Spin Dynamics and Magnetization in Sepia Melanin by Electron Paramagnetic Resonance and Vibrating Sample Magnetometer

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Calculation S1:

We have calculated the transverse relaxation times (T_2) for both dry and wet Sepia melanin samples using the peak-to-peak linewidths (ΔB_{PP}), from derivative curves, reported in Table 1 of the main manuscript.

The transverse relaxation time [1, 2]

$$T_2 = \frac{2}{\sqrt{3} \cdot \gamma \cdot \Delta B_{PP}} \quad \text{..... S1}$$

γ is defined as

$$\gamma = g \frac{e}{2m_e} \quad \text{.....S2}$$

Where:

- γ is the gyromagnetic ratio
- g is the g-factor
- e is the elementary charge
- m_e is the electron's mass
- ΔB_{PP} is peak-to-peak linewidth of the EPR signal

We have g and ΔB_{PP} for dry and wet samples of Sepia melanin in Table 1 (main file).

Using the g-values from Table 1 (dry: 2.0034; wet: 2.0047), we calculated γ values of 28.03 GHz/T and 28.05 GHz/T for the dry and wet samples, respectively. Substituting these into the S2 equation with the corresponding ΔB_{PP} values yield $T_2 = 66.4$ ns (dry) and $T_2 = 76.2$ ns (wet).

Calculation S2:

INAA analysis indicates the presence of Fe at approximately 86 ppm, while Cu (~19 ppm), Ni (<4.4 ppm), and Co (0.137 ppm) are present only at trace levels. Assuming that all Fe atoms contribute fully as ferromagnetic centers, the maximum theoretical magnetization expected from this concentration is two orders of magnitude lower than the experimentally measured magnetization.

According to INAA measurements, for 1 gr of Sepia melanin, there is ~8.6×10^{-5} gr of Fe. Knowing that the mass of 1 mol of Fe is 56 gr, this means that we have 1.02×10^{18} atoms of Fe in 1 gr of Sepia melanin.

We assume that we have Fe^{3+} (5 unpaired electrons), which corresponds to a magnetic moment of $5\mu_B = 4.64 \times 10^{-23}$ A.m^2, where μ_B is the Bohr magneton and equals 9.27×10^{-24} A.m^2.

The total magnetic moment of all Fe^{3+} ions in 1 gr of Sepia melanin is thus $4.64 \times 10^{-23} \times 1.02 \times 10^{18}$=$\mathbf{4.72 \times 10^{-5}}$ A.m^2.

For 1 gr of dry sample of Sepia melanin, we measured ~$\mathbf{4 \times 10^{-3}}$ A.m^2.

For 1 gr of wet sample of Sepia melanin, we measured ~$\mathbf{2 \times 10^{-3}}$ A.m^2.

This indicates that the magnetic contribution of Fe ions is small.

Therefore, trace metal content detected by INAA cannot account for the observed hysteresis and magnetic parameters (*Ms* ~3.6×10^{-3} emu/g, *Mr* ~0.6×10^{-3} emu/g, *Hc* ~23.6 mT), and that the origin of the magnetic behavior is more consistent with interactions between intrinsic radical centers in the melanin structure.

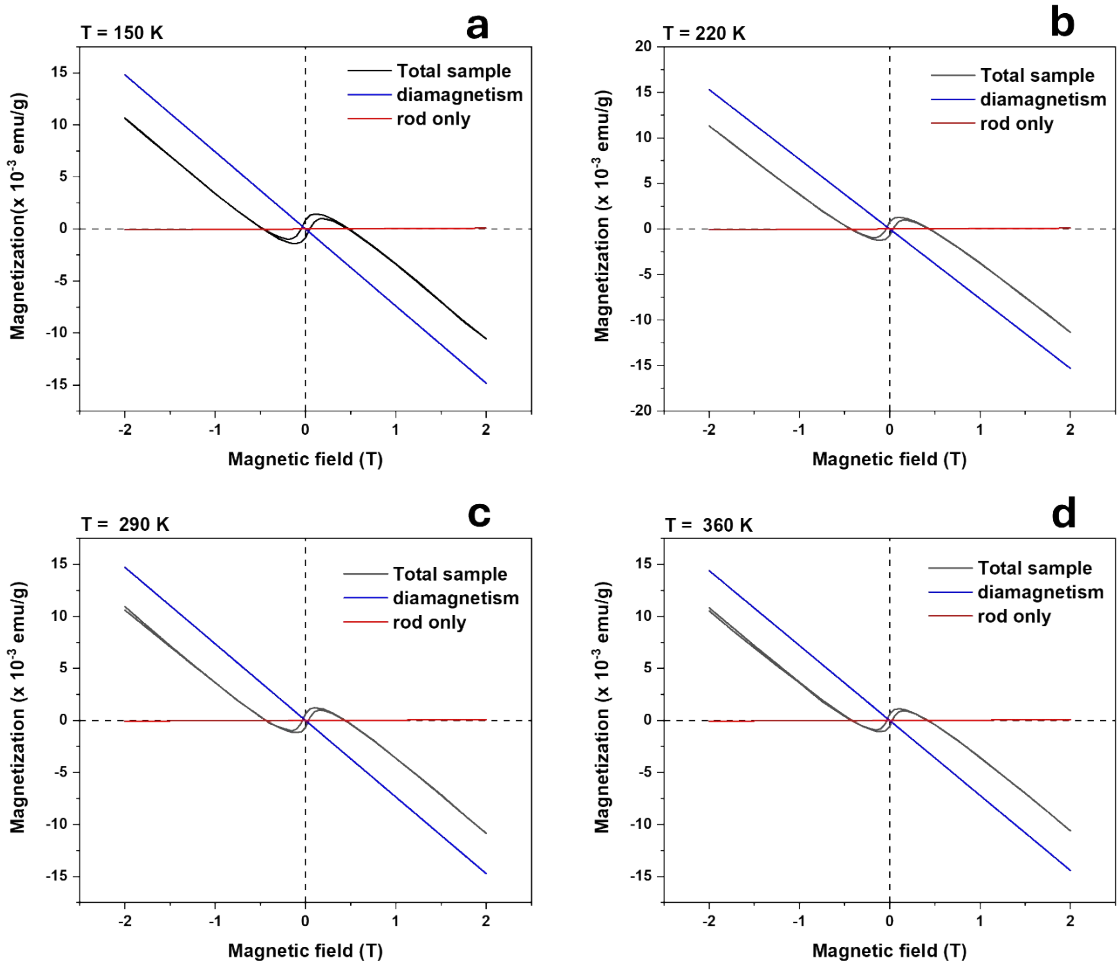

Fig: S1: M-H curve of dry sample (S2_dry_P1) of Sepia melanin total signal including rod (black solid line), diamagnetic contribution (blue line) and rod contribution (red line) at (a) 150 K, (b) 220 K, (c) 290 K and (d) 360 K for a dry sample (1 emu/g = 1 A.m^2/kg).

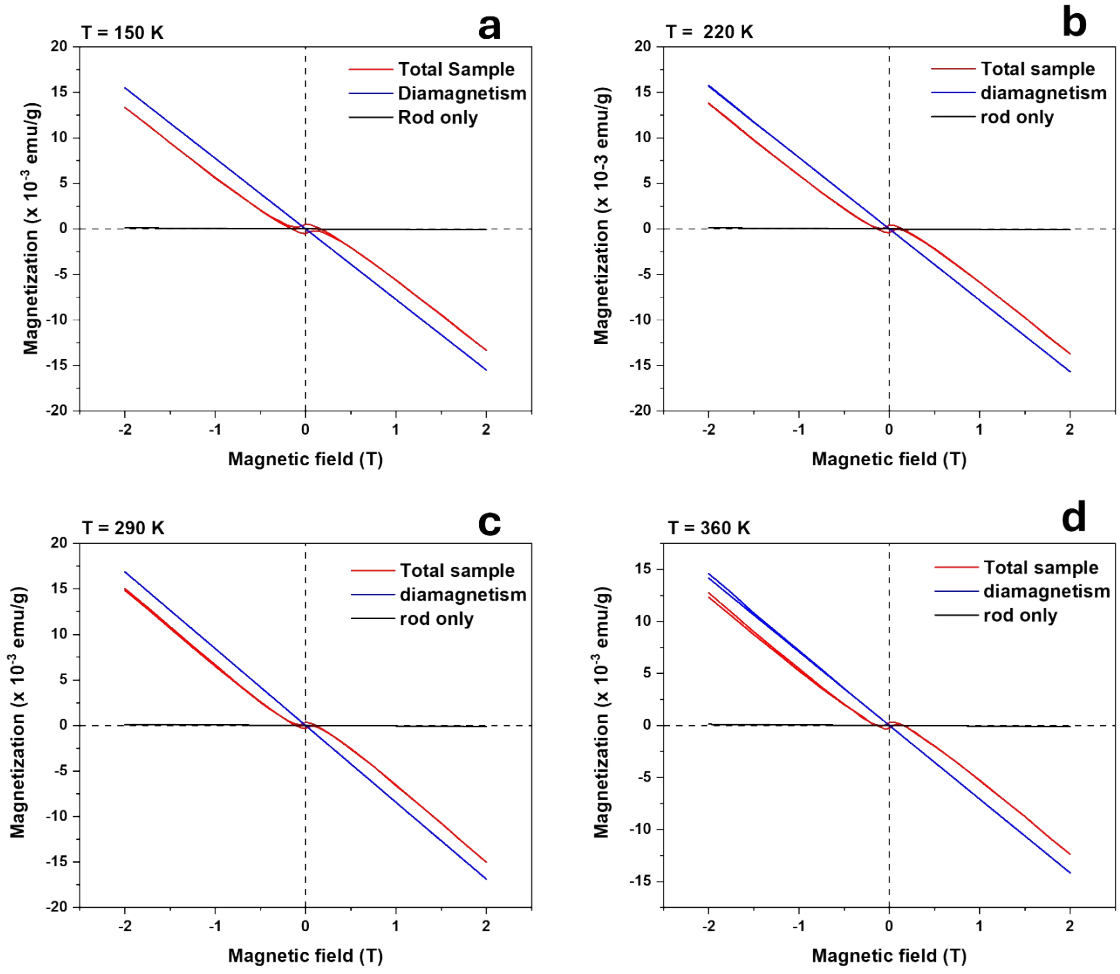

Fig. S2: M-H curve of wet sample (S2_wet_P1) of Sepia melanin total signal including rod (black solid line), diamagnetic contribution (blue line) and rod contribution (red line) at (a) 150 K, (b) 220 K, (c) 290 K and (d) 360 K for a wet sample (1 emu/g = 1 A.m^2/kg).

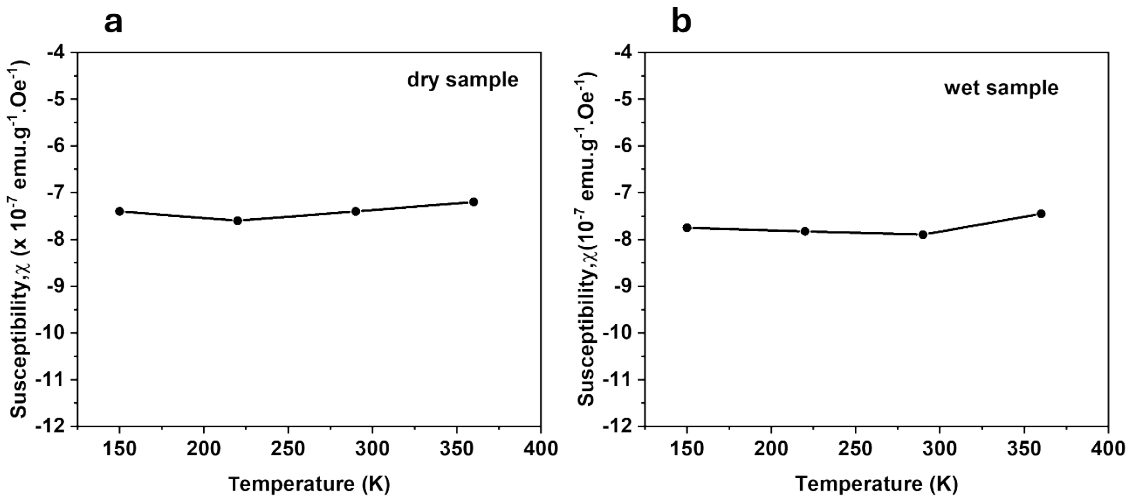

Fig. S3: Susceptibility vs temperature plot for the diamagnetic contribution for (a) dry (S2_dry_P1) and (b) wet (S2_wet_P1) samples of Sepia melanin.

Initially, we subtracted the signal from the sample holder (rod) to isolate the magnetic response of the sample. After that, we removed the sample diamagnetic signals from the total signal. The diamagnetic M–H plot reflects only the diamagnetic behavior of the sample, and the slope of this plot gives the diamagnetic susceptibility.

1 emu/g = 1 $A.m^2/kg$

1 Tesla (T) = 10^{-4} Oersted (Oe)

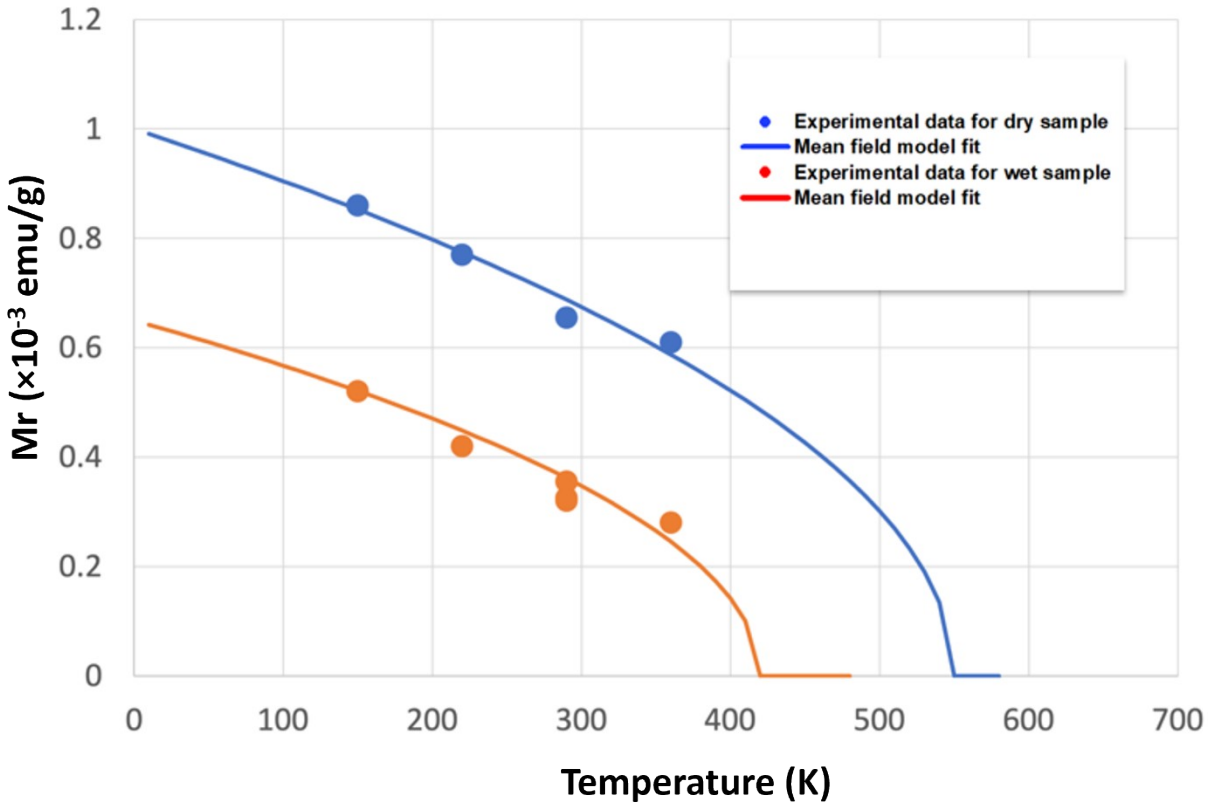

Fig. S4: Remanent Magnetization vs Temperature for dry and wet samples of Sepia melanin [dots are experimental values and solid lines are fitting by mean field model, $M \propto (1-T/Tc)^{1/2}$].

Estimated transition temperature from above graph (Fig. S4) for dry and wet sample of Sepia melanin is approximately 550 and 420 K.

Summary of Saturation Magnetization, Remanence, and Coercivity for Sepia melanin samples obtained from VSM measurements.

Samples of Sepia melanin powder were stored in a N_2 glovebox or a hydration chamber for drying and wetting for ~2 days, respectively. Afterwards, pellets were prepared from the respective powders and put back in their respective places (glovebox or hydration chamber) for drying and wetting for other ~2-3 days, before doing the VSM measurements.

List of symbols in the Table S1:

S1_dry: sample 1 dry.

S1_wet: sample 1 wet … and so on.

Dry: dried in the N_2 glove box.

Wet: hydrated in the hydration chamber with DI water.

P: piece. First, we measured sample S3 twice (with an interval of 3 days between the measurements) then we broke the sample into pieces, and we put two samples in the N_2 glovebox for drying and one sample in the hydration chamber. We weighted the samples twice before and after VSM measurements, to verify if mass was lost while removing them from sample holders.

S3_dry_P1 and S3_wet_P1 are the same sample, which was first measured after drying in the N_2 glovebox (S3_dry_P1). Afterwards, the same sample was put in the hydration chamber and measured again after 3 days (S3_wet_P1).

We broke the S2_dry and S2_wet samples in pieces, and we conducted the temperature-dependent VSM on S2_dry (i.e. S2_dry_P1) and S2_wet (i.e. S2_wet_P1), respectively (see Table S2).

We prepared different samples each time, for dry and wet samples of Sepia melanin, except S3.

For sample S3, first we dried it, then we did the VSM measurements, and finally we broke it into pieces and put pieces in the N_2 glovebox and hydration chamber, for drying and wetting, respectively.

Table S1: Summary of Saturation Magnetization, Remanence, and Coercivity for Sepia melanin samples obtained from VSM measurements.

Sample name	Sample weight before putting in glove box (dry) or hydration chamber (wet) (mg)	Sample weight before VSM measurements (mg)	Time spent in globe box (dry) or hydration chamber (wet) (days)	Ms (m emu/g)	Mr (m emu/g)	Hc (mT)
S1_dry	-	295	~2-3	2.5	0.6	28.2
S1_wet	282	327	~2-3	2.1	0.4	25.1
S2_dry	-	247	~2-3	3.6	0.6	23.6
S2_wet	285	330	~2-3	1.5	0.3	26.0
S2_dry_P1	-	50	~2-3	3.8	0.6	24.6
S2_wet_P2	44	50	~2-3	1.8	0.3	28.1
S3_dry_01	-	275	~2-3	2.4	0.5	26.0
S3_dry_02	275	275	3	2.4	0.5	26.1
S3_dry_P1	36	32	3	2.4	0.5	26.8
S3_dry_P2	64	60	3	2.4	0.6	27.2
S3_dry_P3	29	28	3	2.7	0.5	27.0
S3_wet_P1	32	40	3	1.5	0.3	26.5

Estimation of the uncertainties associated with the measurements of saturation magnetization, remanent magnetization and coercive field was made using the standard deviation σ given by

$$\sigma = \sqrt{\frac{\sum(x_i - \grave{x})^2}{n-1}}.$$

x_i is each individual data point and $\grave{x}$ is the sample mean and n is the number of data point.

For dry samples of Sepia melanin

The saturation magnetization (*Ms*) was measured for eight samples, yielding values of 2.5, 3.6, 3.8, 2.4, 2.4, 2.4, 2.4, and 2.7 × 10^{-3} emu/g. The mean *Ms* was calculated as 2.8 × 10^{-3} emu·g^{-1}, with a standard deviation of 0.5 × 10^{-3} emu/g.

Therefore

$$Ms = (2.8 \pm 0.5) \times 10^{-3} \text{ emu/g}$$

Remanent magnetization (*Mr*) was measured for eight samples, yielding values of 0.6, 0.6, 0.6, 0.5, 0.5, 0.5, 0.6, and 0.5 × 10^{-3} emu·g^{-1}. The mean *Mr* was calculated as 0.55 × 10^{-3} emu·g^{-1}, with a standard deviation of 0.05 × 10^{-3} emu/g.

$$Mr = (0.55 \pm 0.05) \times 10^{-3} \text{ emu/g}$$

Coercive field (*Hc*) was measured for six samples, yielding values of 28.2, 23.6, 24.6, 26.0, 26.1, 26.8, 27.2, and 27.0 mT. The mean *Hc* is 26 mT, with a standard deviation of 2 mT.

$$Hc = 26 \pm 2 \text{ mT}$$

For wet samples of Sepia melanin

The saturation magnetization (*Ms*) was measured for four samples, yielding values of 2.1, 1.5, 1.8 and 1.5 × 10^{-3} emu/g. The mean *Ms* was calculated as 1.7 × 10^{-3} emu·g^{-1}, with a standard deviation of 0.2 × 10^{-3} emu/g.

$$Ms = (1.7 \pm 0.2) \times 10^{-3} \text{ emu/g}$$

The remanent magnetization (*Mr*) was measured for four samples, yielding values of 0.4, 0.3, 0.3 and 0.3 × 10^{-3} emu/g. The mean *Mr* was calculated as 0.33 × 10^{-3} emu·g^{-1}, with a standard deviation of 0.05 × 10^{-3} emu/g.

$$Mr = (0.33 \pm 0.05) \times 10^{-3} \text{ emu/g}$$

Coercive field (*Hc*) was measured for four samples, yielding values of 25.1, 26.0, 28.1 and 26.5 mT. The mean *Hc* is 26 mT, with a standard deviation of 2 mT.

$$Hc = 26 \pm 2 \text{ mT}$$

Table S2: Comparison of magnetic parameters with temperature of dry and wet samples of Sepia melanin (1 emu/g = 1 $A.m^2/kg$).

Temperature (K)	Dry sample (S2_dry_P1)			Wet sample (S2_wet_P2)		
	M_s ($\times 10^{-3}$ emu/g)	M_r ($\times 10^{-3}$ emu/g)	H_c (mT)	M_s ($\times 10^{-3}$ emu/g)	M_r ($\times 10^{-3}$ emu/g)	H_c (mT)
150	4.10	0.86	34.6	2.17	0.52	41.4
220	3.96	0.77	29.0	1.98	0.42	33.4
290	3.85	0.66	24.6	1.87	0.36	28.1
360	3.80	0.61	23.0	1.78	0.28	23.6

For the temperature dependent VSM measurements, we broke the sample S2_dry and sample S2_wet into small pieces (approximately ~50 mg for both dry and wet samples), after doing the VSM measurements in ambient conditions, and kept them in the N_2 glovebox and hydration chamber, for drying and wetting, respectively, for ~2-3 days before doing the temperature-dependent VSM measurements. The weight of dry sample remained approximately the same, whereas the weight of the wet sample increased by ~15% of the weight percentage, after wetting.

(1) Poole, C. P.; Farach, H. A. Electron spin resonance. In *Handbook of Spectroscopy*, CRC Press, 2019; pp 217-314.

(2) Tadyszak, K.; Mrówczyński, R.; Carmieli, R. Electron spin relaxation studies of polydopamine radicals. *The Journal of Physical Chemistry B* **2021**, *125* (3), 841-849.