High-coercivity magnetic minerals in archaeological ceramics: New insights from remanence acquisition and demagnetization measurements at elevated temperatures

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Motivation

What do we know about the magnetic mineralogy of archaeological ceramics?

- From hysteresis/remanence acquisition properties – it always contain a soft magnetic phase and very often an additional hard phase(s);
- Magnetization/susceptibility vs. temperature measurements typically yield Curie temperatures >500 °C;
- However, the Verwey transition indicative of stoichiometric magnetite rarely if ever reported;
- Lowrie 3-axis IRM test often reveals a possible presence of a magnetically hard phase with unblocking temperatures <200 °C (HCLST phase as introduced in McIntosh, G., M. Kovacheva, G. Catanzariti, M. L. Osete, and L. Casas (2007), Widespread occurrence of a novel high coercivity, thermally stable, low unblocking temperature magnetic phase in heated archeological material, *Geophys. Res. Lett.*, **34**, L21302, doi: 10.1029/2007GL031168).

At least three magnetic phases: maghemite (substituted magnetite), hematite, and HCSLT phase (ε-Fe_2O_3 ?)

Obviously, starting material (clay, etc.) normally does not contain all these magnetic phases. They must be therefore formed during the process of ceramics making (intentional or not) and should reflect conditions during the latter.

Our project:

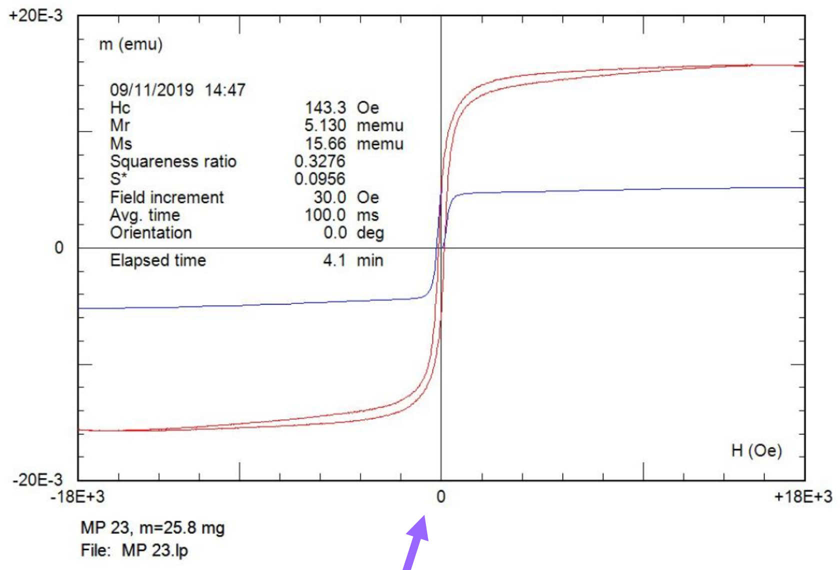
Magnetic minerals in the archaeological ceramics and baked clay: genesis, composition, and applications in geophysics and archaeology
(funded by Russian Foundation for Basic Research and Bulgarian Science Fund)

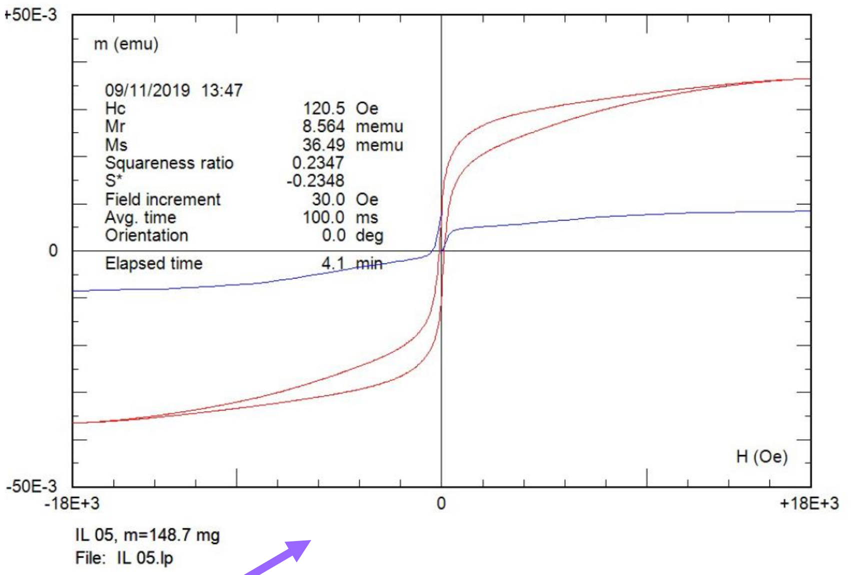
Samples and methods

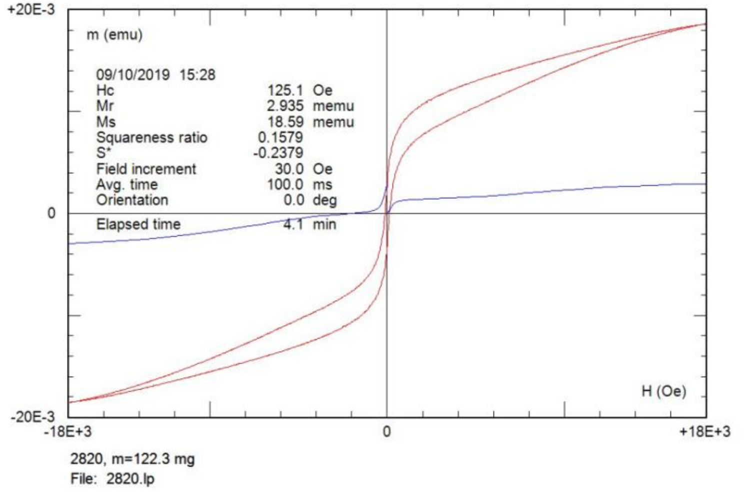
- Samples: baked clay from prehistoric fires and bricks from various archaeological sites in Bulgaria

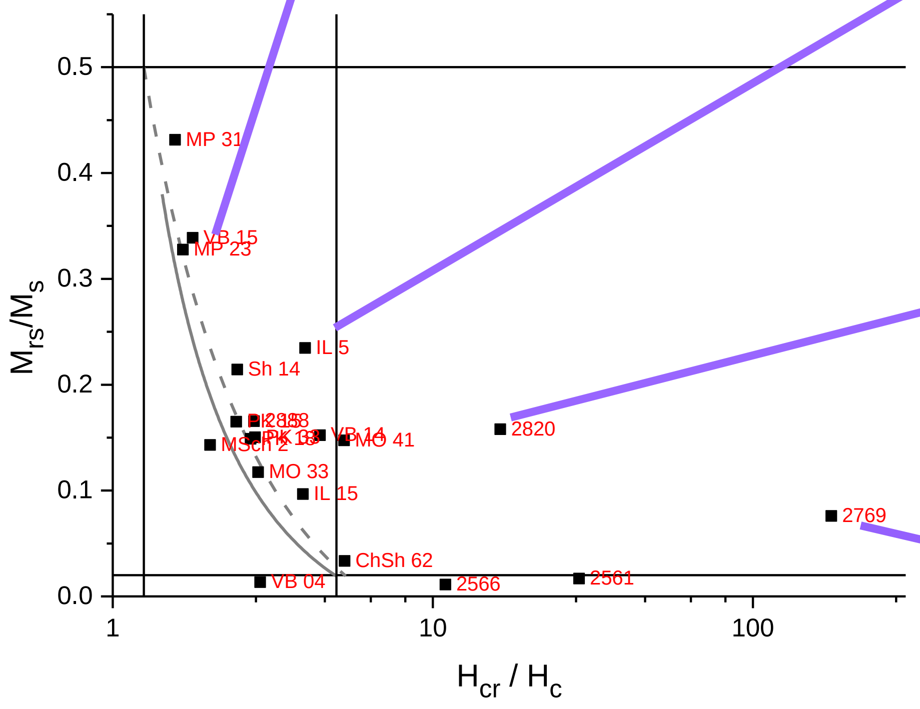
- Experimental methods: IRM acquisition and dc demagnetization curves were measured as a function of temperature between 25°C and the maximal temperature at which ferrimagnetic signal was still resolvable (typically 520 or 540°C, occasionally up to 640°C), using a PMC 3900 vibrating sample magnetometer. For selected samples, hysteresis loops, dc demagnetization curves, and SIRM thermomagnetic curves were measured between 1.8 K and 300 K using a Quantum Design MPMS 3 instrument. Magnetic susceptibility was measured as a function of temperature and ac field frequency in the 2 – 330 K range using a Quantum Design PPMS instrument.

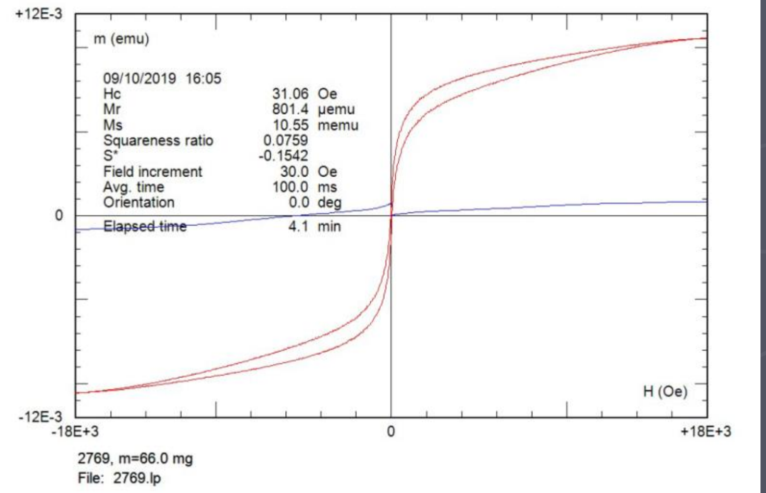
Hysteresis in 1.8 T, room temperature



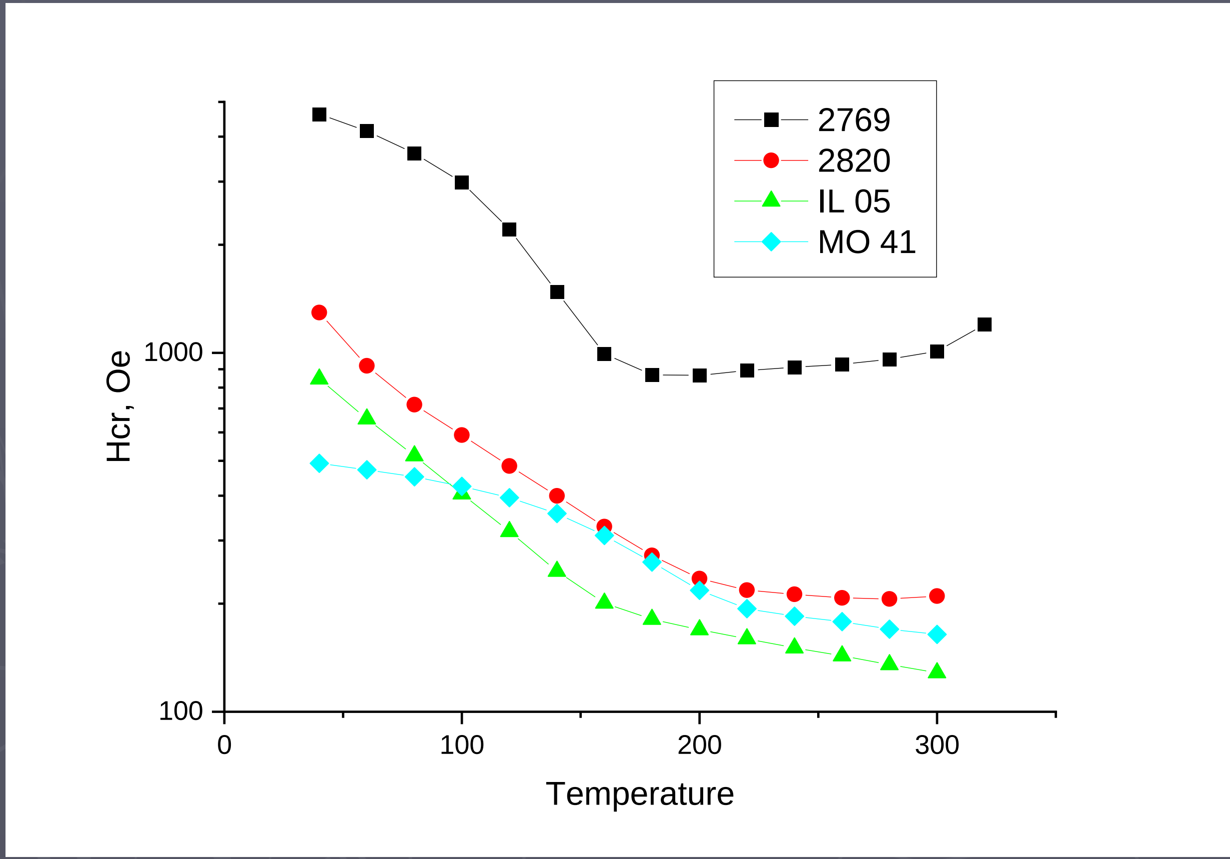


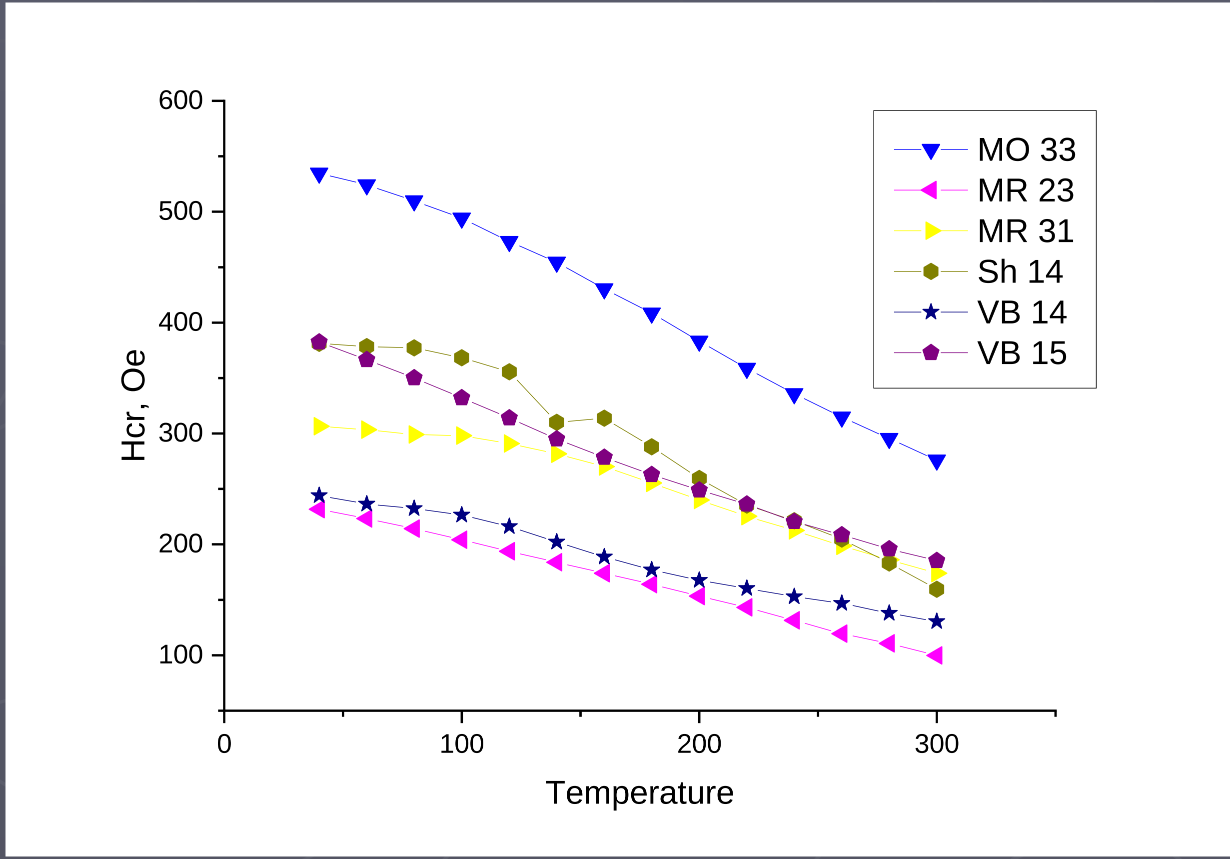




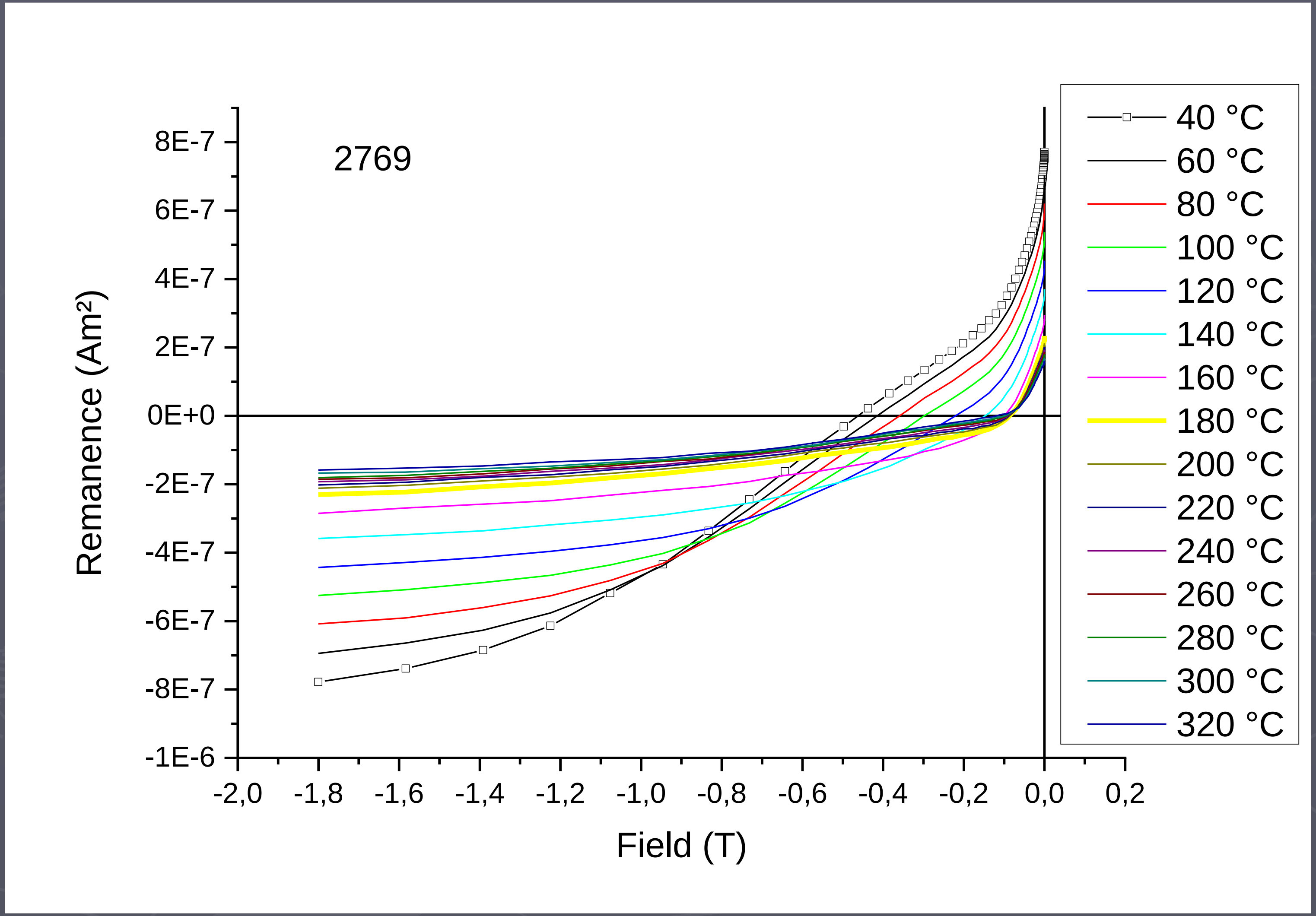


Remanent coercivity vs temperature in the 25 – 300°C range



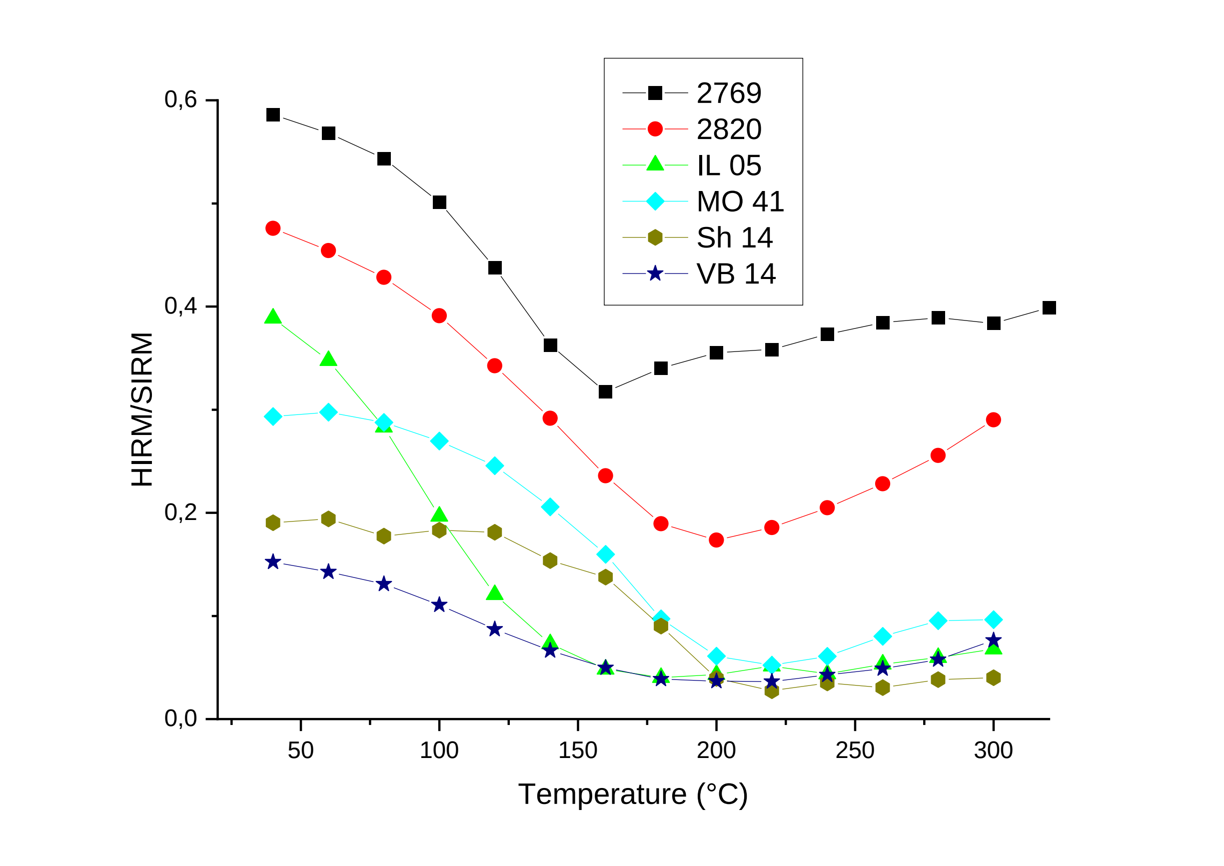


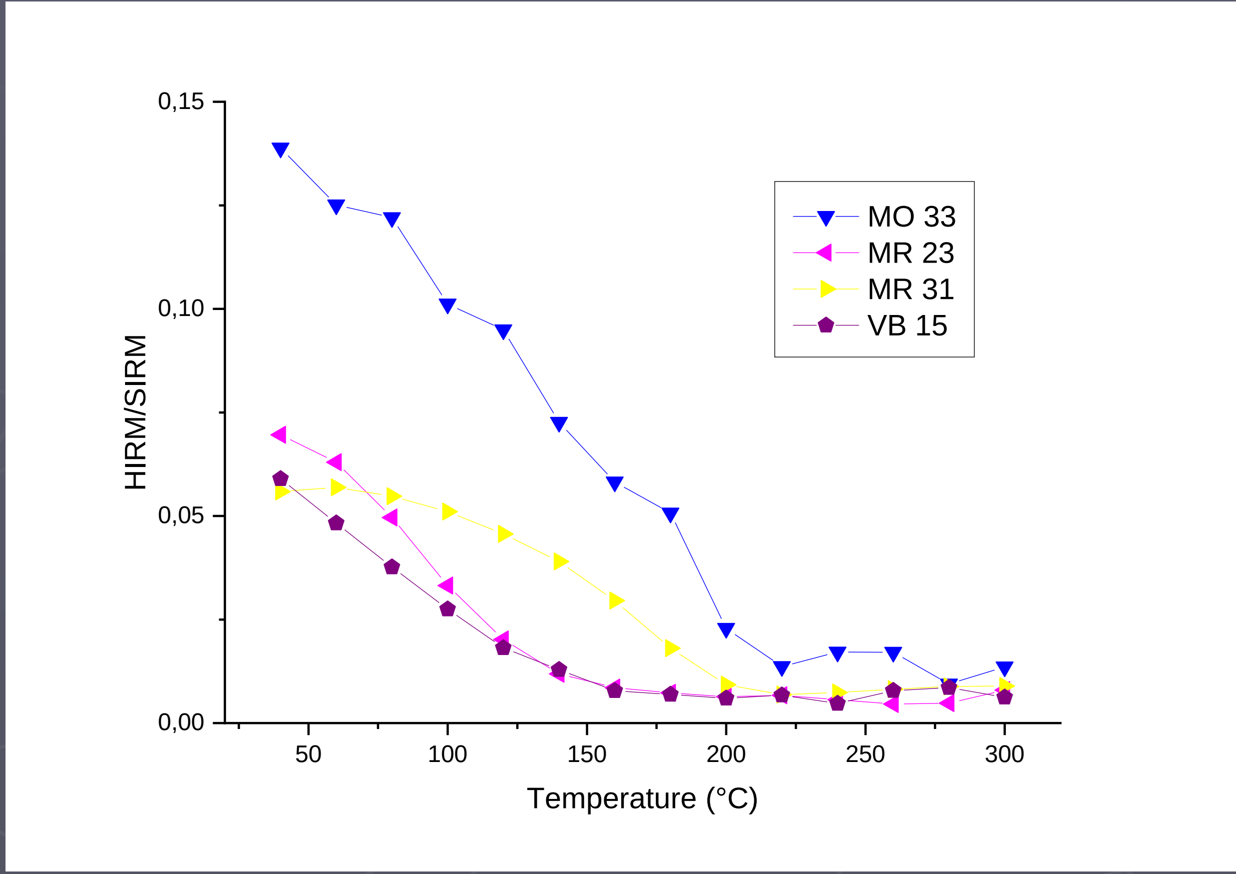
Remanent coercivity vs temperature – Anatomy of $H_{cr}(T)$ dependence



HIRM vs temperature

HIRM ≡ IRM (1.8 T) – IRM (0.3 T)

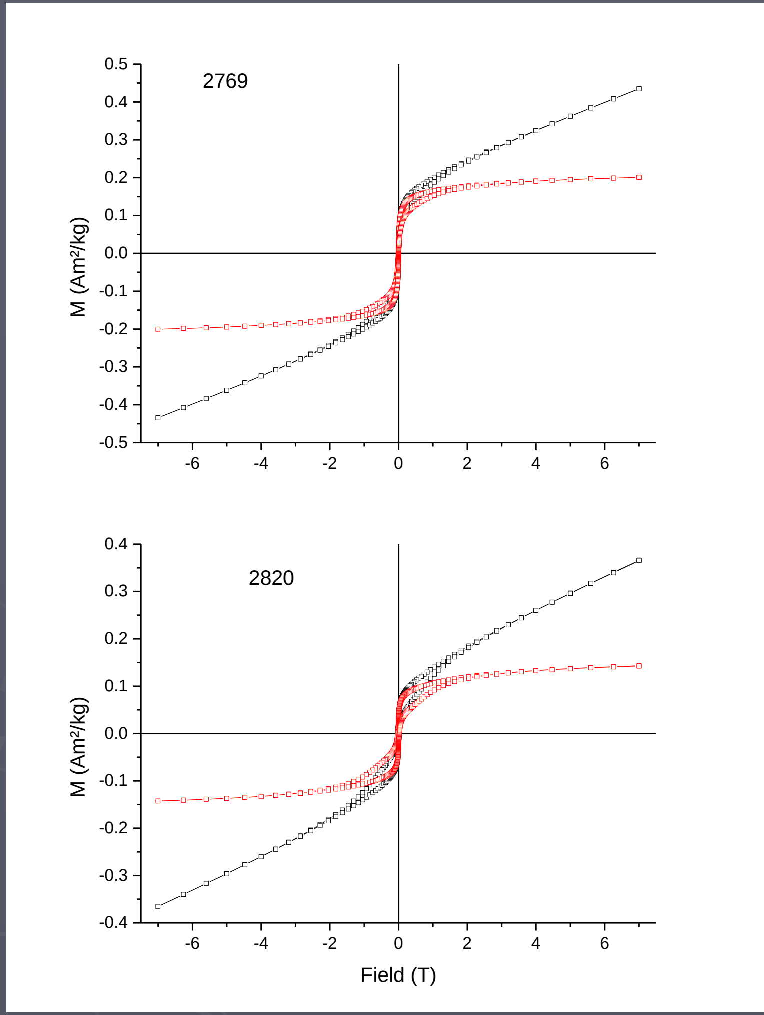


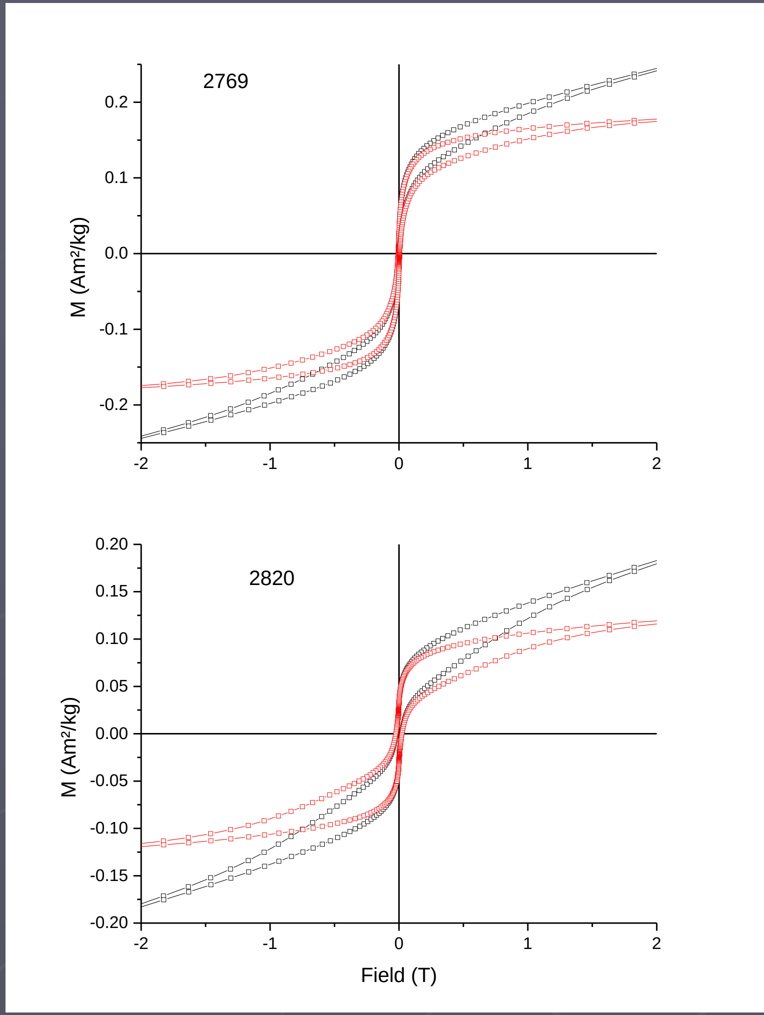


Samples containing both HCSLT and hematite-like phase. HCSLT phase looses its magnetization between 140 and 220°C.

Samples dominated by HCSLT phase.

Hysteresis in ±7 T field at 295 K

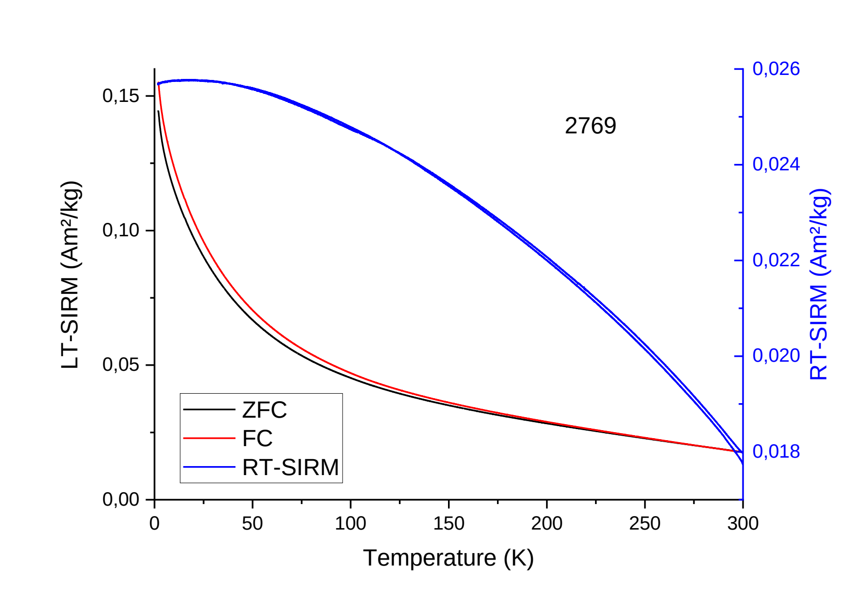


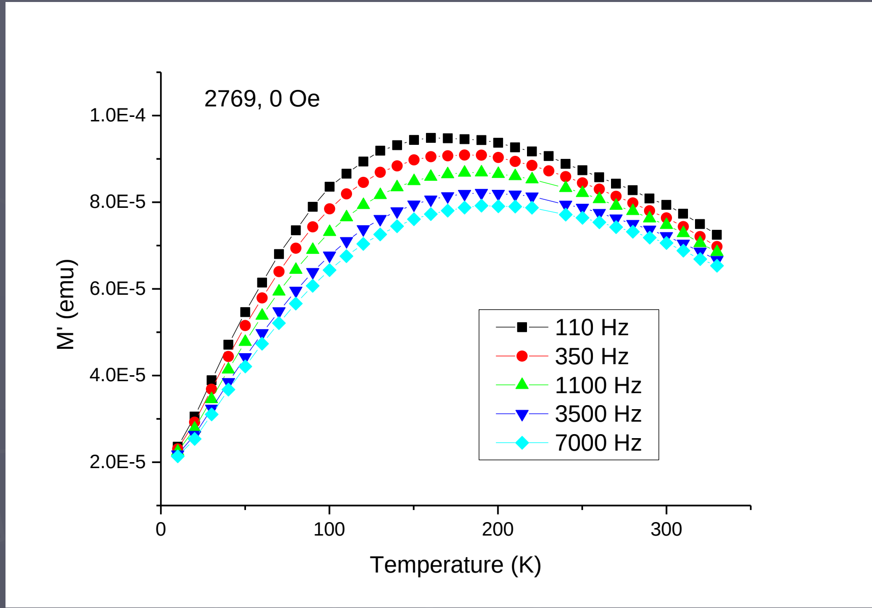


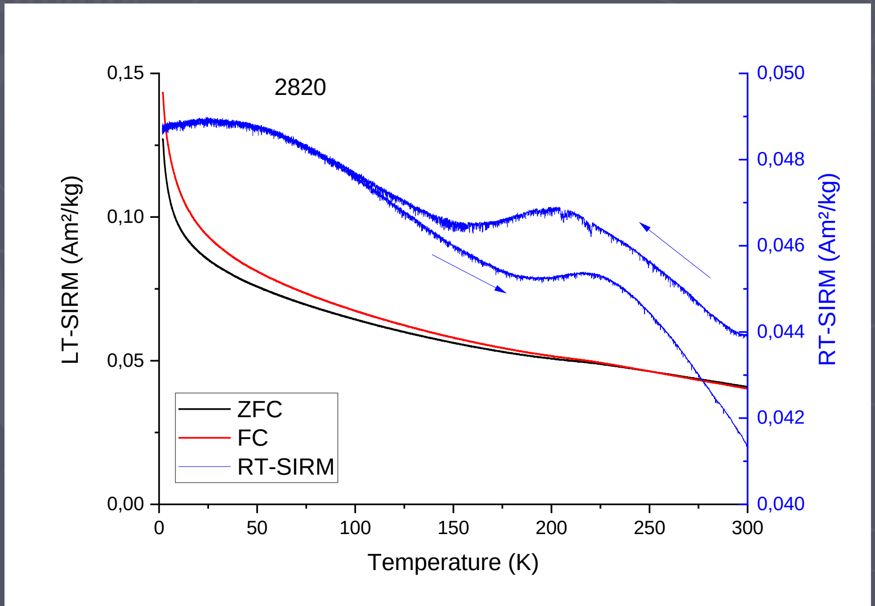
Loops measured in 7 T maximal field. Black are original loops, red – corrected for high-field slope by extrapolating dM/dH vs. 1/H dependency to 20 T field.

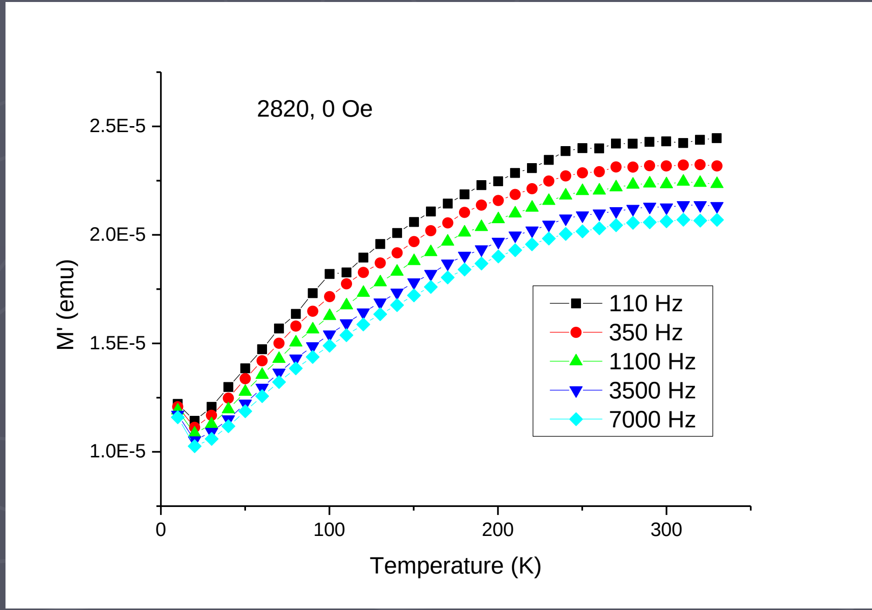
Central parts of ± 7 T loops showing lack of saturation in fields typical for commonly used VSMs.

Remanence and susceptibility at cryogenic temperatures









HCSLT phase — ε-Fe_2O_3 ? Indeed ?

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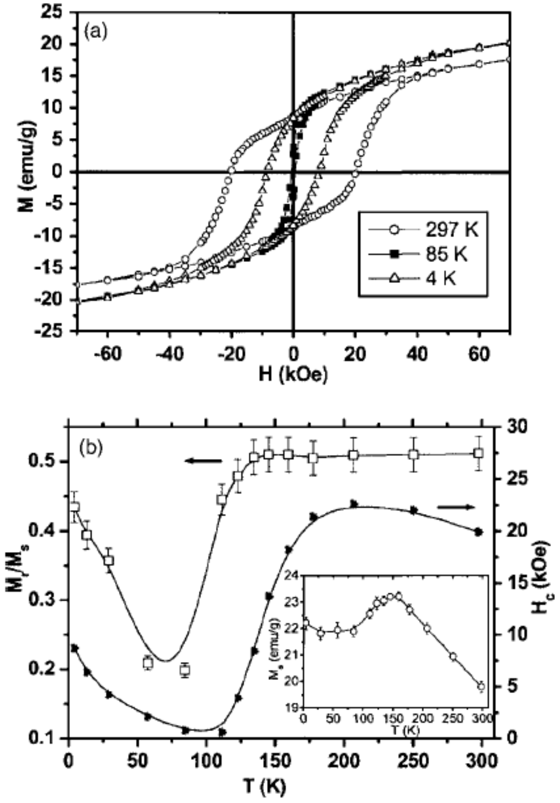


FIG. 3. (a) Magnetization vs magnetic-field hysteresis loops of the ε-Fe_2O_3/SiO_2 composite measured at 4 (△), 85 (■), and 297 K (○). (b) Dependence of the coercive field H_C and the squareness ratio M_R/M_S on temperature. Shown in the inset is the temperature dependence of the saturation magnetization M_S obtained from the law of approach to saturation. The lines are guides to the eye.

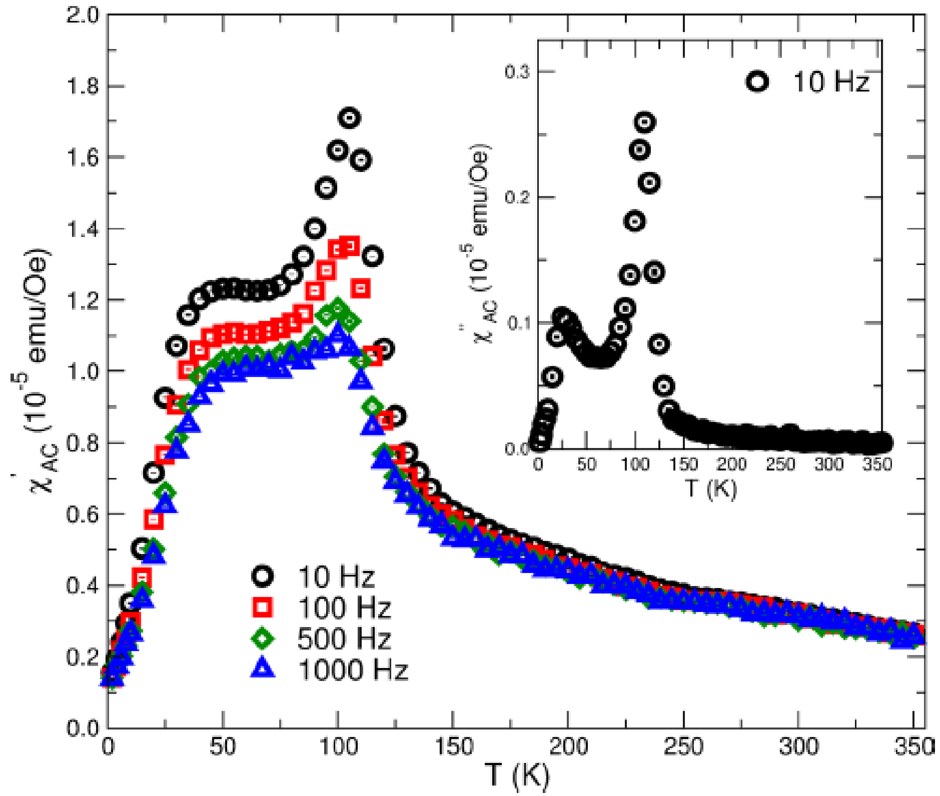


FIG. 4. Temperature and frequency (10 Hz ○, 100 Hz □, 500 Hz ◊, and 1000 Hz △) dependence of the in-phase $\chi'(T,\nu)$ and out-of-phase [$\chi''(T)$ at 10 Hz, inset] AC susceptibility of the ϵ-Fe_2O_3 nanoparticles.

Gich, M. et al. (2005), J. Appl. Phys., 98(4), 044307

Jones, R. et al. (2019), Phys. Rev. B, 100(9), 094425.

HCSLT phase — ε-Fe_2O_3 ? Indeed ?

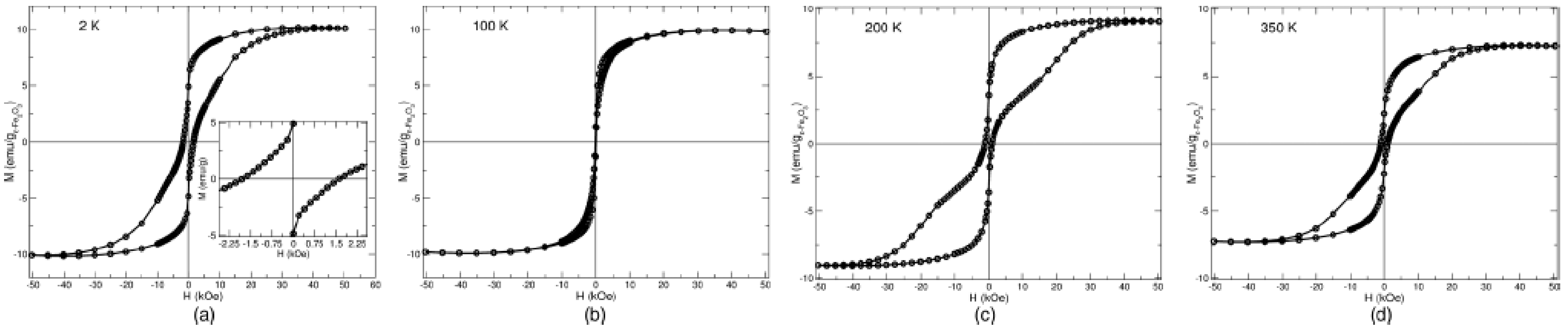
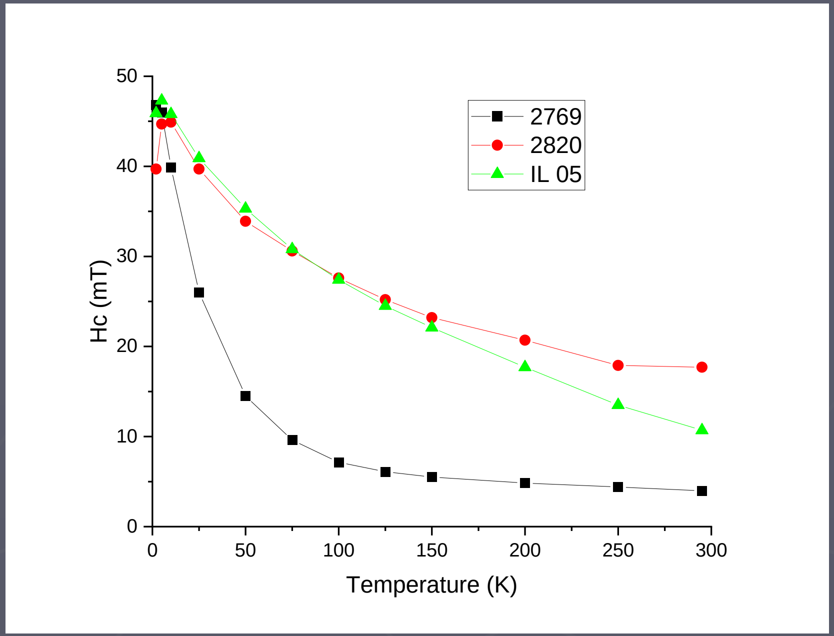
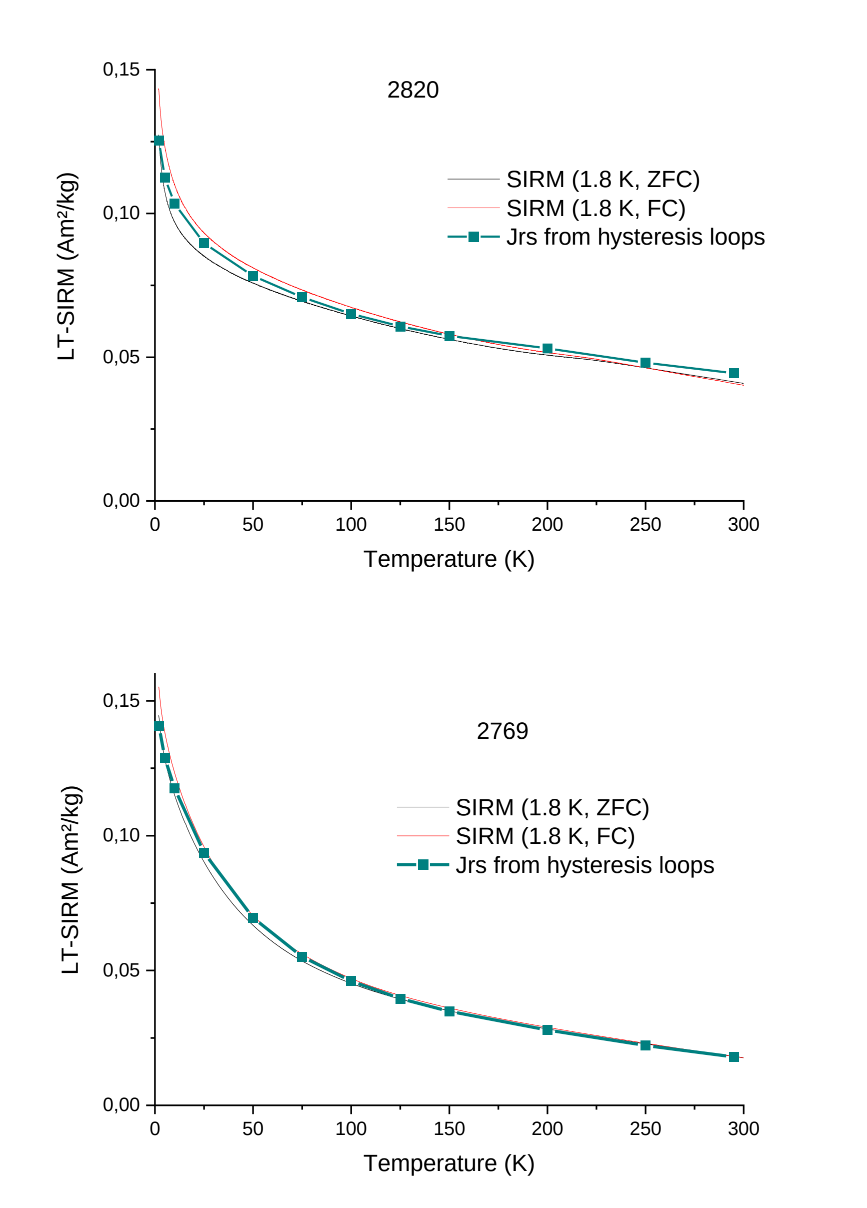


FIG. 6. Respective field-dependent magnetizations of the ϵ-Fe_2O_3 nanoparticles at (a) 2 K, (b) 100 K, (c) 200 K, and (d) 350 K.

Jones, R. et al. (2019), Phys. Rev. B, 100(9), 094425.





Here, we compare magnetic properties of our samples at cryogenic temperatures with those of synthetic ε-Fe_2O_3 (see two previous slides). Even though maghemite or substituted magnetite is also present, we would expect a relatively high coercivity at room T, and a non-monotonous dependence of coercivity and remanence on temperature, were the HCSLT phase be something like pure ε-Fe_2O_3. Neither is observed. Susceptibility vs. temperature curves (slides 10 and 11) are dissimilar too. One tentative possibility to resolve this conundrum is to assume a rather high, up to 0.4 per formula unit, degree of Fe substitution by e.g. Al in the ε-Fe_2O_3 lattice [*c.f.* Namai, A., et al. (2009), Synthesis of an electromagnetic wave absorber for high-speed wireless communication, J. Am. Chem. Soc., 131(3), 1170-1173].

Conclusions

- ✓ Studied samples universally contain at least three magnetic phases. One of these is magnetically soft and two are magnetically hard. Soft phase is likely a substituted magnetite and/or maghemite. Two hard phases show a dramatic difference in their Curie temperatures, the lower one ranging from 140 to 220°C and the higher one from 500 to 640°C. The latter values imply that hematite also contains a considerable amount of impurities.

- ✓ The phase with 140 to 220°C Curie temperatures (HCSLT phase) may be related to orthorhombic iron oxide, ε-Fe_2O_3. However, Curie temperature of the pure phase is somewhat higher, implying that this phase might also be quite heavily substituted with e.g. aluminum. This would also help to reconcile the discrepancy between low-temperature magnetic properties of synthetic ε-Fe_2O_3 and those observed in our study.

Open questions

- ✓ What is really the HCSLT phase as occurs in archaeological samples ?
- ✓ Does stoichiometric magnetite ever occur in archaeological ceramics ? If not, why ?
- ✓ What can we tell about ceramics production from its magnetic mineralogy ?
- ✓ Is there any hope to devise a method for pre-selecting samples for Thellier experiments ?

Acknowledgements

This study has been supported by Russian Foundation for Basic Research (grant 19-55-18006) and Bulgarian Science Fund (grant KP-06-Russia-10). Magnetic measurements have been carried out using the facilities of St. Petersburg State University Research Park and Schmidt Institute of Physics of the Earth RAS, Moscow.

Appendix

Discovery of the HCSLT phase

Cui, Y., and K. L. Verosub (1995), A mineral magnetic study of some pottery samples: possible implications for sample selection in achaeointensity studies, Phys. Earth Planet. Inter., 91, 261-271.

Jordanova, N., E. Petrovský, and M. Kovacheva (1997), Preliminary rock magnetic study of archaeomagnetic samples from Bulgarian prehistoric sites, J. Geomag. Geoelectr., 49, 543-556.

Cui, Y., K. L. Verosub, A. P. Roberts, and M. Kovacheva (1997), Mineral magnetic studies of archaeological samples: Implications for sample selection for paleointensity determinations, J. Geomag. Geoelectr., 49, 567-585.

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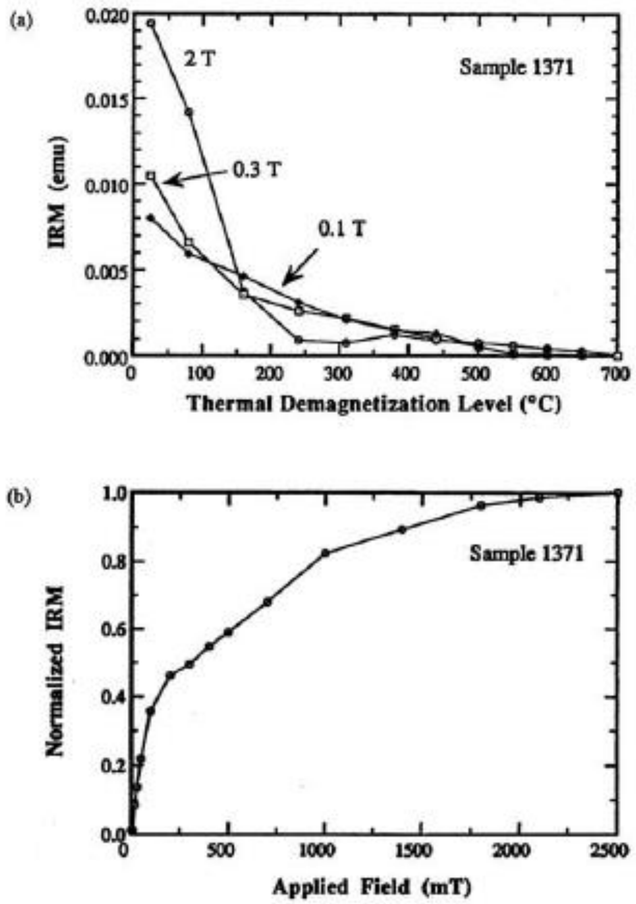

Fig. 9. Data from sample 1371. (a) Thermal demagnetization of a composite three-axis IRM. (b) IRM acquisition curve.

Lack of saturation even at 2.5 T (Fig. 9b) and high stability against AF demagnetization are additional evidence for the dominance of a high-coercivity mineral, which based on the unblocking temperature data, is most likely to be goethite.
Most of the samples with wasp-waisted hysteresis loops listed in Table 1 are bricks. Goethite can be expected as a product of weathering in these samples.

McIntosh, G., M. Kovacheva, G. Catanzariti, M. L. Osete, and L. Casas (2007), Widespread occurrence of a novel high coercivity, thermally stable, low unblocking temperature magnetic phase in heated archeological material, Geophys. Res. Lett., 34, L21302, doi: 10.1029/2007GL031168.

McIntosh, G., M. Kovacheva, G. Catanzariti, F. Donadini, and M. L. Osete Lopez (2011), High coercivity remanence in baked clay materials used in archeomagnetism, Geochem. Geophys. Geosyst., 12(2), Q02003, doi:10.1029/2010GC003310.

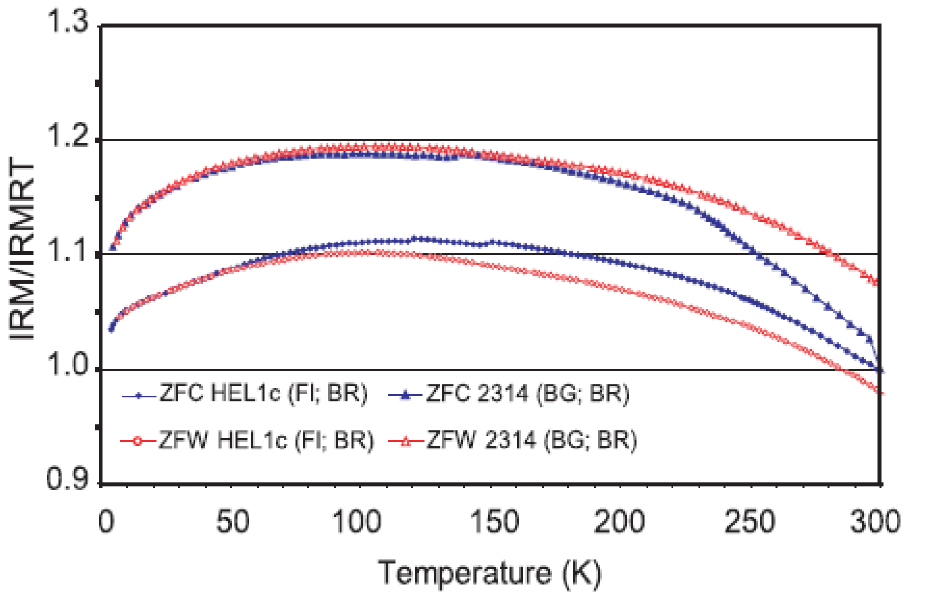

Figure 3. Representative zero-field cooling and warming (ZFC, ZFW resp.) of a 2 T, room temperature isothermal remanence. Country, material given in brackets; for key see, Table 1.

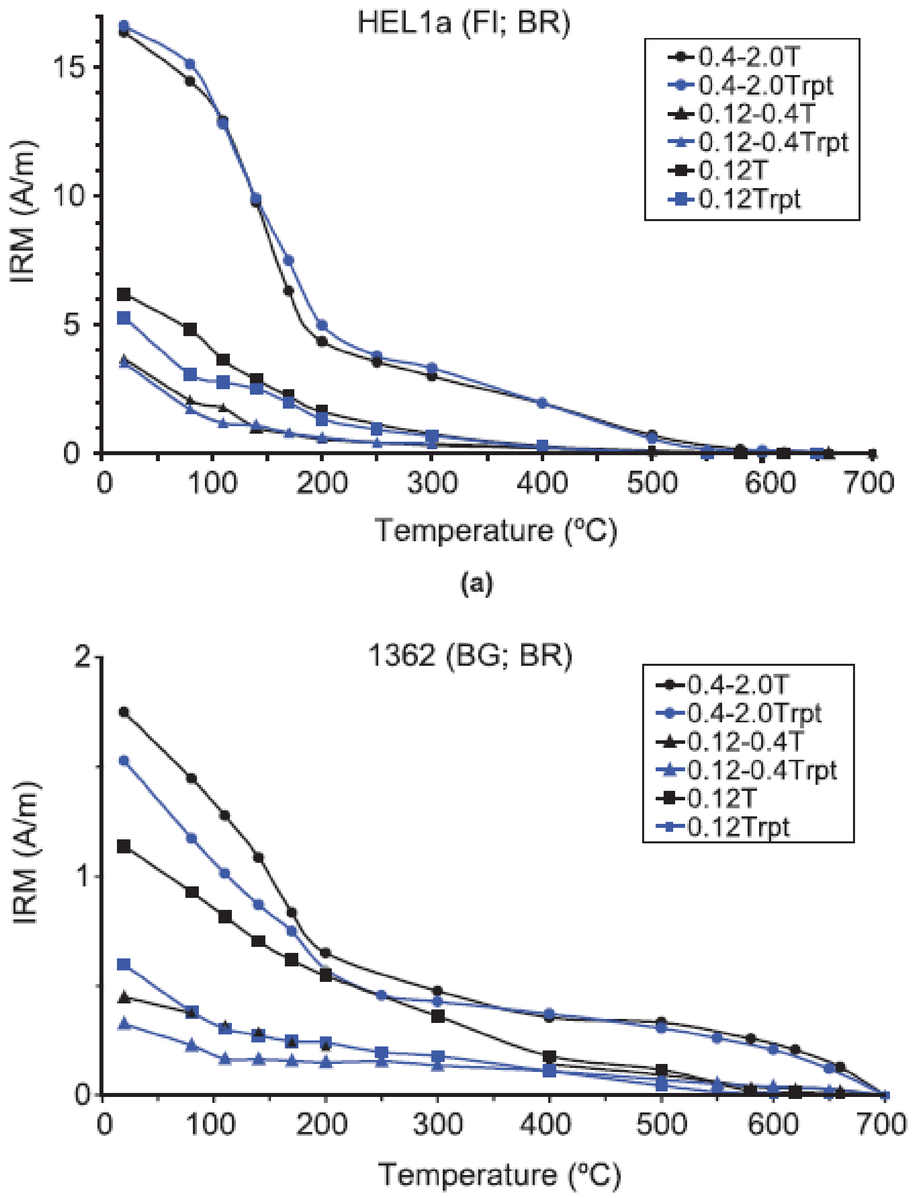

Figure 2. (a) and (b) Representative thermal demagnetisation of orthogonal isothermal remanences. Repeated (rpt) results indicated in grey.

López-Sánchez, J., G. McIntosh, M. L. Osete, A. del Campo, J. J. Villalaín, L. Pérez, M. Kovacheva, and O. Rodríguez de la Fuente (2017), Epsilon iron oxide: Origin of the high coercivity stable low Curie temperature magnetic phase found in heated archeological materials, Geochem., Geophys., Geosyst., 18(7), 2646-2656.

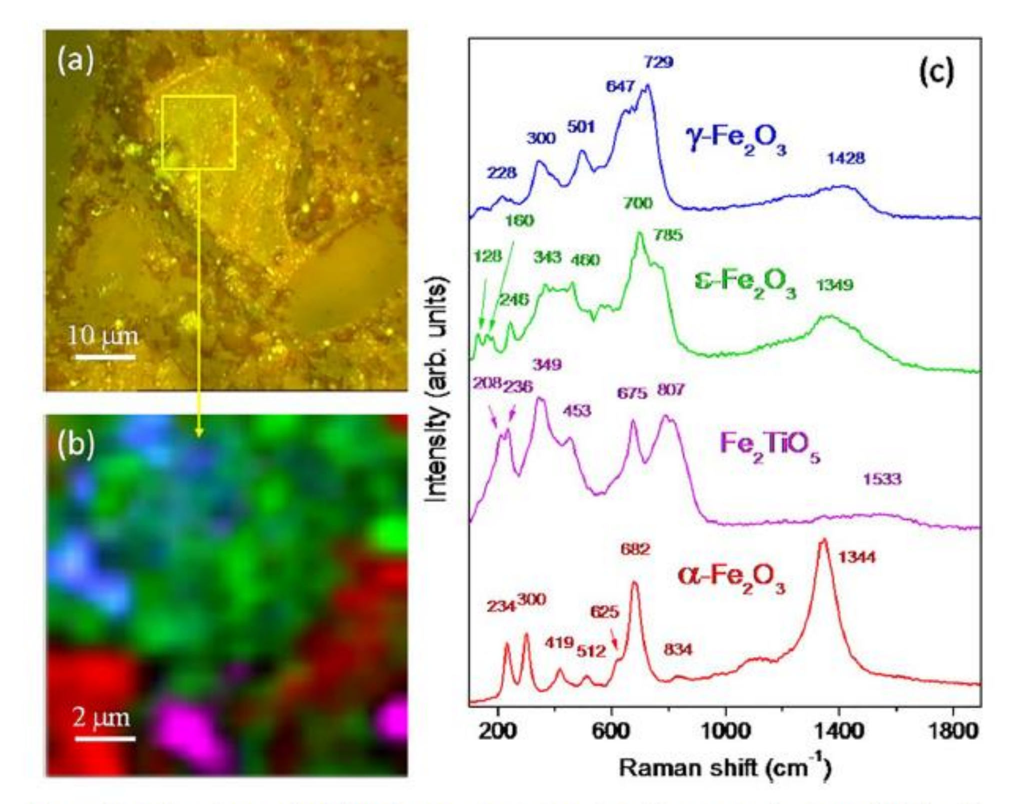

Figure 3. (a) Optical image from sample CO. (b) In-plane Raman intensity image obtained from mapping the region marked with a yellow square in Figure 3a, measuring different single Raman spectra taken each 100 nm with an integration time of 3 s. Maghemite (blue), ε-Fe_2O_3(green), pseudobrookite (violet) and hematite (red) were all detected. (c) Average Raman spectra obtained from in-plane Raman image. Positions of the Raman shifts have been calculated by Lorentzian fitting in each case and the main peaks are labeled.

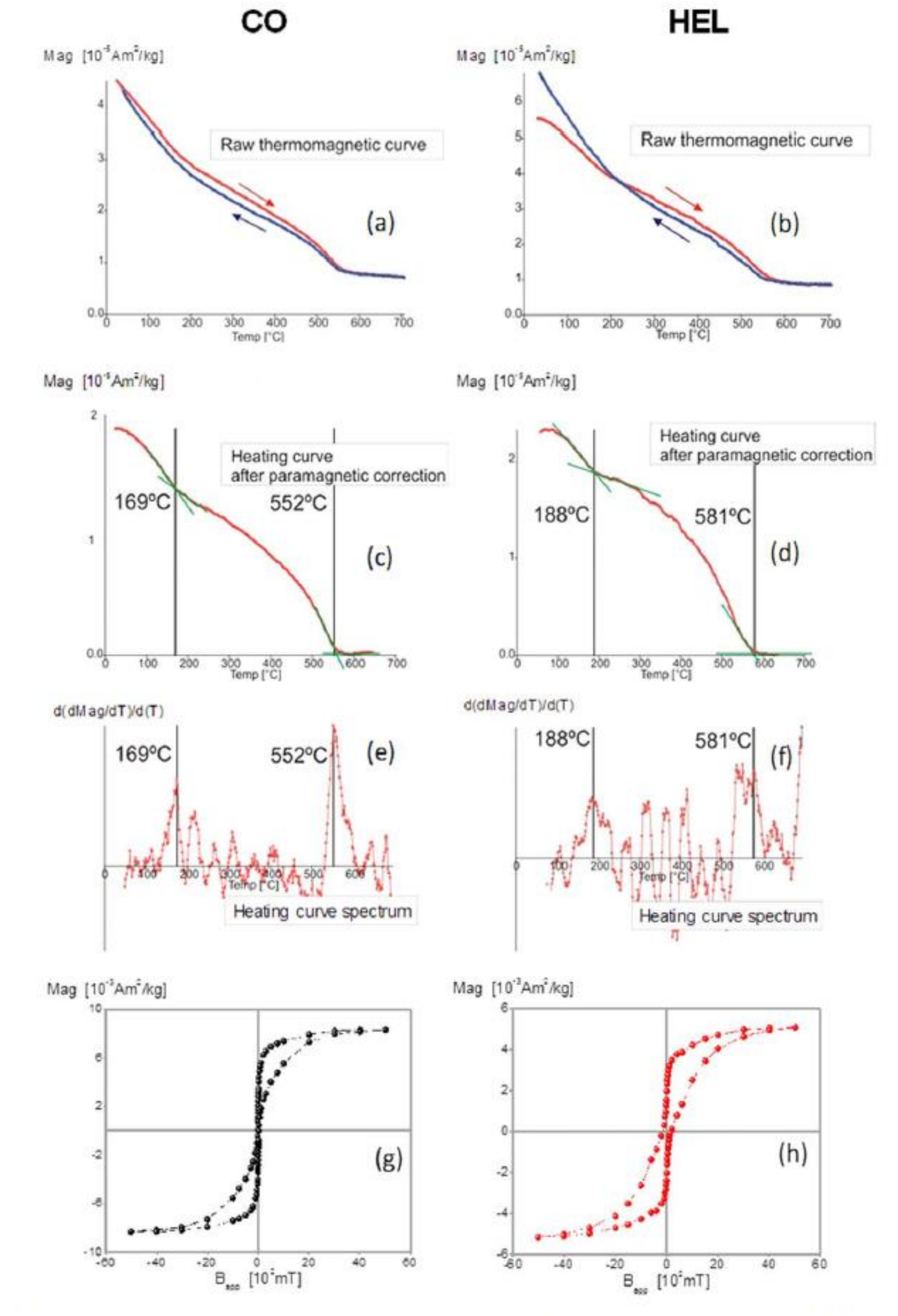

Figure 1. Rock magnetic analyses of representative HEL and CO samples. (a and b) Thermomagnetic curves obtained in a field of 1 T. (c and d) Heating curve corrected for the paramagnetic contribution and Curie temperature determination. (e and f) Second derivative of the heating curve. (g and h) Hysteresis curves at room temperature (corrected by the paramagnetic contribution).