

METHODS FOR ESTIMATING CURIE TEMPERATURES OF TITANOMAGHEMITES FROM EXPERIMENTAL J_s - T DATA

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Methods for determining the Curie temperature (T_c) of titanomaghemites from experimental saturation magnetization-temperature (J_s - T) data are reviewed. J_s - T curves for many submarine basalts and synthetic titanomaghemites are irreversible and determining Curie temperatures from these curves is not a straightforward procedure. Subsequently, differences of sometimes over 100°C in the values of T_c may result just from the method of calculation. Two methods for determining T_c will be discussed: (1) the graphical method, and (2) the extrapolation method. The graphical method is the most common method employed for determining Curie temperatures of submarine basalts and synthetic titanomaghemites. The extrapolation method based on the quantum mechanical and thermodynamic aspects of the temperature variation of saturation magnetization near T_c , although not new to solid state physics, has not been used for estimating Curie temperatures of submarine basalts. The extrapolation method is more objective than the graphical method and uses the actual magnetization data in estimating T_c .

1. Introduction

Curie temperatures (T_c) are frequently used as an aid in the identification of magnetic mineralogy in continental and oceanic rocks. In particular, Curie temperature data from oceanic basalts are important because these data, in conjunction with other magnetic data, are used to infer the extent of alteration and chemical composition of the magnetic oxides responsible for the marine magnetic anomalies [1–8]. In some cases different magnetic minerals have approximately identical Curie temperatures and therefore T_c data alone cannot conclusively determine the magnetic minerals present within a sample. However, T_c data in combination with the shape of the thermomagnetic curve (saturation magnetization as a function of temperature (J_s - T)) and the type of irreversible behavior exhibited by J_s upon heating and cooling can be diagnostic of the particular magnetic

minerals present. Consequently, methods for determining T_c values from experimental data is an essential first step for thermomagnetic analysis to succeed. A better understanding of the methods and assumptions for T_c determination from experimental data is therefore a vital prerequisite for thermomagnetic analysis.

The most popular method in geophysics for Curie temperature determination is the measurement of saturation magnetization as a function of temperature. Theoretically, the temperature at which $J_s = 0$ is T_c . A large class of rocks which contain magnetite, hematite or titanomagnetite exhibit reversible J_s - T curves with sharp, well-defined points where $J_s \approx 0$. Consequently, there is little problem in determining values of T_c from these curves. On the other hand, titanomaghemites, another class of magnetic minerals found in oceanic basalts, do not have reversible J_s - T curves and do not have well defined points where $J_s \approx 0$ (e.g., [1–3]). Typical examples of irreversible J_s - T curves are shown in Fig. 1. This irreversible type of J_s - T behavior of oceanic basalts is due to the un-

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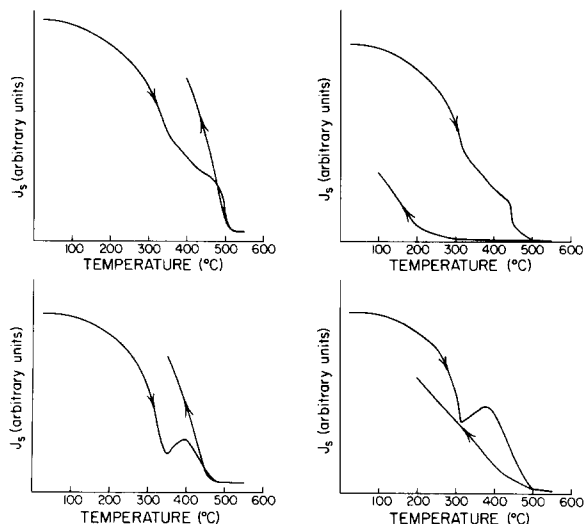


Fig. 1. Saturation magnetization-temperature curves for some oceanic basalts from Site 417D.

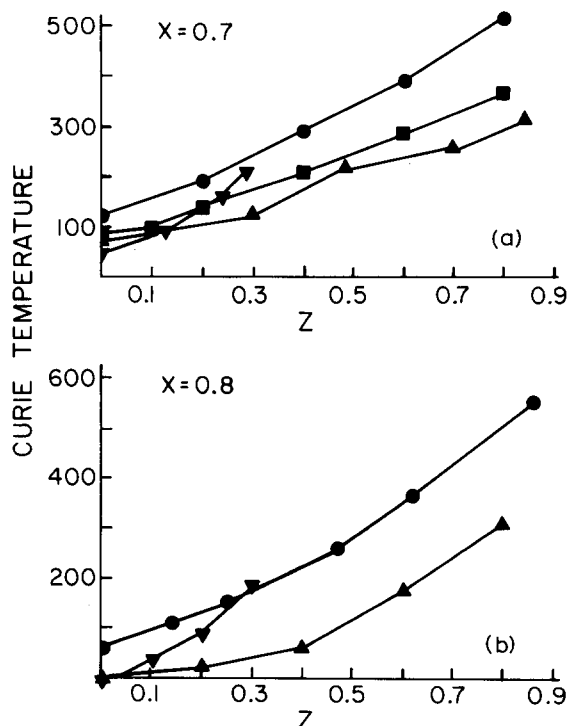


Fig. 2. Curie temperature as a function of oxidation (z) for synthetic titanomaghemites for (a) $x = 0.7$ and (b) $x = 0.8$. The symbols represent the following data: triangles [4], inverted triangles [9], squares [11] and circles [12].

mixing and inversion of the original titanomaghemites to other magnetic and nonmagnetic phases at temperatures of ~ 300 – 400°C [1,4,5]. Because the “true” Curie temperatures of titanomaghemites of most oceanic basalts are usually close to the inversion temperature, the saturation magnetization does not fall to zero and therefore the actual T_c values are difficult to determine.

A better understanding of the magnetic properties of oceanic basalts has come from studies on laboratory-produced synthetic titanomaghemites (e.g. [4, 9–13]). However, a close examination of the synthetic titanomaghemites and natural titanomaghemites on the one hand, and a comparison between the different synthetic titanomaghemite investigations on the other, have revealed a number of discrepancies. This is a particularly severe problem with regard to T_c . Curie temperature as a function of oxidation (z) is shown in Fig. 2 for titanomaghemites with initial values of $x = 0.7$ and $x = 0.8$ (where x is related to the Fe/Ti ratio of the original titanomagnetite) taken from the above sources. While it is apparent that all the studies overlap to some degree, differences of over 100°C in T_c for equal values of z are common. The large scatter in the T_c values is probably related in part to our poor understanding of the cation distribution and mechanisms of oxidation of titanomaghemites. The scatter, in part, may also be due to the uncertainties in determining T_c values from J_s - T curves.

Two methods of estimating Curie temperatures from experimental J_s - T curves will be reviewed. The first method is a graphical technique, which is adequate for determining T_c in many cases. The second method is a numerical extrapolation technique, which can be useful for T_c determinations from irreversible J_s - T data, particularly for estimating T_c values of oceanic basalts. The extrapolation method based on the thermodynamic and quantum mechanical aspects of the temperature dependence of J_s near T_c has not been utilized, to my knowledge, by the geophysical community for estimating Curie temperatures from J_s - T data.

2. Graphical methods

The method most widely used in rock magnetism to determine T_c is a graphical method proposed by

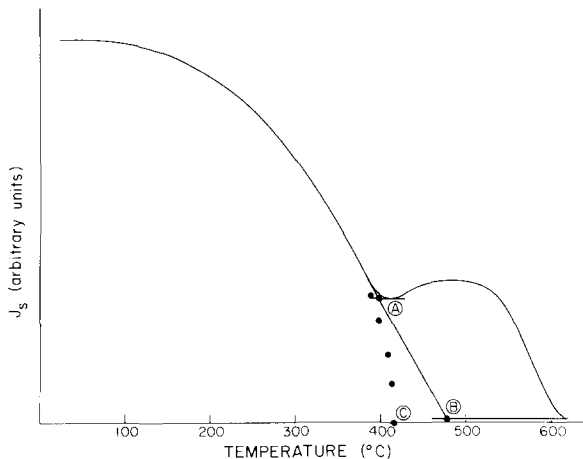


Fig. 3. Comparison of three techniques for determining Curie temperatures from J_s - T curves. Methods A and B are examples of the Grommé et al. [14] graphical method while C is an example of the extrapolation method. The data points are the extrapolated values of J_s . The letters A, B and C denote the values of T_c determined from each method.

Grommé et al. [14]. A theoretical justification for this method is that, at the Curie temperature, the Brillouin function, which is the quantum mechanical description of the temperature variation of J_s , undergoes a discontinuity in slope [15]. This discontinuity in slope causes an inflection in the J_s - T curve.

The graphical method is demonstrated in Fig. 3. Two tangents are drawn to the J_s - T curve; one below the inferred Curie temperature which represents the ferrimagnetic contribution and one above the inferred Curie temperature which represents the paramagnetic contribution. The intersection of these tangents projected to the temperature axis defines T_c . This method may yield either a lower or upper bound to T_c depending on the tangent line used above T_c (Fig. 3, A or B).

The minimum in the J_s - T curve just above 400°C (Fig. 3) is an artifact due to the inversion of the titanomaghemite and does not represent an adequate baseline. Construction A will yield a lower bound to T_c in this particular case because the true J_s - T behavior near T_c is approximately quadratic (e.g. [16,17]) and will curve away towards the temperature axis beyond the T_c value determined by A. However, construction B is also inadequate because the tangent used above T_c is based on the paramagnetic contribu-

tion of an entirely different magnetic phase produced at the expense of the original titanomaghemite. Curie temperatures of samples with low z values (slight oxidation) will not be much in error using either method A or B. Curie temperatures, however, could be overestimated by as much as 100°C for titanomaghemites with high z values using method B. A compromise would be to average the T_c values determined by the above two methods.

Similar graphical methods include defining T_c as the point of inflection or the point of maximum curvature of the J_s - T curve [18], but these methods are more tedious in practice to carry out graphically. Finally, the J_s - T curves can be differentiated numerically to yield the point of inflection or the point of maximum curvature. However, a more straight forward numerical technique will be described in the next section.

3. Extrapolation method

The extrapolation method takes advantage of the true temperature dependence of magnetization near T_c as derived by quantum mechanics and thermodynamics [16,17,19]. The thermodynamic derivation according to Belov [19] will be briefly reviewed.

At the Curie temperature, a magnetic material goes from a ferromagnetic (or ferrimagnetic or antiferromagnetic) state to a paramagnetic state and is a second order phase transition [19]. Accordingly, this phase transition can be described in terms of a thermodynamic potential function.

Near the Curie temperature J_s is small and the thermodynamic potential (ϕ) can be expanded in an even-power series in J_s [19]:

$$\phi = \phi_0 + a(T, P) J_s^2 + b(T, P) J_s^4 + \dots \quad (1)$$

where ϕ_0 is a constant and $a(T, P)$ and $b(T, P)$ are functions of temperature and pressure. The two thermodynamic coefficients $a(T, P)$ and $b(T, P)$ behave differently near T_c . The coefficient $a(T, P)$ close to T_c is small ($a(T, P) < 0$) and can be expanded in powers of $(T - T_c)$, where T and T_c are in K. On the other hand, the coefficient $b(T, P) > 0$ [19,20]. Substituting the expansion of $a(T, P)$ (to first order) into equation (1) yields:

$$\phi = \phi_0 + a'(T - T_c) J_s^2 + b J_s^4 + \dots \quad (2)$$

Neglecting terms higher than fourth order, the equilibrium value of J (below T_c) is found from the condition $d\phi/dJ_s = 0$ [19] and therefore:

$$\frac{d\phi}{dJ_s} = 2a'(T - T_c)J_s + 4bJ_s^3 = 0 \quad (3)$$

The variation of J_s with temperature near T_c is then:

$$J_s \propto (T_c - T)^{1/2} \quad (4)$$

A similar equation for J_s near T_c can be derived by the small argument expansion of the Brillouin function [17]. Experimental results indicate that the critical exponent in equation (4) varies between 0.3 and 0.6 [20] for various metals and ferrites. More relevant data for rock magnetism is given by Tucker and O'Reilly [21] for a number of single crystals of titanomagnetite ($\text{Fe}_{2.4}\text{Ti}_{0.6}\text{O}_4$). They find that the critical exponent varies between 0.32 and 0.52.

Equation (4) is an adequate description of the temperature variation of J_s near T_c for $T/T_c > 0.8$ [19]. This means that for Curie temperatures in the range of 300–500°C, equation (4) is valid from ~100°C below T_c . In order to determine T_c using this method, pick a starting temperature (T_0) approximately within 100°C below the inferred T_c . From equation (4):

$$[J_s(T)/J_{s0}]^2 = \frac{T_c}{T_c - T_0} - \frac{1}{T_c - T_0} T \quad (5)$$

where J_{s0} is the saturation magnetization at T_0 . Starting at T_0 and incrementing T by a fixed amount (say 5°C), calculate $[J_s(T)/J_{s0}]^2$ until T is approximately slightly below the temperature where the J_s - T curve flattens out and changes slope. A linear-least squares fit of the $[J_s(T)/J_{s0}]^2$ - T data will then yield the value of T_c from the slope of the best-fitting straight line to equation (5).

The advantage of this method is that it uses the magnetization data below the Curie temperature to determine T_c . Using a different exponent (<2) in equation (5) will result in a lower estimate of T_c . However, the errors associated with the least squares fit of equation (5) are the least when the exponent = 2 ($\pm 5^\circ\text{C}$) for the samples in Table 1 and 2. Finally, for T_c values between 300 and 500°C, an exponent <2 will result in less than a 10% difference in the calculated values of T_c .

Values of T_c determined by the extrapolation and

TABLE 1

Comparison of graphical and extrapolation methods for determining Curie temperatures for standard samples

Sample	Graphical method		Extrapolation method
	low ^a	high ^b	
CrO ₂	131		133
Ni	360		360
Fe ₃ O ₄	575		572

graphical methods are compared in Table 1 for Fe₃O₄, Ni and CrO₂. The correspondence is excellent. The magnetization data in Fig. 3 were extrapolated by this method and is also shown in Fig. 3 and results in a value of T_c between the two estimates from the graphical methods. Finally, for samples which have initially more than one magnetic phase, only the Curie temperature of the highest T_c phase can be calculated by this method (C.S. Grommé, personal communication, 1980).

4. Conclusions

In many instances, authors fail to mention the technique of estimating Curie temperatures from J_s - T data. Variations of 100°C in T_c may be realized just

TABLE 2

Comparison of graphical and extrapolation methods for determining Curie temperatures for some oceanic basalts and synthetic titanomagemites

Sample	Graphical method			Extrapolation method
	low ^a	high ^b	average	
52-5 ^c	348	444	396	393
53-1	324	412	368	380
54-3	338	354	346	342
50-2	328	386	357	357
9-2 ^d	267	289	278	255
9-3	335	387	361	334
9-5	377	455	416	393
9-4	387	489	438	413

^a Low estimate is based on construction A.

^b High estimate is based on construction B.

^c First 4 samples are oceanic basalts from DSDP Hole 417D and are the same samples as shown in Fig. 1.

^d 9-2 to 9-5 are synthetic titanomagemites [13].

by the method of calculating T_c from irreversible J_s - T data. This may be a contributing factor to the large scatter in reported T_c trends with oxidation for synthetic titanomaghemitites. Summarized in Table 2 are estimates of Curie temperatures determined by the graphical and extrapolation methods for some oceanic basalts and synthetic titanomaghemitites. The different values of T_c determined by the methods are evident.

With the accumulation of more data on the magnetic properties of oceanic basalts, Curie temperature data have become more important. Because of the irreversible type of J_s - T curves for the majority of oceanic basalts and synthetic titanomaghemitites, the estimation of Curie temperatures is not straightforward. The graphical method may estimate Curie temperatures either too low or too high for these materials. The extrapolation method proposed, although not new to solid state physics, has not been used for estimating Curie temperatures of submarine basalts. The extrapolation method is more objective than the graphical method and uses the actual magnetization data in estimating T_c . Although, the extrapolation method can be very useful for estimating T_c for titanomaghemitites, it can also be used for more accurate T_c determinations from reversible J_s - T data.

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References

- 1 M. Ozima and E.E. Larson, Low and high temperature oxidation of titanomagnetite in relation to irreversible changes in the magnetic properties of submarine basalts, *J. Geophys. Res.* 75 (1970) 1003–1008.
- 2 M. Ozima, M. Joshima and H. Kinoshita, Magnetic properties of submarine basalts and implications on the structure of the oceanic crust, *J. Geomag. Geoelectr.* 26 (1974) 335–343.
- 3 M. Marshall, The magnetic properties of some DSDP basalts from the north Pacific and inferences for Pacific plate tectonics, *J. Geophys. Res.* 83 (1978) 289–308.
- 4 R. Readman and W. O'Reilly, Magnetic properties of oxidized (cation deficient) titanomagnetites ($\text{Fe, Ti, } \square\text{)}_3\text{O}_4$, *J. Geomag. Geoelectr.* 24 (1972) 191–210.
- 5 H.P. Johnson and J.M. Hall, A detailed rock magnetic and opaque mineralogy study of the basalts from the Nazca plate, *Geophys. J.* 52 (1978) 45–64.
- 6 C.S. Grommé and E. Mankinen, Natural remanent magnetization, magnetic properties and oxidation of titanomagnetite in basaltic rocks from DSDP, Leg 34, in: F. Aumento, W.G. Melson et al., Initial Reports of the Deep Sea Drilling Project, 37 (1976) 425–445.
- 7 N. Petersen, P. Eisenach and U. Bleil, Low temperature alteration of the magnetic minerals in ocean floor basalts, in: Deep Drilling Results in the Atlantic Ocean: Ocean Crust, M. Talwani, C.G. Harrison and D.E. Hayes, eds. (1979) 169–209.
- 8 M. Prévot, A. Lecaille and R. Hekinian, Magnetism of the Mid-Atlantic crest near 37°N from Famous and DSDP results: a review, in: Deep Drilling Results in the Atlantic Ocean: Ocean Crust, M. Talwani, C.G. Harrison and D.E. Hayes, eds. (1979) 210–229.
- 9 M. Ozima and N. Sakamoto, Magnetic properties of synthesized titanomaghemitite, *J. Geophys. Res.* 76 (1971) 7035–7046.
- 10 J.B. O'Donovan and W. O'Reilly, The preparation, characterization and magnetic properties of synthetic analogues of some carries of the paleomagnetic record, *J. Geomag. Geoelectr.* 29 (1977) 331–344.
- 11 T. Nishitani, Grain size effects on the low-temperature oxidation of titanomagnetites, *Rock Mag. Paleogeoph.* 6 (1979) 128–136.
- 12 C. Keefer and P. Shive, Curie temperature and lattice constant reference contours for synthetic titanomaghemitites, *J. Geophys. Res.* (in press).
- 13 B.M. Moskowitz and S.K. Banerjee, The magnetic properties of synthetic titanomaghemitites and some ocean basalt, I. The oxidation-grain size dilemma (submitted to *J. Geophys. Res.*).
- 14 C.S. Grommé, T.L. Wright and D.L. Peck, Magnetic properties and oxidation of iron-titanium oxide minerals in Alae and Makaopuhi lava lakes, Hawaii, *J. Geophys. Res.* 74 (1969) 5277–5294.
- 15 T.R. McGuire and P.J. Flanders, Direct current magnetic measurements, in: Magnetism and Metallurgy, I, A.E. Berkowitz and E. Kneller, eds. (1969) 124–189.
- 16 A. Morris, The physical principles of Magnetism (Wiley, New York, N.Y., 1965).
- 17 J.S. Smart, Effect Field Theories of Magnetism (Saunders, Philadelphia, Pa., 1966).
- 18 J.M. Ade-Hall, R.L. Wilson and P.J. Smith, The petrology, Curie points and natural magnetization of basic lavas, *Geophys. J.* 9 (1965) 323–336.
- 19 K.P. Belov, Magnetic Transitions (Consultants Bureau, New York, N.Y., 1959).
- 20 S.V. Vonsovskii, Magnetism, 2 (Wiley, New York, N.Y., 1974).
- 21 P. Tucker and W. O'Reilly, A magnetic study of single-crystal titanomagnetite ($\text{Fe}_{2.4}\text{Ti}_{0.6}\text{O}_4$), *Phys. Earth Planet. Inter.* 16 (1978) 183–189.