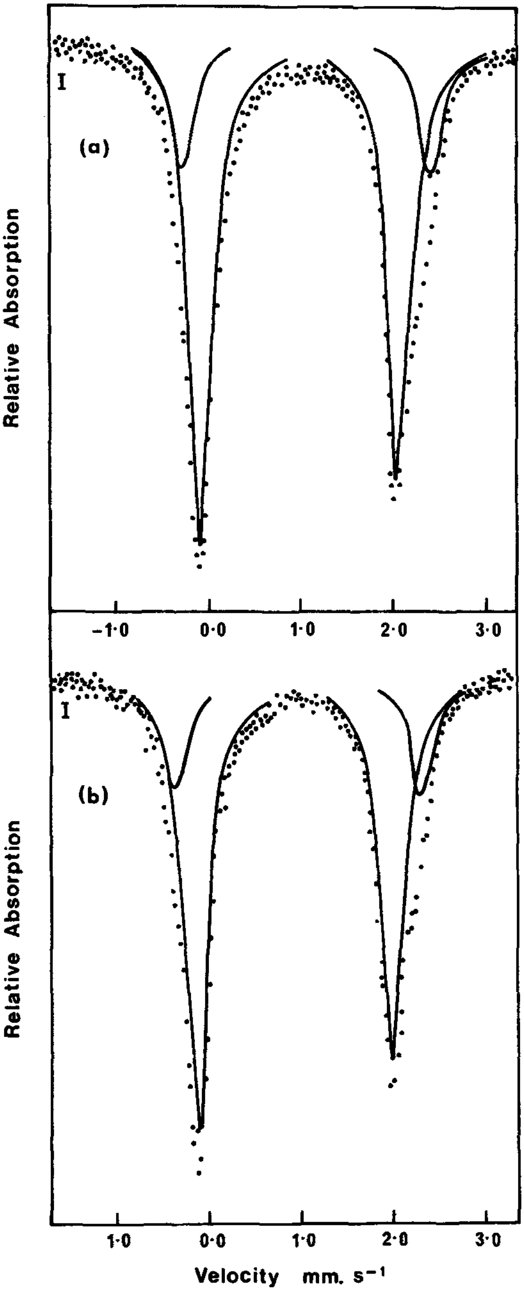

FIG. 3. The experimental and computer-fitted Mössbauer spectra for hypersthene from: (*a*) Upper Taupo Pumice; (*b*) Hatepe Lapilli.

The Δ and δ values are consistent with those quoted by Bancroft *et al.* (1967) for hypersthenes of similar composition (Table III). Typical examples of the Mössbauer spectra with computer-fitted peaks for the Upper Taupo Pumice and Hatepe Lapilli members are shown in fig. 3.

Calculation of site occupancy factors

According to Bancroft *et al.* (1967), Virgo and Hafner (1969, 1970), and Bancroft (1973), the outer Fe^{2+} doublet peaks in the Mössbauer spectrum of hypersthene (fig. 3) arise from ferrous ions in the less distorted M_1 site, and the inner doublet peaks from ferrous ions in the more distorted M_2 site.

Hence, using the appropriate computer-fitted peak areas as a measure of the Fe^{2+} content of the M_1 and M_2 sites respectively, the ratio of Fe^{2+} in each site to the total Fe^{2+} is calculated from:

$$Fe^{2+}_{M_1}/(Fe^{2+}_{M_1}+Fe^{2+}_{M_2}) \text{ and } Fe^{2+}_{M_2}/(Fe^{2+}_{M_1}+Fe^{2+}_{M_2}).$$

For this, however, only the high-velocity peaks of the quadrupole doublets were used, as these are more clearly resolved, and hence have a smaller associated error (see, for example, Dollase, 1975; Johnston, 1977).

The appropriate site-occupancy factor $X^{M_1}_{Fe}$ for the M_1 site etc. is calculated from (Saxena and Ghose, 1971):

$$X^{M_1}_{Fe} = \{Fe^{2+}_{M_1}/(Fe^{2+}_{M_1}+Fe^{2+}_{M_2})\}\{2Fe^{2+}/(Fe^{2+}+Mg^{2+})\}$$

where Fe^{2+} and Mg^{2+} are the atomic fractions of iron and magnesium per formula unit of hypersthene, as determined from the chemical analyses (Table II).

The temperatures corresponding to these resulting site-occupancy factors were then determined from the ideal equilibrium distribution isotherms (Saxena and Ghose, 1971) (see fig. 4). Table IV lists the site-occupancy factors and corresponding temperature for each sample, together with the respective sample-source distances and thickness of the deposit at the sampling site.

Discussion

The stratigraphy, mineralogy, sources of eruption, and aerial distribution of the Upper Taupo Pumice, Taupo Lapilli, and Hatepe Lapilli have been previously determined (Ewart, 1963; Healy, 1964; Poole, 1974). However, the chemical and physical conditions at the time of and subsequent

TABLE III. *Mössbauer parameters for the hypersthene separates*

Sample no.	Inner peaks		Outer peaks	
	δ (mm s^{-1})*	Δ (mm s^{-1})	δ (mm s^{-1})*	Δ (mm s^{-1})
1	0.925±0.007	2.074±0.008	0.951±0.025	2.552±0.019
2	0.923±0.007	2.056±0.007	0.956±0.020	2.534±0.012
5	0.930±0.010	2.077±0.009	0.957±0.031	2.552±0.022
6	0.931±0.008	2.067±0.008	0.963±0.027	2.550±0.021
7	0.937±0.008	2.095±0.008	0.966±0.023	2.576±0.021
10	0.935±0.009	2.079±0.009	0.958±0.023	2.589±0.018
12	0.919±0.008	2.054±0.008	0.959±0.025	2.511±0.019
13	0.924±0.007	2.070±0.008	0.948±0.024	2.567±0.017
14	0.924±0.007	2.061±0.008	0.956±0.023	2.533±0.020
17	0.937±0.009	2.075±0.009	0.967±0.023	2.580±0.018
43.1% Fe^{2+}†	0.92 ±0.02	2.05 ±0.02	0.94 ±0.04	2.35 ±0.04
48.4% Fe^{2+}†	0.90 ±0.02	2.01 ±0.02	0.92 ±0.04	2.39 ±0.04

* With reference to a copper source matrix.

† Mössbauer parameters for orthopyroxenes with varying Fe^{2+} content (after Bancroft *et al.*, 1971).

to the eruptions are less well known. The deposits studied here, erupted within a short time of one another, fed either from one common magma source at depth or separate magma chambers tapping a deeper common parent magma. Ages have been determined by carbon-14 dating of the organic material (mainly carbonized wood) buried by the deposits. These are 1785±80, 1795±70, and 2035±75 years BP for the Upper Taupo Pumice, Taupo Lapilli, and Hatepe Lapilli members respectively (Grant Taylor and Rafter, 1971). Isopach maps show that the volume of erupted material is greatest for the Taupo Lapilli and least for the Hatepe Lapilli (Healy, 1964).

The temperatures obtained (Table IV) for these volcanic hypersthenes range from 480-680 °C and therefore reflect the cooling history rather than the crystallization temperatures. This range, in particular the temperature of 680°, is greater than that reported by Virgo and Hafner (1970) for orthopyroxenes of volcanic rocks. Temperatures obtained for the Upper Taupo Pumice member at all the sites are consistent with the limiting temperature of 480 °C for maximum ordering, and suggest this member was subject to conditions of gradual cooling (Table IV). The Upper Taupo Pumice is considered to be an airflow deposit. In this, the erupted mixture comprises gas and solid particles, and behaves as a fluidized mass, which is propelled close to ground level (Baumgart and Healy, 1956). Such a mass would not be subjected to rapid cooling in transit, and once deposited would cool slowly, hence resulting in maximum cation order. No correlations with distance from the source or thickness of the deposit are apparent (Table IV).

Both the Taupo and Hatepe Lapilli members are considered to be airfall deposits, which may therefore undergo more rapid cooling, hence reflect higher temperatures. The temperatures for the Taupo Lapilli range from 480-585 °C and the

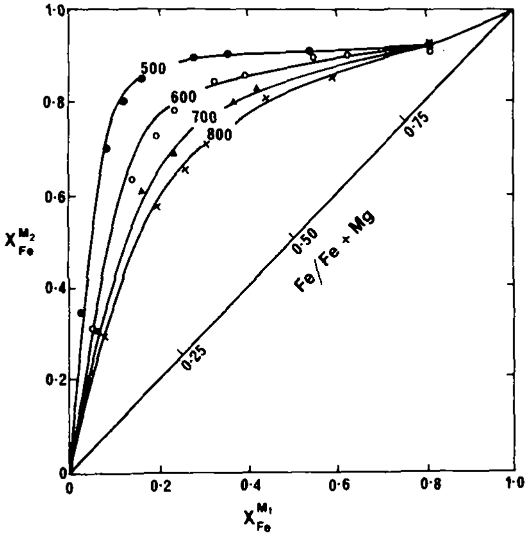

FIG. 4. The ideal equilibrium distribution isotherms for the Mg^{2+}-Fe^{2+} partitioning between the M_1 and M_2 sites in heated natural orthopyroxenes (after Saxena and Ghose, 1971).

TABLE IV. *Site-occupancy factors, corresponding equilibrium temperatures, and physical characteristics of the respective members of the Taupo Pumice formation*

Member	Site	Sample no.	$\frac{Fe^{2+}*}{Fe^{2+}+Mg^{2+}}$	$\frac{Fe^{2+}_{M_1}\dagger}{Fe^{2+}_{M_1}+Fe^{2+}_{M_2}}$	$\frac{Fe^{2+}_{M_2}\dagger}{Fe^{2+}_{M_1}+Fe^{2+}_{M_2}}$	$X^{M_1}_{Fe}$	$X^{M_2}_{Fe}$	Temperature °C ±30	Sample-source distance (km)	Thickness of deposit (m)
Upper	I	1	0.549	0.190±0.015	0.810±0.016	0.209±0.016	0.889±0.018	500	13.4	0.7
Taupo	II	6	0.549	0.182±0.016	0.818±0.017	0.200±0.017	0.898±0.019	485	11.7	0.7
Pumice	IV	13	0.549	0.169±0.013	0.831±0.016	0.186±0.014	0.912±0.024	480	3.2	0.5
Taupo	I	2	0.546	0.181±0.014	0.819±0.015	0.198±0.015	0.894±0.017	480	6.1	1.8
Lapilli	II	7	0.551	0.227±0.019	0.773±0.020	0.250±0.021	0.852±0.022	560	4.0	1.6
	IV	14	0.546	0.238±0.020	0.762±0.020	0.260±0.022	0.832±0.021	585	4.1	1.2
Hatepe	I	5	0.550	0.181±0.015	0.819±0.018	0.199±0.017	0.901±0.020	480	16.1	2.0
Lapilli	II	10	0.542	0.191±0.013	0.809±0.014	0.207±0.014	0.877±0.015	500	14.9	2.0
	III	12	0.541	0.276±0.020	0.724±0.020	0.299±0.022	0.783±0.022	680	15.0	1.5
	IV	17	0.558	0.196±0.013	0.804±0.015	0.218±0.014	0.897±0.016	480	12.8	2.0

* Determined from X-ray fluorescence analytical data.

† Determined from the computer-fitted Mössbauer peak areas.

Hatepe Lapilli from 480–680 °C (Table IV). The sample-source distances for the Taupo Lapilli are shorter than those for the Hatepe Lapilli, which could suggest that the airborne times of the former are shorter and hence cooling would be less rapid and temperatures lower. A comparison of such temperatures for sites II and IV in fact oppose this argument. Unfortunately, it was not possible to sample the Taupo Lapilli at site III to provide a further comparison for the high (680°) temperature of the Hatepe Lapilli at this site. However, from the isopach map, Poole (1974) suggested a strong south-west wind was blowing at the time of the Taupo Lapilli eruption. This could assist in quenching the airborne deposit thereby producing higher temperatures at sites II and IV for the Taupo Lapilli than for corresponding Hatepe Lapilli members. Also, for these Lapilli deposits, there is a possible correlation of temperature with deposit thickness (Table IV) showing the thicker deposits are more slowly cooled. This suggests the deposit thickness may well be significant in the cooling of airfall as well as airflow deposits. Finally, at this stage it is noted that the highest temperature of 680° recorded for the Hatepe Lapilli site III is higher than any similar previously observed temperatures for natural pyroxenes. As previously mentioned, this is in the region of rapid short-range diffusion and suggests this particular sample was cooled very rapidly indeed.

In conclusion, it appears that from this study utilizing a relatively small suite of samples, this cooling-history geothermometer is indeed useful in providing information about the physical conditions prevailing at the time of the eruption, the method of tephra transport and characteristics of the deposit. However, as with most measurements of this type, it is necessary to collect and process a much wider range of samples before any definite conclusions can be drawn or trends established.

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