Measuring the Curie Temperature

MagIC Global Seminar Series
November 19th, 2013 4:30pm PST

Maggie Avery, UCSD

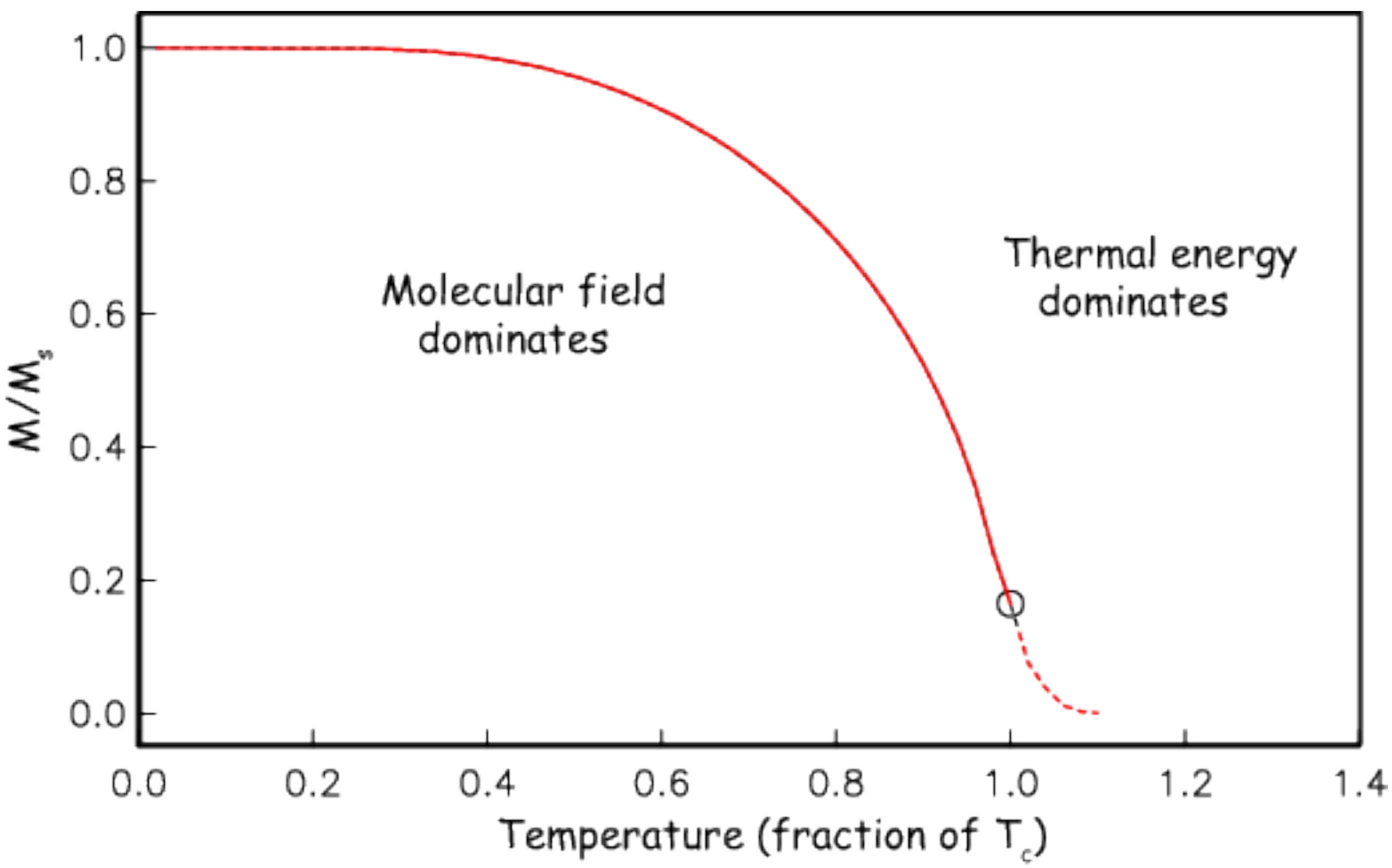
Outline

- Basic background info
- How we measure T_C at SIO
- Discuss THE PAPER
- How do you put it into the database?

Basic Background Information

- Curie point temperature: what it is?
- For ferromagnetic, ferrimagnetic, or antiferromagnetic material, the Curie temperature (T_C) is the temperature where uncompensated spins in zero-field undergo a second-order phase transition from a thermally disordered high-temp state to a magnetically ordered low-temp state.

Basic Background Information

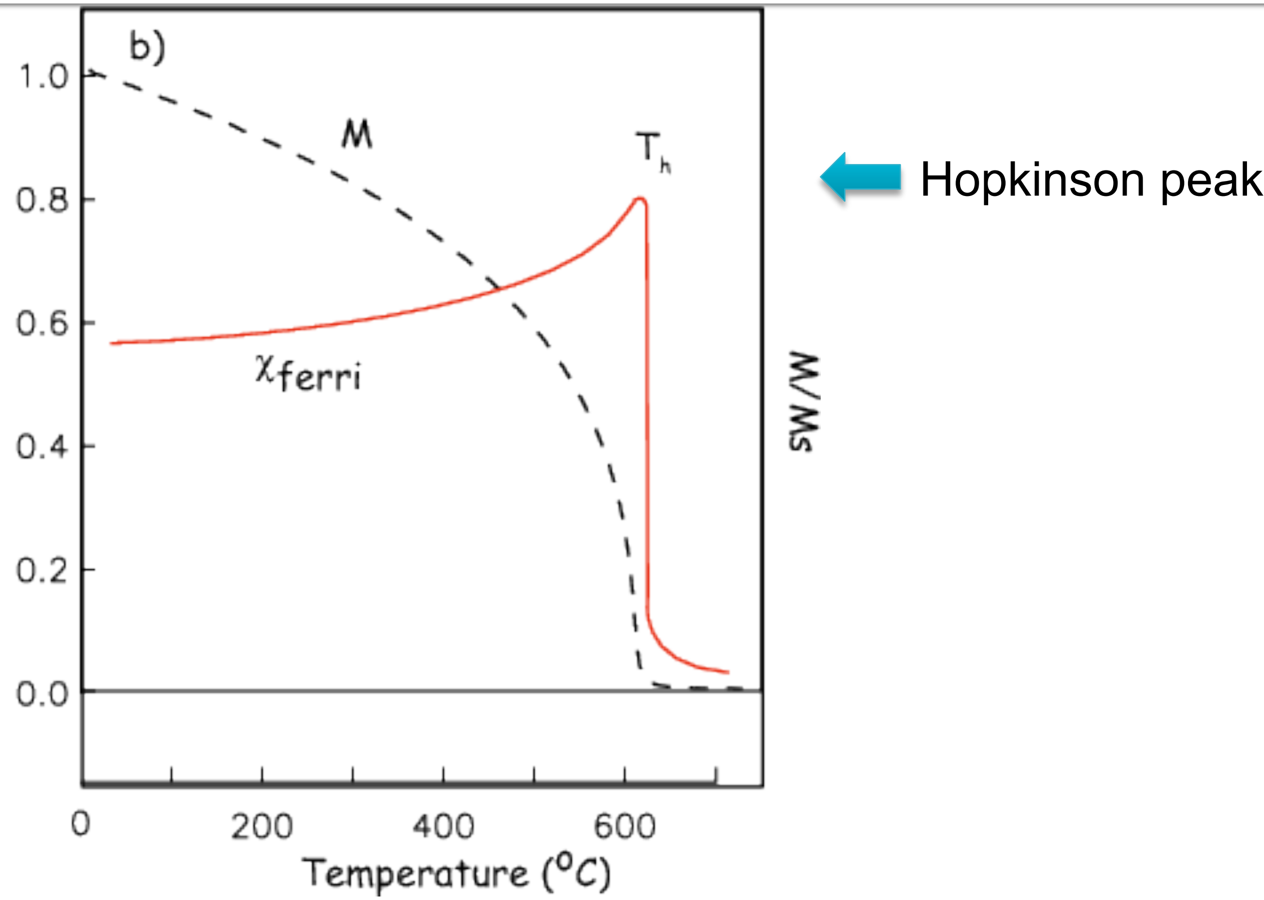


- Variation of spontaneous magnetization, M_s, with temperature in magnetite
- Figure 3.7 from Tauxe, 2nd web ed. 2012

Basic Background Information

- Curie point temperature: what do you measure to determine it?
- magnetization or susceptibility as a function of temperature

Basic Background Information



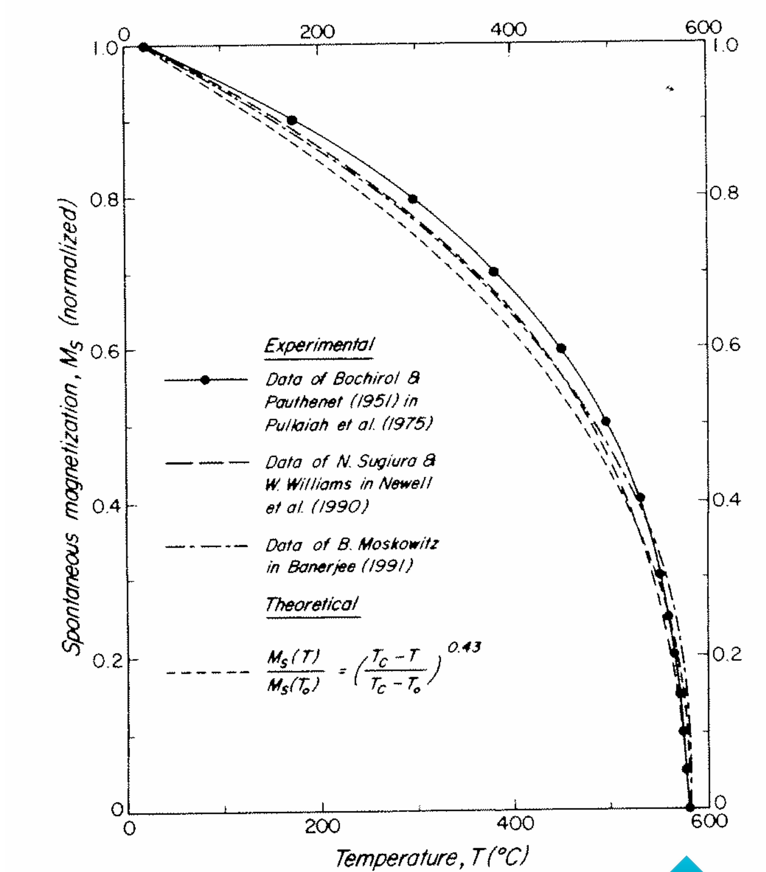
- Behavior of ferromagnetic susceptibility (solid line) as the material approaches its Curie temperature (M_s-T data shown as dashed line).
- Figure 8.5 b) from Tauxe, 2nd web ed. 2012

Basic Background Information

- Curie point temperature: what is it good for?

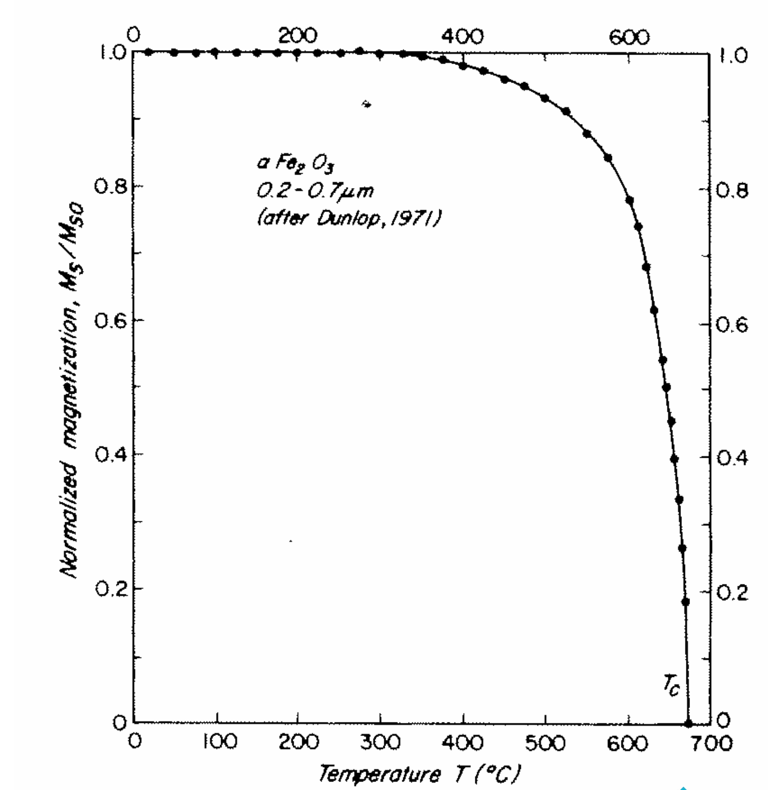
- Magnetic mineral identification!

Basic Background Information



Magnetite

578ºC

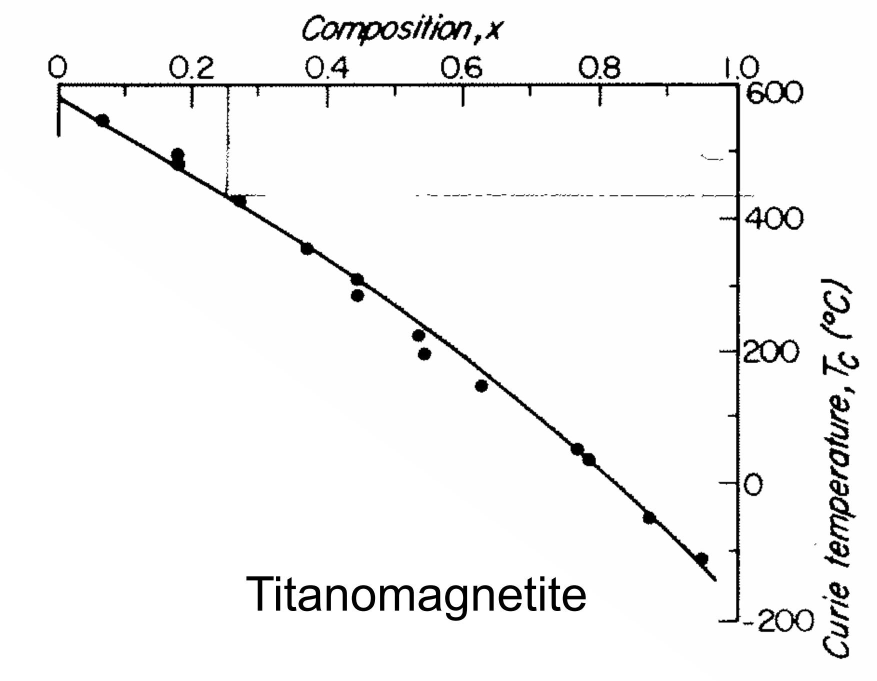


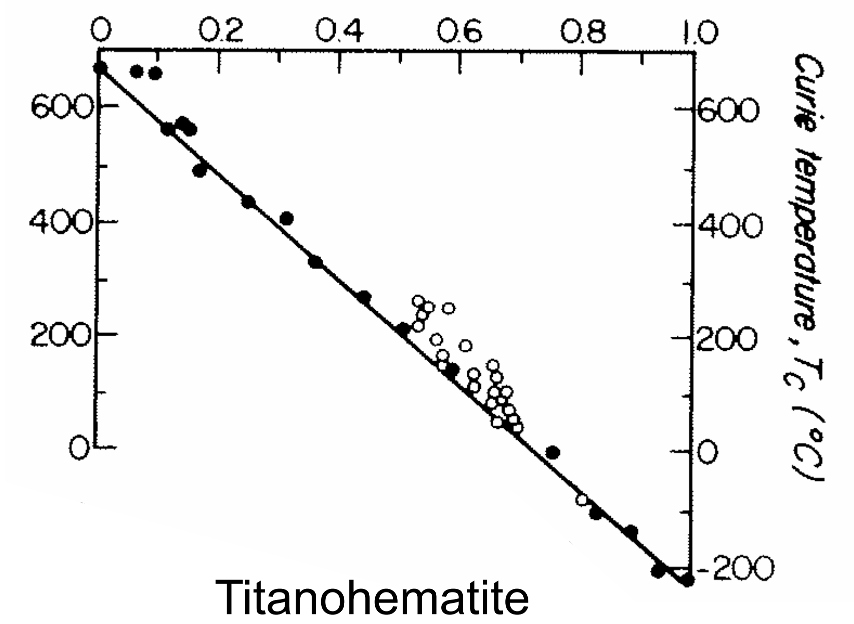
Hematite

680ºC

- Variation of spontaneous magnetization, M_s, with temperature in magnetite and hematite
- Figures 3.5 and 3.20 from Dunlop and Özdemir, 1997

Basic Background Information

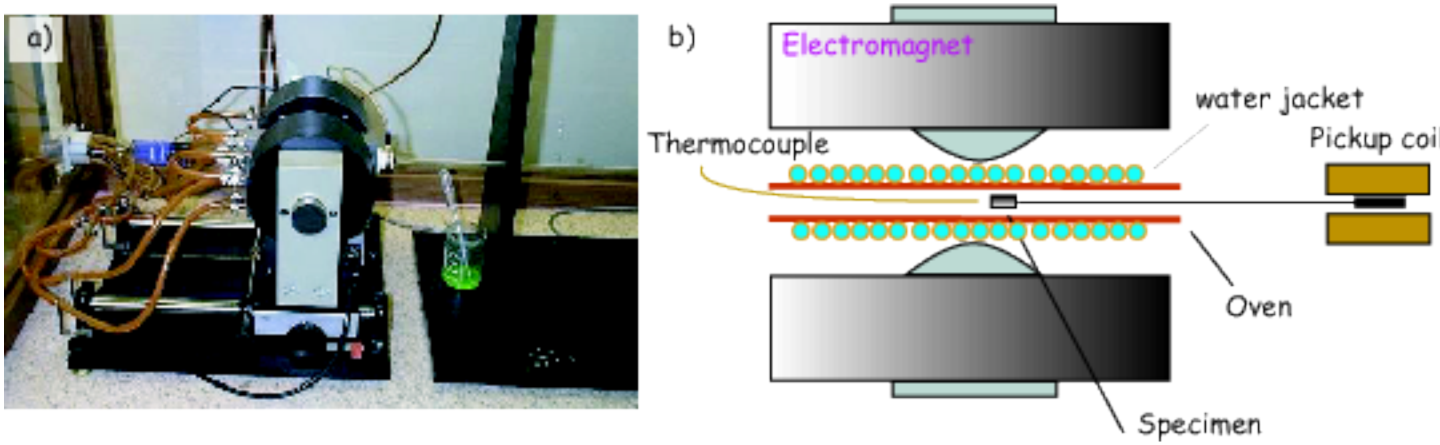




- Curie temperature of a function of titanium content, x, in titanomagnetite and titanohematite
- Figures 3.11 and 3.23 from Dunlop and Özdemir, 1997

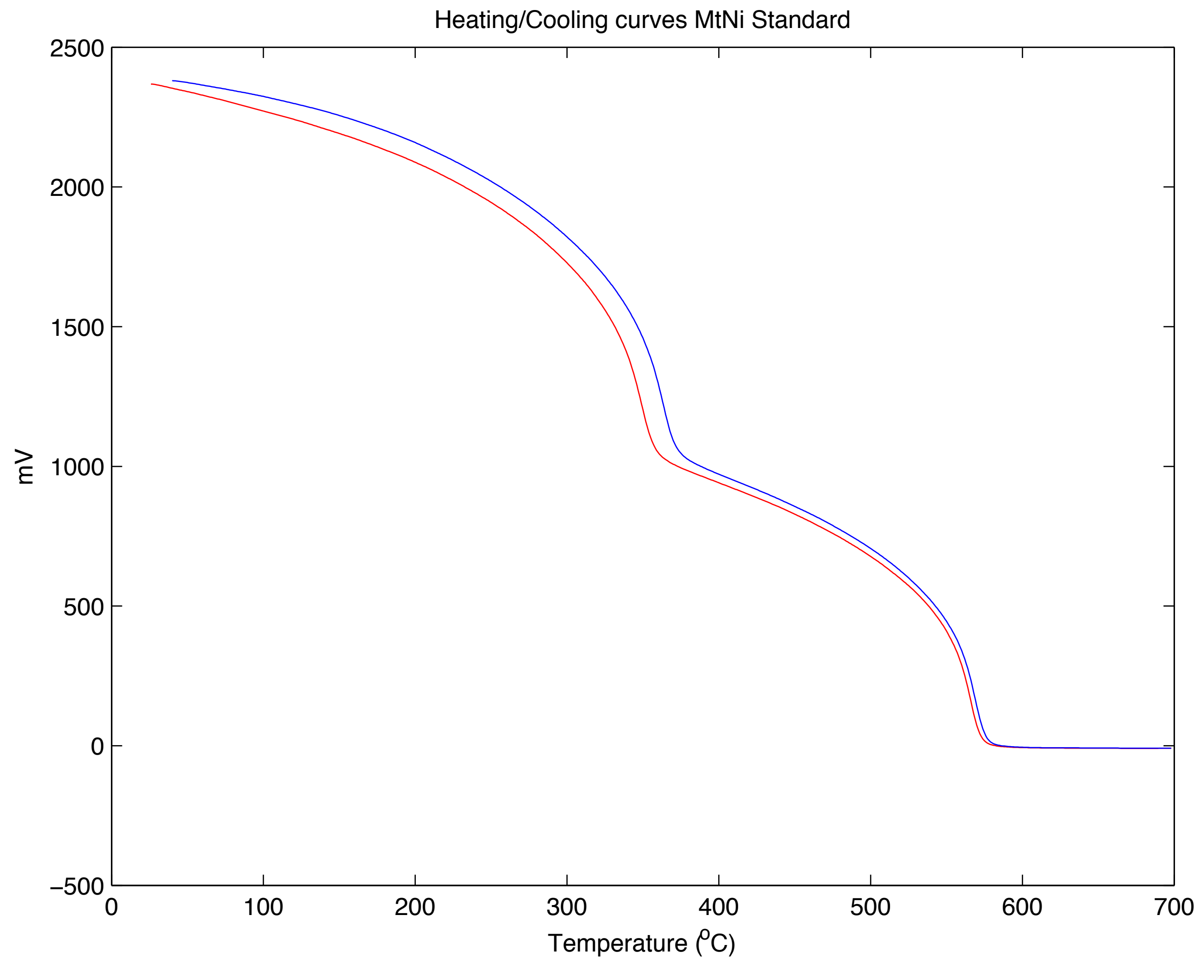
What we do at SIO

What we do at SIO

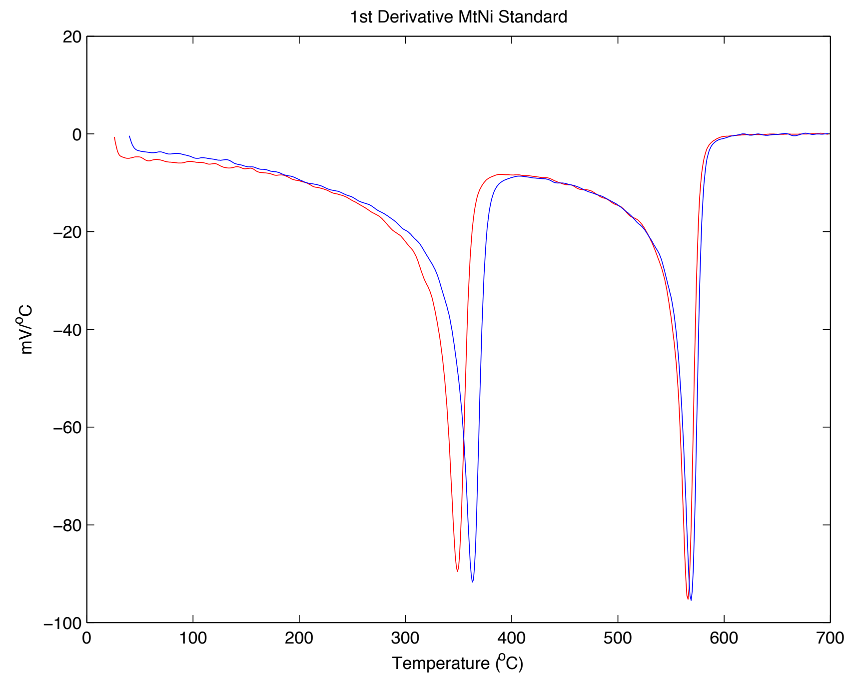


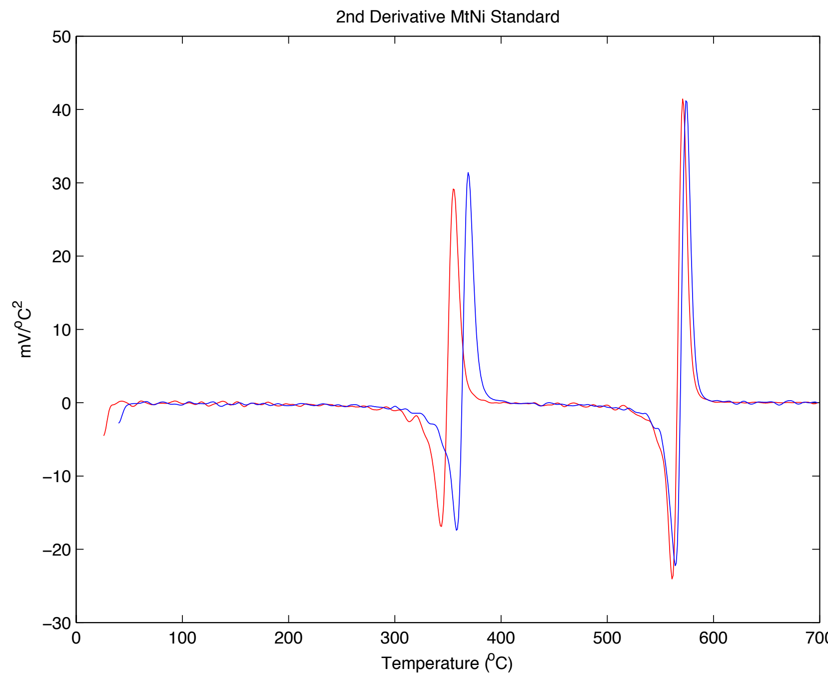
- Horizontal Curie balance
  - A specimen is placed near the pole pieces of a strong electromagnet. The field gradient will pull a magnetic specimen in. A pick-up coil counteracts this force with a restoring force of equal magnitude. The current required to keep the specimen stationary is proportional to the magnetization. A thermocouple monitors the temperature as the specimen heats in a water cooled oven. Both the output of the pickup coil and the thermocouple can be put into a computer to make a graph of saturation magnetization versus temperature
- Figure 8.2 from Tauxe, 2nd web ed. 2012

What we do at SIO

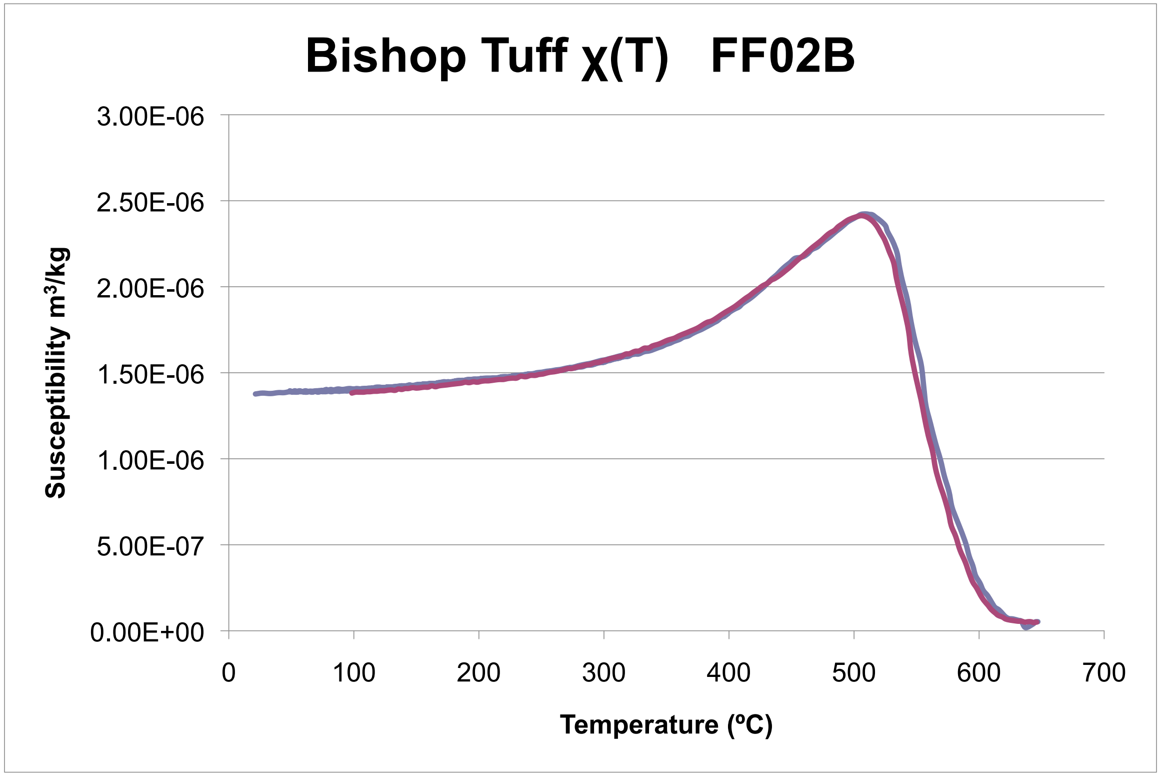


What we do at SIO





Example from Tuff project



- Where do you pick T_C? Min. dχ/dT on heating (556.5ºC) or cooling (541.7ºC)?
- Measured at the IRM by Julie Bowles

Why is it so hard to measure T_C?

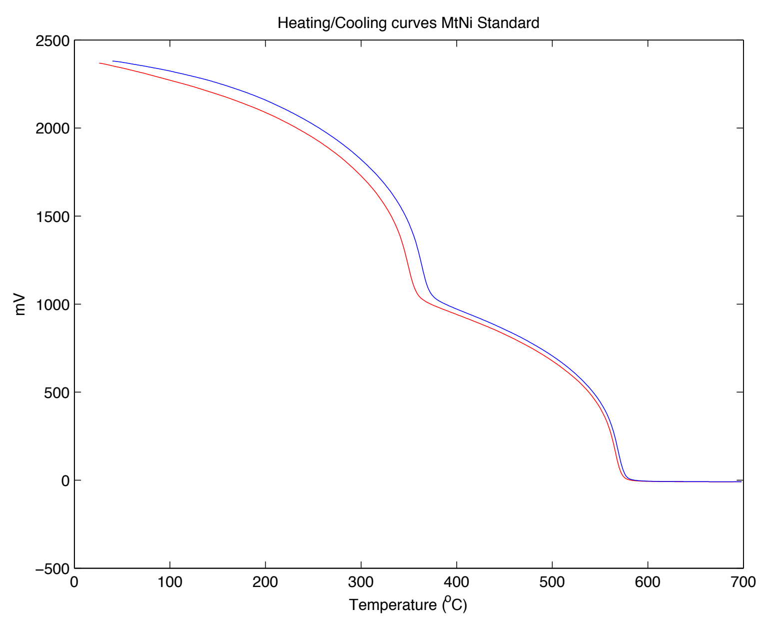
- The transition from a less magnetized to a more magnetized state happens over 10-30ºC, within that interval where is T_C?

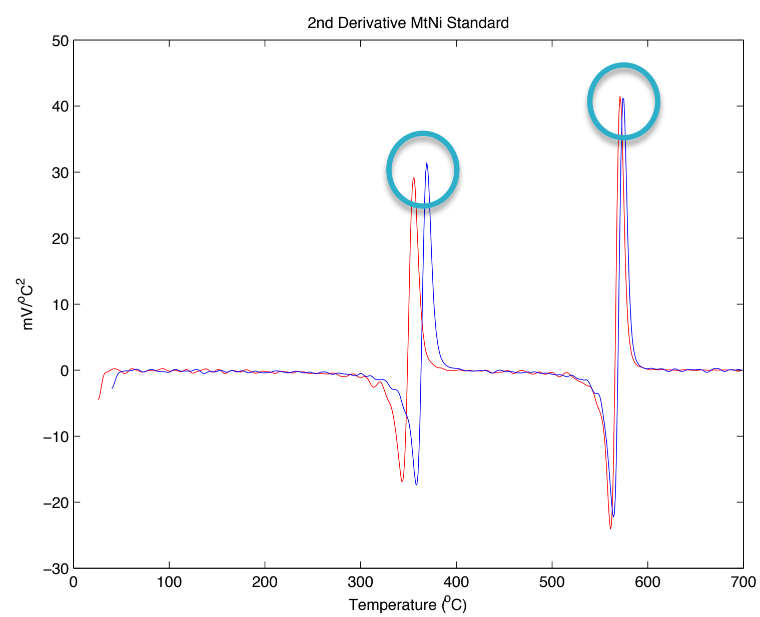
- Factors that smooth phase transition:
  - Paramagnetic minerals
  - Inhomogeneity of the ferromagnetic material
  - Temperature gradient inside the sample

- Zero-field theory used to interpret in-field measurements

Common methods to determine T_C

- Maximum curvature-
  - the temperature at which the curvature of the concave part of the heating curve is a maximum





Common methods to determine T_C

- Graphical
  - Two-tangent crossing – Draw straight lines approximately coinciding with the J-T curve above and below the estimated Curie point, and project their intersection to the temperature axis
  - Moskowitz 1981 – extrapolate using only data acquired below T_C

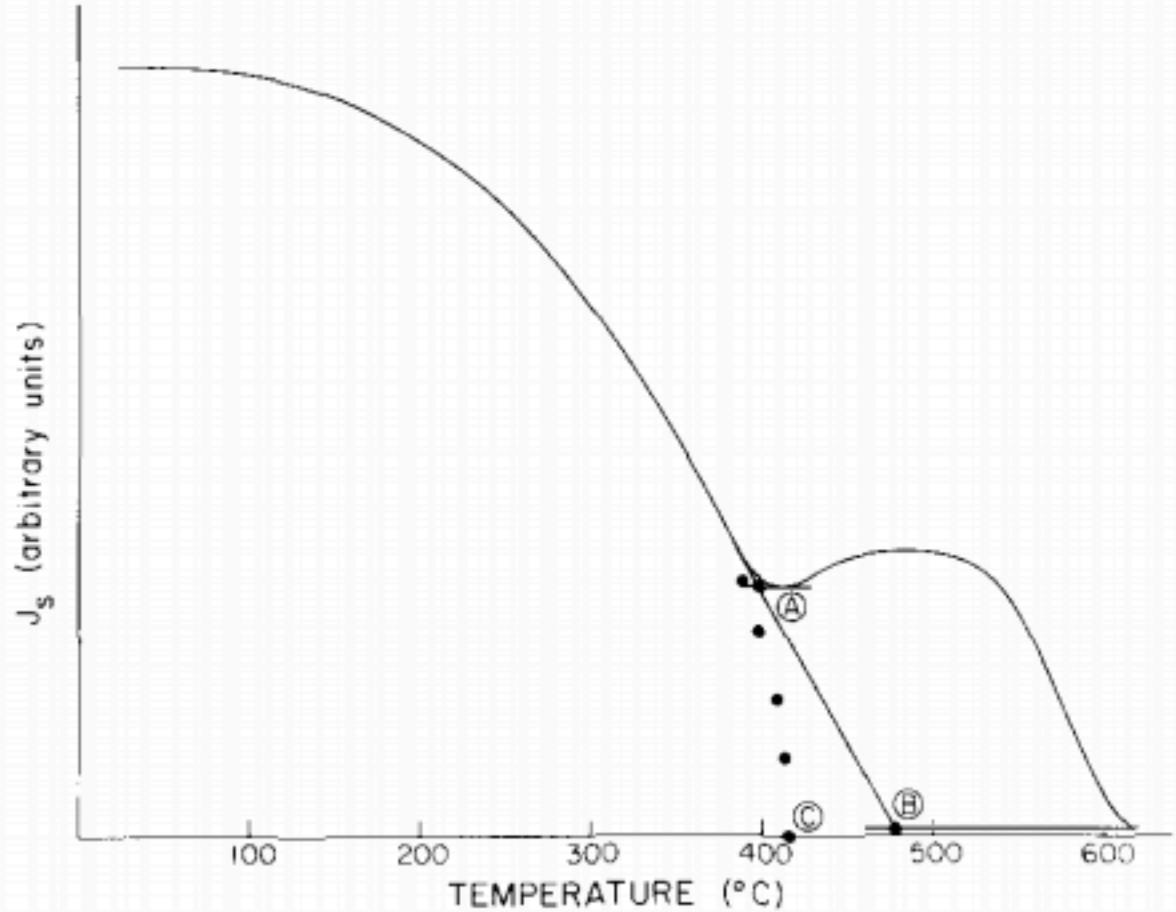


Fig. 3. Comparison of three techniques for determining Curie temperatures from J_s-T curves. Methods A and B are examples of the Grommé et al. [14] graphical method while C is an example of the extrapolation method. The data points are the extrapolated values of J_s. The letters *A*, *B* and *C* denote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

- Figure 3 Moskowitz 1981

Geochemistry Geophysics Geosystems G^3

Article
Volume 14, Number 4
24 April 2013
doi:10.1029/2012GC004440
ISSN: 1525-2027

Published by AGU and the Geochemical Society

Measuring the Curie temperature

K. Fabian
Geological Survey of Norway, Leiv Eirikssons vei 39, Postboks 6315 Sluppen, 7491 Trondheim, Norway (karl.fabian@ngu.no)

V. P. Shcherbakov
Geophysical Observatory 'Borok', Yaroslavskaja Oblast, 151742, Russia

S. A. McEnroe
Department of Geology and Mineral Engineering, NTNU Trondheim, 7491 Trondheim, Norway

[1] Curie point temperatures (T_C) of natural and synthetic magnetic materials are commonly determined in rock magnetism by several measurement methods that can be mutually incompatible and may lead to inconsistent results. Here the common evaluation routines for high-temperature magnetization and magnetic initial susceptibility curves are analyzed and revised based on Landau's theory of second-order phase transitions. It is confirmed that in high-field magnetization curves T_C corresponds to the inflection point, below the temperature of maximum curvature or the double-tangent intersection point. At least four different physical processes contribute to the initial magnetic susceptibility near the ordering temperature. They include variation of saturation magnetization, superparamagnetic behavior, magnetization rotation, and magnetic domain wall motion. Because each of these processes may influence the apparent position of T_C, initial susceptibility and high-field curves can yield deviating estimates of T_C. A new procedure is proposed to efficiently determine the temperature variation of several magnetic parameters on a vibrating-sample magnetometer, by repeatedly measuring quarter-hysteresis loops during a single heating cycle. This procedure takes measurements during the inevitable waiting time necessary for thermal equilibration of the sample, whereby it is not slower than the commonly performed measurements on a Curie balance. However, it returns saturation magnetization, saturation remanence, high-field and low-field slopes, and other parameters as a function of temperature, which provide independent information about T_C and other sample properties.

The authors and their expertise

- Karl Fabian – Geological Survey of Norway
- Valera P. Shcherbakov – Geophysical Observatory ‘Borok’
- Suzanne A. McEnroe – Department of Geology and Mineral Engineering, NTNU Trondheim

Brief outline of the paper

- Introduction
- The Curie Point Temperature in Landau Theory with Field Term
- Initial Susceptibility Near the Curie Point
  - Due to Variation of $M_s(H)$
  - Due to Anisotropy
  - Due to Domain Wall Motion
  - Due to Superparamagnetism
- New Procedure to Improve Curie Point Measurements
- Discussion and Conclusions

Brief outline of the paper

- Introduction (Done)
- The Curie Point Temperature in Landau Theory with Field Term
- Initial Susceptibility Near the Curie Point
  - Due to Variation of $M_s(H)$
  - Due to Anisotropy (Time)
  - Due to Domain Wall Motion
  - Due to Superparamagnetism
- New Procedure to Improve Curie Point Measurements
- Discussion and Conclusions

Curie Point Temperature in Landau Theory with Field Term

- Approximate fourth-order expansion of the zero-field free energy near T_C with an additional field energy term

$$F = F_0 + bm^4 + a\tau m^2 - mH$$

$\tau = (T-T_C)/T_C$

  - dF/dm=0

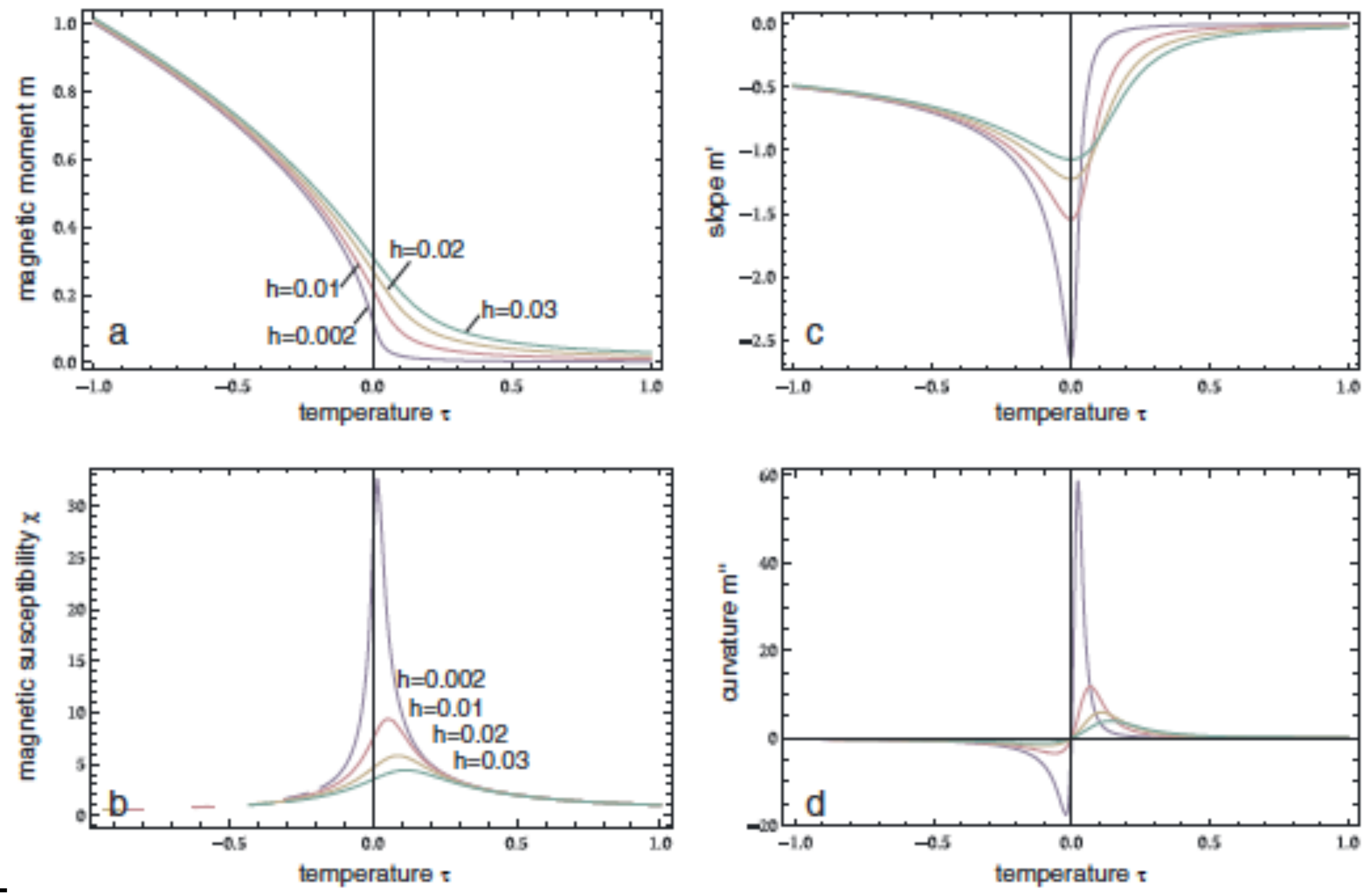
$$m^3 + \tau m = h, \qquad h = \frac{\sqrt{2b}}{2a\sqrt{a}}H$$

$$3m^2 m' + m + \tau m' = 0$$

$$3m^2 m'' + 6m(m')^2 + 2m' + \tau m'' = 0$$

- $\tau=0$ (T_C) at an inflection point with m''=0 and m'≠0

Curie Point Temperature in Landau Theory with Field Term



$\tau = (T-T_C)/T_C$

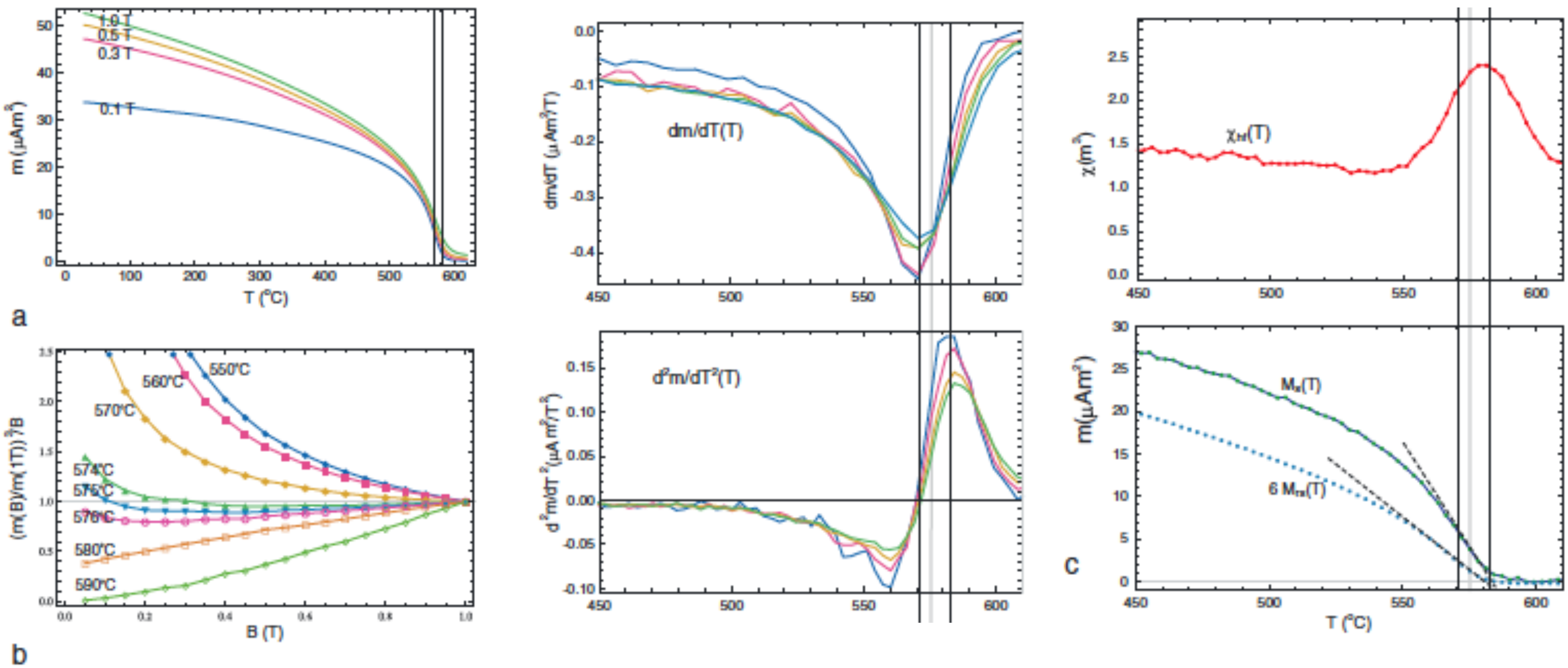
T_C T_C

- Figure 2. Plots of (a) magnetic moment m(τ), (b) susceptibility χ (τ), (c) slope m' (τ), and (d) curvature m" (τ) as a function of normalized field h temperature τ for the phase transition in the scaled Landau theory.

Curie Point Temperature in Landau Theory with Field Term

- T_C corresponds to the temperature at the inflection point of the magnetization curve, (min. of m' and m''=0)
  - Figure 8 c)
- At T_C ***m=h^{1/3}***, so T_C can be determined by plotting m^3/h as a function of h for different temperatures, and choosing the temperature where for high h the plot flattens
  - Figure 8 b)

Curie Point Temperature in Landau Theory with Field Term



T_C=574 ºC

- Figure 8. High-temperature measurements on an Icelandic basalt ST107A, containing fine-grained magnetite.

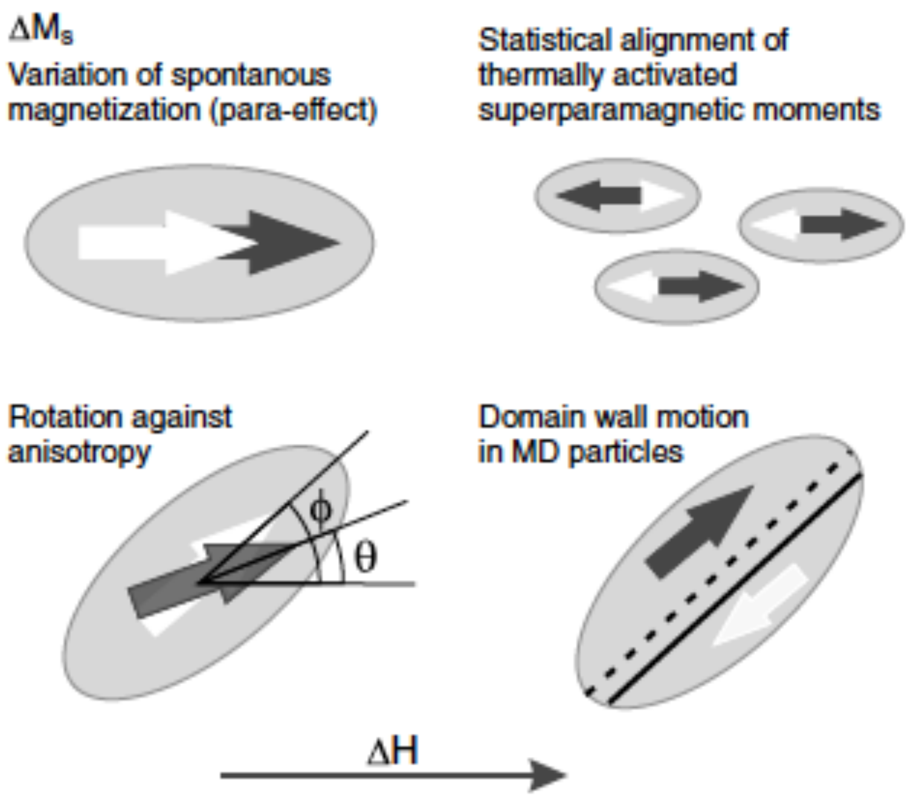
Initial Susceptibility Near the Curie Point

$$\frac{\mathrm{d}M}{\mathrm{d}H} = \frac{1}{v}\sum_i \left(\frac{\mathrm{d}M_s}{\mathrm{d}H} v_i \mathbf{m}_i + M_s \frac{\mathrm{d}v_i}{\mathrm{d}H} \mathbf{m}_i + M_s v_i \frac{\mathrm{d}\mathbf{m}_i}{\mathrm{d}H} \right)$$

Para-effect | Domain wall motion | Rotation of magnetization against anisotropy

- v = volume, $\mathbf{m}_i$ = magnetization direction
- Their relative contributions at any temperature depend on the grain-size distribution

Initial Susceptibility Near the Curie Point

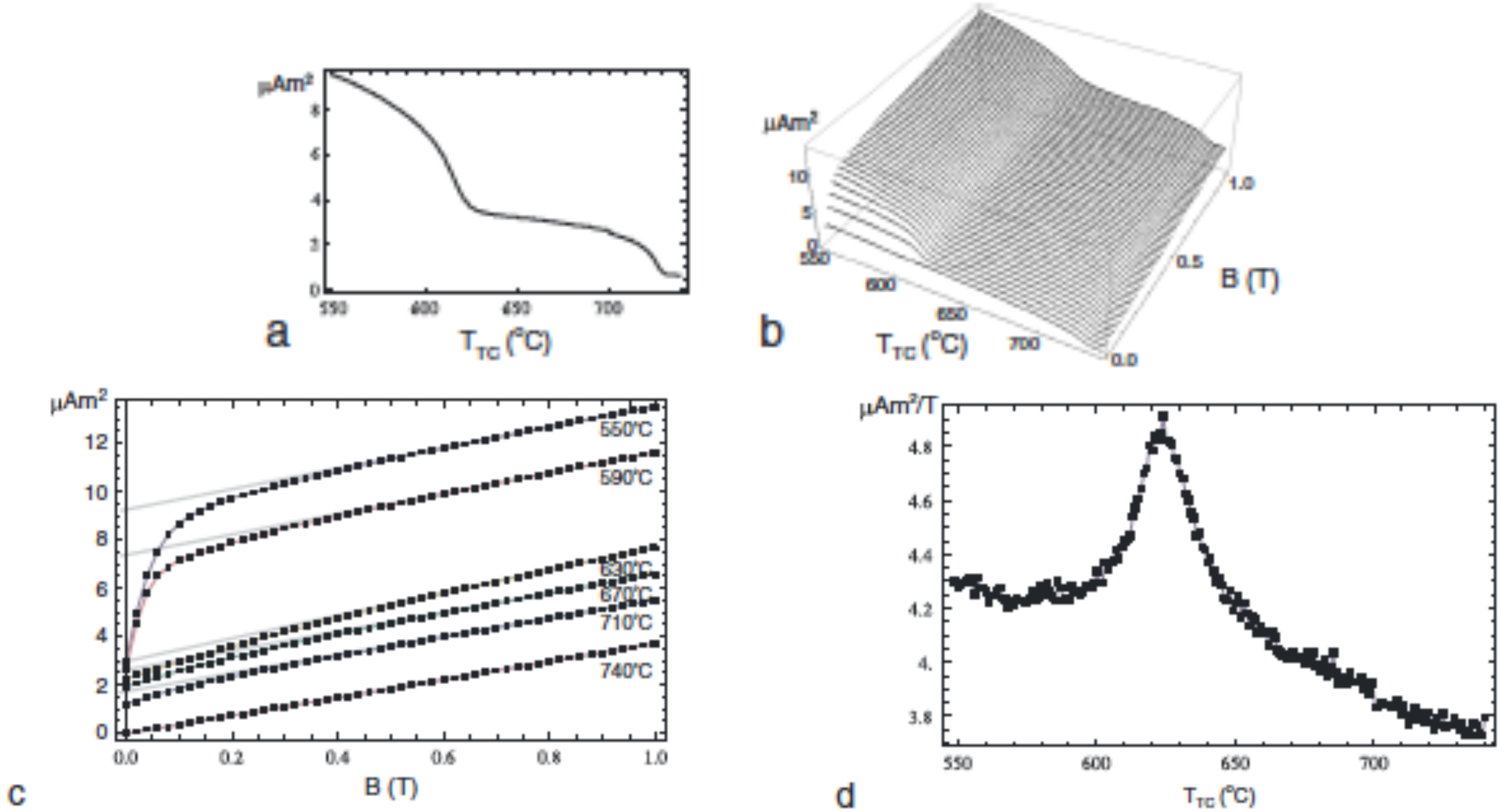


- Figure 3. Four independent mechanisms of magnetic susceptibility in a ferrimagnet as discussed in the text. When increasing the field by a vector ΔH the magnetic moment aligned with this direction (black) also increases as compared to the initial or opposite magnetization (white).

New Procedure to Improve Curie Point Measurment

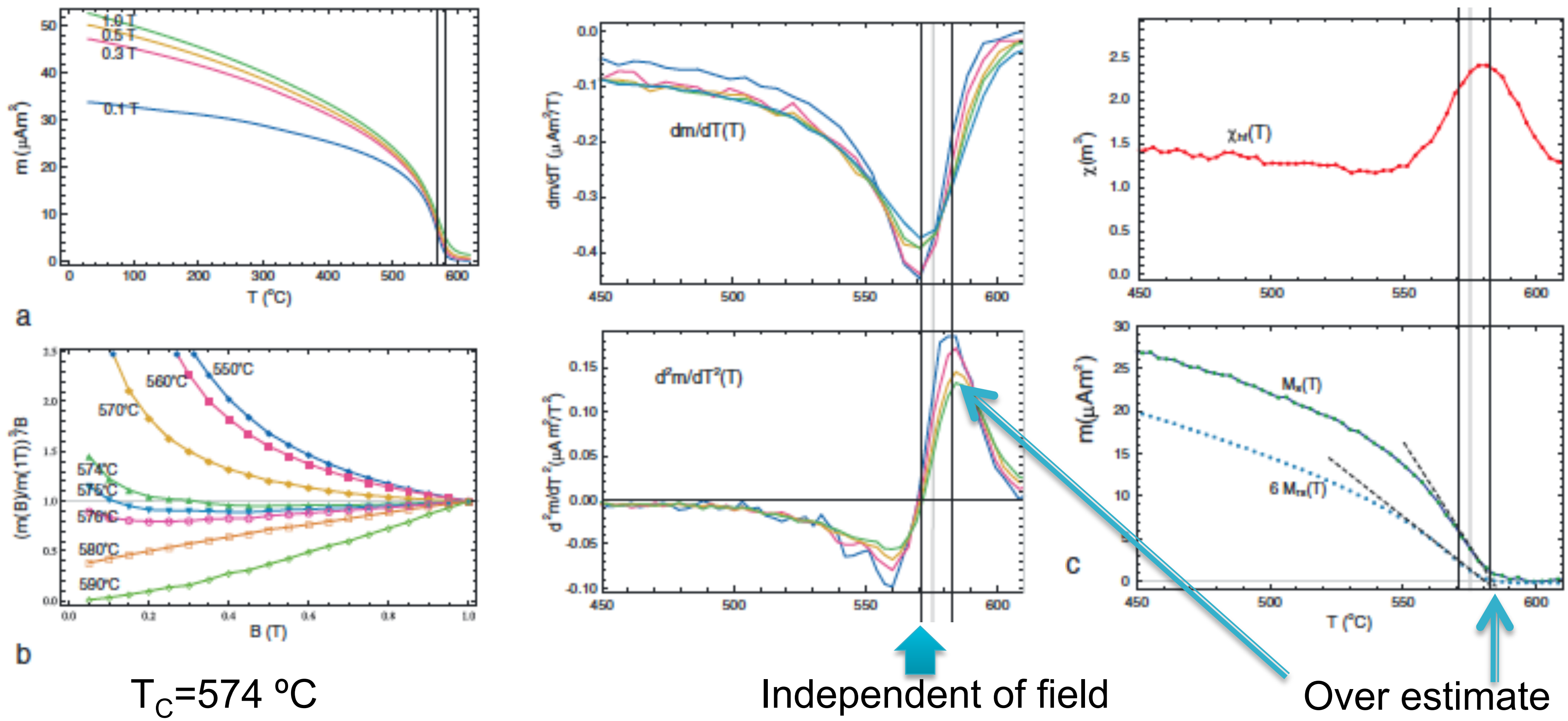
- Measurements made on a Vibrating Sample Magnetometer (VSM) fit with a furnace
- At each temperature step, T_i to T_{i+1}, the sample is heated in zero field to T_{i+1}. The field is then increased to the max field (e.g.,1.5T). $M_{si}(H, T_{i+1})$ is measured. The field is turned off before further heating.
- ΔT = 1-3 ºC, ΔH=50mT

New Procedure to Improve Curie Point Measurment



- Figure 7. High-temperature calibration measurements for a hematite-magnetite sample. At the thermocouple the temperature, T_{TC}, is measured. The offset between sample temperature and T_{TC} is calibrated to the Curie points of magnetite at 578 ºC and hematite at 680 ºC.

New Procedure to Improve Curie Point Measurment



- Figure 8. High-temperature measurements on an Icelandic basalt ST107A, containing fine-grained magnetite.

Discussion

- The methods previously used for determining the Curie point systematically overestimate T_C
- For most practical purposes the errors are negligible
- Serious problems occur when you compare T_C obtained by different physical measurements (for example comparing across studies in a database)

Discussion

- A coexisting paramagnetic mineral that contains 100-1000 times more Fe than the ferrimagnetic mineral will mess up T_C estimation.
  - The new procedure helps this because you can extrapolate to H=0, where the paramagnetic phase has a smaller effect.

Conclusions

- At least four different physical processes contribute to the initial magnetic susceptibility near the ordering temperature.
- In high-field magnetization curves T_C corresponds to the inflection point.
  - So the point of maximum curvature and double-tangent methods overestimate T_C
- The outcome of T_C determination depends on grain size and measurement method.
- Measuring quarter-hysteresis loops at each temperature step, M(H,T), is the way to go.

Were they successful in making a convincing case for their conclusions?

- Discuss

Questions raised by this work

- Can most labs make this measurement?
- Is this new procedure a big improvement?
- It really isn't slower than usual measurements made on a Curie balance?
- In Figure 8, why don't the T_C estimates from (b)=574ºC and (c)=571ºC agree?
- How would you put it into the MagIC database?
- How do you in general put Curie temp. measurements into the database, for comparison (or not) across studies?
- Others?

MagIC method codes – Statistical Method

MagIC Method Codes

Code	Method Type	IAGA7	URL	Description
SM-1D	Statistical Method			First derivative.
SM-1DMAX	Statistical Method			Maximum on first derivative.
SM-1DZERO	Statistical Method			Zero on first derivative.
SM-2D	Statistical Method			Second derivative.
SM-2DMAX	Statistical Method			Maximum on second derivative.
SM-2DZERO	Statistical Method			Zero on second derivative.
SM-2TAN	Statistical Method			Two tangents.
SM-AVE	Statistical Method			Arithmetic mean.
SM-DIG-GRAPH	Statistical Method			Digitization of data from diagrams and plots.
SM-EXT	Statistical Method			Extrapolation.
SM-EXT-LIN	Statistical Method			Linear extrapolation from above critical temperature. Linear temperature dependence of inverse susceptibility above ordering temperature of ferromagnets. Petrovsky & Kapicka 2006.
SM-EXT-NL1	Statistical Method			Non-linear extrapolation from above critical temperature. Hyperbolic temperature dependence of inverse susceptibility above ordering temperature of ferromagnets. Petrovsky & Kapicka 2006.
SM-EXT-NL2	Statistical Method			Non-linear extrapolation from below critical temperature. Theoretical decay of Ms versus T to estimate Curie temperature. Moskowitz 1981.
SM-EYE	Statistical Method			Eyeball estimation.
SM-FISHER	Statistical Method			Fisher transformation.

MagIC method codes – Lab Protocol

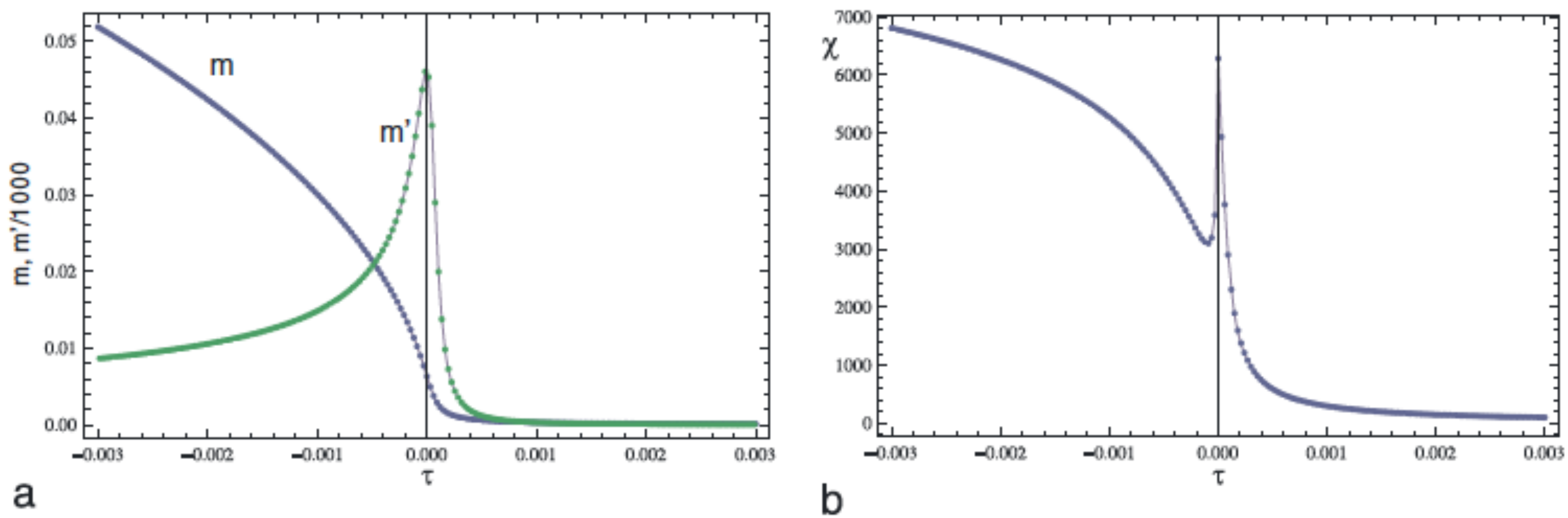
LP-LT	Lab Protocol			Lab protocol involving low temperature treatments.
LP-MC	Lab Protocol			Measured while cooling.
LP-MC-I	Lab Protocol			Measured while cooling: In laboratory field.
LP-MC-Z	Lab Protocol			Measured while cooling: In zero field.
LP-MRM	Lab Protocol			MRM acquisition: Microwave induced TRM.
LP-MRT	Lab Protocol			Remanent magnetization as a function of temperature.
LP-MST	Lab Protocol			Saturation magnetization as a function of temperature.
LP-MW	Lab Protocol			Measured while warming.
LP-MW-I	Lab Protocol			Measured while warming: In laboratory field.
LP-MW-Z	Lab Protocol			Measured while warming: In zero field.

LP-X	Lab Protocol			Susceptibility measurement.
LP-X-F	Lab Protocol			Susceptibility measurement: As a function of frequency.
LP-X-FERRO	Lab Protocol			Susceptibility measurement: Independent measurements of low field and highfield susceptibility for getting ferromagnetic susceptibility. Ferromagnetic susceptibility is the low-field minus the high-field susceptibility to correct for paramagnetic contribution.
LP-X-H	Lab Protocol			Susceptibility measurement: As a function of amplitude.
LP-X-T	Lab Protocol			Susceptibility measurement: As a function of temperature.

Thank you for your attention!

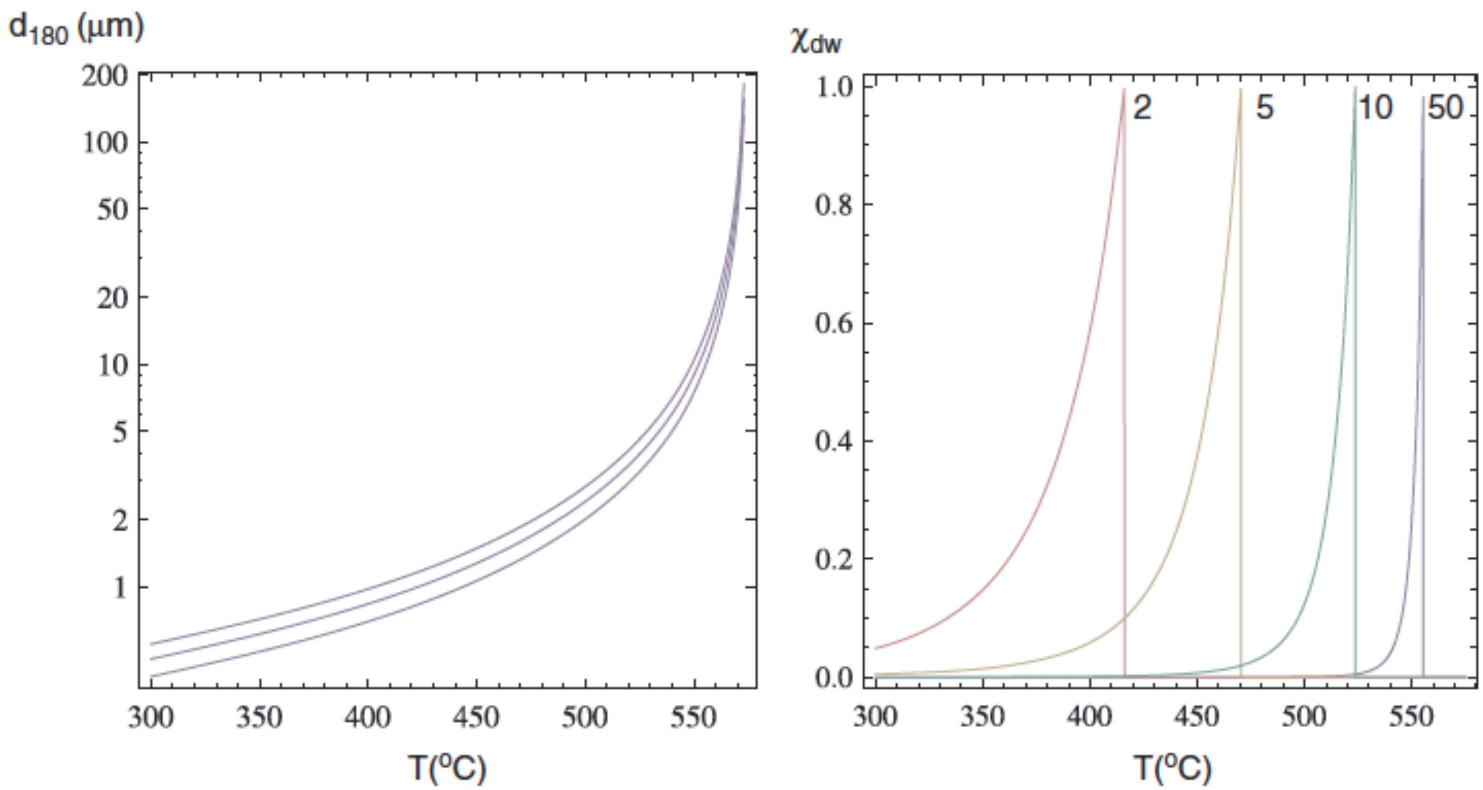
- SIO AGU pitches:
  - Maggie Avery - Poster, Fri. PM
    - “Analysis of Growth and Decay of the Axial Dipole in Geodynamo Models”
  - Cathy Constable - Poster, Fri. PM
    - “Long-term geomagnetic field variations inferred from geodynamo simulations”
  - Geoff Cromwell - Poster, Fri. PM
    - “A new estimate of the average dipole field strength for the last five million years”
  - Jeff Gee - Talk, Wed. 5:00 PM
    - “How Big is the Dufek Intrusion? Paleomagnetic Constraints on the Cooling History of the Dufek Layered Intrusion”
  - Nick Jarboe - Poster, Thurs. AM
    - “Introducing a New Interface for the Online MagIC Database by Integrating Data Uploading, Searching, and Visualization”
  - Sanja Panovska - Talk, Wed. 9:45 AM
    - “Towards global geomagnetic field reconstruction for the past 100 thousand years”
  - Ron Shaar - Poster, Thurs. AM
    - “Decadal to millennial scale archaeointensity variations in the Levan”

Initial Susceptibility Near the Curie Point Due to Anisotropy



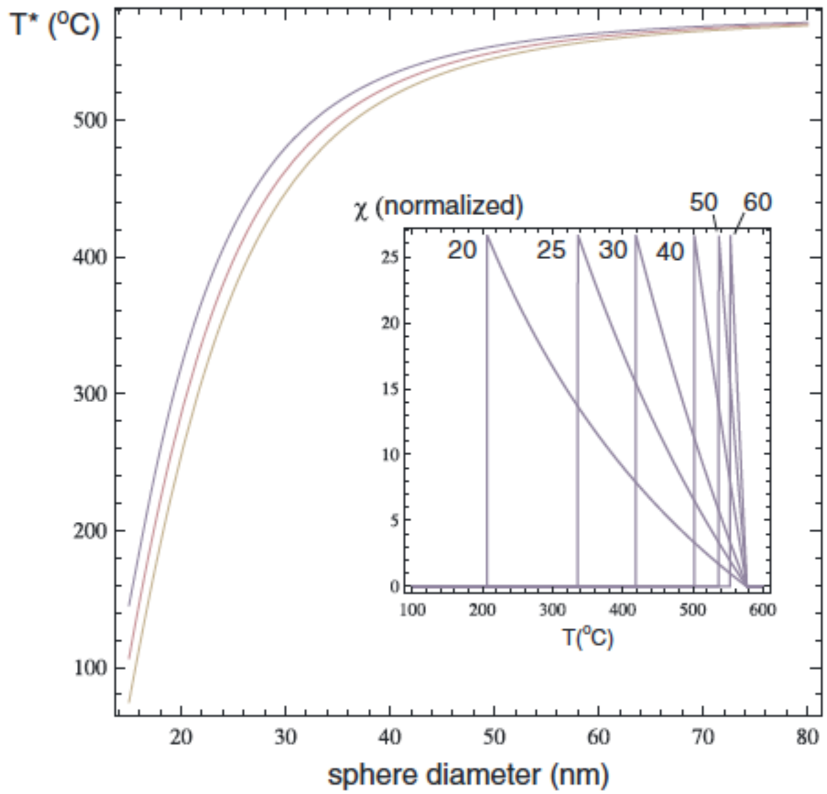
- Figure 4. Magnetic moment m, and slope m' (a), as well as low-field susceptibility χ_0 , as a function of normalized temperature $\tau = T/T_C - 1$ and normalized field h for the phase transition in the scaled Landau theory with anisotropy term.

Initial Susceptibility Near the Curie Point Due to Domain Wall Motion



- Figure 5. (a) Approximate width of 180º Bloch walls in magnetite as a function of temperature. This width determines the minimal size for particles which contribute susceptibility due to domain wall movement at the given temperature. (b) Approximate relative susceptibility variation due to domain-wall motion for four particle sizes in magnetite. The numbers indicate approximate particle diameter in micrometers.

Initial Susceptibility Near the Curie Point Due to Superparamagnetism



- Figure 6. Approximate peak temperature T* for the Hopkinson peak in magnetite as estimated from (31). Volume is transferred to an equivalent spherical diameter, and the error band takes into account a range of relaxation time=0.01-1s and of the demagnetizing factor N=1/4-1/3.