Timing-dependent in vivo cobalt doping of magnetosome chains

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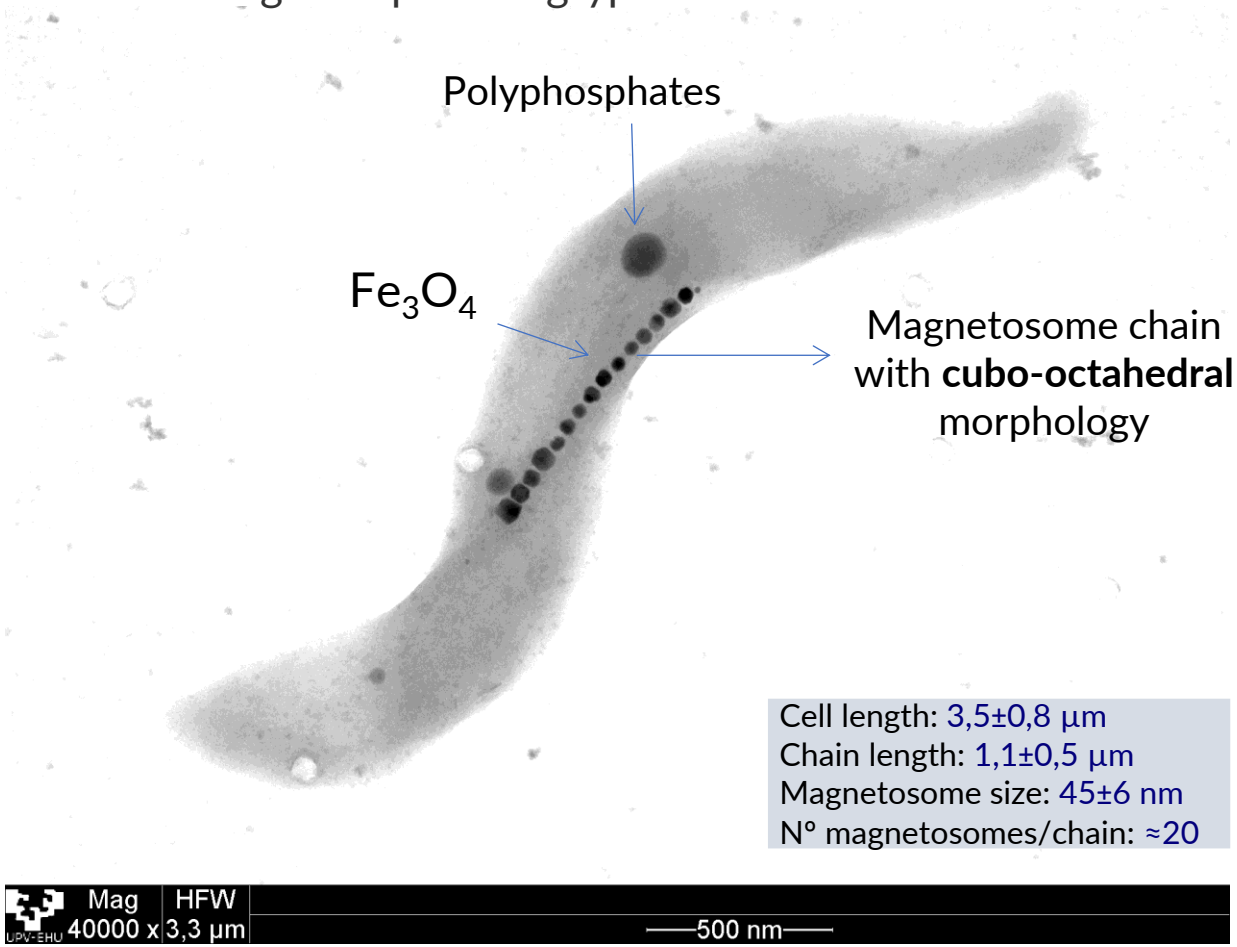
Magnetosomes provide an ideal magnetic nanoparticle system

- Single-domain magnetite nanoparticles
- High crystallinity & chemical purity
- Controlled morphology, size and chain organization
- Magnetosome membrane provides a biocompatible interface

Excellent structural control makes magnetosomes a powerful model system

Magnetospirillum gryphiswaldense



Marcano et al., J. Phys. Chem. C 2018, 122, 7541–7550.

A key limitation: magnetosome composition is difficult to tune

Natural biomineralization gives precise control over:

- **Size**
- **Morphology**
- **Chain organization**

Strong biological control

Composition
difficult to modify

Fe_3O_4

Natural magnetite composition

Can transition-metal doping overcome this compositional limitation?

Most M. gryphiswaldense magnetosomes are biomineralized magnetite (Fe_3O_4).

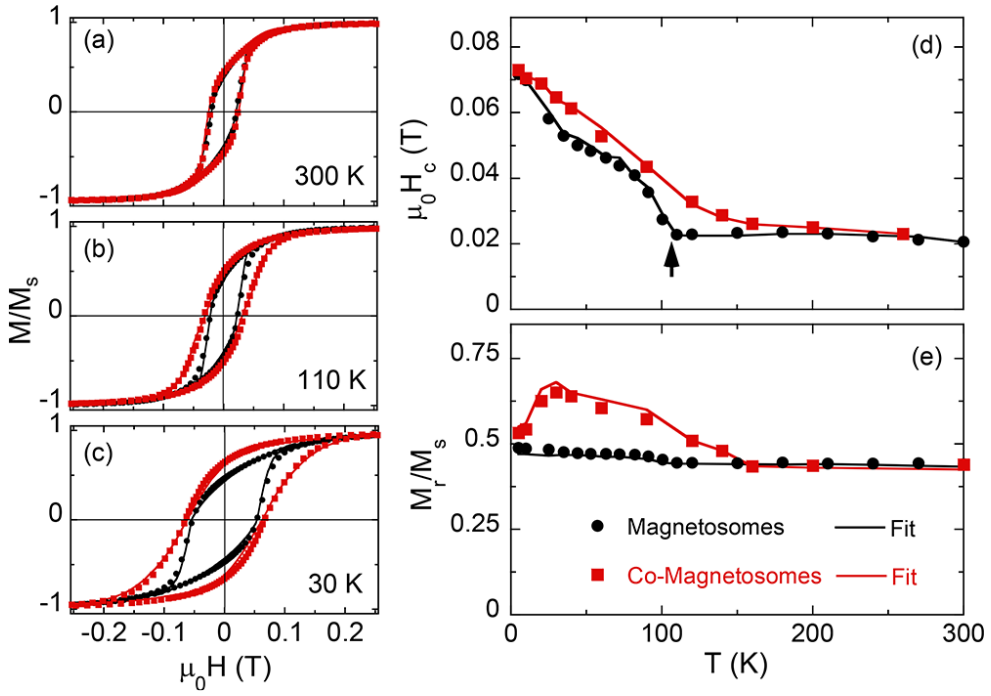
Previous Co doping: strong magnetic effect, but low incorporation

Previous in vivo Co-doping work established that:

~1% Co^{2+}_{Oh}

substitutes Fe^{2+} in octahedral sites

- Co increase Coercivity and magnetic hardness
- The magnetic anisotropy becomes strongly temperature dependent
- The effect is large despite the very small Co



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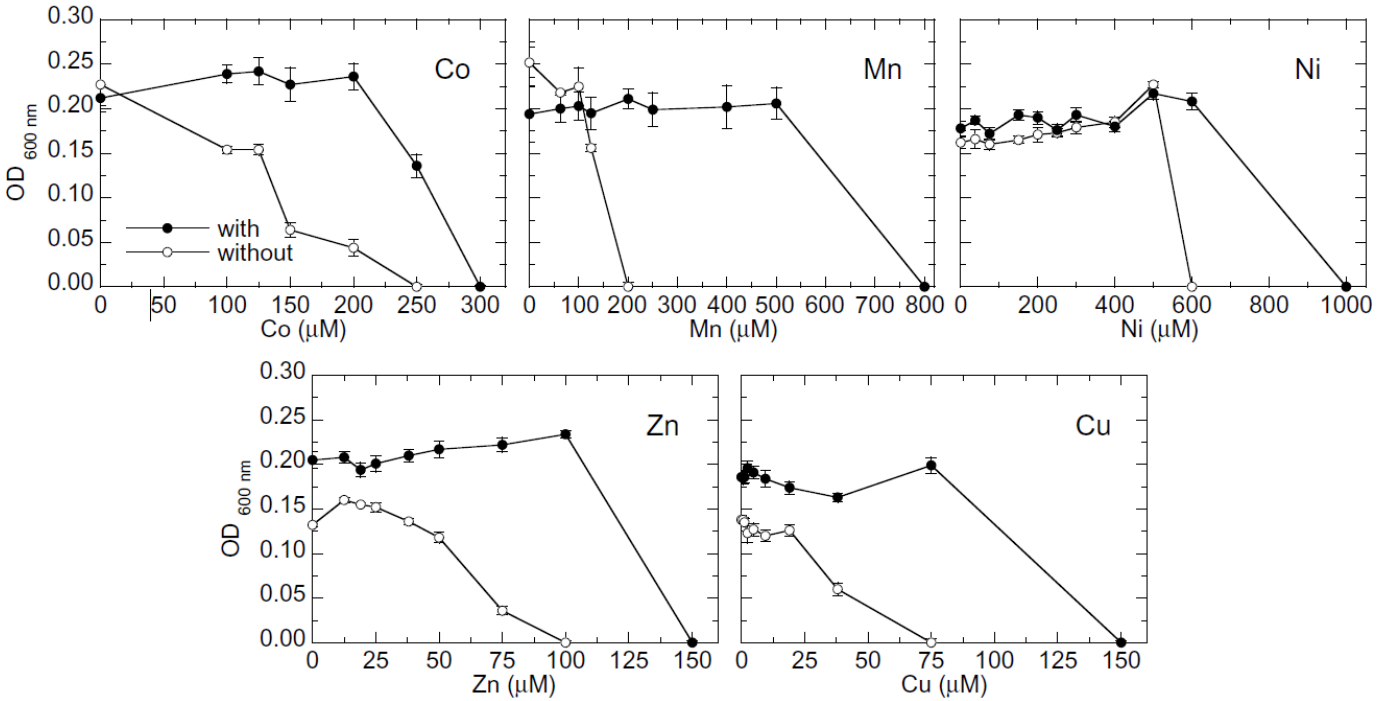
Open question:
can we increase or better control Co incorporation?

Magnetosomes increase tolerance to transition-metal stress

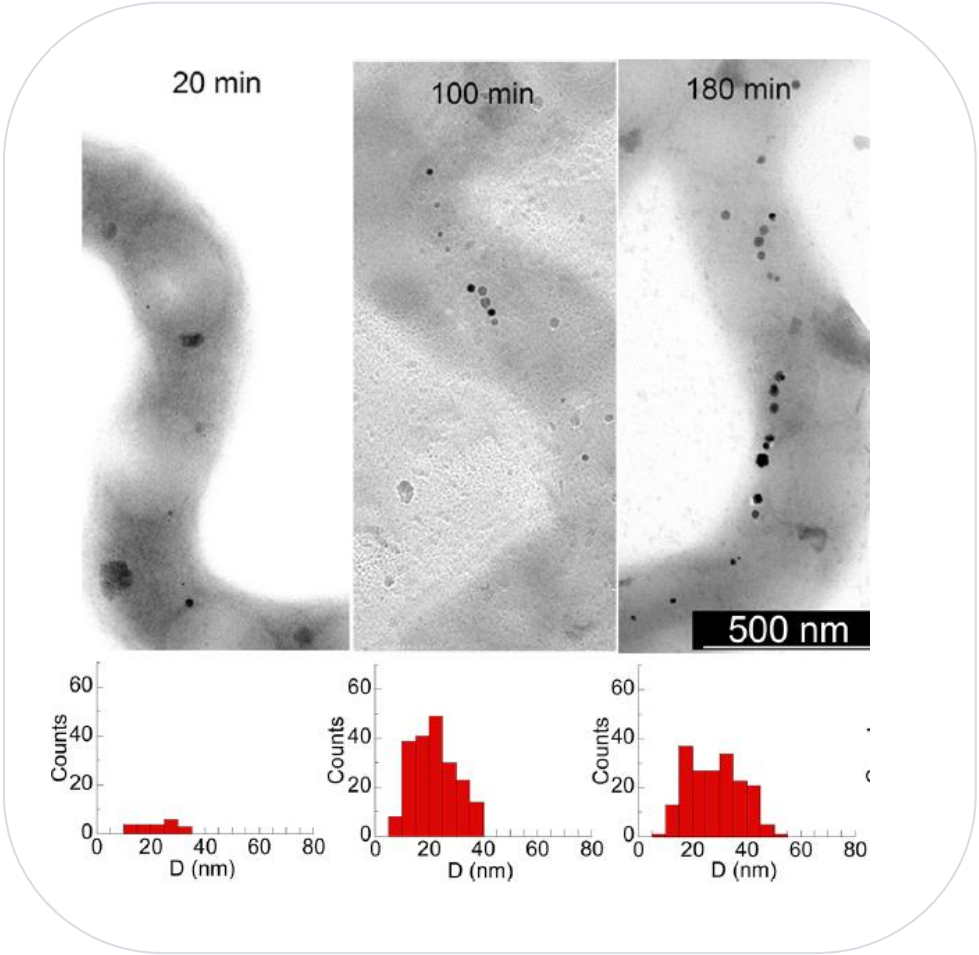


- Bacteria containing magnetosomes tolerate higher concentrations of transition metals
- The protective effect is observed for Co, Mn, Ni, Zn and Cu
- For Co, the excess metal is incorporated specifically into the magnetosomes

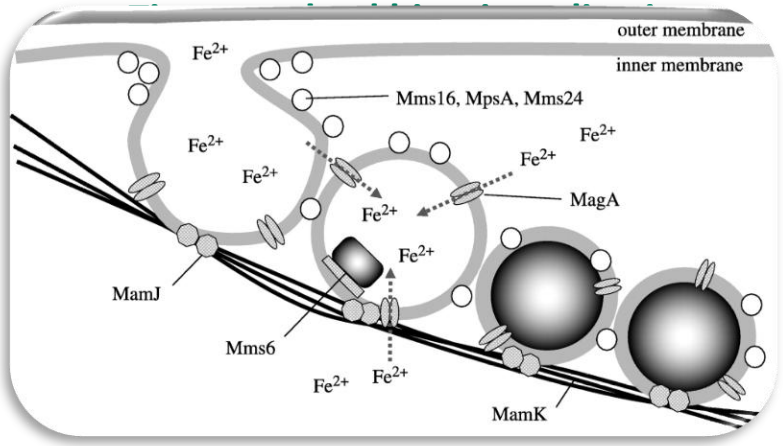
Key idea: having magnetosomes already present may help the cells accommodate Co

Muñoz et al., Sci. Rep. 2020, 10, 11430.

Magnetosome biomineralization is time-dependent



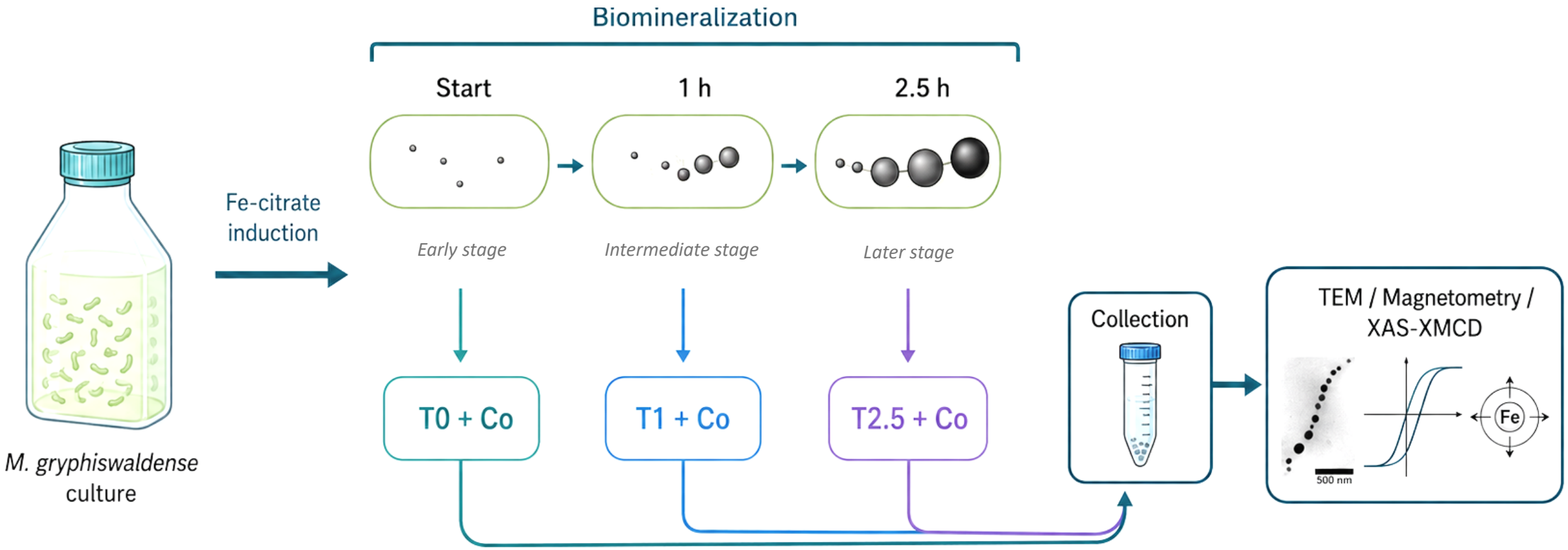
Fdez-Gubieda et al., ACS Nano 2013, 7, 3297–3305.



- Small magnetite crystals appear first and grow progressively during biomineralization after Fe addition
- Therefore, adding the same Co dose at different times exposes it to different growth stages

Timing determines whether Co is supplied at an early, intermediate, or later biomineralization stage

Magnetosome biomineralization is time-dependent



Same Co dose; different addition stage → different biomninelalization

Characterization strategy

Each technique answers a different question

TEM

Does Co-addition timing alter magnetosome formation?

- morphology
- particle diameter and distribution
- magnetosomes per chain

Magnetometry

Do those structural/doping changes modify magnetic behavior?

- ZFC/FC M(T)
- M(H) at 300 and 30 K
- Hc(T), Mr(T), loop shape

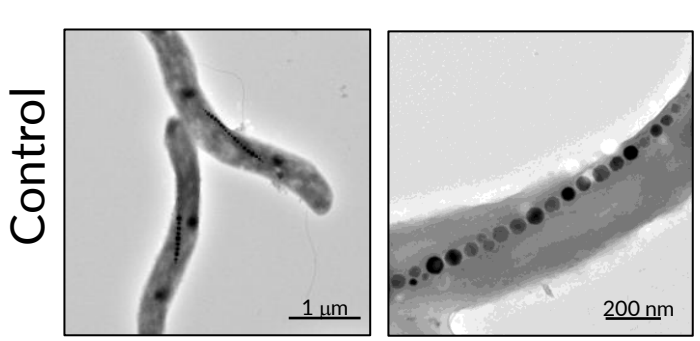
XAS / XMCD

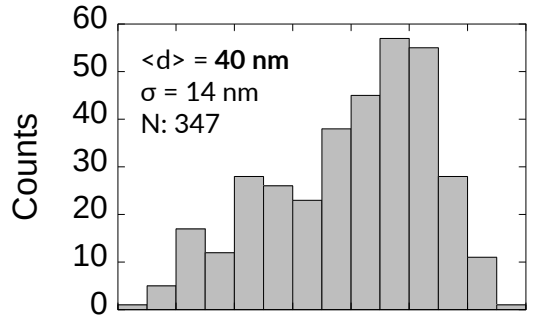
Where does the magnetic change come from at the element-specific level?

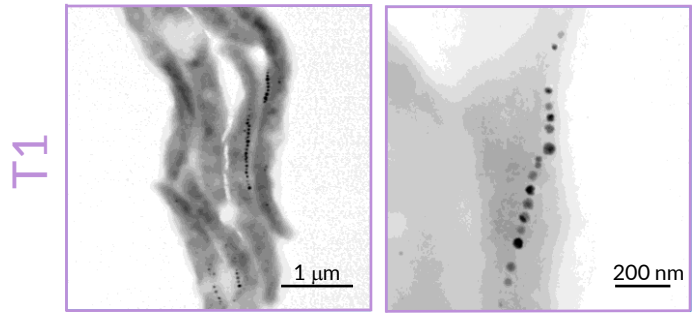
- Fe and Co edges
- transmission vs TEY

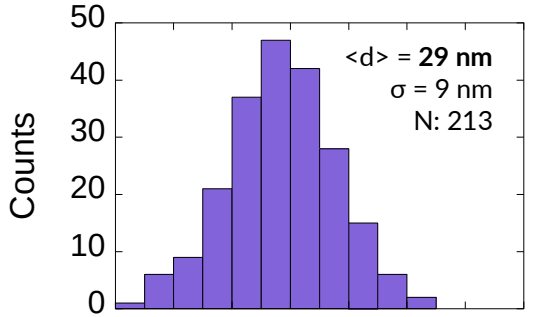
Structure → magnetic response → microscopic origin

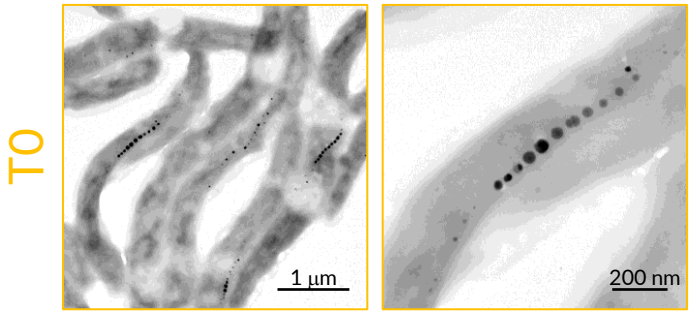
TEM: Co timing modifies magnetosome size distributions

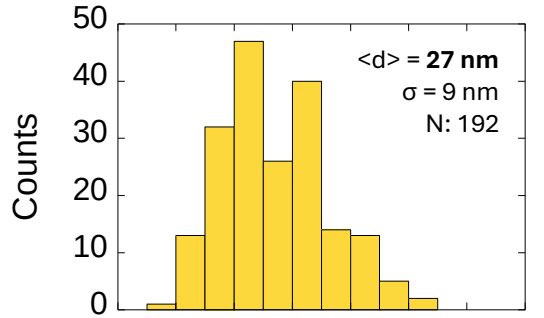


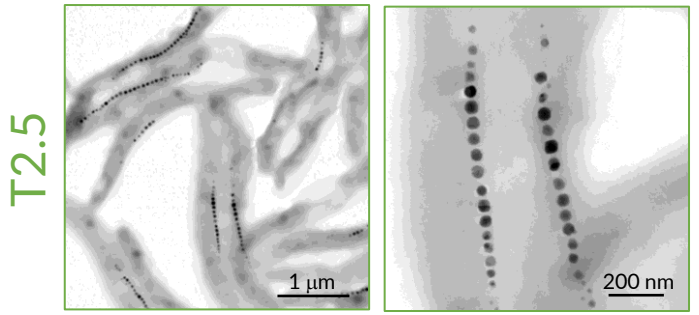


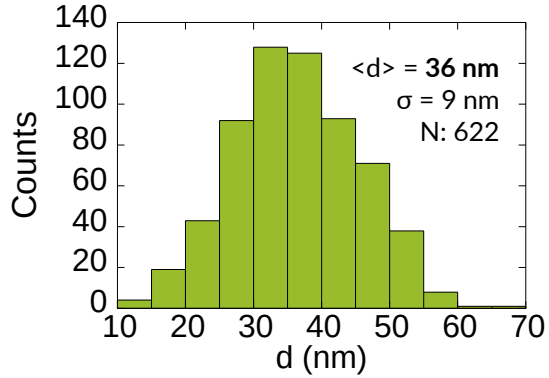








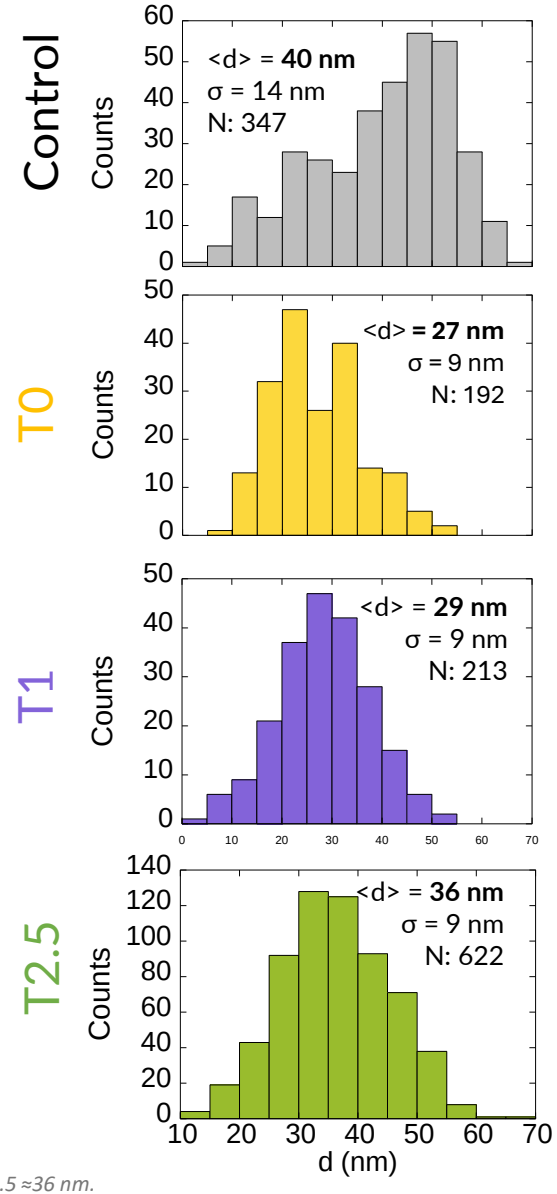


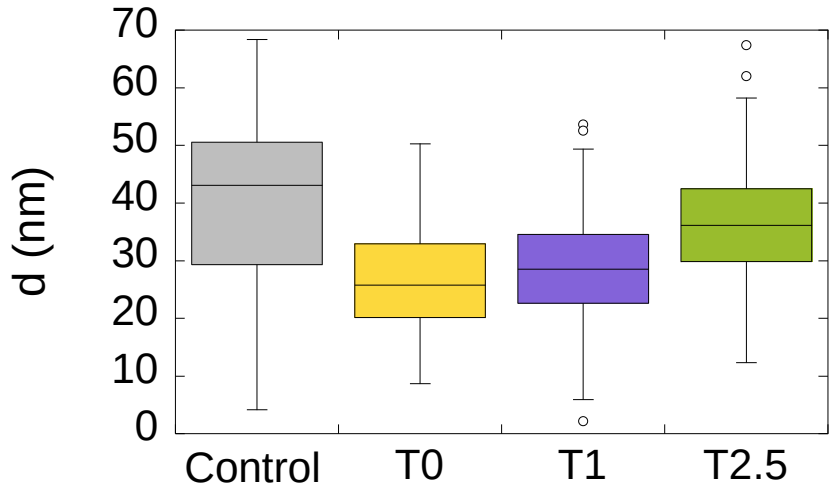


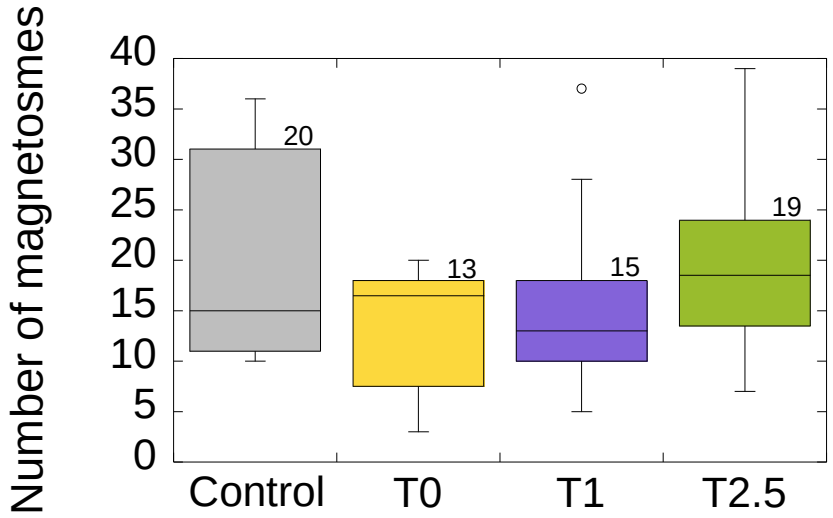
All samples still form magnetosome chains; the particle-size distribution depends on when Co is added

TEM summary: early Co addition gives smaller magnetosomes

Trend: T0/T1 reduce the particle diameter, while T2.5 approaches the control size again; chain statistics also evolve with timing





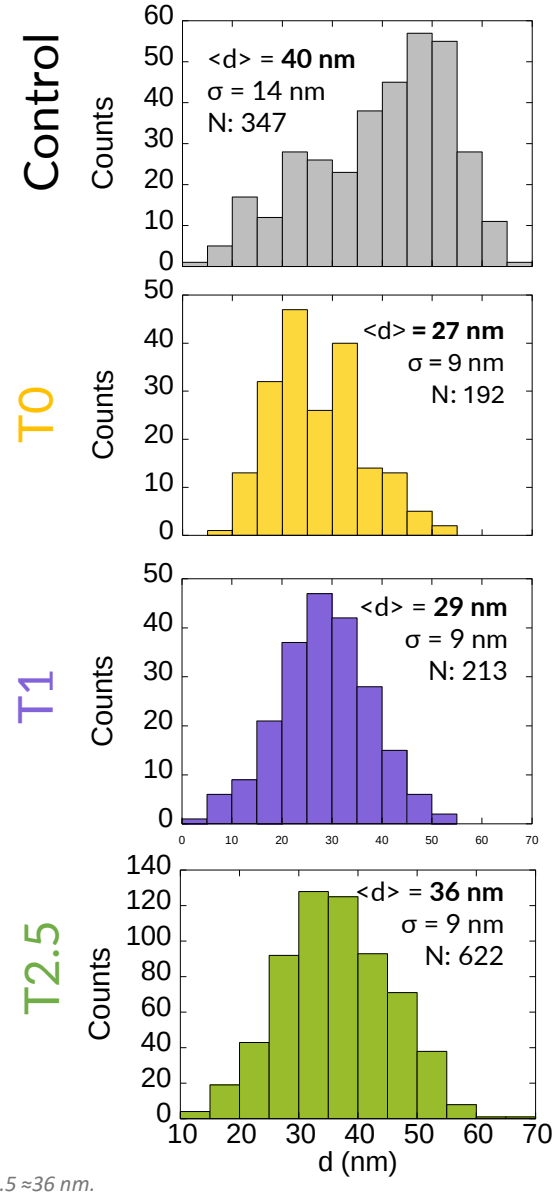


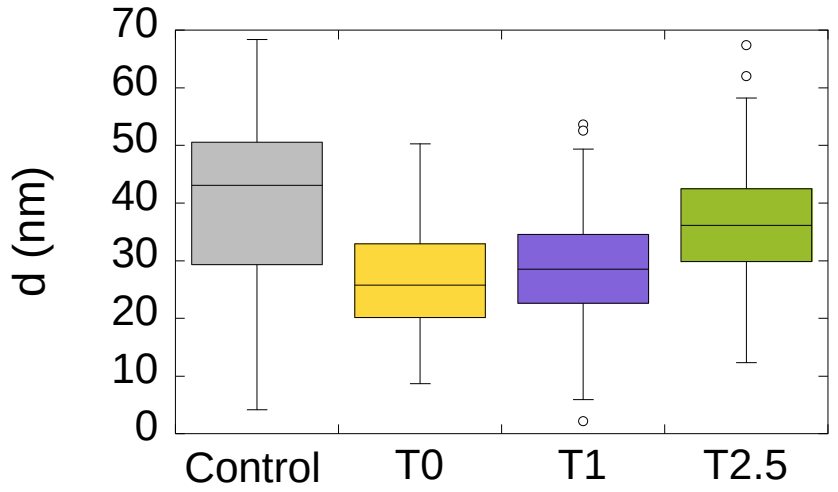
Mean diameter: Control ≈40 nm; T0 ≈27 nm; T1 ≈29 nm; T2.5 ≈36 nm.

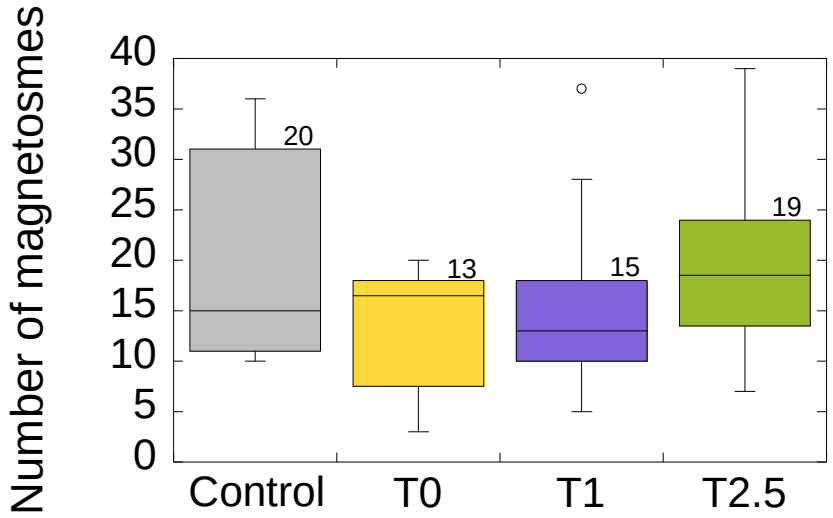
TEM summary: early Co addition gives smaller magnetosomes

Trend: T0/T1 reduce the particle diameter, while T2.5 approaches the control size again; chain statistics also evolve with timing

Open question: can this structural differences translate into magnetic properties?



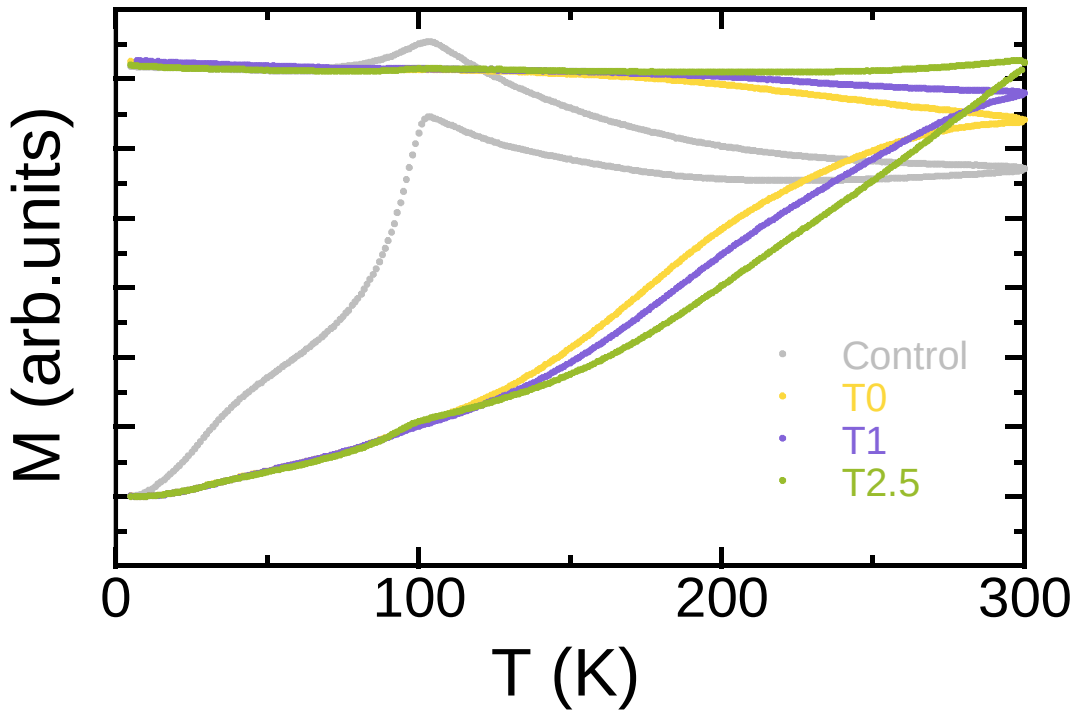




Mean diameter: Control ≈40 nm; T0 ≈27 nm; T1 ≈29 nm; T2.5 ≈36 nm.

Magnetic overview: Co addition strongly modifies the low-temperature temperature response

- Control: a sharp magnetite-related Verwey feature is visible around 100 K
- After Co addition, this feature is strongly broadened or suppressed
- The Co-containing samples retain strong ZFC/FC irreversibility
- This points to a modified temperature-dependent magnetic-energy landscape



M(T) tells us where magnetic/structural changes occur; hysteresis tells us how hard magnetization reversal becomes

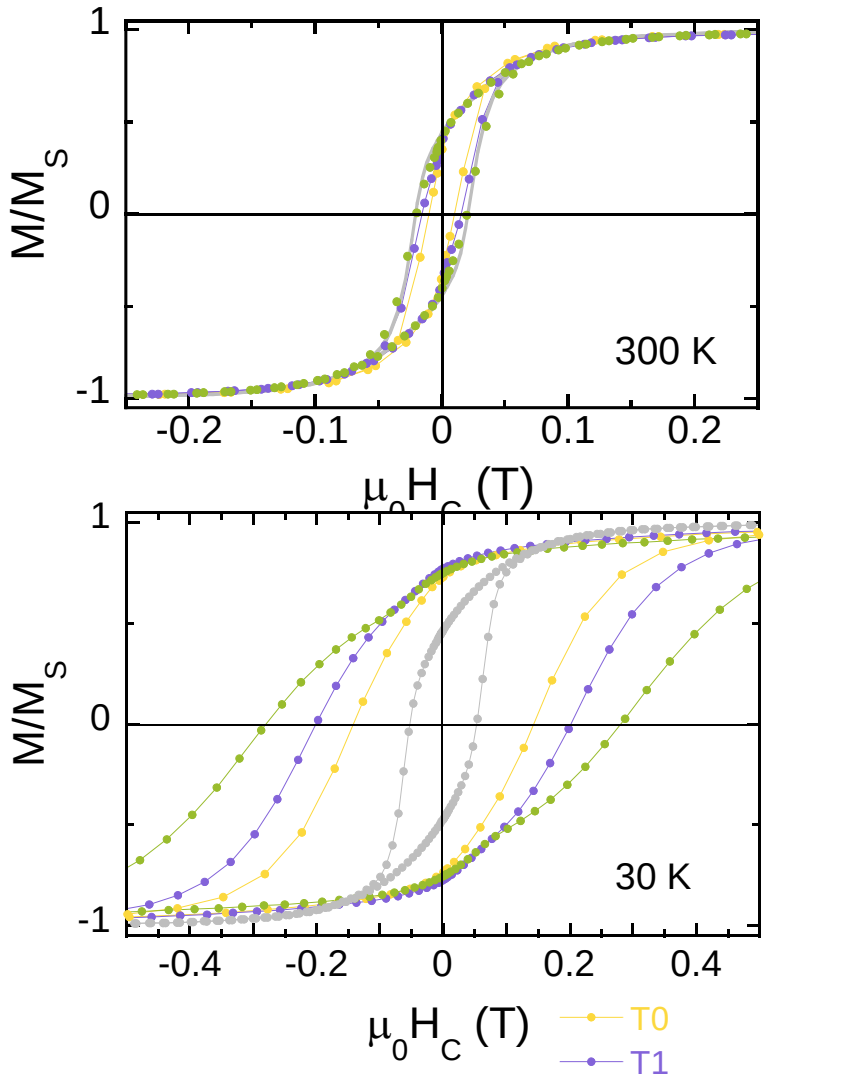
Later Co addition produces the strongest magnetic hardening

300 K

The hysteresis loops are relatively similar at room temperature

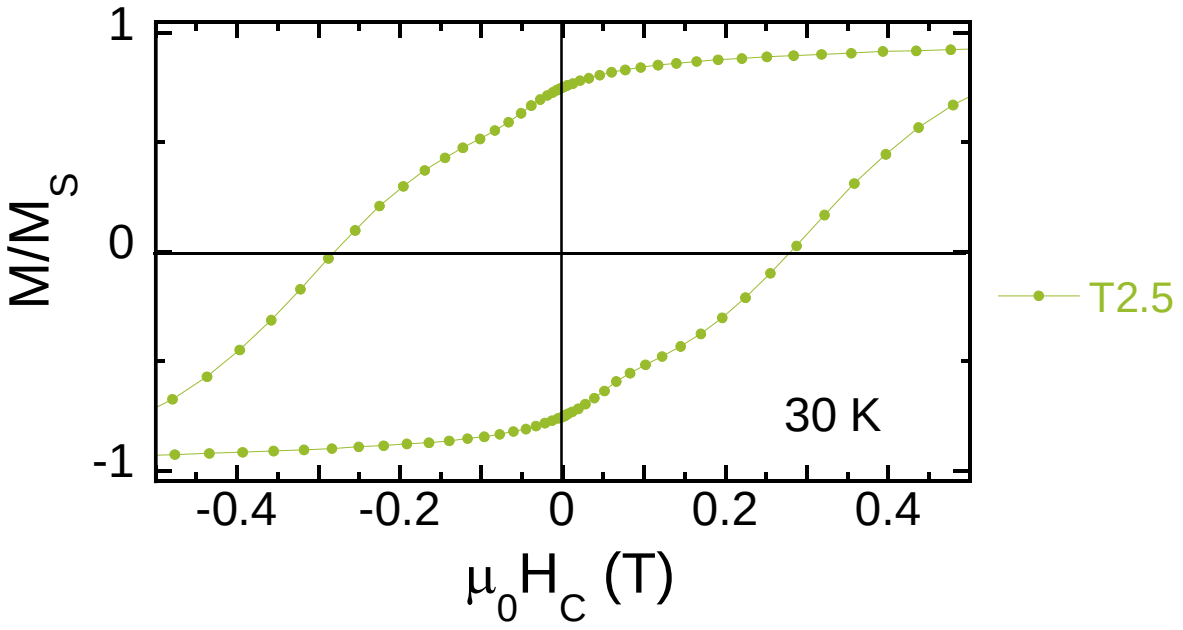
30 K

The differences become much larger on cooling. T2.5 requires the largest reverse field to reach M = 0

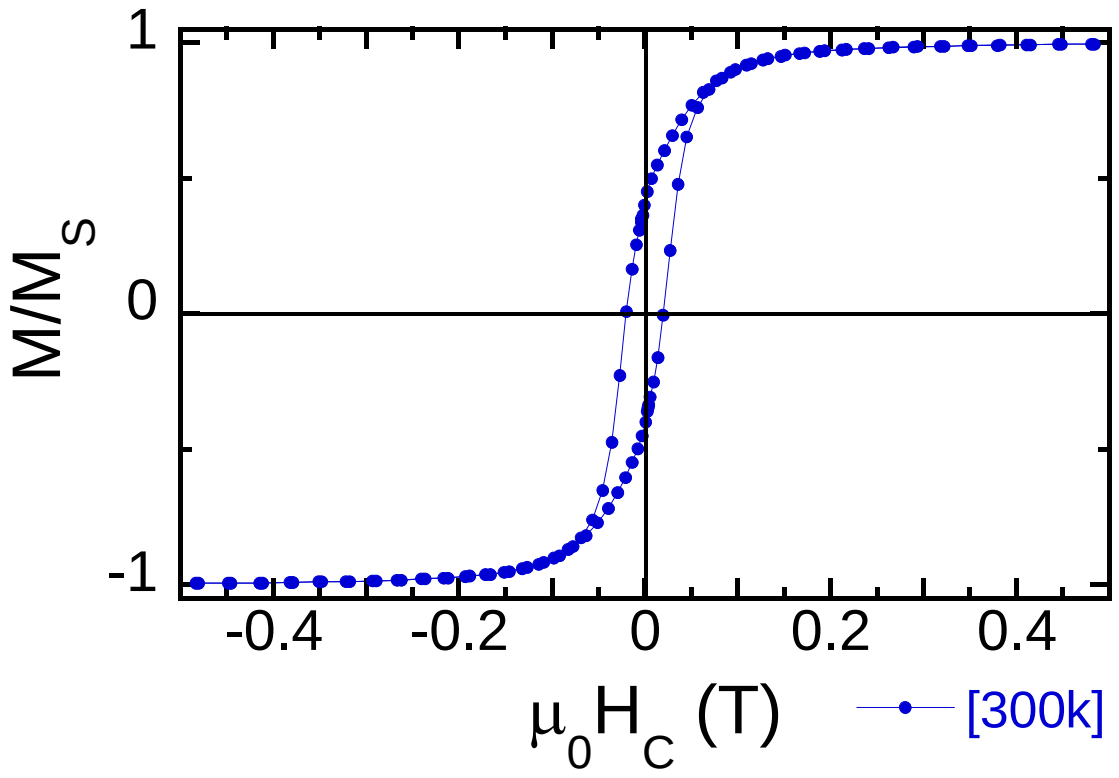


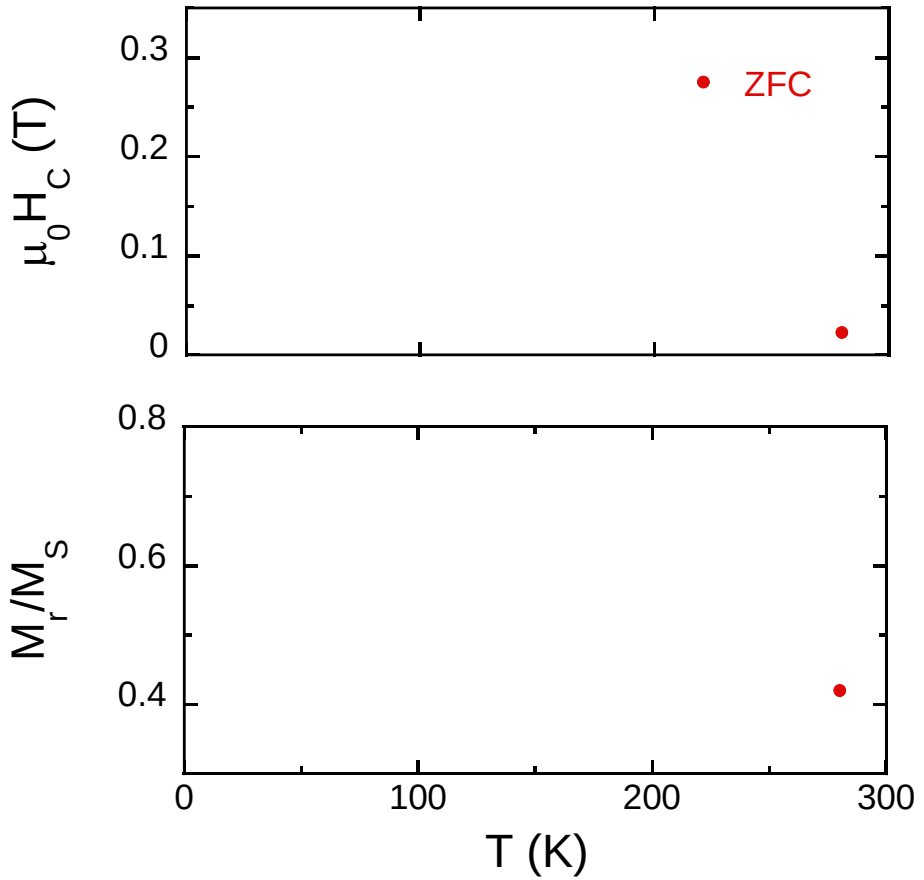
Later Co addition produces the strongest magnetic hardening

T2.5 is therefore the key sample for the detailed temperature-dependent analysis



T2.5: temperature evolution reveals a more complex reversal process





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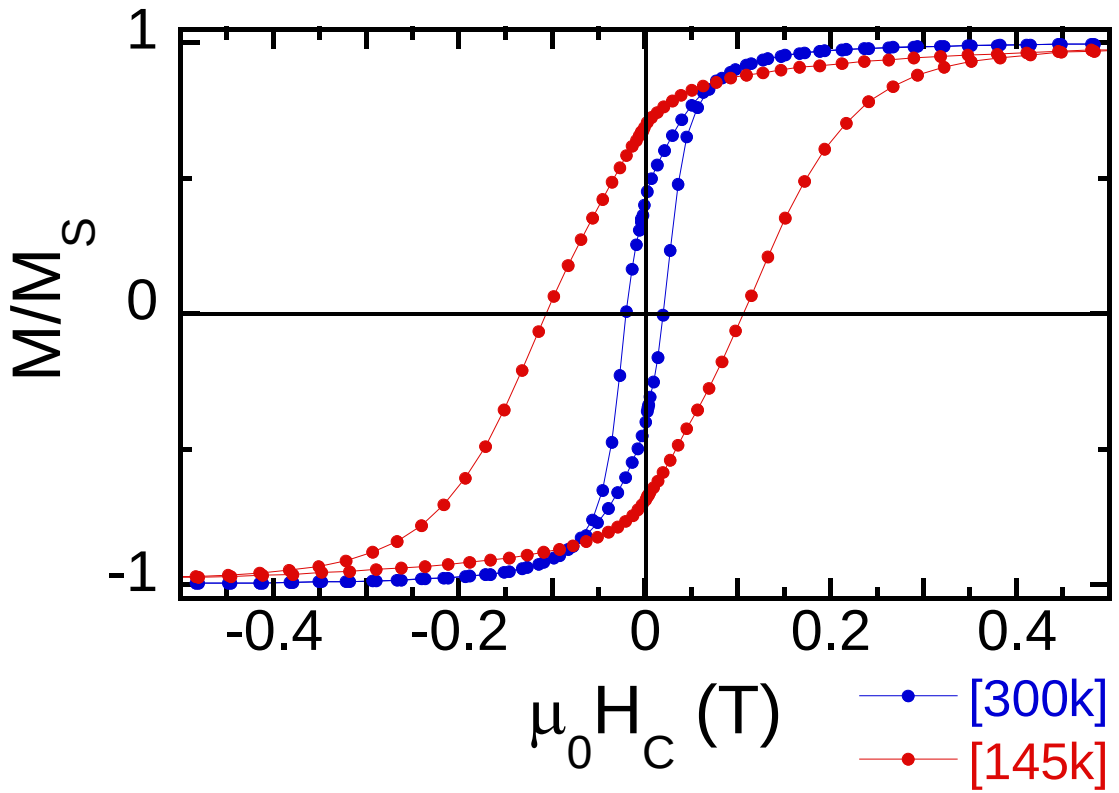

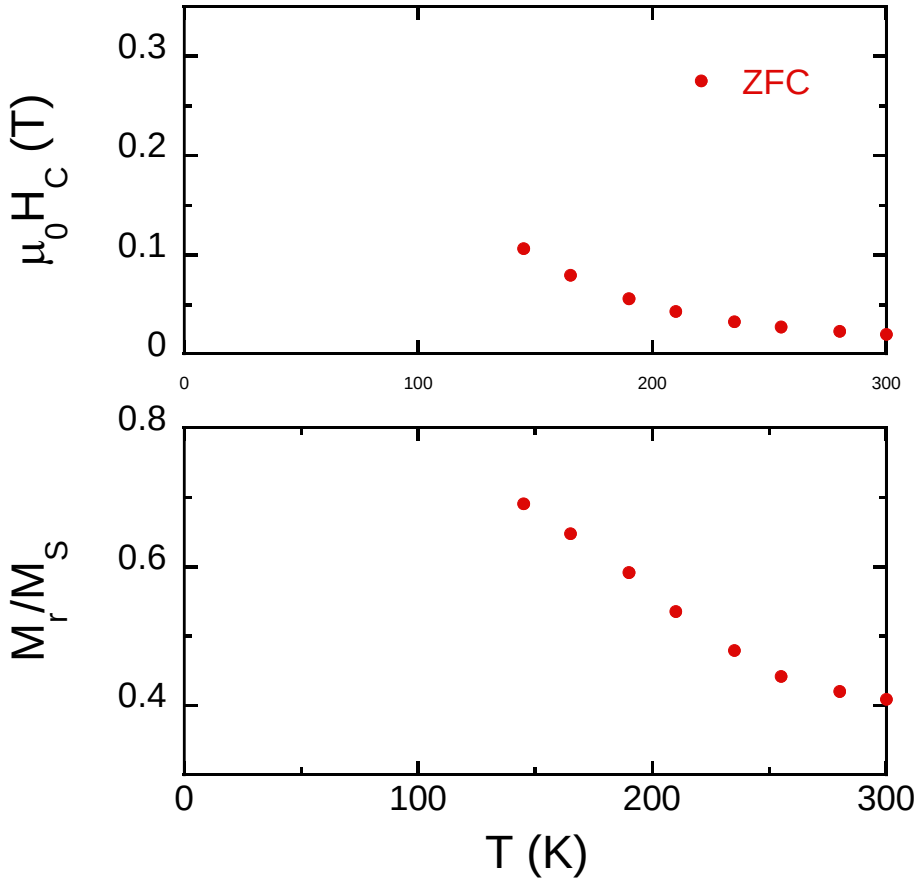

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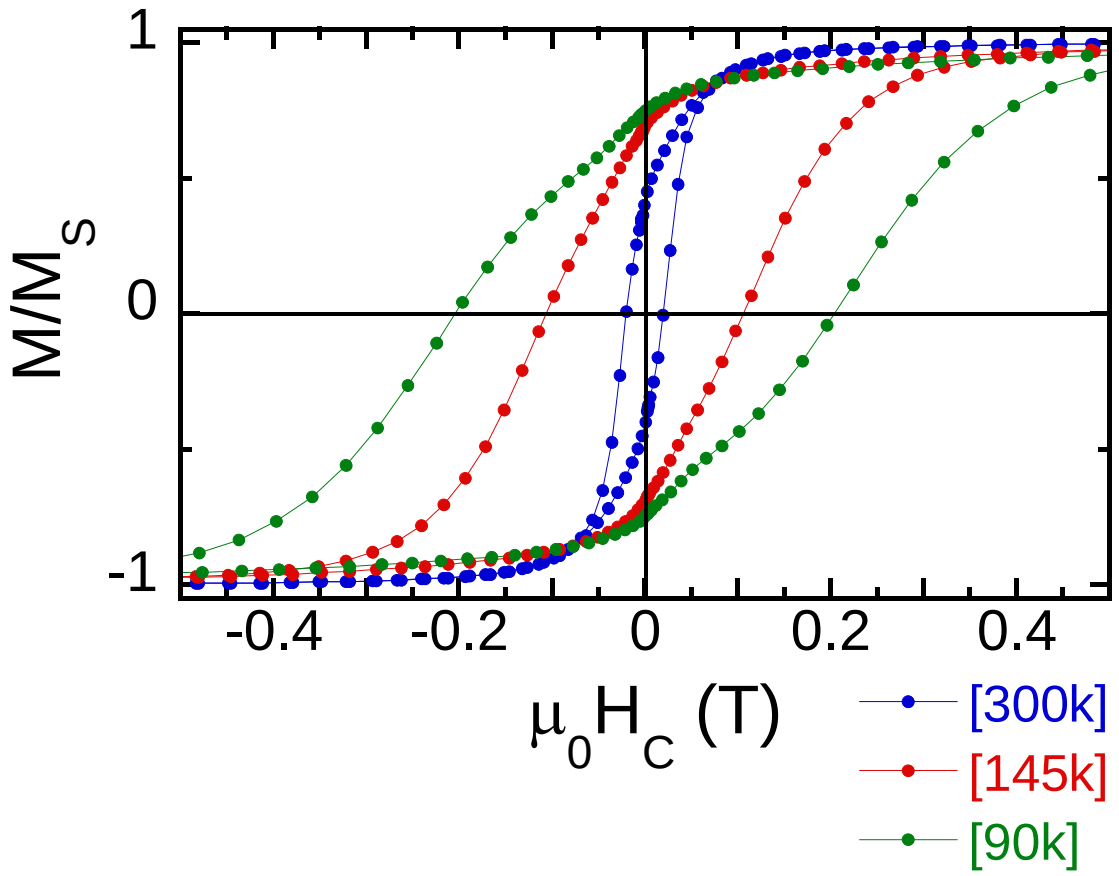

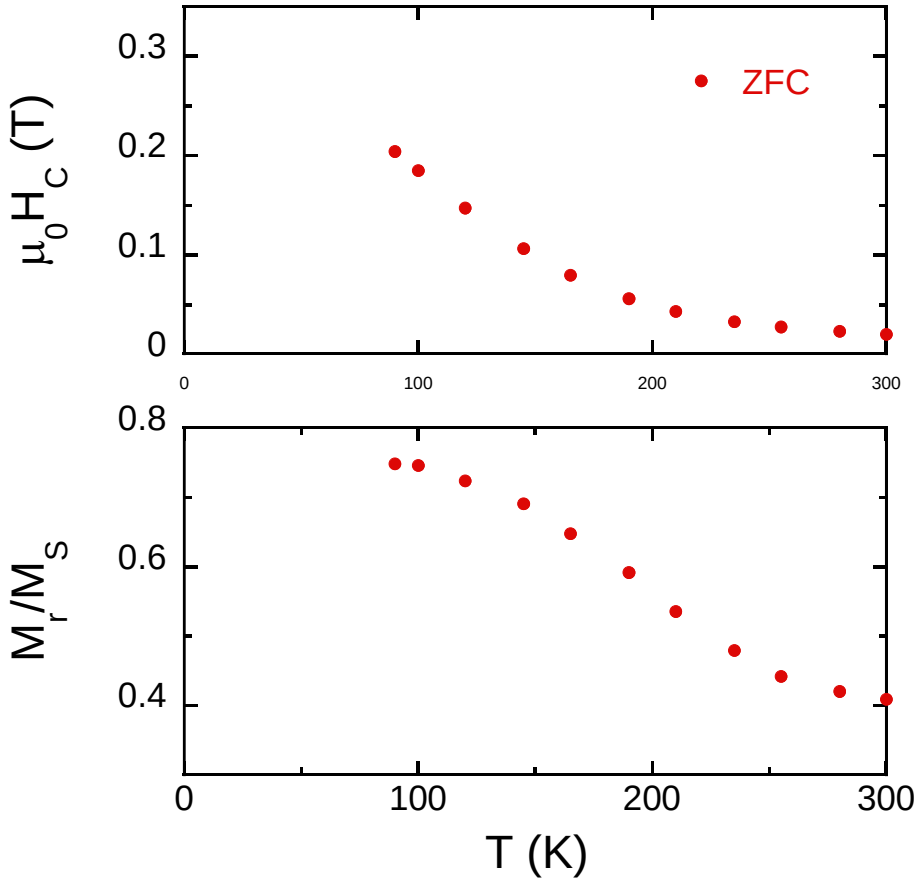

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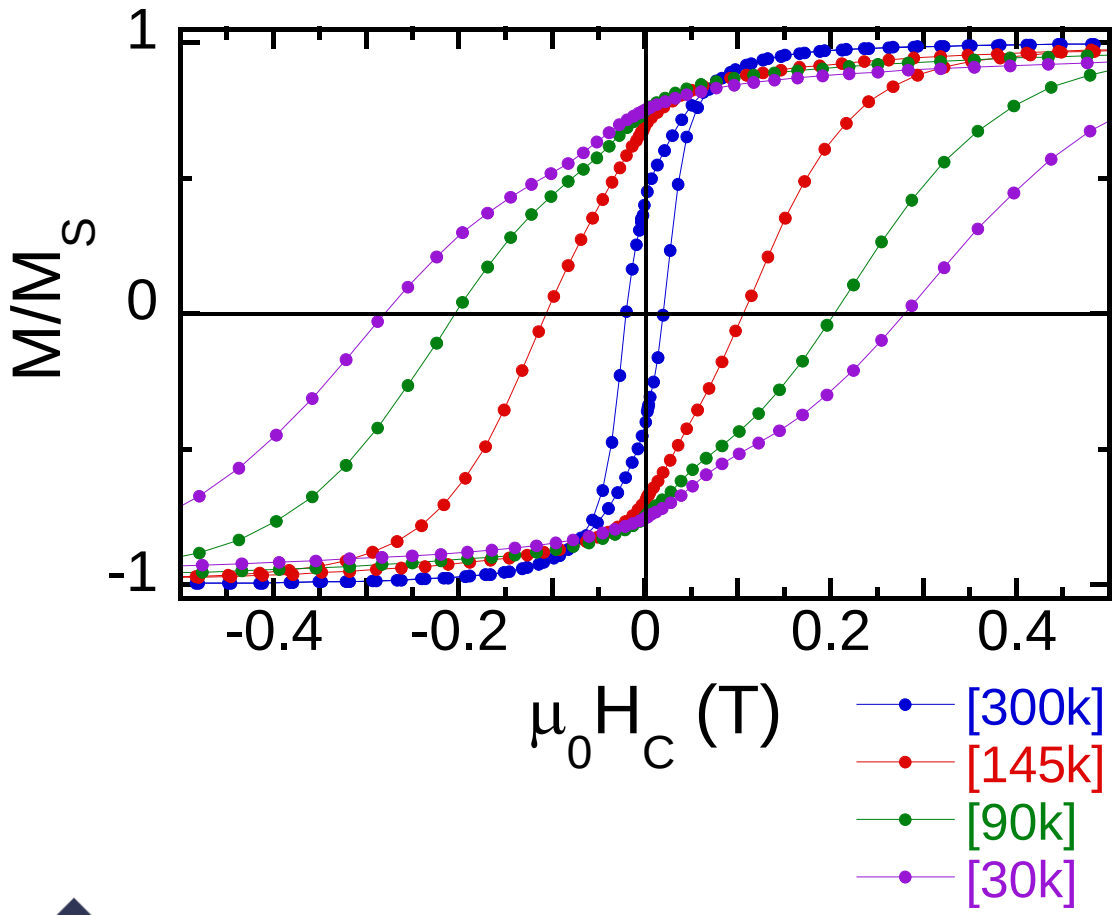
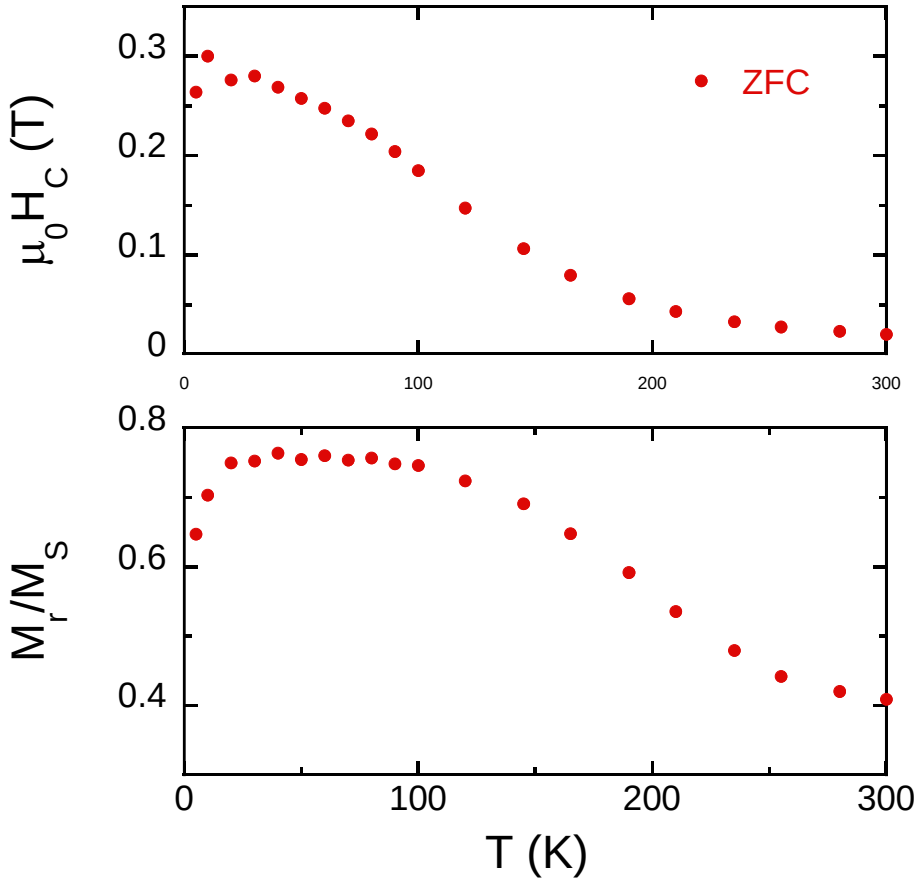
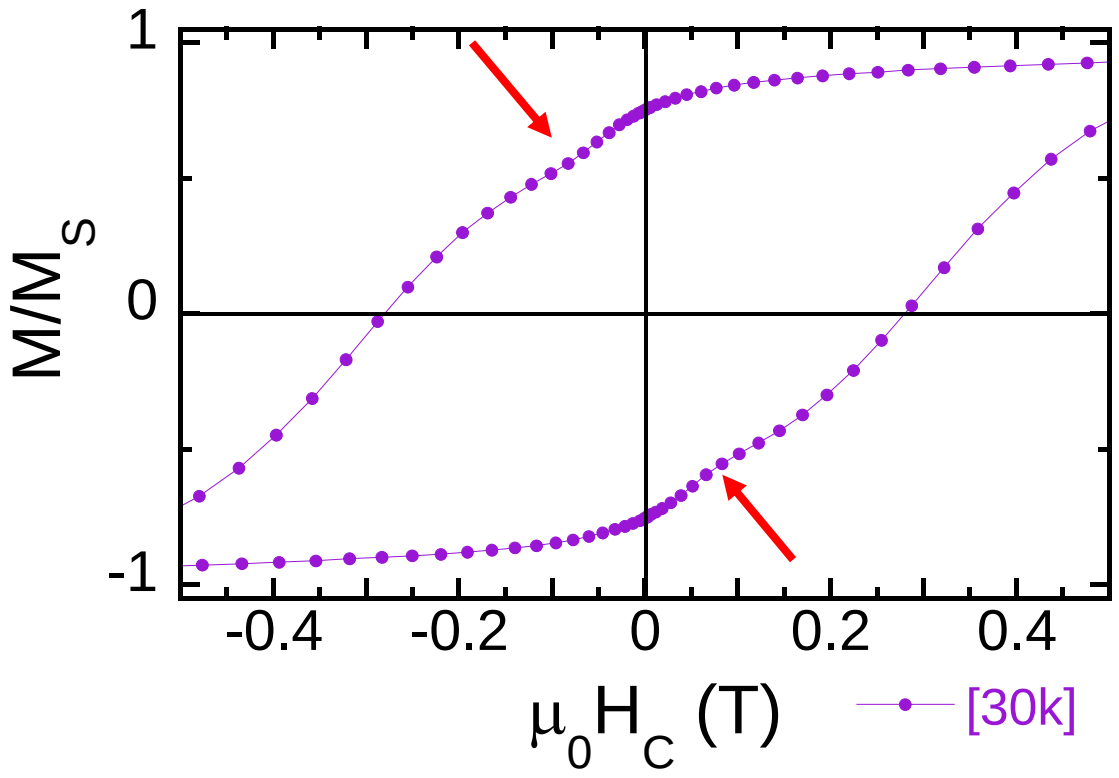




T2.5: the kink reveals a heterogeneous magnetic response



Magnetic heterogeneity

Possible 1: core -shell

Possible origin 2 : coexistence of Fe_3O_4 and $Co_xFe_{3-x}O_4$

Magnetometry alone cannot distinguish between these scenarios

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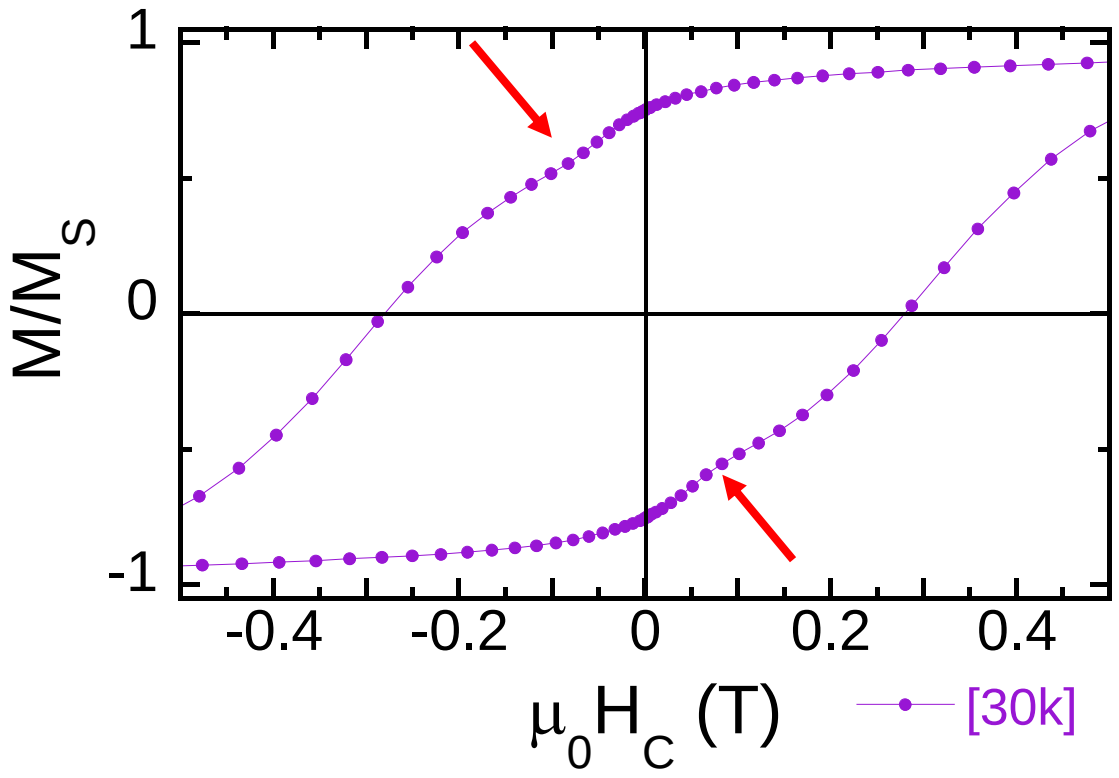

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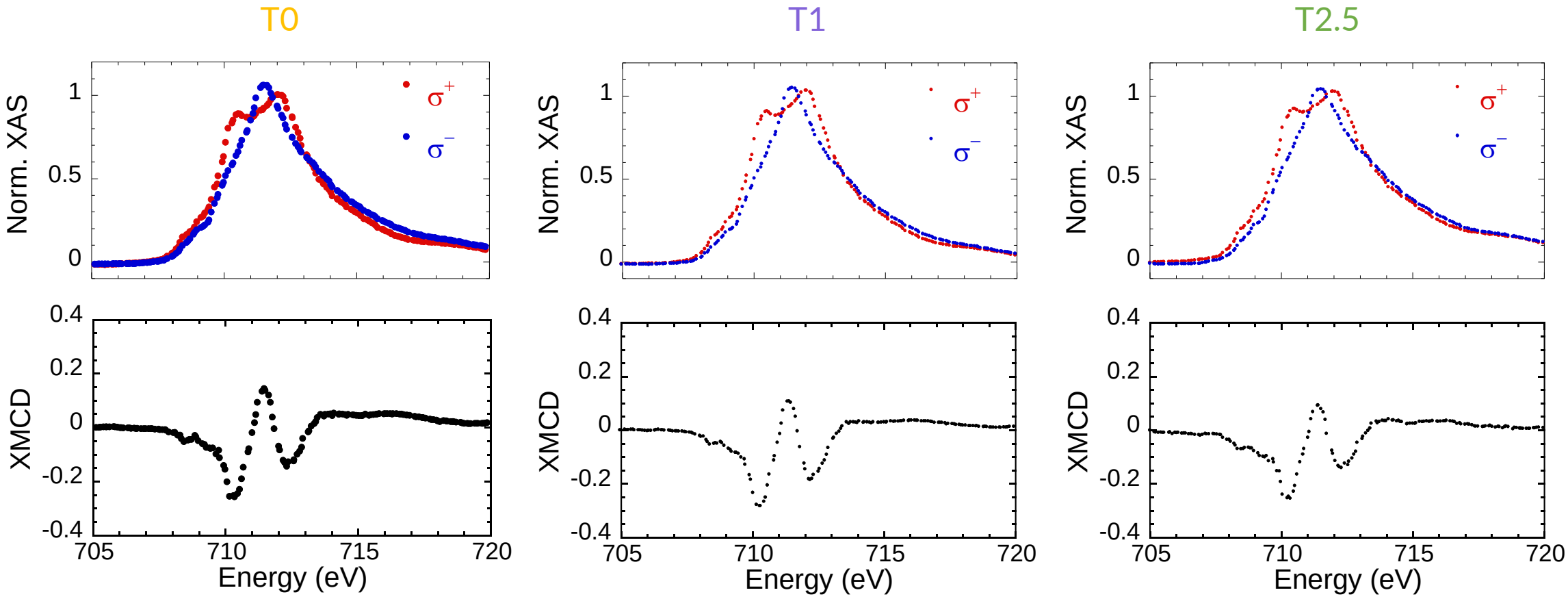
XAS/XMCD

Fe XAS/XMCD: transmision similar spectra

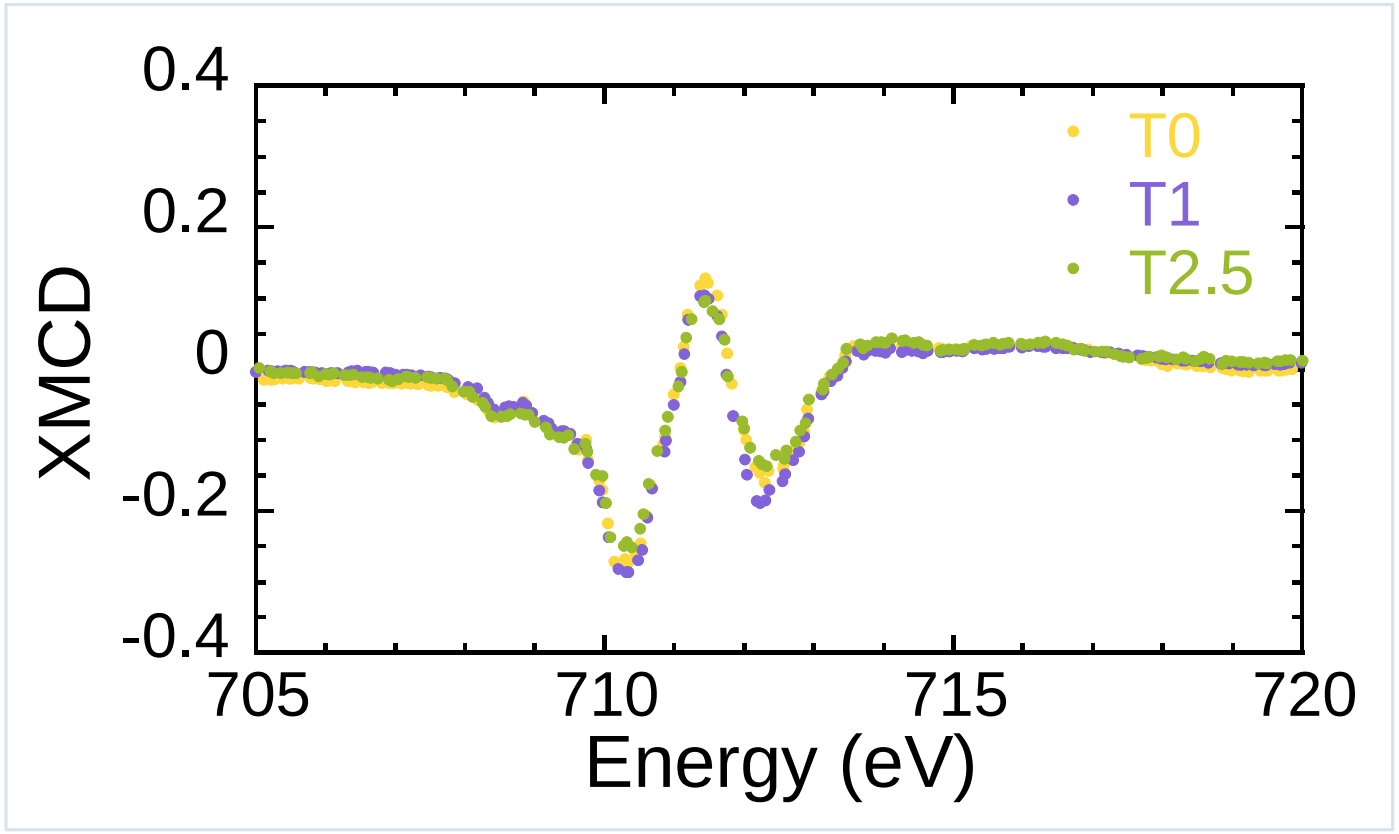
Extracted magnetosomes | Fe $L_{2,3}$ edge



Fe XAS/XMCD: in transmission magnetite is preserved

Extracted magnetosomes | Fe $L_{2,3}$ edge

Transmission — more bulk sensitive



Whole-bacteria transmission gives the same overall magnetite-like Fe fingerprint.

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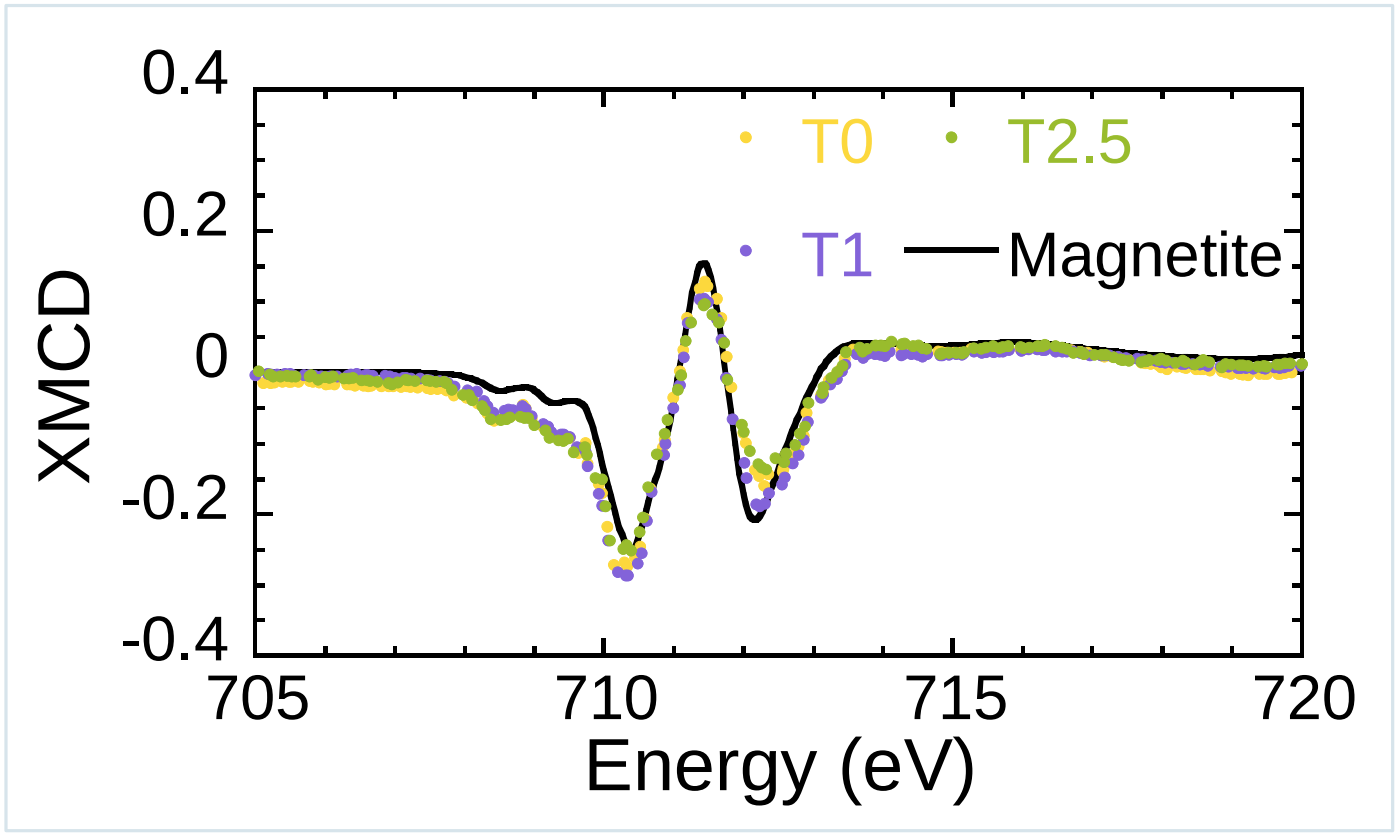


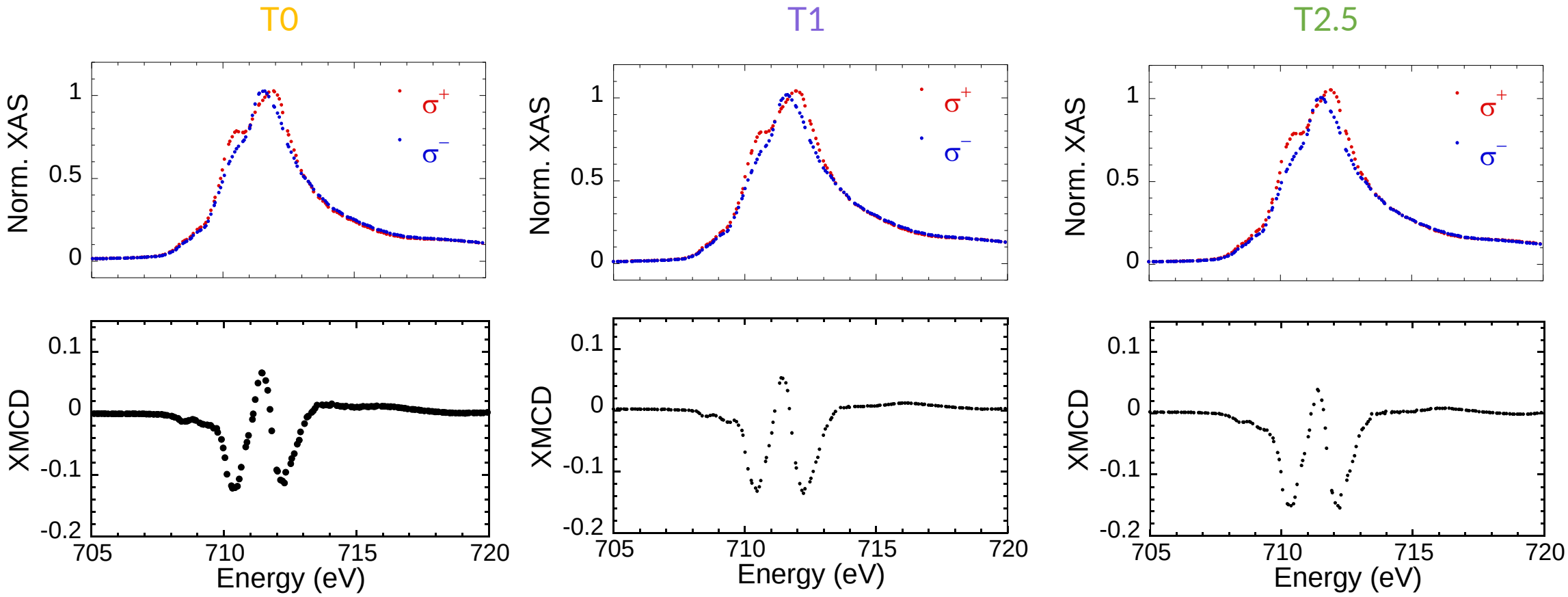
T0 / T1 / T2.5 remain magnetite-like

→ dominant bulk Fe phase remains magnetite

Whole-bacteria transmission gives the same overall magnetite-like Fe fingerprint.

Fe XAS/XMCD: TEY suggests surface oxidation

Extracted magnetosomes | Fe $L_{2,3}$ edge



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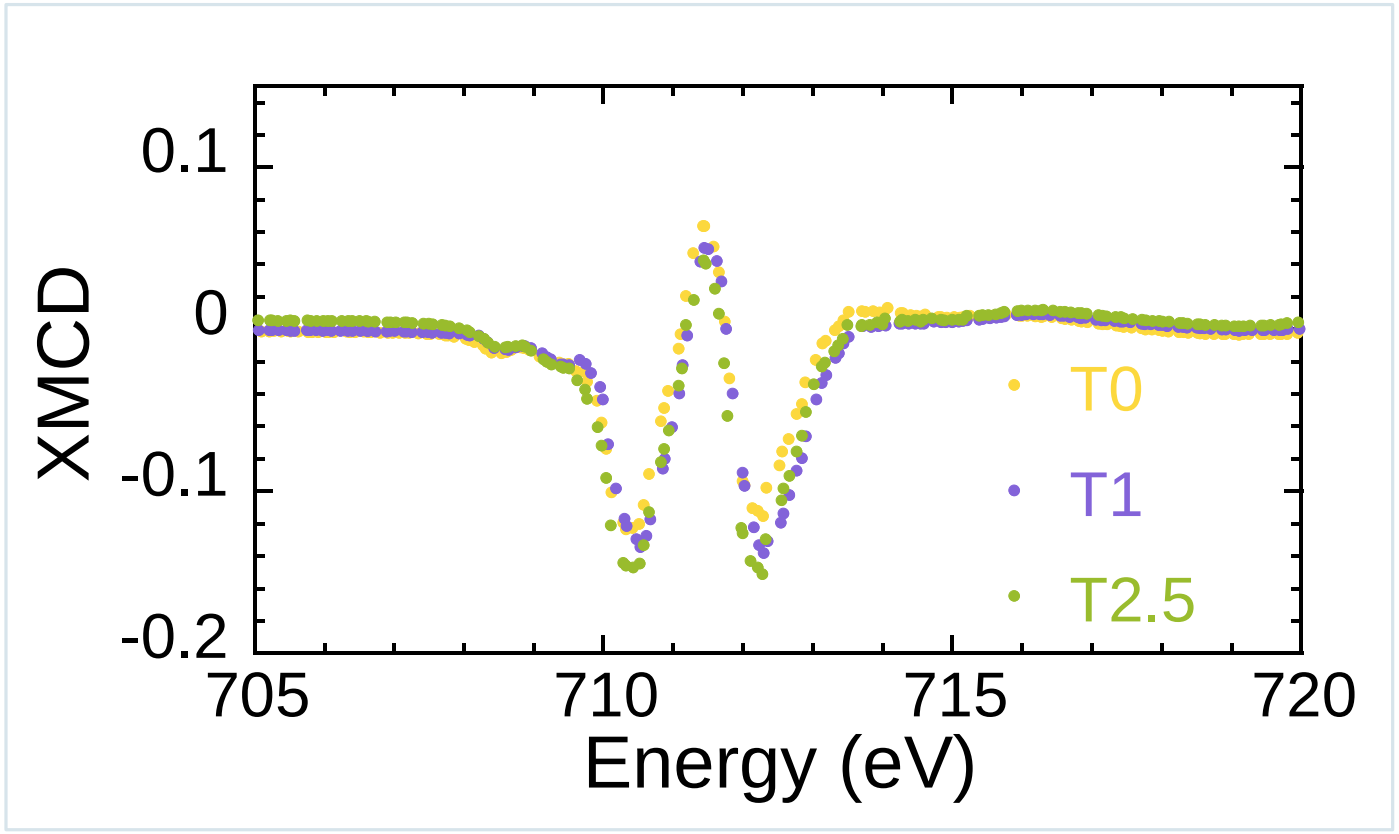

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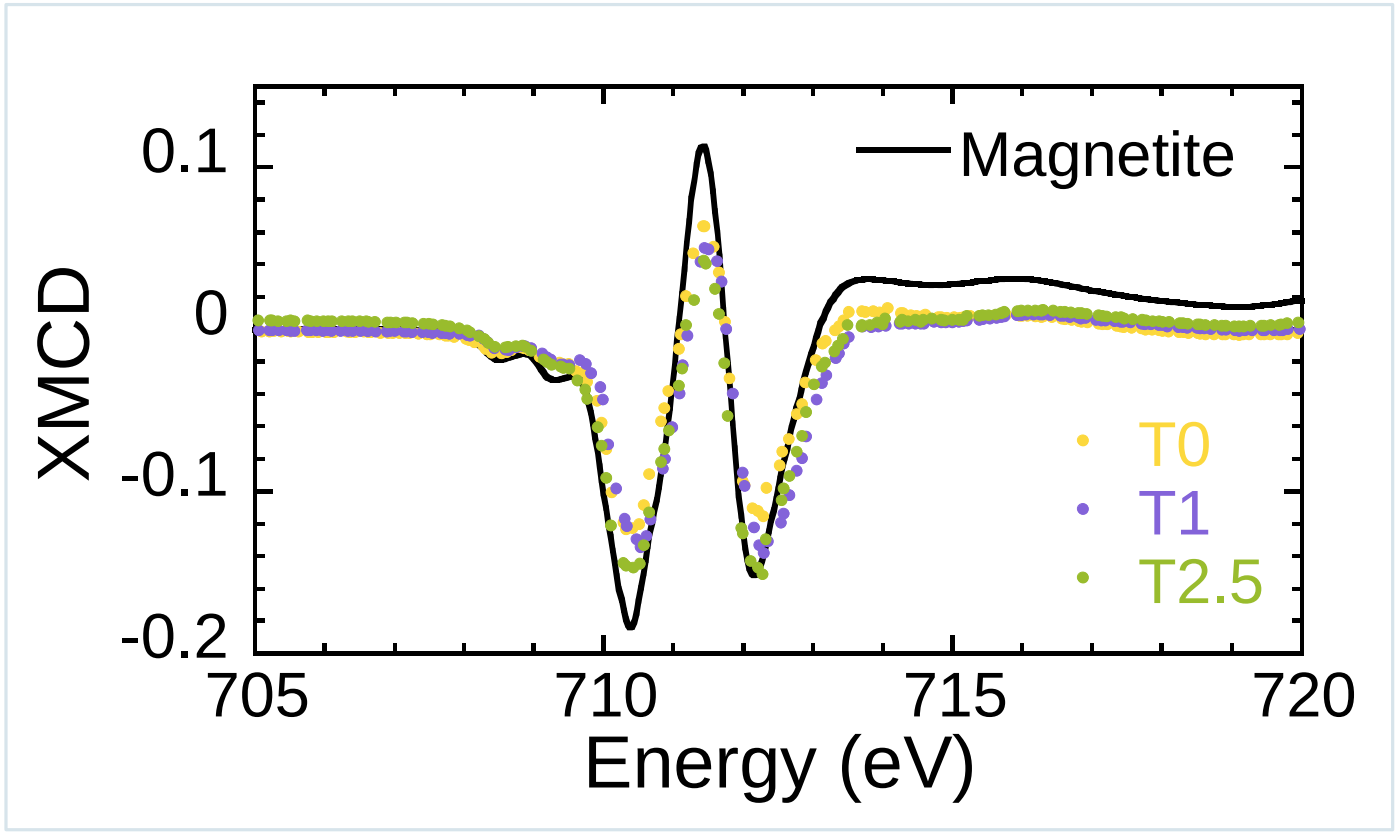

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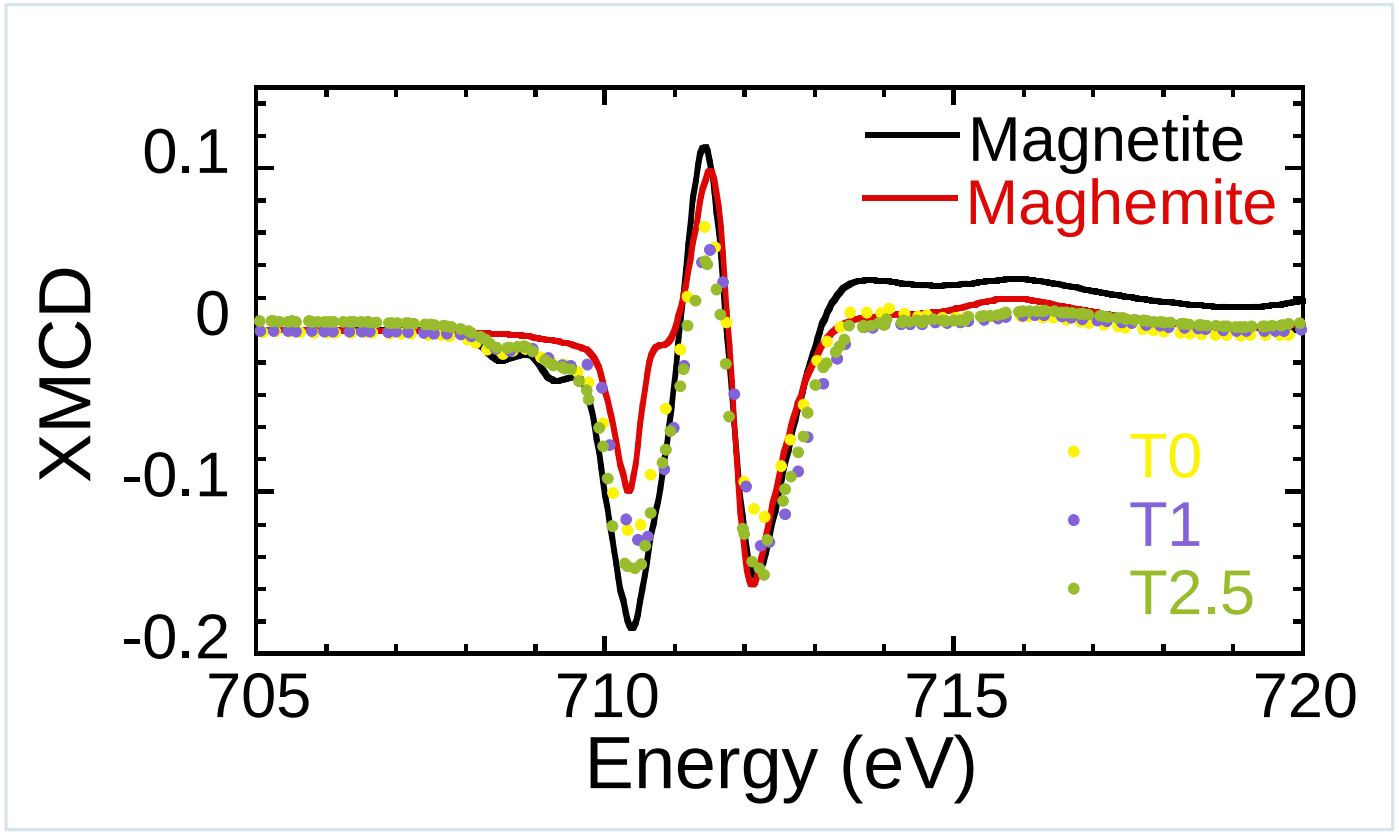

Spectra become more maghemite-like

→ consistent with partial surface oxidation

Fe XAS/XMCD: bulk magnetite is preserved; TEY suggests surface oxidation

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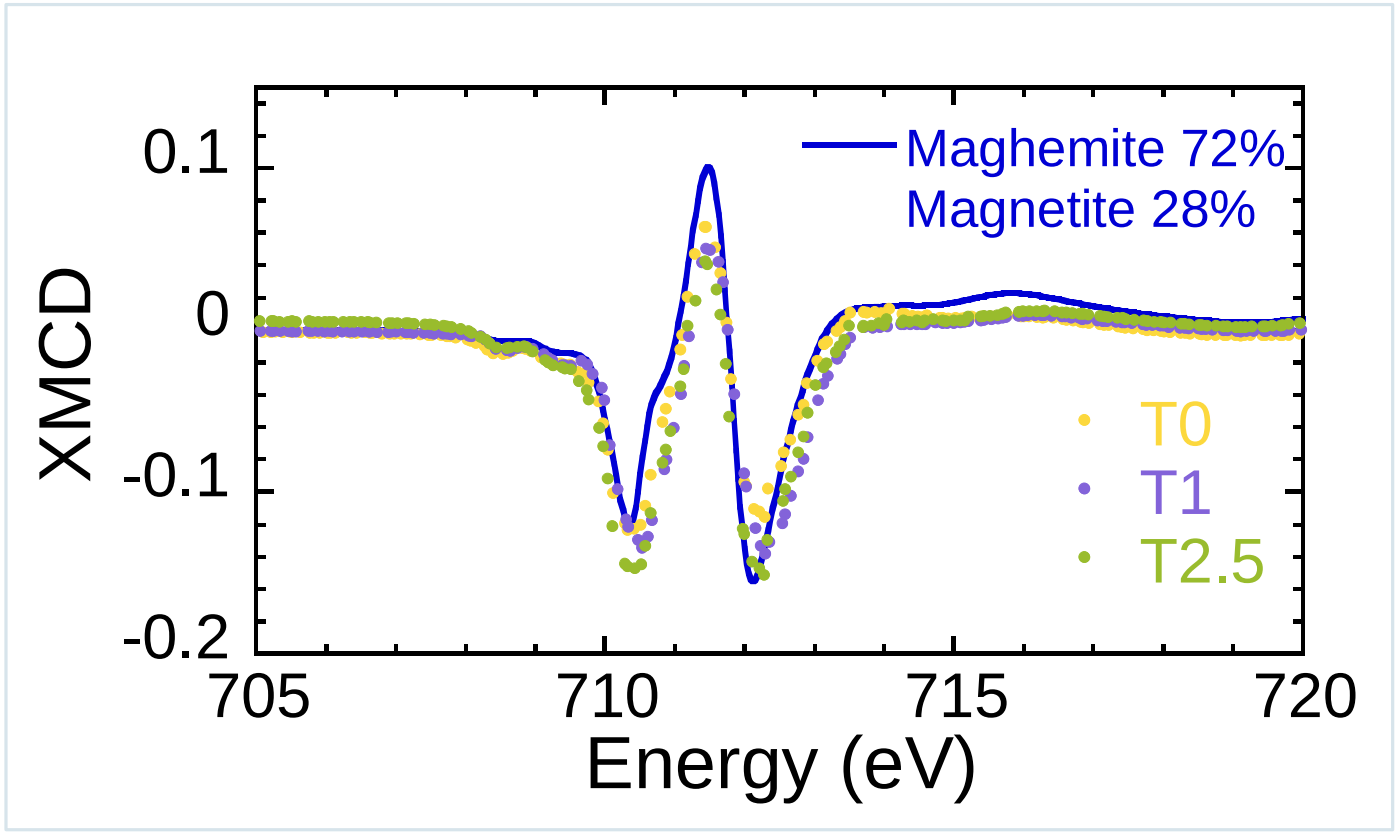

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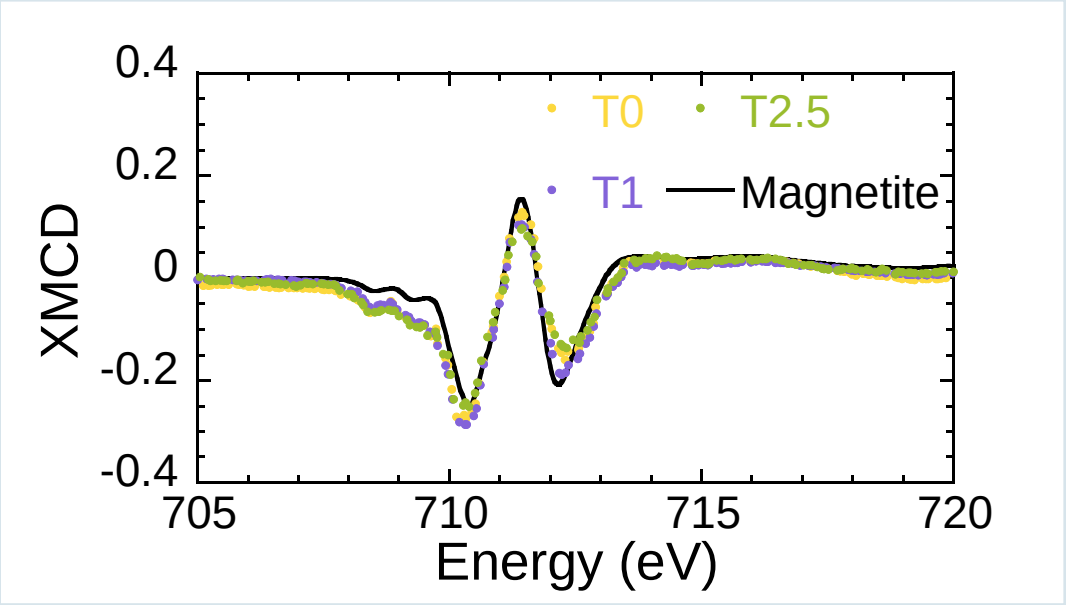

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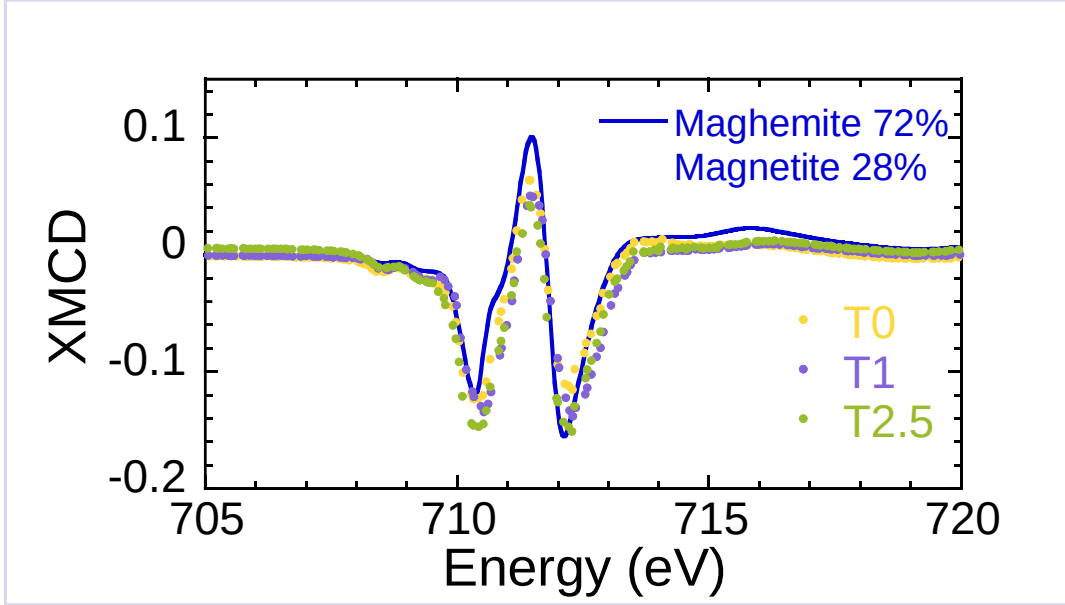


T0 / T1 / T2.5 remain magnetite-like

→ dominant bulk Fe phase remains magnetite

Spectra become more maghemite-like

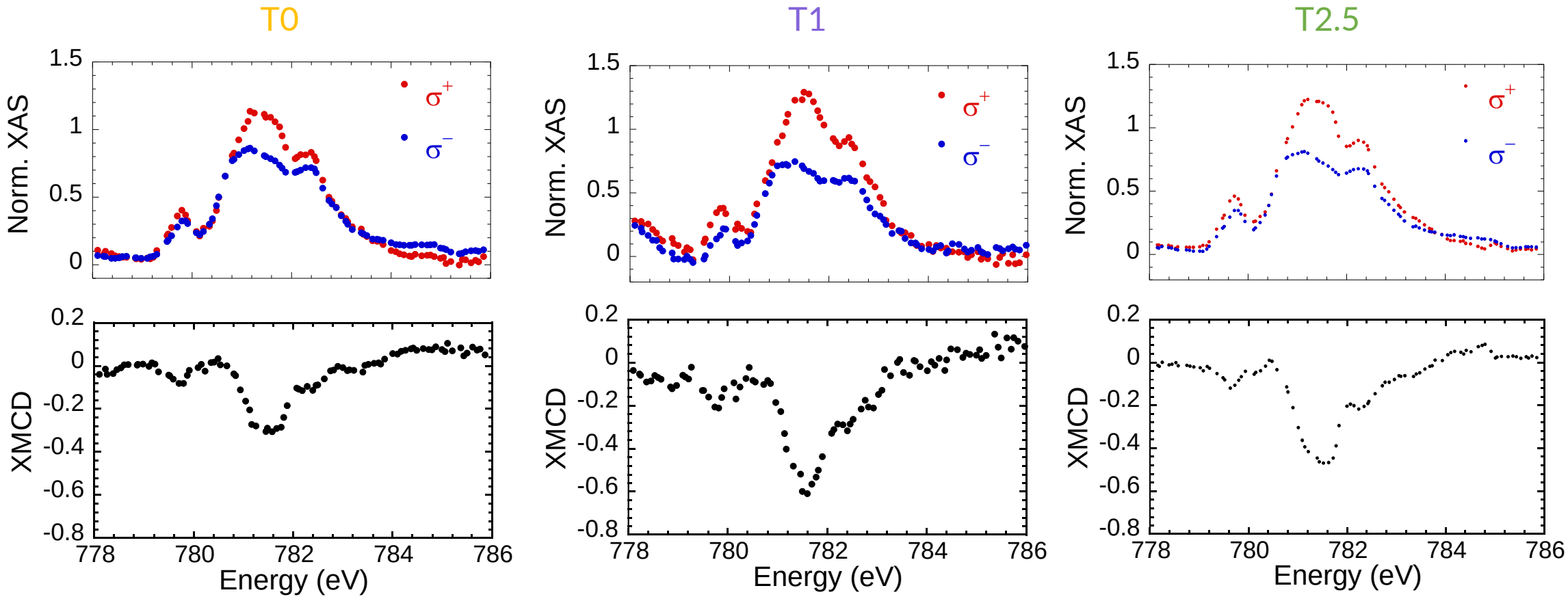
→ consistent with partial surface oxidation

Surface oxidation changes the Fe^{2+}/Fe^{3+} balance, so TEY alone cannot quantify Co substitution

Whole-bacteria transmission gives the same overall magnetite-like Fe fingerprint.

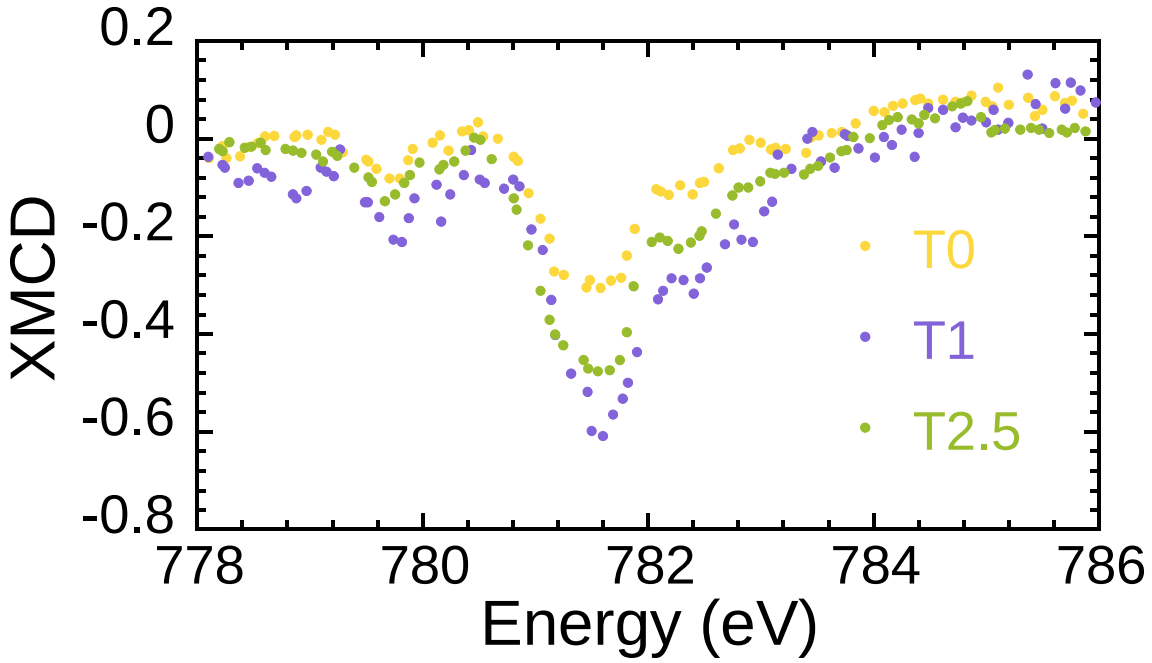
Fe XAS/XMCD: extracted magnetosomes- TEY

Extracted magnetosomes | TEY | Co $L_{2,3}$ edge



Co XAS/XMCD confirms Co^{2+} in octahedral coordination

Extracted magnetosomes | TEY | Co $L_{2,3}$ edge

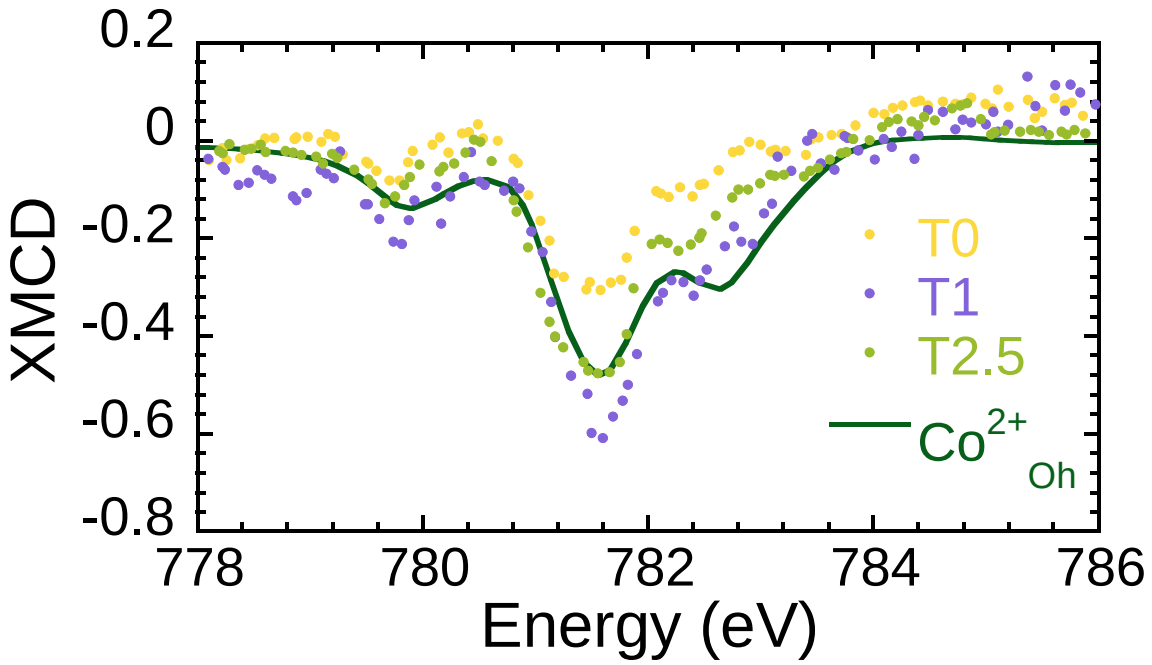


Final Co fit

- A well-defined Co XMCD signal is observed in T0, T1 and T2.5

Co XAS/XMCD confirms Co^{2+} in octahedral coordination

Extracted magnetosomes | TEY | Co $L_{2,3}$ edge



Final Co fit

- A well-defined Co XMCD signal is observed in T0, T1 and T2.5
- The experimental line shape is consistent with Co^{2+} in octahedral coordination
- No additional Co contribution is required to reproduce the spectra

Same Co chemical state in all samples

Co^{2+} in octahedral sites
No second Co species detected

Timing strongly modifies the magnetic response without changing the detected Co^{2+} octahedral signature

Consistent with Marcano et al. (2018): predominantly octahedral Co^{2+} in earlier Co-doped magnetosomes.

Conclusions

What does the timing of Co addition actually control?

1 Biomineralization

- Early addition (T0/T1) gives smaller magnetosomes
- T2.5 approaches a more control-like particle size

2 Magnetic response

- T2.5 shows the strongest magnetic hardening
- Magnetic heterogeneity is observed

3 Element-specific picture

- Transmission Fe-spectra remains magnetite-like; TEY is consistent with surface oxidation
- Co is Co^{2+} in octahedral coordination in all samples

TAKE-HOME MESSAGE **Co-addition timing is a synthetic control parameter for magnetosome magnetic anisotropy**

THANK YOU

FOR YOUR ATTENTION

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T2.5: temperature evolution reveals a more complex reversal process