Supporting Information for

Long Range Magnetic Ordering in Iron Jarosites Prepared by Redox-Based Hydrothermal Methods

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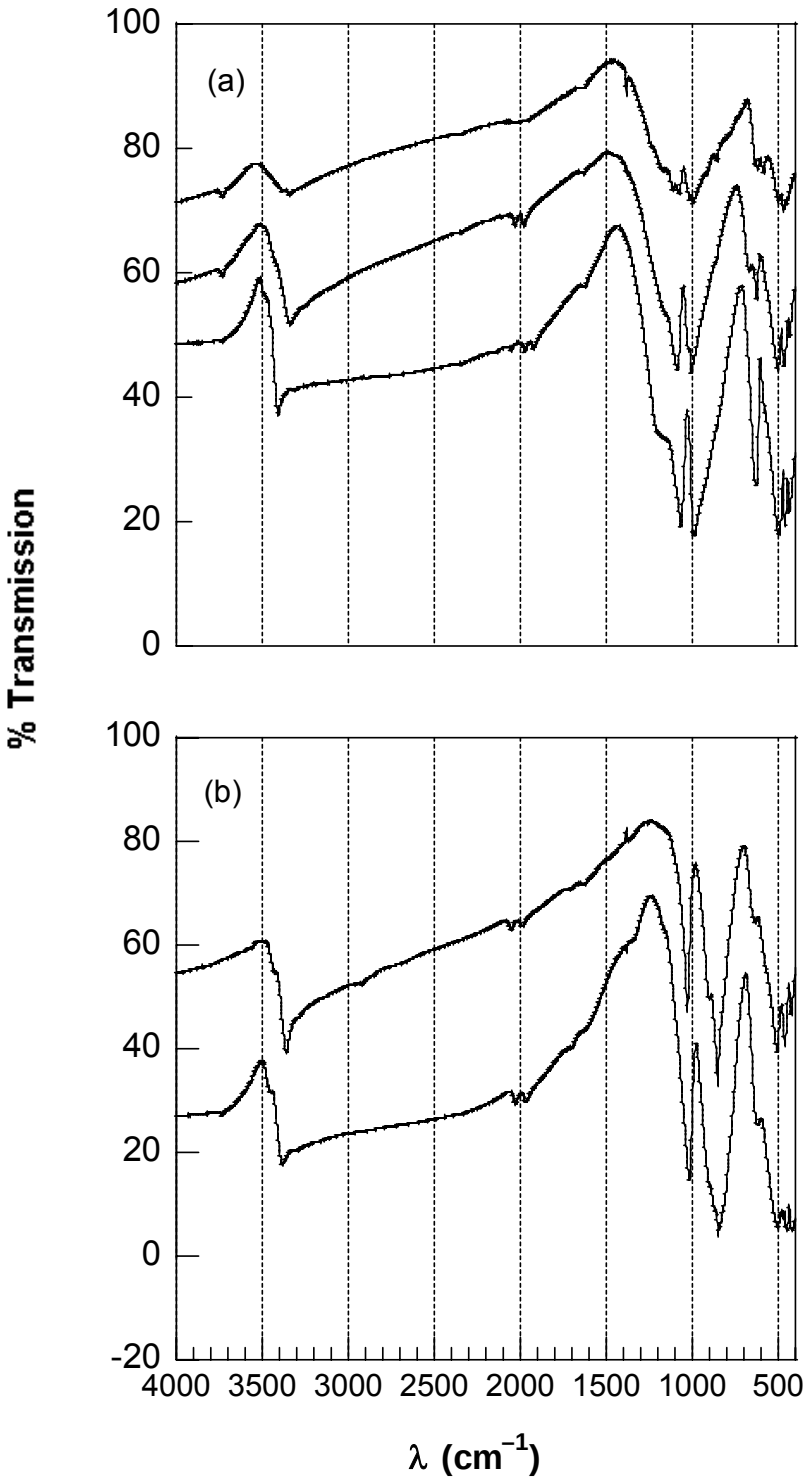

Figure S1. IR spectra of the (a) sulfate-capped iron jarosites, $Pb_{0.5}Fe_3(OH)_6(SO_4)_2$ (top) $AgFe_3(OH)_6(SO_4)_2$ (middle), and $TlFe_3(OH)_6(SO_4)_2$ (bottom) and (b) selenate-capped iron jarosite analogs $KFe_3(OH)_6(SO_4)_2$ (top) and $RbFe_3(OH)_6(SO_4)_2$ (bottom).

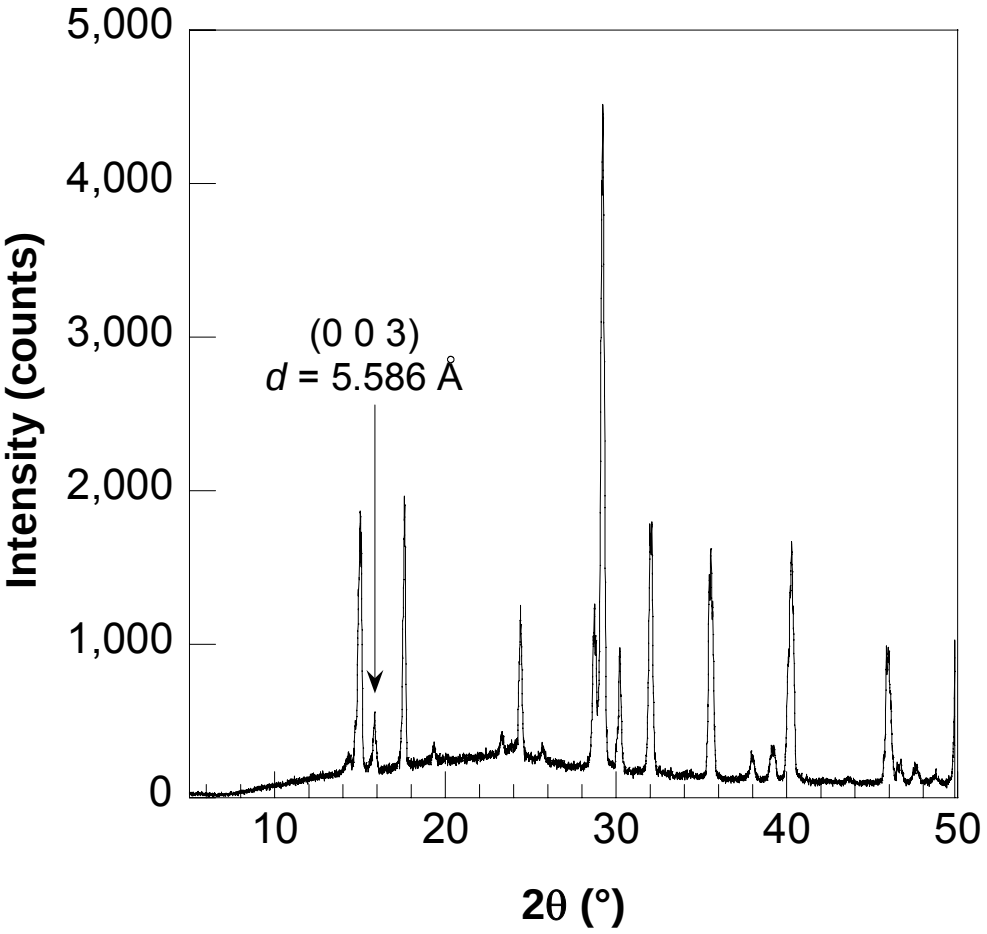

Figure S2. Powder X-ray diffraction pattern of $Pb_{0.5}Fe_3(OH)_6(SO_4)_2$, emphasizing the (003) reflection at 15.85° 2θ.

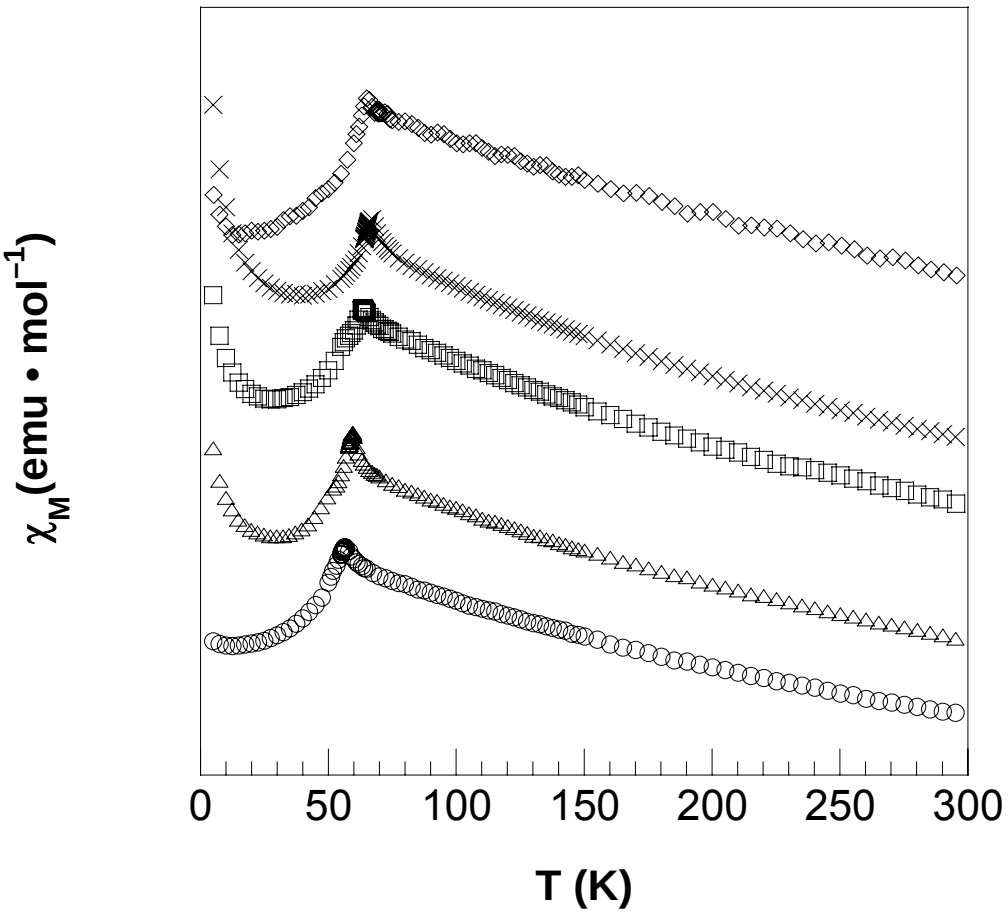

Figure S3. ZFC susceptibilities for the new jarosite compounds $Pb_{0.5}Fe_3(OH)_6(SO_4)_2$ (○),$AgFe_3(OH)_6(SO_4)_2$ (Δ), $TlFe_3(OH)_6(SO_4)_2$ (□), $KFe_3(OH)_6(SeO_4)_2$ (×), and $RbFe_3(OH)_6(SeO_4)_2$ (◊). The maximum in T_N ranges from 56.4 66.5 K. Plots are offset for clarity.

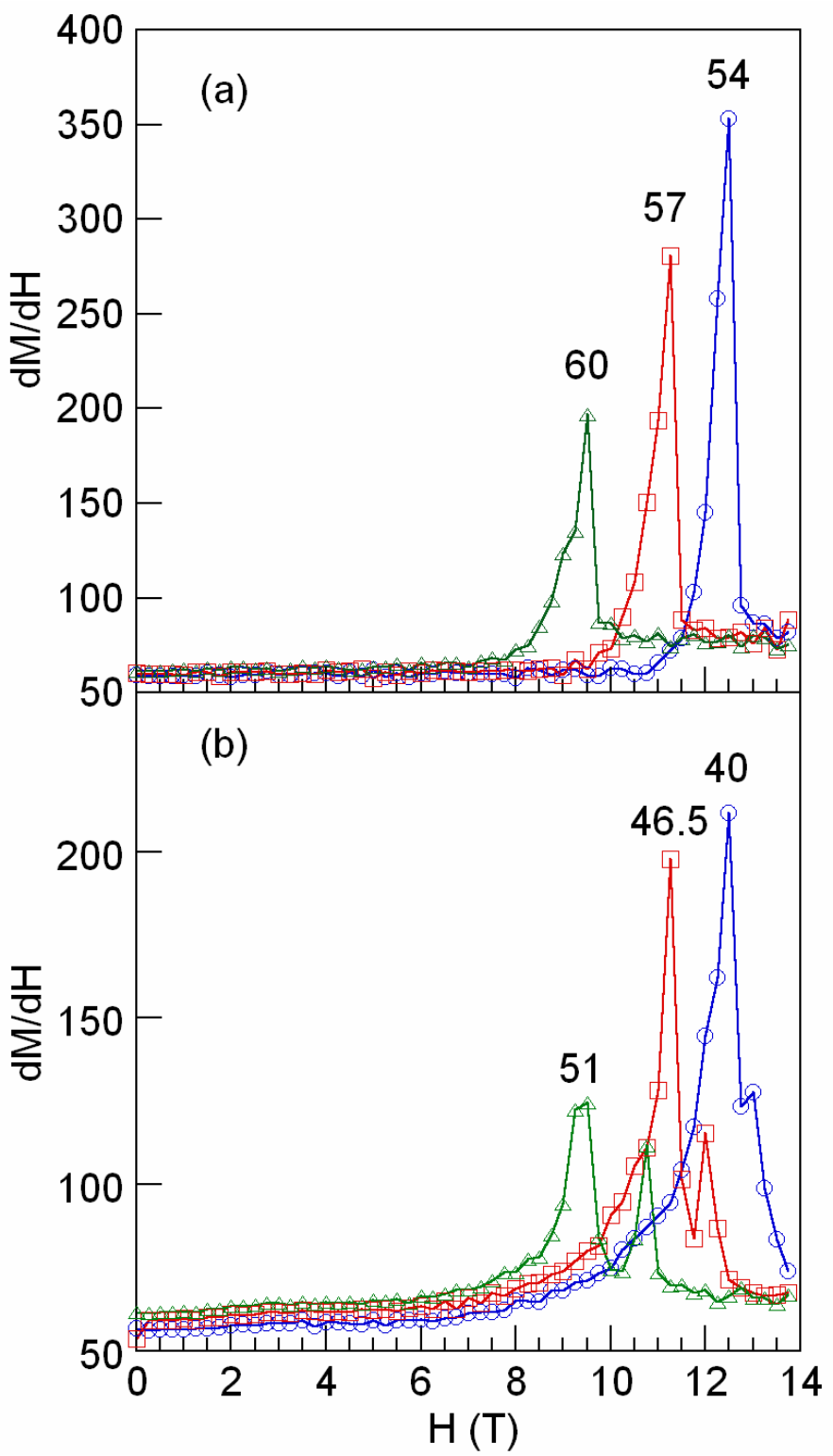

Figure S4. First derivative plots of the magnetization with applied field at a given temperature for (a) $RbFe_3(OH)_6(SO_4)_2$ and (b) $Pb_{0.5}Fe_3(OH)_6(SO_4)_2$. The maximum gives the critical field for the ferromagnetic alignment of canted spins between layers.

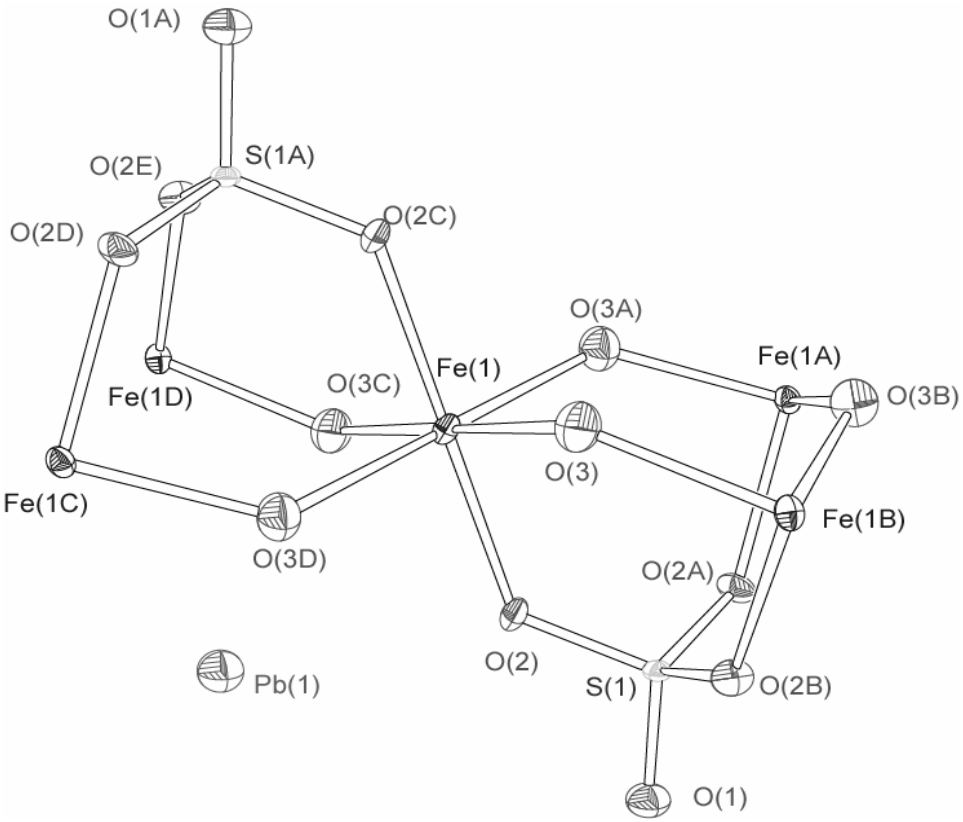

Figure S5. Atom labeling scheme for $Pb_{0.5}Fe_3(OH)_6(SO_4)_2$.

Table S1. Crystal data and structure refinement for $Pb_{0.5}Fe_3(OH)_6(SO_4)_2$.

Identification code	001206m	
Empirical formula	$H_6Fe_3O_{14}Pb_{0.5}S_2$	
Formula weight	565.31	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	*R*-3m	
Unit cell dimensions	a = 7.328(2) Å	α = 90°
	b = 7.328(2) Å	β = 90°
	c = 16.795(6) Å	γ = 120°
Volume	781.1(4) $Å^3$	
Z	3	
Density (calculated)	3.606 Mg/m^3	
Absorption coefficient	15.334 mm^{-1}	
F(000)	848	
Crystal size	0.04 ×0.04 × 0.04 mm^3	
Theta range for data collection	3.43 to 23.22°.	
Index ranges	$-4 \le h \le 8$	
	$-8 \le k \le 5$	
	$-18 \le l \le 17$	
Reflections collected	937	
Independent reflections	164 [$R_{(int)}$ = 0.0833]	
Completeness to theta = 23.22°	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	164 / 1 / 34	
Goodness-of-fit on F^2	1.190	
Final R indices [I > 2σ (I)]	*R1* = 0.0268	*wR2* = 0.0538
R indices (all data)	*R1* = 0.0297	*wR2* = 0.0552
Largest diff. peak and hole	0.736 $eÅ^{-3}$	–0.593 $eÅ^{-3}$

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $Pb_{0.5}Fe_3(OH)_6(SO_4)_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
Pb(1)	0	0	0	21(1)
S(1)	0	0	3109(2)	7(1)
Fe(1)	3333	1667	1667	8(1)
O(1)	0	0	3973(4)	20(3)
O(2)	2200(7)	1100(3)	2810(2)	15(2)
O(3)	1266(3)	2532(7)	1343(2)	18(2)

Table S3. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $Pb_{0.5}Fe_3(OH)_6(SO_4)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb(1)	22(1)	22(1)	20(1)	0	0	11(1)
S(1)	8(1)	8(1)	5(1)	0	0	4(1)
Fe(1)	7(1)	8(1)	10(1)	1(1)	2(1)	4(1)
O(1)	22(4)	22(4)	14(4)	0	0	11(2)
O(3)	16(2)	16(3)	22(2)	3(2)	1(1)	8(1)
O(2)	10(3)	19(2)	13(2)	1(1)	3(2)	5(1)

Table S4. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $Pb_{0.5}Fe_3(OH)_6(SO_4)_2$.

	x	*y*	*z*	U(eq)
H(1)	1920(40)	3840(70)	1050(40)	60(50)

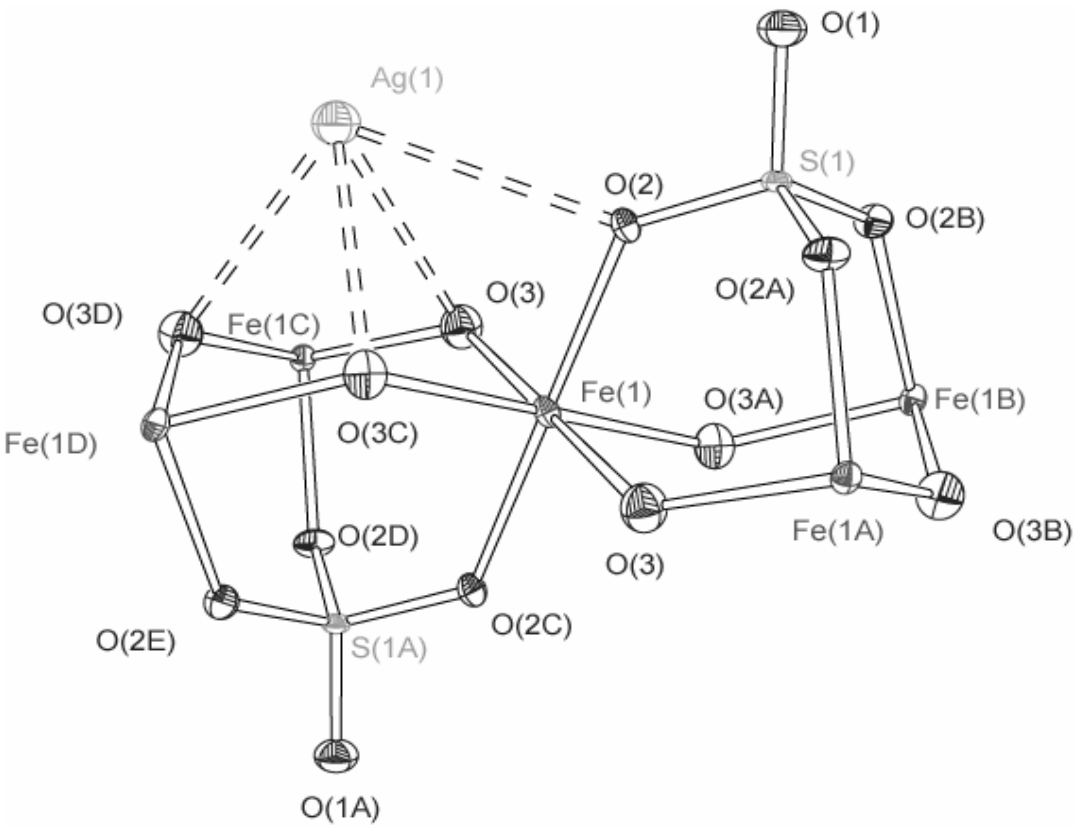

Figure S6. Atom labeling scheme for $AgFe_3(OH)_6(SO_4)_2$.

Table S5. Crystal data and structure refinement for $AgFe_3(OH)_6(SO_4)_2$.

Identification code	002032m	
Empirical formula	$H_6Fe_3O_{14}AgS_2$	
Formula weight	569.59	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	*R*-3m	
Unit cell dimensions	a = 7.3300(9) Å	α = 90°
	b = 7.3300(9) Å	β = 90°
	c = 16.497(3) Å	γ = 120°
Volume	767.62(19) $Å^3$	
Z	3	
Density (calculated)	3.696 Mg/m^3	
Absorption coefficient	6.547 mm^{-1}	
F(000)	825	
Crystal size	0.04 ×0.04 × 0.04 mm^3	
Theta range for data collection	3.44 to 23.27°.	
Index ranges	$-8 \le h \le 8$	
	$-8 \le k \le 8$	
	$-7 \le l \le 18$	
Reflections collected	1039	
Independent reflections	161 [$R_{(int)}$ = 0.0459]	
Completeness to theta = 23.27°	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	161 / 1 / 29	
Goodness-of-fit on F^2	1.224	
Final R indices [I > 2σ (I)]	*R1* = 0.0255	*wR2* = 0.0642
R indices (all data)	*R1* = 0.0259	*wR2* = 0.0644
Largest diff. peak and hole	0.508 $eÅ^{-3}$	–0.906 $eÅ^{-3}$

Table S6. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $AgFe_3(OH)_6(SO_4)_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
Ag(1)	0	0	0	27(1)
S(1)	0	0	3123(2)	7(1)
Fe(1)	3333	1667	1667	7(1)
O(1)	0	0	4009(5)	8(2)
O(2)	2194(8)	1097(4)	2823(3)	10(1)
O(3)	1256(4)	2512(8)	1331(3)	8(1)

Table S7. Anisotropic displacement parameters (Å^2 × 10^3) for $AgFe_3(OH)_6(SO_4)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag(1)	34(1)	34(1)	13(1)	0	0	17(1)
S(1)	8(1)	8(1)	5(2)	0	0	4(1)
Fe(1)	5(1)	7(1)	8(1)	0(1)	1(1)	3(1)
O(1)	12(3)	12(3)	1(4)	0	0	6(2)
O(2)	6(3)	13(2)	7(2)	0(1)	0(2)	3(1)
O(3)	7(2)	7(3)	11(2)	1(2)	1(1)	4(2)

Table S8. Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3) for $AgFe_3(OH)_6(SO_4)_2$.

	x	*y*	*z*	U(eq)
H(1)	2000(20)	3990(50)	1180(70)	120(70)

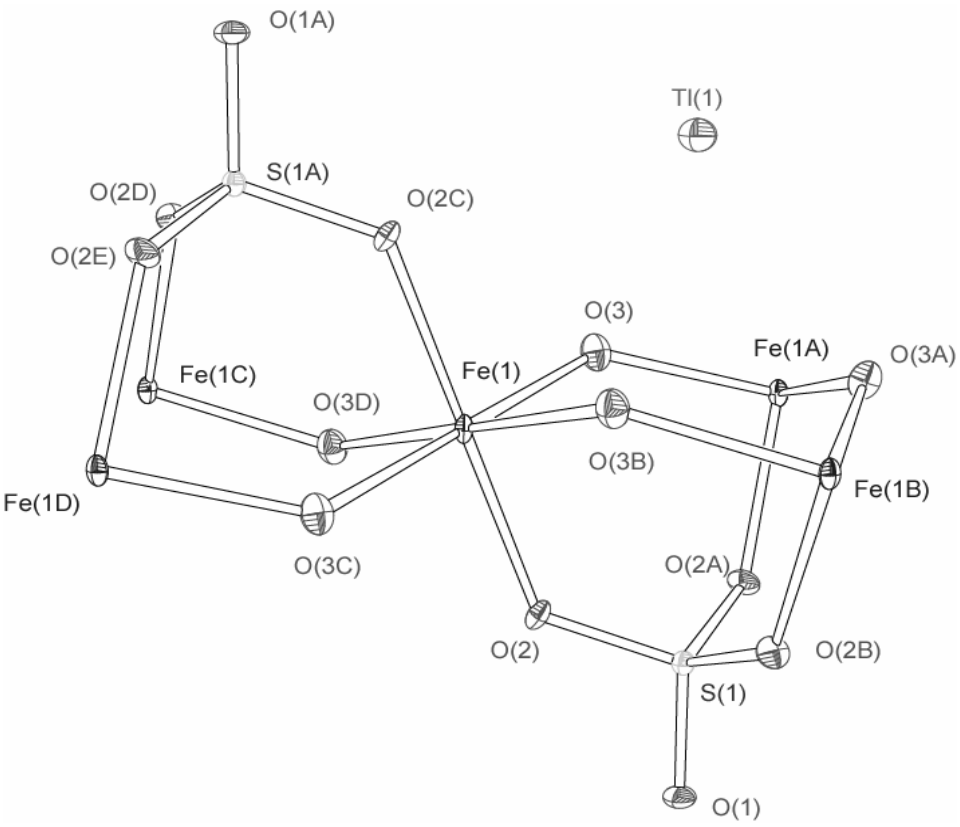

Figure S7. Atom labeling scheme for $TlFe_3(OH)_6(SO_4)_2$.

Table S9. Crystal data and structure refinement for $TlFe_3(OH)_6(SO_4)_2$.

Identification code	002124m	
Empirical formula	$H_6Fe_3O_{14}TlS_2$	
Formula weight	666.09	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	*R*-3m	
Unit cell dimensions	a = 7.3226(7) Å	α = 90°
	b = 7.3226(7) Å	β = 90°
	c = 17.610(2) Å	γ = 120°
Volume	817.74(15) $Å^3$	
Z	3	
Density (calculated)	4.058 Mg/m^3	
Absorption coefficient	19.111 mm^{-1}	
F(000)	927	
Crystal size	0.04 ×0.04 × 0.04 mm^3	
Theta range for data collection	3.41 to 23.22°.	
Index ranges	$-6 \le h \le 8$	
	$-7 \le k \le 8$	
	$-18 \le l \le 19$	
Reflections collected	1080	
Independent reflections	169 [$R_{(int)}$ = 0.0589]	
Completeness to theta = 23.22°	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	169 / 1 / 29	
Goodness-of-fit on F^2	1.292	
Final R indices [I > 2σ (I)]	*R1* = 0.0207	*wR2* = 0.0546
R indices (all data)	*R1* = 0.0207	*wR2* = 0.0546
Largest diff. peak and hole	0.754 $eÅ^{-3}$	–0.649 $eÅ^{-3}$

Table S10. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $TlFe_3(OH)_6(SO_4)_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
Tl(1)	0	0	0	12(1)
S(1)	0	0	3050(2)	6(1)
Fe(1)	3333	1667	1667	5(1)
O(1)	0	0	3873(6)	9(2)
O(2)	2202(10)	1101(5)	2762(3)	9(1)
O(3)	1283(5)	2565(10)	1374(3)	12(2)

Table S11. Anisotropic displacement parameters ($Å^2 \times 10^3$) for $TlFe_3(OH)_6(SO_4)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tl(1)	13(1)	13(1)	11(1)	0	0	7(1)
S(1)	5(1)	5(1)	7(2)	0	0	3(1)
Fe(1)	3(1)	4(1)	9(1)	0(1)	0(1)	2(1)
O(1)	11(4)	11(4)	5(5)	0	0	6(2)
O(2)	6(3)	11(2)	9(3)	2(1)	3(3)	3(2)
O(3)	9(3)	10(4)	16(4)	-2(3)	-1(1)	5(2)

Table S12. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for $TlFe_3(OH)_6(SO_4)_2$.

	x	*y*	*z*	U(eq)
H(1)	1300(300)	2700(500)	824(15)	230(160)

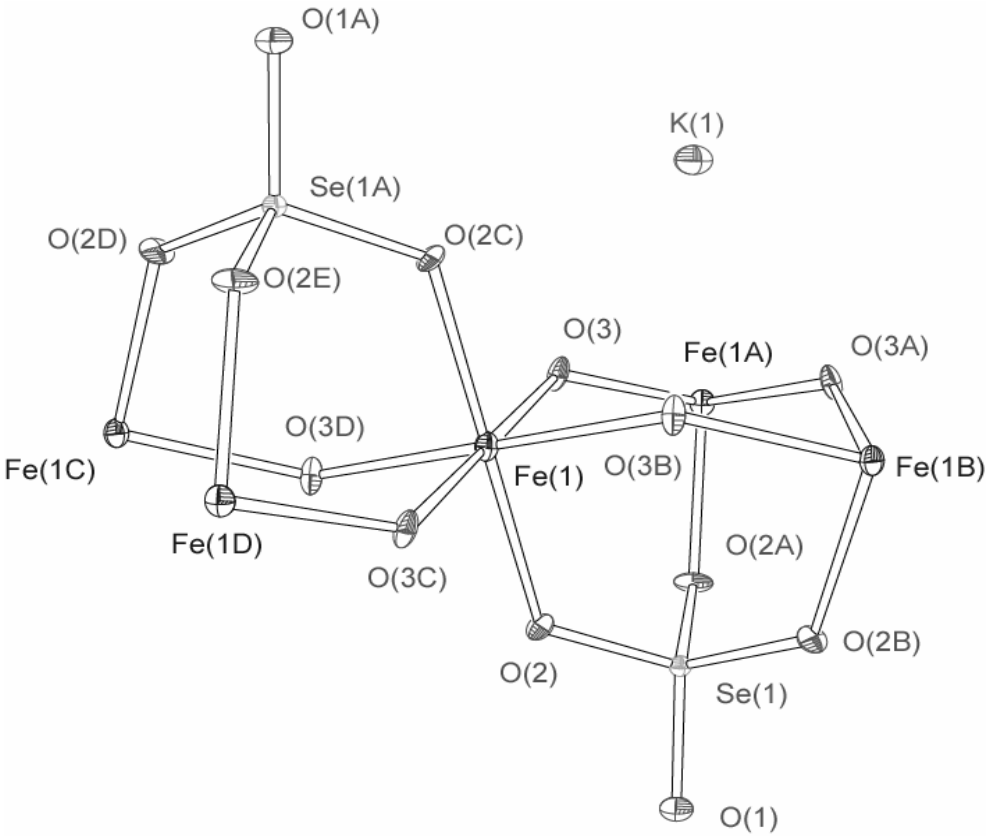

Figure S8. Atomic labeling scheme for $KFe_3(OH)_6(SeO_4)_2$.

Table S13. Crystal data and structure refinement for $KFe_3(OH)_6(SeO_4)_2$.

Identification code	002127m	
Empirical formula	$H_6Fe_3O_{14}KSe_2$	
Formula weight	594.62	
Temperature	183(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	*R*-3m	
Unit cell dimensions	a = 7.3902(9) Å	α = 90°
	b = 7.3902(9) Å	β = 90°
	c = 17.498(3) Å	γ = 120°
Volume	827.6(2) $Å^3$	
Z	3	
Density (calculated)	3.579 Mg/m^3	
Absorption coefficient	10.947 mm^{-1}	
F(000)	849	
Crystal size	0.04 ×0.04 × 0.02 mm^3	
Theta range for data collection	3.39 to 23.27°.	
Index ranges	$-7 \le h \le 8$	
	$-7 \le k \le 8$	
	$-19 \le l \le 19$	
Reflections collected	1130	
Independent reflections	171 [$R_{(int)}$ = 0.0706]	
Completeness to theta = 23.27°	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	171 / 1 / 29	
Goodness-of-fit on F^2	1.245	
Final R indices [I > 2σ (I)]	*R1* = 0.0367	*wR2* = 0.0781
R indices (all data)	*R1* = 0.0374	*wR2* = 0.0786
Largest diff. peak and hole	0.913 $eÅ^{-3}$	–0.690 $eÅ^{-3}$

Table S14. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $KFe_3(OH)_6(SeO_4)_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
K(1)	0	0	0	13(1)
Se(1)	0	0	3115(1)	5(1)
Fe(1)	3333	1667	1667	7(1)
O(1)	0	0	4036(7)	11(3)
O(2)	2410(11)	1205(6)	2792(3)	10(2)
O(3)	1258(6)	2516(12)	1387(4)	9(2)

Table S15. Anisotropic displacement parameters (Å^2 × 10^3) for $KFe_3(OH)_6(SeO_4)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K(1)	15(2)	15(2)	10(3)	0	0	7(1)
Se(1)	5(1)	5(1)	5(1)	0	0	3(1)
Fe(1)	5(1)	7(1)	10(1)	0(1)	1(1)	3(1)
O(1)	12(5)	12(5)	7(6)	0	0	6(2)
O(2)	6(4)	6(4)	7(3)	2(1)	4(3)	3(2)
O(3)	5(3)	6(4)	16(4)	4(3)	2(2)	3(2)

Table S16. Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3) for $KFe_3(OH)_6(SeO_4)_2$.

	x	*y*	*z*	U(eq)
H(1)	1930(40)	3860(80)	1130(50)	40(50)

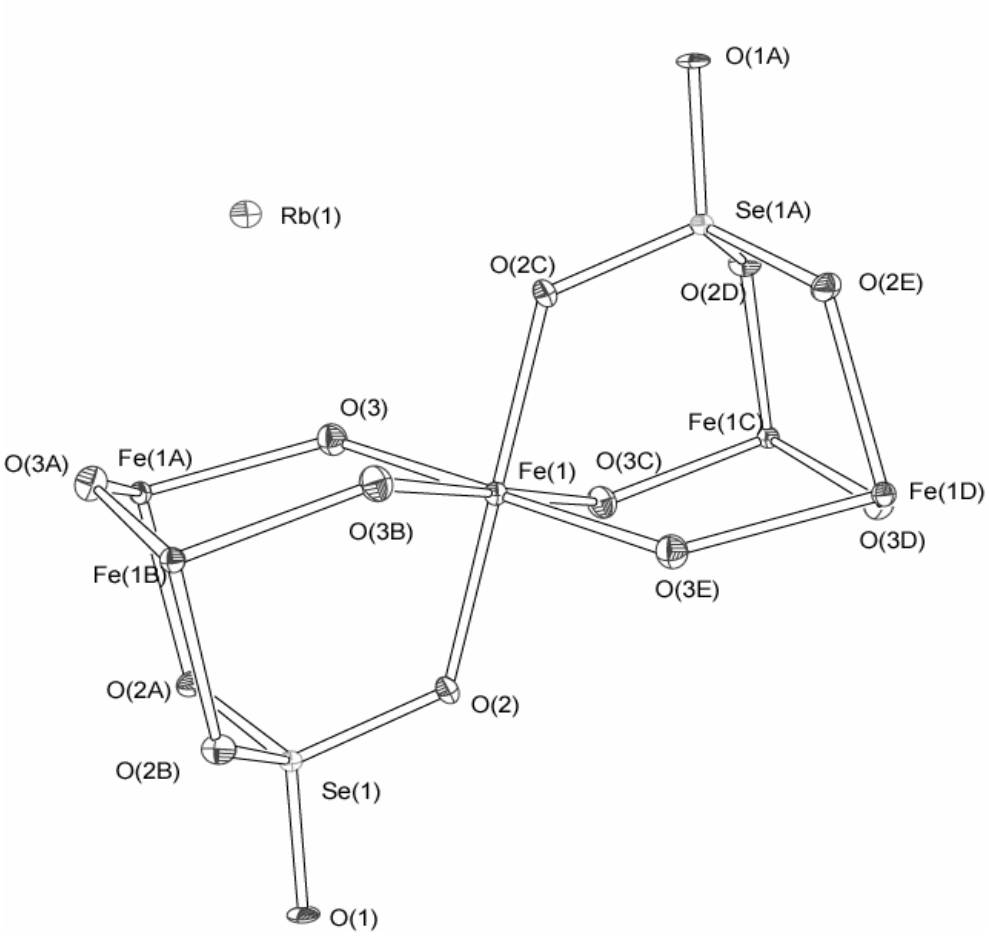

Figure S8. Atomic labeling scheme for $RbFe_3(OH)_6(SeO_4)_2$.

Table S17. Crystal data and structure refinement for $RbFe_3(OH)_6(SeO_4)_2$.

Identification code	003096m	
Empirical formula	$H_6Fe_3O_{14}RbSe_2$	
Formula weight	640.99	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	*R*-3m	
Unit cell dimensions	a = 7.4022(16) Å	α = 90°
	b = 7.4022(16) Å	β = 90°
	c = 17.816(5) Å	γ = 120°
Volume	845.4(4) $Å^3$	
Z	3	
Density (calculated)	3.777 Mg/m^3	
Absorption coefficient	4.879 mm^{-1}	
F(000)	301	
Crystal size	0.04 ×0.04 × 0.03 mm^3	
Theta range for data collection	3.38 to 28.47°.	
Index ranges	$-9 \le h \le 9$	
	$-9 \le k \le 9$	
	$-23 \le l \le 23$	
Reflections collected	5356	
Independent reflections	293 [$R_{(int)}$ = 0.0323]	
Completeness to theta = 23.27°	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	293 / 1 / 29	
Goodness-of-fit on F^2	1.116	
Final R indices [I > 2σ (I)]	*R1* = 0.0156	*wR2* = 0.0433
R indices (all data)	*R1* = 0.0162	*wR2* = 0.0436
Largest diff. peak and hole	0.617 $eÅ^{-3}$	–0.812 $eÅ^{-3}$

Table S18. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for $RbFe_3(OH)_6(SeO_4)_2$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
Rb(1)	0	0	0	8(1)
Se(1)	0	0	3093(1)	5(1)
Fe(1)	3333	1667	1667	5(1)
O(1)	0	0	4002(2)	8(1)
O(2)	2409(3)	1204(2)	2774(1)	8(1)
O(3)	1264(2)	2527(3)	1408(1)	10(1)

Table S19. Anisotropic displacement parameters (Å^2 × 10^3) for $RbFe_3(OH)_6(SeO_4)_2$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Rb(1)	8(1)	8(1)	7(1)	0	0	4(1)
Se(1)	5(1)	5(1)	5(1)	0	0	3(1)
Fe(1)	5(1)	5(1)	6(1)	0(1)	1(1)	2(1)
O(1)	10(1)	10(10	2(2)	0	0	5(1)
O(2)	5(1)	10(1)	8(1)	1(1)	1(1)	2(1)
O(3)	9(1)	10(1)	12(1)	1(1)	1(1)	5(1)

Table S20. Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3) for $RbFe_3(OH)_6(SeO_4)_2$.

	x	*y*	*z*	U(eq)
H(1)	1959(14)	3920(30)	1210(20)	19(10)