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Supporting information for article:

**Role of lone-pair electron localization in temperature-induced
phase transitions in mimetite]**

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Table S1 Experimental details of mimetite at 173, 273, and 353 K.

	Mimetite-M (173 K)	Mimetite-M (273 K)	Mimetite-M (353 K)
Crystal data			
Chemical formula	As ₄ Cl _{1.33} O ₁₆ Pb _{6.67}	As ₃ ClO ₁₂ Pb ₅	As ₄ Cl _{1.33} O ₁₆ Pb _{6.67}
Crystal system, space group	Monoclinic, <i>P</i> 112 ₁ / <i>b</i>	Monoclinic, <i>P</i> 112 ₁ / <i>b</i>	Monoclinic, <i>P</i> 112 ₁ / <i>b</i>
Temperature (K)	173	273	353
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.2378 (3), 20.4573 (7), 7.4457 (2)	10.2398 (4), 20.4774 (9), 7.4554 (3)	10.2544 (4), 20.5052 (7), 7.4568 (2)
α , β , γ (°)	90, 90, 120.039 (5)	90, 90, 119.981 (6)	90, 90, 119.971 (5)
<i>V</i> (Å ³)	1349.96 (9)	1354.10 (12)	1358.26 (10)
<i>Z</i>	3	4	3
Radiation type	Ag <i>K</i> α , λ = 0.56087 Å	Ag <i>K</i> α , λ = 0.56087 Å	Ag <i>K</i> α , λ = 0.56087 Å
μ (mm ⁻¹)	37.69	37.57	37.71
Crystal size (mm)	0.10 × 0.06 × 0.04	0.10 × 0.06 × 0.04	0.10 × 0.06 × 0.04
Data collection			
Diffractometer	XtaLAB Synergy, Dualflex, Hypix	XtaLAB Synergy, Dualflex, Hypix	XtaLAB Synergy, Dualflex, Hypix
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	23244, 5558, 4813	27265, 5414, 4531	24325, 5534, 4410
<i>R</i> _{int}	0.046	0.047	0.038
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.794	0.794	0.794
Refinement			
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.039, 0.086, 1.14	0.032, 0.071, 1.05	0.029, 0.069, 1.08
No. of reflections	5558	5414	5534
No. of parameters	192	190	190
	$w = 1/[\sigma^2(F_o^2) + (0.0142P)^2 + 76.360P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2 + 19.508P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 2.9140P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	4.44, -5.28	2.96, -4.32	4.22, -3.78

Table S2. Selected geometric parameters (Å) of mimetite-2M at 123 K.

Pb11—O19	2.46 (2)	Pb12—O112	2.48 (3)	Pb13—O18	2.40 (2)
Pb11—O17	2.48 (3)	Pb12—O110	2.53 (3)	Pb13—O19	2.52 (3)
Pb11—O18	2.54 (3)	Pb12—O111	2.57 (3)	Pb13—O27 ⁱⁱⁱ	2.56 (2)
Pb11—O32	2.62 (2)	Pb12—O212	2.60 (2)	Pb13—O17	2.62 (3)
Pb11—O29 ⁱ	2.66 (2)	Pb12—O316 ⁱ	2.62 (3)	Pb13—O28 ^{iv}	2.65 (2)
Pb11—O320 ⁱ	2.72 (2)	Pb12—O211 ⁱⁱ	2.81 (2)	Pb13—O317 ⁱⁱⁱ	2.72 (3)
Pb11—O28	3.00 (2)	Pb12—O210 ⁱ	2.82 (2)	Pb13—O29 ⁱⁱⁱ	2.87 (3)
Pb11—O27 ⁱ	3.17 (2)	Pb12—O318 ⁱⁱ	3.10 (3)	Pb13—O321 ⁱⁱⁱ	3.11 (2)
Pb11—O313 ⁱ	3.22 (3)			Pb13—O31 ^{iv}	3.18 (3)
Pb14—O110	2.42 (3)	Pb15—O12	2.38 (2)	Pb16—O14	2.44 (3)
Pb14—O111	2.50 (3)	Pb15—O11	2.56 (2)	Pb16—O16	2.47 (3)
Pb14—O312 ^{iv}	2.57 (2)	Pb15—O13 ⁱⁱⁱ	2.57 (3)	Pb16—O33	2.53 (2)
Pb14—O112	2.62 (2)	Pb15—O310 ^{vi}	2.67 (3)	Pb16—O24 ^{viii}	2.56 (3)
Pb14—O322 ^v	2.76 (2)	Pb15—O323 ⁱⁱⁱ	2.71 (3)	Pb16—O15	2.62 (3)
Pb14—O211 ^v	2.79 (2)	Pb15—O22 ^{vii}	2.72 (3)	Pb16—O26	2.71 (2)
Pb14—O210 ⁱⁱⁱ	2.81 (2)	Pb15—O21 ⁱⁱⁱ	2.79 (2)	Pb16—O25	2.91 (3)
Pb14—O212 ^{iv}	2.96 (2)	Pb15—O23 ^{vi}	3.11 (2)	Pb16—O34	3.28 (3)
Pb14—O38 ⁱⁱⁱ	3.12 (3)	Pb15—O315 ^{vii}	3.12 (2)	Pb16—O39 ^{viii}	3.33 (3)
Pb17—O15^{iv}	2.46 (2)	Pb18—O11	2.51 (3)		
Pb17—O14 ^{iv}	2.48 (2)	Pb18—O13 ⁱⁱⁱ	2.53 (3)		
Pb17—O16 ^{iv}	2.49 (3)	Pb18—O23 ^{ix}	2.57 (3)		
Pb17—O35	2.60 (2)	Pb18—O12	2.63 (3)		
Pb17—O37 ^{viii}	2.66 (3)	Pb18—O324 ^x	2.67 (2)		
Pb17—O25	2.71 (3)	Pb18—O21 ⁱ	2.75 (2)		
Pb17—O26	2.99 (2)	Pb18—O22 ^x	2.82 (3)		
Pb17—O24 ^{viii}	3.03 (3)	Pb18—O319 ⁱ	3.15 (3)		
Pb17—O314	3.35 (2)	Pb18—O311 ^{ix}	3.40 (3)		
Pb21—O23 ^{ix}	2.33 (2)	Pb22—O212	2.38 (2)	Pb23—O211	2.37 (2)
Pb21—O37 ^{xi}	2.50 (3)	Pb22—O35 ^{xi}	2.40 (3)	Pb23—O36 ^{xiii}	2.45 (2)
Pb21—O315 ^x	2.63 (3)	Pb22—O38 ⁱ	2.42 (3)	Pb23—O315 ^{xiii}	2.55 (3)

Pb21—O39	2.70 (3)	Pb22—O34	2.95 (3)	Pb23—O324 ^{xiv}	2.68 (3)
Pb21—O324 ^x	2.82 (2)	Pb22—O16	3.10 (2)	Pb23—O11 ⁱ	2.95 (3)
Pb21—O15 ^{ix}	3.05 (3)	Pb22—Cl2 ⁱ	3.120 (9)	Pb23—O312 ^{xiii}	3.07 (2)
Pb21—Cl4 ^{xii}	3.100 (8)	Pb22—O316 ⁱ	3.18 (2)	Pb23—Cl4 ^{xv}	3.130 (9)
Pb21—Cl4 ⁱⁱ	3.232 (8)	Pb22—Cl2	3.218 (9)	Pb23—Cl4 ^{viii}	3.187 (9)
Pb24—O27	2.35 (2)	Pb25—O24	2.41 (2)	Pb26—O28	2.32 (2)
Pb24—O323 ⁱⁱⁱ	2.43 (3)	Pb25—O314 ^{ix}	2.41 (3)	Pb26—O33	2.55 (3)
Pb24—O313	2.44 (3)	Pb25—O310 ^{vi}	2.43 (3)	Pb26—O321 ⁱ	2.59 (2)
Pb24—O319 ⁱ	2.85 (3)	Pb25—O311 ^{ix}	2.88 (3)	Pb26—O314 ^{xi}	2.73 (3)
Pb24—O317	2.86 (2)	Pb25—O12	2.95 (3)	Pb26—O320 ⁱ	2.78 (2)
Pb24—O13 ⁱⁱⁱ	2.97 (2)	Pb25—Cl1 ⁱⁱⁱ	3.062 (8)	Pb26—O14	3.08 (3)
Pb24—Cl3	3.175 (8)	Pb25—O33 ^{ix}	3.11 (2)	Pb26—Cl1 ^{xvi}	3.141 (8)
Pb24—Cl3 ^{vii}	3.177 (7)	Pb25—Cl1 ^{ix}	3.258 (8)	Pb26—Cl1	3.156 (8)
Pb27—O26	2.35 (2)	Pb28—O34	2.37 (3)	Pb29—O316 ⁱ	2.34 (3)
Pb27—O39 ^{viii}	2.39 (3)	Pb28—O32	2.41 (3)	Pb29—O31 ⁱⁱⁱ	2.39 (3)
Pb27—O36	2.49 (3)	Pb28—O25	2.42 (2)	Pb29—O29	2.42 (2)
Pb27—O312 ^{iv}	2.74 (3)	Pb28—O31 ^{iv}	2.86 (3)	Pb29—O38 ⁱⁱⁱ	2.95 (3)
Pb27—O110	3.11 (2)	Pb28—O19	2.96 (2)	Pb29—O111	3.05 (3)
Pb27—Cl4 ⁱⁱⁱ	3.118 (9)	Pb28—Cl2	3.040 (9)	Pb29—Cl2 ⁱⁱⁱ	3.087 (8)
Pb27—Cl4 ^{xvii}	3.154 (9)	Pb28—Cl2 ⁱⁱⁱ	3.229 (9)	Pb29—O32 ⁱⁱⁱ	3.19 (3)
Pb27—O37 ^{viii}	3.24 (2)	Pb28—O35	3.33 (3)	Pb29—Cl2	3.190 (8)
P210—O22 ^{xiii}	2.29 (3)	P211—O210	2.32 (2)	P212—O21	2.35 (2)
P210—O322 ^{iv}	2.38 (3)	P211—O318 ^{xviii}	2.45 (3)	P212—O311 ^{xix}	2.36 (2)
P210—O319	2.46 (3)	P211—O317 ⁱⁱⁱ	2.54 (2)	P212—O321 ⁱⁱⁱ	2.42 (3)
P210—O318	2.90 (3)	P211—O313 ⁱ	2.75 (3)	P212—O320 ⁱ	2.87 (3)
P210—O112 ^{xiii}	3.08 (3)	P211—O18	3.08 (3)	P212—O17	2.94 (2)
P210—Cl3 ^{xiii}	3.134 (7)	P211—Cl3 ⁱⁱⁱ	3.088 (7)	P212—Cl1	3.065 (9)
P210—Cl3 ⁱⁱⁱ	3.162 (7)	P211—Cl3 ^{xiii}	3.168 (7)	P212—Cl1 ^{xix}	3.189 (8)
P210—O323	3.19 (3)	P211—O322 ^{xviii}	3.22 (3)	P212—O310 ^{xix}	3.29 (2)
				P212—O314	3.47 (2)

As1—O38	1.68 (3)	As11—O112	1.64 (2)	As2—O323	1.66 (3)
As1—O210	1.69 (3)	As11—O317	1.65 (2)	As2—O319	1.68 (3)
As1—O316	1.71 (2)	As11—O29	1.69 (3)	As2—O18	1.72 (2)
As1—O19	1.76 (2)	As11—O313	1.69 (3)	As2—O21	1.74 (2)
As21—O320	1.67 (3)	As3—O111	1.64 (2)	As31—O15	1.67 (2)
As21—O27	1.68 (3)	As3—O35	1.68 (3)	As31—O312	1.69 (3)
As21—O321	1.69 (3)	As3—O26	1.69 (2)	As31—O36	1.70 (3)
As21—O12	1.75 (2)	As3—O34	1.70 (3)	As31—O212	1.71 (3)
As4—O324	1.68 (3)	As41—O318	1.61 (3)	As5—O25	1.63 (2)
As4—O110	1.69 (3)	As41—O211	1.62 (2)	As5—O314	1.66 (3)
As4—O315	1.72 (3)	As41—O13	1.67 (3)	As5—O17	1.69 (3)
As4—O22	1.77 (2)	As41—O322	1.74 (3)	As5—O33	1.71 (3)
As51—O32	1.66 (3)	As6—O310	1.67 (3)	As61—O11	1.66 (3)
As51—O16	1.70 (3)	As6—O311	1.70 (3)	As61—O24	1.69 (3)
As51—O31	1.74 (3)	As6—O23	1.70 (3)	As61—O39	1.69 (3)
As51—O28	1.78 (2)	As6—O14	1.71 (3)	As61—O37	1.74 (3)

Symmetry codes: : (i) $-x+1, y+1/2, -z+1$; (ii) $x, y, z+1$; (iii) $-x+1, y-1/2, -z+1$; (iv) $x, y-1, z$; (v) $x, y-1, z+1$; (vi) $-x+1, y-1/2, -z+2$; (vii) $x-1, y-1, z$; (viii) $x+1, y, z$; (ix) $-x+1, y+1/2, -z+2$; (x) $x-1, y, z$; (xi) $x, y+1, z$; (xii) $-x, y+1/2, -z+1$; (xiii) $x, y, z-1$; (xiv) $x, y+1, z-1$; (xv) $-x+1, y+1/2, -z$; (xvi) $-x+2, y+1/2, -z+1$; (xvii) $x+1, y, z+1$; (xviii) $-x+1, y-1/2, -z$; (xix) $-x+2, y-1/2, -z+1$; (xx) $x+1, y+1, z$; (xxi) $-x, y-1/2, -z+1$; (xxii) $x-1, y, z-1$.”