Supplementary information for:

Magnetic diffusion anomaly at the Néel temperature of pyrrhotite, Fe_{1-x}S

F. William Herbert,^{*a,b,c*} Aravind Krishnamoorthy,^{*a,b*} Lucy Rands,^{*d*} Krystyn J. Van Vliet,^{*a,c*} and Bilge Yildiz *^{*a,b*}

S1 Bulk, natural pyrrhotite sample characterization

Energy-dispersive x-ray spectroscopy (EDS) was carried out on representative $Fe_{1-x}S$ crystals in a JEOL 6610LV scanning electron microscope (SEM), to check for impurities. Chemical composition maps of multiplel areas were made (Figure S1), revealing thin seams of oxide inclusions but no major presence of impurity elements.



Figure S1: (Color online) (a, b) optical microscopy images of polished natural pyrrhotite crystals. (c-h) Energy-dispersive X-ray spectroscopy (EDS) maps of an unpolished surface from a natural crystal used in this study. The scanning electron microscope (SEM) picture is reproduced and overlaid with chemical analysis maps of sulfur, iron, oxygen, silicon and aluminium, as labelled.

^aDept. of Materials Science and Eng., Massachusetts Institute of Technology, Cambridge, MA, USA

^bLab. for Electrochemical Interfaces, Massachusetts Institute of Technology, Cambridge, MA, USA

^cLab. for Material Chemomechanics, Massachusetts Institute of Technology, Cambridge, MA, USA

^dDept. of Materials Science, University of Oxford, Oxford, UK

^{*}Corresponding author: byildiz@mit.edu

Magnetization as a function of temperature $\sigma(T)$ was meaured in a vibrating sample magnetometer (VSM). In Figure S2a we show the results from a powdered natural Fe_{1-x}S sample. The $\sigma(T)$ behavior during the heating portion is characterized by a peak-like, antiferromagnetic to ferrimagnetic λ -transition, typically observed in "NC"-type pyrrhotites in the compositon range $0.08 \le x \le 0.11$ in Fe_{1-x}S. ^{1,2} During the cooling portion, the magnetization remains ferrimagnetic, but flattens off near zero above ~ 300 °C. These complex magnetic properties arise from a redistribution of vacancies upon heating, which alters local magnetic moments on planes stacked along the *c*-axis. ³ However, it is known that a composition-independent, critical spontaneous ordering temperature $T_{\rm N}$ occurs for all pyrrhotites at approx. 315 °C. For a clearer example, in Figure S2b we present $\sigma(T)$ measurements on a synthetic sample of fully ferrimagnetic "4C" pyrrhotite, with a composition of Fe_7S_8 . Here, the Néel temperature of 315 °C is more obviously visible as a sudden drop in σ during both the heating and cooling cycles. The complex magnetic behavior of pyrrhotites is described in more detail in Ref.⁴.



Figure S2: Temperature-dependent magnetization $\sigma(T)$ of: (a) crushed, natural Fe_{1-x}S sample, as used to measure diffusivity in this work. The result is typical of an "NC"-type pyrrhotite that undergoes an antiferromagnetic-ferrimagnetic λ -transition. The Néel point T_N is not clear; (b) for comparision, a synthetically-fabricated, 4C-type pyrrhotite sample with the composition Fe₇S₈. This pyrrhotite is fully ferrimagnetic, and has a clear T_N at approximately 315 °C.

S2 Annealing schedules and diffusivity results for bulk samples

Table S1 details the experimental conditions of annealing temperature and time, and corresponding measured diffusivities from SIMS profiles, for the individual data points from Figure 5 of the main text.

Temperature	Annealing	$^{*}D_{\rm Fe}~({\rm cm}^{2}{\rm s}^{-1})$	Error in [*] D _{Fe}
(°C)	time (s)		(cm^2s^{-1})
170	1976400	5.14 x 10 ⁻¹⁶	6.12 x 10 ⁻¹⁷
186	54000	9.24 x 10 ⁻¹⁵	3.25 x 10 ⁻¹⁵
202	72000	3.02 x 10 ⁻¹⁴	7.75 x 10 ⁻¹⁵
202	72000	4.99 x 10 ⁻¹⁴	7.43 x 10 ⁻¹⁵
205	5762	1.27 x 10 ⁻¹³	1.78 x 10 ⁻¹⁴
209	145800	3.33 x 10 ⁻¹⁴	3.96 x 10 ⁻¹⁵
225	1794	4.63 x 10 ⁻¹³	7.47 x 10 ⁻¹⁴
225	12900	3.40 x 10 ⁻¹³	4.37 x 10 ⁻¹⁴
249	3348	1.08 x 10 ⁻¹²	1.36 x 10 ⁻¹³
249	19830	2.22 x 10 ⁻¹²	2.71 x 10 ⁻¹³
251	573	8.39 x 10 ⁻¹³	4.00 x 10 ⁻¹⁶
288	116	7.56 x 10 ⁻¹²	6.06 x 10 ⁻¹³
298	449	8.77 x 10 ⁻¹²	1.52 x 10 ⁻¹²
326	596	1.89 x 10 ⁻¹¹	2.98 x 10 ⁻¹²
350	86	1.53 x 10 ⁻¹⁰	6.56 x 10 ⁻¹¹
352	410	1.76 x 10 ⁻¹⁰	3.29 x 10 ⁻¹¹
376	94	2.87 x 10 ⁻¹⁰	4.57 x 10 ⁻¹¹
377	276	1.54 x 10 ⁻¹⁰	3.16 x 10 ⁻¹¹
403	98	5.19 x 10 ⁻¹⁰	8.60 x 10 ⁻¹¹

Table S1: Iron self-diffusion $^*D_{\text{Fe}}$ measurement results for Fe_{1-x}S crystals.

S3 Depth profiles and error analysis for bulk sample diffusion analysis

Crystals were mounted on a custom stage and inserted into the hot part of the furnace for a predetermined period of time before being removed outside the tube furnace for cooling under the H_2S/H_2 atmosphere. A thermocouple allowed *in situ* temperature profile recording for each annealing run (for example, see Figure S3a) for an example. The "time error" for each measurement was estimated as the time taken between the start of the experiment and when the temperature reached 95% of the desired setpoint.



Figure S3: Sources of error considered in statistical analysis of diffusion data. (a) representative annealing profile. The time used for each measurement was total time within 5% of the setpoint. (b) optical micrograph of a tilted SIMS crater, indicating the position of the depth profile line scan in (c). (d) One way to quantify the effects of sputtering error is to take the entire sample set and measure sputtering rate (= crater depth/sputter time). This should be linearly correlated with primary ion sputter power; the standard deviation is used to estimate error in the depth of the diffusion profiles.

Conversion of sputtering time to profile depth was achieved by measuring the depth of the SIMS craters using a Dektak profilometer and assuming a constant sputtering rate (Fig. S3b and c). The main factors contributing to error in depth profiling are surface roughness and sample tilt. Tilt can be seen clearly in Figure S3b with a distortion of the square SIMS profile. However, the sputter rate was found to be correlated with primary beam current, which could only be controlled accurately to within \pm 25 nA but was displayed on the instrument for every run (Fig. S3d). An ordinary linear regression of the measured sputter rate on primary beam current was used to estimate a standard deviation for diffusion profiles that are subjected to such systematic errors.

S4 Reduced magnetization of pyrrhotite

Figure S4: Intensity of (001)_{NiAs} magnetic reflection *M* in Fe₇S₈, used to calculate reduced magnetization S(T) = M(T K) / M(T= 0 K). Reproduced from Ref. ⁵

Rreduced magnetization S(T) for pyrrhotite was calculated from digitized data from Powell *et al.*, representing the relative intensity of the (001)_{NiAs} magnetic reflection as a function of temperature obtained using powder neutron diffraction on Fe₇S₈ (Figure S4). ⁵

Parameter	Mean	Lower S.D. bound	Upper S.D. bound
D_o	$4.65 imes10^{-4}$	$2.74 imes10^{-4}$	$7.91 imes10^{-4}$
Q_p	0.83	0.80	0.86
α	0.41	0.47	0.34
$Q_{M,max}$	1.24	1.27	1.21

Table S2: Summary of fitting parameters used for the plot in Figure 5 of the main text. D_o and Q_P values were fit from linear regression of data from above the Néel temperature. The best fit α for each linear regression was then obtained from the entire set of data using Eq. S1. We show the mean linear regression and upper and lower standard deviation (S.D.) bounds.

S5 Fitting of diffusion data with magnetic contribution

We first selected all literature data from Figure 1 in the main text that corresponded to a similar stoichiometry as the samples used in this work (x = 0.04 in Fe_{1-x}S). We then added our data obtained above the Néel temperature of 315 °C and performed a linear regression on the plot of log(${}^*D_{\text{Fe}}$) to obtain an average and standard deviation fits with intercepts giving values of D_0 and slopes corresonding to an activation energy Q_{P} of 0.83 \pm 0.03 eV. We input this range of D_0 and Q_{P} into Eq. S1 to find the single unknown α .

$$D(T) = D_o \exp\left[-\frac{Q_p (1 + \alpha S(T)^2)}{k_B T}\right]$$
(S1)

The full results of the fitting are detailed in Table S2. Each value of α represents the best fit to the data, given by the smallest sum of square residuals from the data.

References

- Townsend, M., Webster, A., Horwood, J. & Roux-Buisson, H. Ferrimagnetic transition in Fe_{0.9}S: Magnetic, thermodynamic and kinetic aspects. *Journal of Physics and Chemistry of Solids* 40, 183–189 (1979).
- 2. Marusak, L. A. & Mulay, L. N. Polytypism in the cation-deficient iron sulfide, Fe₉S₁₀, and the magnetokinetics of the diffusion process at temperatures about the antiferro- to ferrimagnetic λ phase transition. *Physical Review B* **21**, 238–244 (1980).
- 3. Herbert, F., Krishnamoorthy, A., Van Vliet, K. & Yildiz, B. Diffusion limited kinetics of the antiferromagnetic to ferrimagnetic λ -transition in $Fe_{1-x}S$. *In preparation* (2014).

- 4. Wang, H. & Salveson, I. A review on the mineral chemistry of the nonstoichiometric iron sulphide, $Fe_{1-x}S$ (0 < x < 0.125): polymorphs, phase relations and transitions, electronic and magnetic structures. *Phase Transitions* **78**, 547–567 (2005).
- 5. Powell, A. V., Vaqueiro, P., Knight, K. S., Chapon, L. C. & Sánchez, R. D. Structure and magnetism in synthetic pyrrhotite Fe₇S₈: A powder neutrondiffraction study. *Physical Review B* **70**, 014415 (2004).