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Key Points:

- High temperature magnetic susceptibility bridges can detect endothermic and exothermic reactions in Fe- and non-Fe-bearing minerals
- Data can be acquired without any new equipment and resemble thermodynamic data acquired during differential thermal analysis
- These methods expand the capabilities of a common rock magnetic instrument for characterizing the mineralogy of natural samples

Supporting Information:

Supporting Information may be found in the online version of this article.

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Differential Thermal Analysis Using High Temperature Susceptibility Instruments

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Abstract Measurements of susceptibility as a function of temperature are an important, standard method of quantifying a sample's magnetic mineralogy. These measurements are used to identify the Curie/Néel temperatures of constituent minerals and show evidence of thermally induced oxidation and formation of magnetic minerals. For these reasons, the High Temperature Susceptibility Bridge (HTSB) is a common instrument in paleomagnetism laboratories around the world. Here, we argue that HTSBs can be used to perform simple differential thermal analysis, a technique used to identify phase transitions and exo-/endothermic reactions by measuring deviations in temperature from a steady heating rate. Because HTSBs are designed to heat samples at a relatively constant rate, the standard susceptibility measurement can be used to obtain similar information, albeit crude, about the phase transitions taking place. For standard samples of vivianite, goethite, and maghemite, we compare the heating curves of the sample and a blank run, to identify DTA-analogous information. In the case of goethite and vivianite, the reactions identified do not have a corresponding expression in susceptibility, demonstrating that this approach expands the utility of this common piece of equipment. We estimate the minimum enthalpy of reactions detectable and their mass dependence. Additionally, we show that this approach is successful in detecting the dehydration of vivianite in a mixed mineralogy natural sample.

Plain Language Summary Magnetic susceptibility is a measurement of how a sample responds to the presence of a small applied magnetic field. Measuring magnetic susceptibility on heating and cooling can be used to determine the types of minerals in the sample and how they alter. This is a relatively quick measurement with minimal sample preparation, hence, it is commonly measured in paleomagnetism laboratories. However, not all characteristic changes experienced by the sample have an effect on magnetic susceptibility. This study offers a complementary analysis that can be done concurrently with magnetic susceptibility on a High Temperature Susceptibility Bridge. It determines whether reactions are producing or absorbing heat by detecting fluctuations in the temperature. The method is tested using three iron-bearing standards (maghemite, goethite, and vivianite) and a natural, vivianite-rich sample. This analysis was able to detect the temperature fluctuation caused by the loss of structural water in both goethite and vivianite, a reaction that does not affect the magnetic susceptibility. Additionally, we explored the sensitivity of these measurements on varying amounts of sample and different grain sizes.

1. Introduction

Measurements of susceptibility as a function of temperature, X(T), are an important and standard method of characterizing a sample's magnetic mineralogy. High temperature susceptibility bridges (HTSBs) (often referred to as "KappaBridges," based on the popular instrument from AGICO) are commonly used to measure magnetic susceptibility as a function of temperature. Such measurements provide information about a specimen's initial magnetic susceptibility, its Curie and/or Néel temperatures, the existence of a Hopkinson peak, and any phase transformations that may occur during temperature cycling (e.g., Matasova et al., 2001; Petrovskỳ and Kapička, 2006; Zan et al., 2011). In turn, these observations are often used to infer a specimen's magnetic mineral composition and to determine when mineral alteration and growth may occur during thermal demagnetization experiments. These measurements of mineral composition and alteration can be used in environmental magnetism studies as a proxies for the paleoenvironment. For example, measurements of X(T) have been used to estimate paleoprecipitation rates in Chinese loess (Gao et al., 2019). Overall, the interpretation of magnetic susceptibility measurements is vital to many types of magnetic studies.



Although less utilized within the paleomagnetic community, differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are complementary techniques used to detect thermally induced phase transitions and reactions, which can be used to determine composition (Dekkers, 1990; Kulp & Trites, 1951; Viti, 2010). In both, a sample is heated in a controlled setting alongside a carefully calibrated standard. In DTA, the power is applied equally to the sample and standard, and the temperature differences are measured. In DSC, the same heating rate is maintained for both and the difference in power applied is measured. The most basic interpretation of DSC and DTA data is the identification of endothermic or exothermic reactions. An endothermic reaction is characterized by a relative decrease in temperature (DTA) or an increase in power supplied (DSC) in the sample. An exothermic reaction is characterized by an increase in temperature (DTA) or a decrease in power supplied (DSC). The ability to identify diagnostic exothermic and endothermic reactions in paleomagnetic or environmental magnetic materials would help provide more unambiguous characterization of magnetic mineral assemblages (Jordanova & Jordanova, 2016).

HTSBs are designed to heat samples at a relatively constant rate. Power is applied to its furnace as a function of time and does not include a feedback system to regulate the temperature of the sample. Here we show how this feature can be leveraged to obtain data broadly similar to that of classic thermal analyses. Detected reactions sometimes coincide with changes in bulk susceptibility, but often they do not. This approach demonstrates a promising new way to gather additional diagnostic information without modifying the instrument in any way. This paper is separated into three parts. The first describes the methodology and demonstrates the manner in which data are processed using a data set for the iron-phosphate mineral vivianite, found commonly in marine and lacustrine sediments. The second part applies the technique to mono-mineralic standards of goethite an maghemite and goethite, minerals frequently encountered in paleomagnetic and environmental magnetic studies. The third part applies the technique to a natural sediment sample. We demonstrate that the approach works successfully on different models of HTSBs and offer it as a means to expand the ways materials are commonly characterized in paleomagnetic laboratories.

2. Methodology

Magnetic susceptibility was measured on two HTSBs. The majority of measurements were made on the Geofyzika KLY-2 KappaBridge (sensitivity of 4×10^{-8} SI) at a 920 Hz frequency 300 A/m field. Samples were heated with the attached CS2 furnace. The measurements were made in air using the fast heating rate (~10°C/min). Additionally, some measurements were made on the AGICO MFK1 (sensitivity of 2×10^{-8} SI) at a 976 Hz frequency 200 A/m field. Samples were heated with the attached CS4 furnace. These measurements were made in air (in a sealed tube) using the medium heating rate (~11.8°C/min). An HTSB run involves measuring magnetic susceptibility as a function of temperature upon heating up to a user-defined peak temperature and cooling back to 50°C. For each round of sample analysis, first an empty tube (blank) is measured on the HTSB over the temperature range. Then, the tube is used to measure the sample of interest. Classically, magnetic susceptibility is plotted as a function of temperature and the derivative is often used to determine critical temperatures, such as Curie and/or Néel temperature (Avery et al., 2018; Fabian et al., 2013; Petrovskỳ and Kapička, 2006).

2.1. Developing Methodology With Vivianite $Fe_3 (PO_4)_2 \cdot 8H_2O$

To identify deviations in temperature, the heating curves (temperature vs. time) of a blank and the sample are compared, as seen in Figure 1. Though not typically used, these data are collected by the HTSB while measuring magnetic susceptibility. During an endothermic reaction, thermal energy is absorbed into the system. In this case, the heating curve will stagnate at a constant temperature while the reaction takes place before continuing to heat up (blue line in Figure 1). An exothermic reaction is one in which heat is released from the system and will result in an increased heating rate.

To process the data so that the deviations can be identified, first, both the blank and sample heating curves are linearly interpolated to create a regularly spaced time series. The interpolated sample data set is subtracted from that of the blank to calculate the residual temperature. To account for subtle differences in average heating rate or initial temperature, a best fit line is subtracted from the residual if possible. Lastly, to minimize the effect of noise and minor fluctuations caused by adjustments to the instrument, the resultant data set is smoothed using locally weighted smoothing (LOESS) over a 3%–8% window depending on the sharpness and noise of the curve. The



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Figure 1. (a) Flow chart describing the procedure for data collection and processing (b) Excerpted data from vivianite heating curve showing the relationship between measured temperatures, interpolated points, and residual temperature during the endothermic dehydration reaction.

results are displayed as residual temperature versus sample temperature (Figure 2b). This basic calculation can be done using code available at https://github.com/RDoctor786/kDTA. At first glance, the peaks in this result can be classified as positive or negative, indicating a exothermic or endothermic reaction respectively.

The same analysis can be done on cooling. The cooling rate on the HTSB is also nearly linear and consistent. Cooling information can be useful to find reversible reactions, like phase changes (Hidvégi et al., 1977). However, much of the DSC and DTA literature used for comparison only includes thermal analysis upon heating, so, this study focuses on the heating curves.

The dehydration of vivianite can be characterized on the DSC as an endothermic process with a peak at 193°C and an enthalpy (ΔH) of -381.8 J/g (Ogorodova et al., 2017). This study used a powdered, natural crystal of vivianite with trace amounts of magnetite. The heating rate analysis of vivianite, as described earlier, results in an endothermic peak that aligns well with the DSC result, and coincides with the temperature corresponding to the maximum rate of change in the residual temperature (negative peak in the first derivative) of Figure 2b. This thermal analysis data can be juxtaposed with the classic susceptibility data measurement. Upon heating, vivianite's magnetic susceptibility (Figure 2a, red) is inversely proportional to the temperature, as expected for a paramagnetic material (Minyuk et al., 2013). Upon cooling, there is an increase of susceptibility near the Curie temperature of magnetite and a decrease in susceptibility near 200°C. The dehydration of vivianite does not affect the magnetic susceptibility and characteristic magnetic transitions in vivianite occur at low temperatures, not observable on the HTSB. Thus, this analysis provides further information for the identification of vivianite without additional measurements.

2.2. Applications to Mineral Standards

2.2.1. Goethite

Goethite is an iron oxide-hydroxide commonly found in soils and sediments, as well as a range of altered volcanic materials. It is often used as a magnetic proxy for paleoprecipitation studies (Balsam et al., 2004; Maxbauer et al., 2016), but identifying goethite is complicated by its high coercivity and low magnetization (Bilardello, 2019). The commercially available Pfizer YLO-1888D, with a nominal grain size of 0.35 μ m (Morris et al., 1985) was used as the goethite mineral standard. The low-field magnetic susceptibility of the goethite is relatively featureless during heating up to 400°C (Figure 2c). Above 400°C, the goethite decomposes to a lower coercivity material with a higher measured susceptibility, likely magnetite based on the sharp decrease in





Figure 2. Graphs (a–f) show mineral standards measured on KLY-2 with the upper plot showing the low-field magnetic susceptibility during heating (red) and cooling (blue) and the lower plot showing the repeat heating rate analyses results and a comparative differential scanning calorimetry/differential thermal analysis (DSC/DTA) plotted in purple. The extent of each reaction as detected by DSC/DTA is highlighted in gray with the peak temperature indicated by a dotted line. The standards include (a and b) Vivianite in which the heating rate analyses in (b) do not include detrending (c and d) Goethite, and (e and f) maghemite. (g) Bay Horse Lake natural samples magnetic susceptibility and (h) heating rate analysis without detrending. The extent of the vivianite standards peaks is highlighted with the standard peak temperature indicated by a dotted line.



susceptibility near 580°C. Above that temperature, some of the material may react to form another high coercivity material, likely hematite, since the susceptibility upon cooling is lower.

The heating rate analysis of goethite (Figure 2d) resulted in a well-defined, reproducible endothermic peak near 300°C, which aligns with the overall range of peaks found by Walter et al. (2001) via DTA at 278°C ($\Delta H = -355.9 \text{ J/g}$) and 304°C ($\Delta H = -223.0 \text{ J/g}$). These peaks correspond to the dehydration of goethite, which forms channels lined by hematite as water is driven off from the crystal lattice. The double peakedness could be the result of a surface hematite layer that halts dehydration, and could promote the formation of maghemite (Walter et al., 2001; Özdemir & Dunlop, 2000). The peak susceptibility value results in an estimated 13% magnetite formed by mass during heating. Like with vivianite, the dehydration of goethite has no noticeable effect on the magnetic susceptibility, so capturing this characteristic reaction expands the utility of the HTSB. The same analysis was repeated for another commercially available goethite sample, Pfizer YO-5087, which has a larger nominal grain size of 0.90 µm.

2.2.2. Maghemite

Weathering or low-temperature oxidation of magnetite causes maghematization. Maghemite is often the main remanence holding mineral in paleomagnetic studies. The maghemite measured in this study is the commercially available Wright 4200 Lot-897, with a nominal grain size of 0.05 μ m (Solheid & Jackson, 2001). As seen in Figure 2e, the maghemite undergoes a relatively steady increase in susceptibility during heating. Starting near 480°C, the susceptibility drops, indicating maghemite's inversion to the higher-coercivity mineral hematite. Upon cooling, the susceptibility is much lower than its starting value, which suggests that almost all of the maghemite has inverted.

The DSC measurement was taken on the TA Instruments DSC Q1000 at a heating rate of 10°C/min. The maghemite undergoes a small exothermic reaction that takes place between 220 and 320°C with a peak at 270°C (Figure 2f, purple), that does not appear to correspond to any significant feature in the low-field susceptibility data. The enthalpy of this reaction can be found by integrating the area between the peak and the baseline trend. This reaction has a normalized energy of 17.24 J/g, over 20 times lower than that of vivianite. This reaction could indicate the mobilization of vacancies within its structure or recrystallization (Majzlan et al., 2003). At 500°C, the DSC captures the beginning of another exothermic peak that is much larger in magnitude. As evidenced by the magnetic susceptibility data, this exothermic reaction corresponds to the inversion of maghemite to hematite (Gorshe, 1998).

The heating rate analysis on maghemite (Figure 2f) does not have a well-defined peak corresponding to the 270°C peak on the DSC data. However, there is a broad peak just prior to 300°C and there is a clear start to an exothermic peak at around 500°C. The temperature of the peak near 300°C is relatively close to the peak observed at 270°C in the DSC data and we propose that the observation of this relatively low energy reaction is close to the minimum resolution of this approach.

2.3. Using Approach on Natural Sediment

To determine the effectiveness of this method on natural, multi-mineral samples, we measured a lake core sample from Bay Horse Lake, Idaho. These cores are composed of organic-poor late Pleistocene sediments with occasional vivianite-rich layers (Mark Shapley, pers. comm.). One such layer containing vivianite nodules, with large bladed grains, was measured on the HTSB. The presence of vivianite was independently corroborated via XRD (Figure S1 in Supporting Information S1). For comparison, another sample, taken from a vivianite-poor layer, was also measured on the HTSB.

The magnetic susceptibility measurement (Figure 2g) shows an increase in susceptibility between 300 and 500°C and a decrease in susceptibility between 500 and 550°C that is consistent with the Curie temperature of magnetite with a minor degree of Fe-substitution. Upon cooling, the increase in susceptibility is still consistent with that of magnetite. Near 350°C, there is a secondary increase in susceptibility. The previous measurements on the vivianite standards show a strong endothermic reaction at 200°C. The heating rate analysis of the natural sediment (Figure 2h) also has an endothermic peak that aligns with that of the standards. This demonstrates that this method can be used on natural samples to detect characteristic phase transitions that are not always readily observable using magnetic susceptibility data alone.



The analysis of the vivianite-poor sample showed almost no signal in its magnetic susceptibility measurement. The heating rate analysis does not show a peak at 200°C, demonstrating that this approach to detect vivianite can successfully differentiate between the presence and absence of vivianite. In the absence of the vivianite peak, another endothermic peak near 150°C was observable, likely due to the dehydration of a nonmagnetic mineral, such as a clay. Since this method is not reliant on magnetic properties, nonmagnetic minerals can also be characterized.

3. Variability and Limitations to the Approach

3.1. Peak Temperature

Comparing the well understood DSC/DTA curves to those produced by our analysis is useful in determining which aspects of the data are most reliable and meaningful. The beginnings of the peaks, or the onset of the deviation from the background near-zero slope, line up well between the two methods of analysis. This implies that our method is accurately capturing the temperature at which the reactions start causing a deviation from the baseline heating rate. In classic thermal analyses, it is common to report reactions by their peak temperature. The peak temperatures found via this method are consistently higher than those measured by DSC/DTA and the temperature of the greatest rate of change in the heating rate analysis often coincides with the peak position identified using DSC/DTA. Similarly, the ending temperatures are also consistently higher than the DSC/DTA ones. These higher values could be a consequence of the much larger sample volumes used in HTSB experiments than those used for DSC/DTA, as larger samples take a longer time to react and then reequilibrate with the furnace temperature.

Peak temperature is the most consistent value across HTSB measurements of the same sample. As seen in the repeat vivianite and goethite measurements, the peak temperature detected remains steady. In the analysis of the natural sediments, its peak temperature lines up almost exactly with the standards' peak temperatures. The ending of the peak, or where the residual temperature returns to the background value, also closely matches the endings of the standard peaks. Interestingly, the beginning of the peak, or where the deflection from the average starts, is at a lower temperature than that of the standards. As evidenced by the vivianite-poor sample, this inconsistency can be explained by the presence of another mineral with an endothermic reaction near 150°C. The combination of these two reactions could result in the wide measured peak.

The characteristic peak(s) used for sample identification in DSC/DTA can be grain size dependent. Walter et al. (2001) determined the grain size dependence of goethite's dehydration, with larger grains resulting in higher peak temperatures and double-peaked reactions. Differential scanning calorimetry measurements of a coarser grain size of goethite yielded endothermic peaks at 278°C ($\Delta H = -464.8 \text{ J/g}$) and 314°C ($\Delta H = -298.9 \text{ J/g}$), a 20°C shift in temperature for the second peak (Walter et al., 2001). As seen in Figure S2 in Supporting Information S1, there is a consistent shift to higher peak temperatures for coarser-grained material in the heating rate analysis, though the shift in peak temperature is greater than expected.

3.2. Peak Size and Sensitivity Limits

DTA measurements are most often used for qualitative interpretations. However, it is possible to indirectly determine the enthalpy of reaction, ΔH , as a function of the peak area. The two are related by

$$\Delta H = \Phi\left(T_r\right) \int_{t_1}^{t_2} \Delta T dt$$

where H is the enthalpy, Φ is a proportionality constant, T_r is the reaction temperature, ΔT is the residual temperature, and t_1 and t_2 are the temperature limits of the peak. The proportionality constant that relates residual temperature and enthalpy is dependent on the reaction temperature (e.g., peak temperature). $\Phi(T_r)$ can be determined empirically for a given set of experimental conditions, and, for DTA, has a positive linear dependence on the reaction temperature (Hoffman & Pan, 1991).

The positive relationship between the proportionality constant and the reaction temperature has significant consequences for the sensitivity of the heating rate analysis. For a given reaction enthalpy, its expression on the heating rate will decrease in area as the reaction temperature increases. Using the proportionality constant equation found by Hoffman and Pan (1991), if the dehydration reaction temperature of goethite shifted 200°C higher while maintaining the same enthalpy, the peak area would reduce by 30%. Hence, reactions at higher temperatures are harder to resolve.

Using reactions barely distinguishable from the baseline signal, we can find the minimum resolvable reaction enthalpy for reactions in a given temperature range. The endothermic peak at 300°C for goethite corresponds to its dehydration. Walter et al. (2001) found that goethite of similar grain size to our second goethite sample has a double-peaked reaction with enthalpies of 465 and 298 J/g (Figure 2d), which corresponds to a total energy of 30 J for the smallest goethite sample run. By comparison, the maghemite heating rate analysis shows only a broad, poorly defined peak at its 17.24 J/g exothermic reaction at around 270°C (Figure 2f). The largest example of maghemite had a reaction enthalpy of 10 J. So, near 300°C, the minimum resolvable reaction enthalpy must be between 10 and 30 J. This minimum value will decrease (become more sensitive) for lower temperatures. Because many characteristic dehydration and dehydroxylation reactions occur in the temperature range between 100 and 400°C (Table 1), this minimum energy estimate lets us anticipate the phase transformations detectable.

For a given reaction, the peak area is related to the sample mass (Figure 3). The goethite sample masses span the range of sample volumes allowed by the HTSB sample holder. Over this range, there is a statistically significant linear relationship between peak area and sample mass. Because this does not tend toward the origin, the relationship cannot be purely linear. However, for this limited range of masses, a linear approximation is a good fit. This type of analysis is best suited for comparisons between like samples, as grain size and other mixed minerals could affect the signal.

Heating rate affects both the peak area and peak temperature. In general, higher heating rates result in a greater heat flow. Hence, to maximize the chance of detecting a reaction, a faster heating rate is preferable. Reaction peak temperatures can be heating rate dependent as well, partially due to lagging of internal temperature or other kinetic considerations of the reaction (Thomas, 2001). This study uses the closest heating rate to 10°C/min for all measurements. This heating rate was most common in the comparative measurements and is the fastest rate available on the KLY-2.

3.3. Repeatability

To determine this method's compatibility with other HTSBs, we measured goethite on the AGICO MFK1. The curves obtained have peaks spanning the same temperature range as those produced via the KLY-2 (Figure 4a).

The major difference between the two is the size of the peaks (Figure 4b); the MFK1 peaks are smaller than those from the KLY-2. The dehydration of the smallest MFK1 goethite sample measured has a calculated energy of 49 J using Walter et al. (2001)'s enthalpy values, and is at the edge of being visually distinguishable from the noise. This suggests that the general shape of the curve is common between instruments, but peak areas are dependent on the experimental conditions unique to each instrument, and therefore, should be calibrated for each individual HTSB.

Specifically, for the instrumentation used in this study, one major difference between these two HTSBs is the thermocouple. The thermocouple on the KLY-2 is much thinner than the sample tube and is in direct contact with the powdered sample. On the other hand, the thermocouple for the MFK1 is encased in glass, increasing the sensor-sample distance. Additionally, the glass casing increases the size of the device and makes it difficult to completely surround it with the sample inside of the sample tube. These differences likely contribute to the MFK1's muted measurements in comparison to those on the KLY-2. Hence, as recommended above, measuring reference mineral standards on each HTSB would account for these kinds of instrumental differences.

3.4. Applicability to Natural Samples

This method was successful in getting a complementary analysis on the magnetic minerals while measuring the susceptibility. However, in many natural samples, magnetic minerals often occur in concentrations of less than 1%. Since our ability to detect a reaction is limited by the total enthalpy of the reaction, it is possible that the magnetic minerals in many natural samples may have little to no signal, even when measured on the much more sensitive DTA/DSC. The analysis on magnetic material may be particularly useful for high density mineral separates collected from natural samples (Lagroix et al., 2004; Strehlau et al., 2014). However, as evidenced by the



Table 1

Thermal Decomposition of Some Fe-Bearing Minerals

Mineral	Sample description	Reaction temperature	Δ H (+ is	Reaction description	Atmosphere	Additional notes	Citation
Maghemite $\gamma - Fe_2O_3$	Wright 4200 (grain size 0.05µm)	270	+17.24 J/g		Air	heating rate 10°C/min	This study
		550	+104.5 J/g	Inversion to hematite	-	heating rate 7°C/min	Gorshe (1998)
Siderite FeCO ₃	Ground to 85% passing 0.074 mm; 96.23% of iron carbonate iron	510	−563.3 J/g	Siderite to FeO, almost immediately becomes magnetite	Nitrogen	Shifts to higher temperature with higher heating rates	Zhang et al. (2017)
Vivianite $Fe_2(PO_4) \cdot 8(H_2O)$	High purity, from crystal	194	-831.8 J/g	Dehydration	Nitrogen		Ogorodova et al. (2017)
		195	-381.8 J/g	Dehydration + oxidation	Air	-	
Geothite α – FeO(OH)	$(1.2 \times 0.25 \times 0.25)$ μm^3	274.3	—578.8 J/g	Dehydration + reaction	Iration + reaction to magnetite/ hematite	DTA – 5°C/min DSC – sealed container at 20°/min	Walter et al. (2001)
		321.4	-331.9 J/g	to magnetite/ - hematite			
	$(1.0 \times 0.15 \times 0.15)$ μm^3	278.1	-464.8 J/g				
		314.0	-298.9 J/g				
	$(0.3 \times 0.03 \times 0.03)$ μm^3	278.1	-355.9 J/g				
		304.8	-223.0 J/g	-			
	$(0.1 \times 0.01 \times 0.01)$ μm^3	272.1	−290.9 J/g				
Lepidocrocite γ-FeO(OH)		255	Endothermic	Dehydroxylation leading to formation of maghemite	Nitrogen	DSC at 10°C/min	Dinesen et al. (2001) Nauer et al. (1985)
		475	Exothermic	Maghemite to hematite			
Akaganeite Ideal: <i>β</i> - FeO(OH) <i>Fe</i> ₈ O _{7.1} OH _{8.9} Cl _{0.9}	50 × 6 nm, 3.8% Cl	105	Endothermic	Loss of adsorbed water	Air -	Not seen in larger grains	Paterson et al. (1982)
		180	Endothermic	Dehydroxylation		Shifted higher for larger grains	
		260	Endothermic	Dehydroxylation			
		505	Exothermic	Loss of structural Cl as chlorine		Much higher for larger grains	
		100	Endothermic	Loss of adsorbed water	Nitrogen -	Not seen in larger grains	
		180	Endothermic	Dehydroxylation		Shifter higher for larger grains	
		250	Endothermic	Dehydroxylation			
		420	Exothermic	Loss of structural Cl as HCl			
Feroxyhyte δ -FeO(OH)		80	Endothermic		_	Different temperatures in literature	Nauer et al. (1985)
		305	Endothermic				
Pyrite FeS ₂	Pyrite flotation concentrate (0.09–0.1 mm)	125	-3.9 J/g	Vaporization of volatile inclusions	Argon		Kirilov et al. (1994)
		299	-2.5 J/g			Not seen in DTA	
		538	-49.6 J/g	Formation of pyrrhotite and S_2			
		705	-456.0 J/g				



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Figure 3. (a) Heating rate analysis on goethite samples of different masses measured on KLY-2. (b) Peak area is linearly related to mass.

natural sample measurement, the heating rate analysis contains information about non-magnetic minerals in a sample as well. The strongest signals measured by this study were dehydration reactions, a reaction common and often characteristic in clay minerals. These minerals often make up a large portion of natural samples. Hence, since this method is not reliant on magnetic properties, it can be used to characterize both the magnetic and non-magnetic minerals in a sample.

4. Future Research

To develop this method further and make it more broadly applicable to paleomagnetic and environmental magnetic studies, it would be useful to measure a wider range of mineral standards. Table 1 outlines the thermal decomposition of several iron-bearing minerals as measured by DTA and/or DSC. As determined earlier, this method is most sensitive for lower temperature reactions. Conveniently, this temperature range corresponds with the dehydration and dehydroxylation of many commonly occurring, environmentally sensitive minerals.

5. Conclusions

In this study, we show how the temperature data collected during a regular measurement on the HTSB can be used to find DTA-analogous information about the endo- and exothermic reactions that occur in natural samples during heating. Many minerals go through phase transitions that do not necessarily affect the magnetic susceptibility and this method adds to the information gained about mineralogical alteration of the sample. This method







is particularly useful in identifying minerals that are normally expressionless in magnetic susceptibility measurements, such as those that are paramagnetic or have a high coercivity. Samples of goethite and vivianite demonstrate that this method can detect known phase transitions with reproducible peak shape and size. Using a natural sample of a vivianite-rich sediment, we were able to match the peak produced by the vivianite standards and identify its presence in a mixed-mineral sample.

Data Availability Statement

Magnetic data used in this paper can be found on the MagIC Database at 10.7288/V4/MAGIC/19369. All data can be found in the DRUM Repository at https://hdl.handle.net/11299/225302.

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