Supplementary Information

Tables

Figures

Table S1 Lattice parameters from the powder X-ray refinements of $Ni_3(PO_4)_3$ and $Fe_3(PO_4)_2$

Sample	*a* / Å	*b* / Å	*c* / Å	β / °
$Ni_3(PO_4)_2$	5.8310(2)	4.6978(2)	10.1098(3)	91.129(2)
$Fe_3(PO_4)_2$	8.8828(3)	11.1738(3)	6.1440(2)	99.348(3)

Table S2 Fit statistics from the powder X-ray refinements of $Ni_3(PO_4)_3$ and $Fe_3(PO_4)_2$

	Modelled				Lebail	
	R_p / %	R_{wp} / %	R_{F**2} / %	Obs.	R_p / %	R_{wp} / %
$Ni_3(PO_4)_2$	15.95	24.90	10.61	469	13.11	23.30
$Fe_3(PO_4)_2$	23.60	33.10	15.63	531	22.90	32.50

Table S3 Atomic model of $Fe_3(PO_4)_2$ from powder X-ray Rietveld refinement.

Atom	x	y	Z	occupancy	$U_{iso} \times 100$/ Å^2
Fe(1)	0.9276(9)	0.1168(6)	0.8692(12)	1.0	3.34(10)
Fe(2)	0.7235(9)	0.0811(6)	0.3308(14)	1.0	4.62(12)
Fe(3)	0.3631(8)	0.1939(7)	0.1221(13)	1.0	3.89(12)
P(1)	0.0946(15)	0.1360(11)	0.3893(24)	1.0	3.69(34)
P(2)	0.6047(16)	0.0889(11)	0.8030(26)	1.0	3.69(34)
O(1)	0.0764(28)	0.0654(20)	0.1741(29)	1.0	2.05(30)
O(2)	0.4810(21)	0.1806(19)	0.8257(40)	1.0	2.05(3)
O(3)	0.9463(19)	0.2035(19)	0.3963(40)	1.0	2.05(30)
O(4)	0.6982(23)	0.1220(21)	0.6245(32)	1.0	2.05(30)
O(5)	0.2256(20)	0.2233(17)	0.3811(41)	1.0	2.05(30)
O(6)	0.7195(24)	0.0900(23)	0.0165(32)	1.0	2.05(3)
O(7)	0.1312(26)	0.0600(19)	0.5975(29)	1.0	2.05(30)
O(8)	0.5302(26)	-0.0337(14)	0.7602(42)	1.0	2.05(30)

Table S4 Atomic model of $Ni_3(PO_4)_2$ from powder X-ray Rietveld refinement.

Atom	x	y	z	occupancy	$U_{iso} \times 100/ Å^2$
Ni(1)	0	0	0	1.0	1.86(9)
Ni(2)	0.2382(4)	-0.0133(7)	0.2749(3)	1.0	1.38(8)
P(1)	0.2396(9)	0.4232(10)	0.0945(5)	1.0	1.54(17)
O(1)	0.2464(18)	0.7483(11)	0.0971(11)	1.0	0.89(16)
O(2)	0.2403(19)	0.1996(19)	0.4541(60	1.0	0.89(16)
O(3)	0.0410(13)	0.2959(21)	0.1715(9)	1.0	0.89(16)
O(4)	0.4489(13)	0.2705(19)	0.1538(10)	1.0	0.89(16)

Table S5 Anisotropic thermal displacement parameters from $Fe_2{}^{58}Ni(PO_4)_2$ Rietveld refinement of the powder neutron data from HRPD.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{12} / Å^2	U_{13} / Å^2	U_{23} / Å^2
Ni/Fe(1)	1.10(7)	0.70(7)	0.95(7)	0.19(5)	0.11(5)	-0.08(6)
Ni/Fe(2)	1.60(6)	1.63(6)	1.41(5)	0.02(5)	0.22(4)	0.18(5)
P(1)	1.27(10)	0.19(10)	1.12(11)	0.00(8)	0.33(8)	0.63(8)
O(1)	1.59(10)	0.35(11)	1.59(10)	-0.27(9)	-0.03(8)	-0.36(8)
O(2)	1.71(10)	1.11(9)	0.95(10)	0.20(8)	0.35(8)	-0.08(7)
O(3)	1.76(11)	1.22(9)	0.92(9)	-0.14(7)	0.38(8)	0.69(8)
O(4)	1.54(9)	1.21(10)	1.47(9)	0.37(8)	0.05(7)	0.83(9)

Table S6 Anisotropic thermal displacement parameters from $Fe_2{}^{60}Ni(PO_4)_2$ Rietveld refinement of the powder neutron data from HRPD.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{12} / Å^2	U_{13} / Å^2	U_{23} / Å^2
Ni/Fe(1)	1.37(14)	0.57(15)	1.01(14)	0.23(11)	0.07(10)	-0.22(11)
Ni/Fe(2)	1.41(5)	1.67(5)	1.42(5)	-0.03(4)	0.17(4)	0.19(4)
P(1)	1.12(8)	0.77(7)	1.00(8)	-0.05(7)	0.14(7)	0.66(7)
O(1)	1.42(8)	0.96(8)	1.59(7)	-0.11(7)	0.06(6)	-0.17(6)
O(2)	1.67(7)	1.24(7)	1.27(8)	0.03(6)	0.38(6)	0.09(6)
O(3)	1.69(8)	1.20(8)	1.22(7)	-0.06(5)	0.50(6)	0.55(6)
O(4)	1.66(7)	1.00(8)	1.33(7)	0.14(6)	0.02(6)	0.58(6)

Table S7 Anisotropic thermal displacement parameters from $Fe_2{}^{62}Ni(PO_4)_2$ Rietveld refinement of the powder neutron data from HRPD.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{12} / Å^2	U_{13} / Å^2	U_{23} / Å^2
Ni/Fe(1)	1.63(27)	2.70(31)	1.84(29)	-0.39(25)	0.20(19)	-0.34(26)
Ni/Fe(2)	0.90(7)	0.92(8)	0.93(8)	0.05(7)	0.15(5)	0.03(6)
P(1)	1.31(10)	0.54(9)	1.26(11)	-0.20(9)	0.16(9)	0.87(9)
O(1)	1.54(10)	1.33(10)	1.48(9)	-0.04(10)	0.20(8)	-0.04(9)
O(2)	1.86(9)	1.21(11)	1.24(11)	-0.25(9)	0.32(7)	0.08(8)
O(3)	1.65(11)	1.50(11)	1.38(10)	0.14(8)	0.49(8)	0.35(7)
O(4)	1.70(9)	1.34(10)	1.18(9)	0.04(8)	-0.09(7)	0.36(9)

Table S8 Anisotropic thermal displacement parameters from $Fe_2^{Nat}Ni(PO_4)_2$ Rietveld refinement of the powder neutron data from HRPD.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{12} / Å^2	U_{13} / Å^2	U_{23} / Å^2
Ni/Fe(1)	1.43(3)	0.61(3)	1.08(3)	0.23(3)	0.02(2)	0.12(2)
Ni/Fe(2)	1.04(3)	1.10(3)	1.10(2)	-0.04(2)	-0.01(1)	-0.22(2)
P(1)	1.51(40	1.19(4)	1.16(4)	-0.28(3)	0.37(3)	-0.04(3)
O(1)	1.58(3)	1.87(4)	1.23(4)	-0.15(3)	0.10(2)	-0.23(2)
O(2)	1.78(30	1.61(3)	0.87(4)	-0.24(2)	0.03(2)	-0.07(2)
O(3)	1.04(4)	1.69(3)	1.64(3)	0.23(2)	0.22(2)	0.32(3)
O(4)	1.56(3)	0.92(4)	1.56(3)	0.16(3)	-0.19(2)	0.27(3)

Table S9 Anisotropic thermal displacement parameters from $Fe_2^{Mul}Ni(PO_4)_2$ Rietveld refinement of the powder neutron data from HRPD.

Atom	U_{11} / Å^2	U_{22} / Å^2	U_{33} / Å^2	U_{12} / Å^2	U_{13} / Å^2	U_{23} / Å^2
Ni/Fe(1)	1.21(5)	0.71(5)	0.96(5)	0.11(5)	0.13(4)	0.06(5)
Ni/Fe(2)	0.82(3)	0.98(4)	0.80(3)	0.08(3)	0.13(2)	0.05(3)
P(1)	1.04(5)	0.52(5)	0.81(6)	-0.03(4)	0.07(4)	0.12(5)
O(1)	1.46(60	0.71(5)	1.13(5)	-0.03(5)	0.13(4)	0.00(5)
O(2)	1.44(5)	1.02(6)	0.80(5)	-0.03(4)	0.04(4)	0.01(4)
O(3)	0.95(6)	0.95(5)	1.29(5)	0.03(4)	0.56(4)	0.30(4)
O(4)	0.92(5)	0.92(5)	1.01(5)	0.08(4)	-0.06(4)	0.20(4)

Table S10 Interatomic distances from $Fe_2Ni(PO_4)_2$ single data-set Rietveld refinements.

Bond	^{58}Ni	^{60}Ni	^{62}Ni	^{Nat}Ni
M(1) – O(1) (×2)	2.0911(15)	2.0866(11)	2.0898(15)	2.0888(4)
M(1) – O(2) (×2)	2.1135(14)	2.1083(11)	2.1055(14)	2.1019(4)
M(1) – O(4) (×2)	2.1201(16)	2.1166(12)	2.1131(15)	2.1118(5)
Average	2.1082	2.1038	2.1028	2.1008
M(2) – O(1)	2.1804(17)	2.1759(14)	2.1710(18)	2.1658(5)
M(2) – O(2)	2.0974(17)	2.1007(14)	2.1069(18)	2.1138(5)
M(2) – O(3)	2.1637(16)	2.1661(14)	2.1716(20)	2.1587(5)
M(2) – O(3)`	2.0312(16)	2.0227(12)	2.0138(17)	2.0343(4)
M(2) – O(4)	2.3526(17)	2.3587(13)	2.3679(19)	2.3522(5)
M(2) – O(4)`	2.0800(18)	2.0795(15)	2.0808(19)	2.0877(5)
Average	2.1509	2.1506	2.1520	2.1521
P(1) – O(1)	1.4962(20)	1.5099(15)	1.5191(20)	1.5310(6)
P(1) – O(2)	1.5277(19)	1.5310(16)	1.5255(22)	1.5250(5)
P(1) – O(3)	1.5286(21)	1.5285(17)	1.5271(21)	1.5277(6)
P(1) – O(4)	1.5806(21)	1.5810(17)	1.5746(22)	1.5777(6)
Average	1.5333	1.5376	1.5366	1.5403

Table S11 Interatomic distances for $Fe_2Ni(PO_4)_2$ from previous AXS (X1 and X2) and TOF neutron work (N) of Warner *et al.* (1995) compared with this work using ISND (N2).

Bond	X1	X2	N	N2
M(1) – O(1) (×2)	2.091(4)	2.075(5)	2.092(4)	2.0804(9)
M(1) – O(2) (×2)	2.128(4)	2.129(5)	2.110(3)	2.1066(9)
M(1) – O(4) (×2)	2.120(5)	2.125(6)	2.117(4)	2.1109(9)
Average	2.113	2.110	2.106	2.0993
M(2) – O(1)	2.161(5)	2.146(6)	2.164(5)	2.1717(11)
M(2) – O(2)	2.056(4)	2.104(5)	2.115(4)	2.1015(11)
M(2) – O(3)	2.174(4)	2.171(5)	2.152(4)	2.1619(11)
M(2) – O(3)`	2.109(4)	2.046(5)	2.043(3)	2.0246(10)
M(2) – O(4)	2.335(5)	2.333(5)	2.336(4)	2.3528(11)
M(2) – O(4)`	2.040(4)	2.048(5)	2.093(4)	2.0853(11)
Average	2.146	2.141	2.151	2.1496
P(1) – O(1)	1.527(3)	1.537(4)	1.531(4)	1.5276(13)
P(1) – O(2)	1.593(5)	1.555(6)	1.528(4)	1.5277(14)
P(1) – O(3)	1.472(5)	1.517(6)	1.529(5)	1.5263(14)
P(1) – O(4)	1.619(5)	1.636(7)	1.582(5)	1.5756(14)
Average	1.553	1.561	1.543	1.5393

Table S12 Refined fractional occupancies for M(1) and M(2) from Rietveld refinements. Type 1 refinements contain occupancy constraints only and type 2 have no constraints on occupancy or Fe:Ni ratio. Ni content per unit cell is also calculated, where possible, which has an ideal value of 2 as Z = 2.

Sample	Type	M(1)		M(2)		Ni content
		Fe	Ni	Fe	Ni	
^{Nat}Ni	1	0.2 – 0.4	0.8 – 0.6	0.9 – 0.8	0.1 – 0.2	1.8 – 2.2
	2	INS	INS	INS	INS	
^{58}Ni	1	0.367(10)	0.633(10)	0.838(10)	0.162(10)	1.91(6)
	2	INS	INS	INS	INS	
^{60}Ni	1	0.258(4)	0.742(4)	0.880(4)	0.120(4)	1.964(24)
	2	INS	INS	INS	INS	
^{62}Ni	1	0.303(2)	0.697(2)	0.867(2)	0.133(2)	1.926(12)
	2	INS	INS	INS	INS	
MUL	1	0.300(2)	0.700(2)	0.871(2)	0.129(2)	1.916(12)
	2	0.291(2)	0.692(4)	0.864(3)	0.129(2)	1.900(16)

INS – refinement insoluble

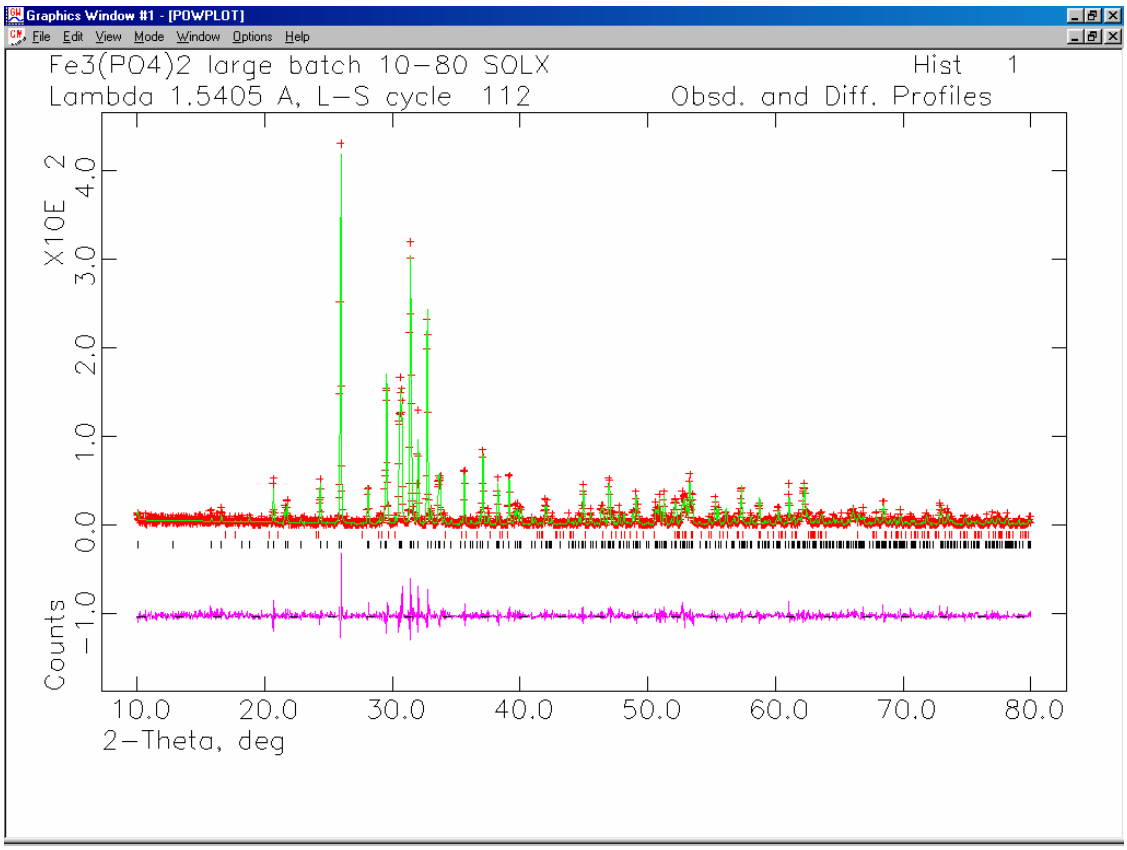

Figure S1 Profile fit from the X-ray Rietveld refinement of $Fe_3(PO_4)_2$.

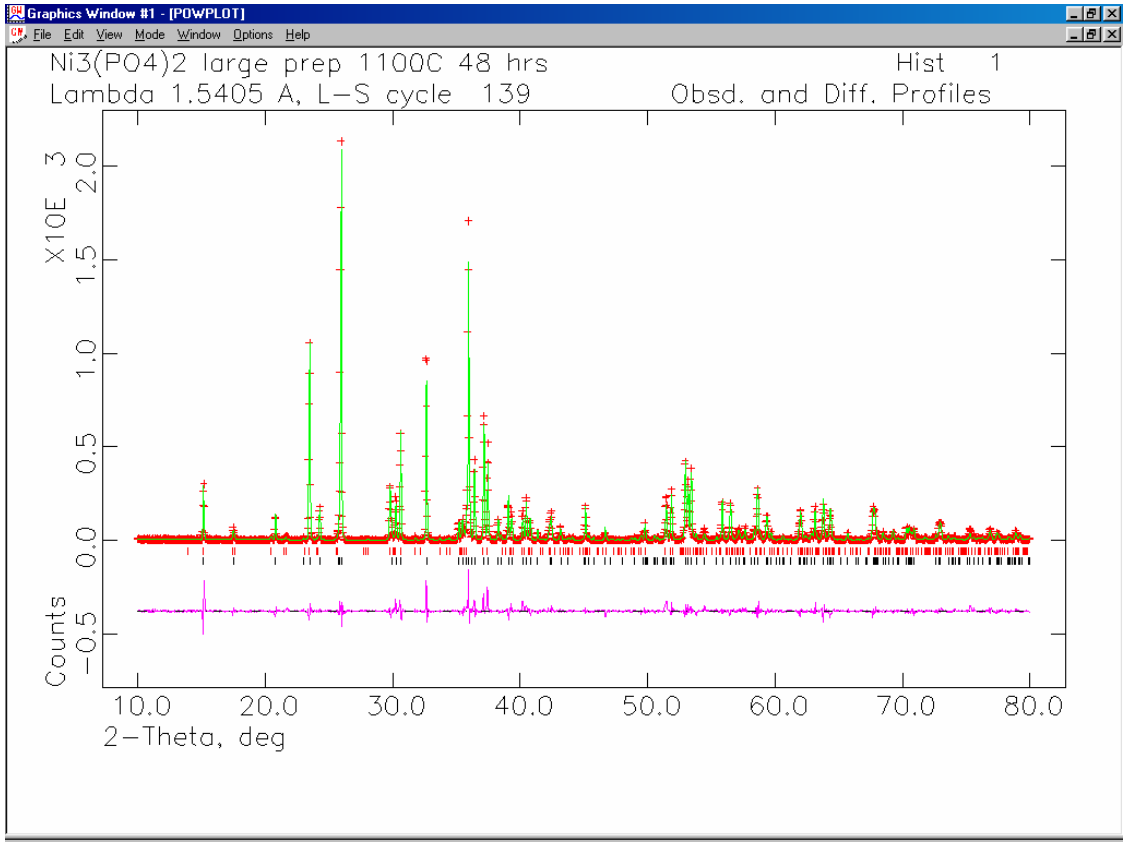

Figure S2 Profile fit from the X-ray Rietveld refinement of $Ni_3(PO_4)_2$.

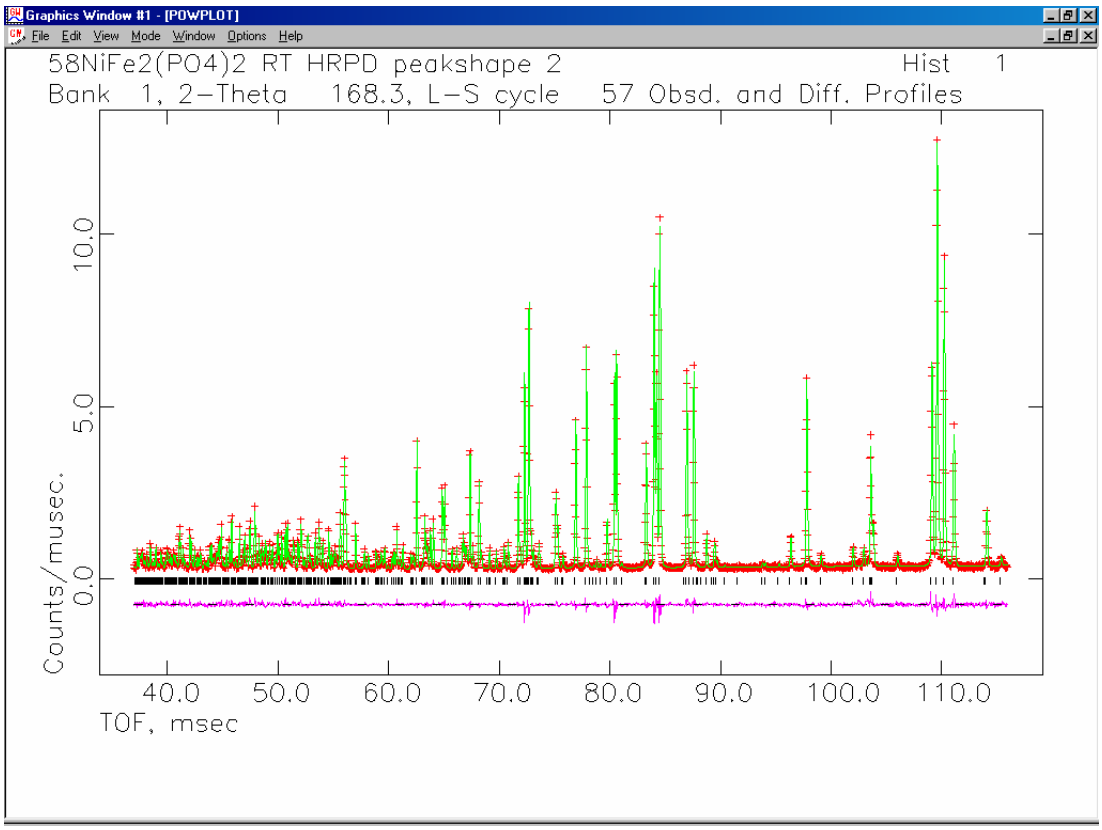

Figure S3 Profile fit from the neutron single data-set Rietveld refinement of $Fe_2{}^{58}Ni(PO_4)_2$.

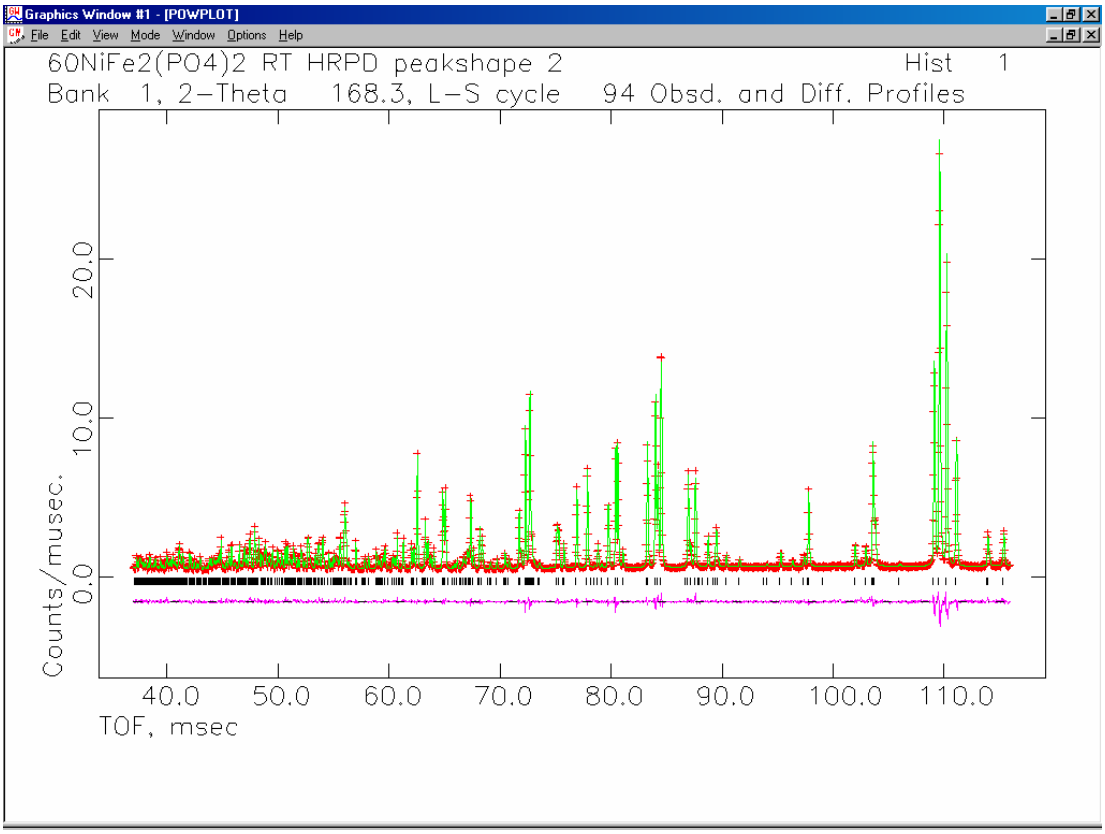

Figure S4 Profile fit from the neutron single data-set Rietveld refinement of $Fe_2{}^{60}Ni(PO_4)_2$.

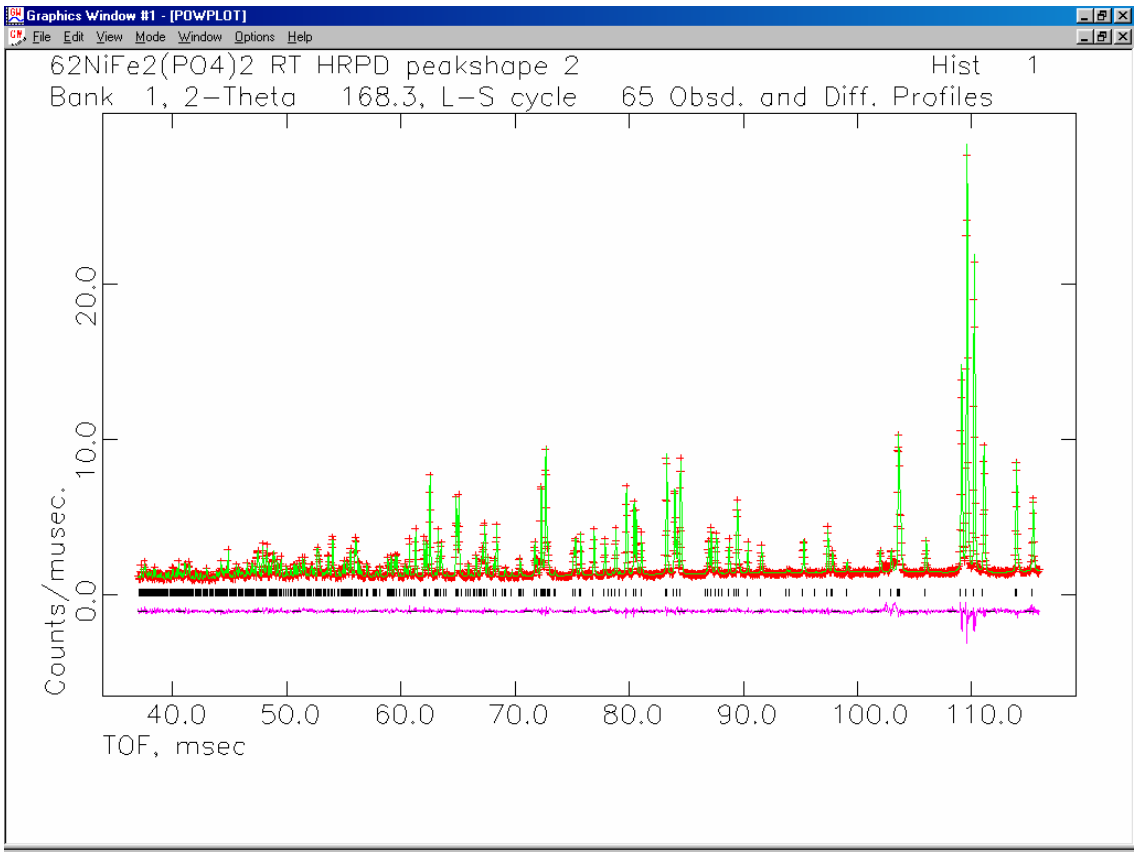

Figure S5 Profile fit from the neutron single data-set Rietveld refinement of $Fe_2{}^{62}Ni(PO_4)_2$.

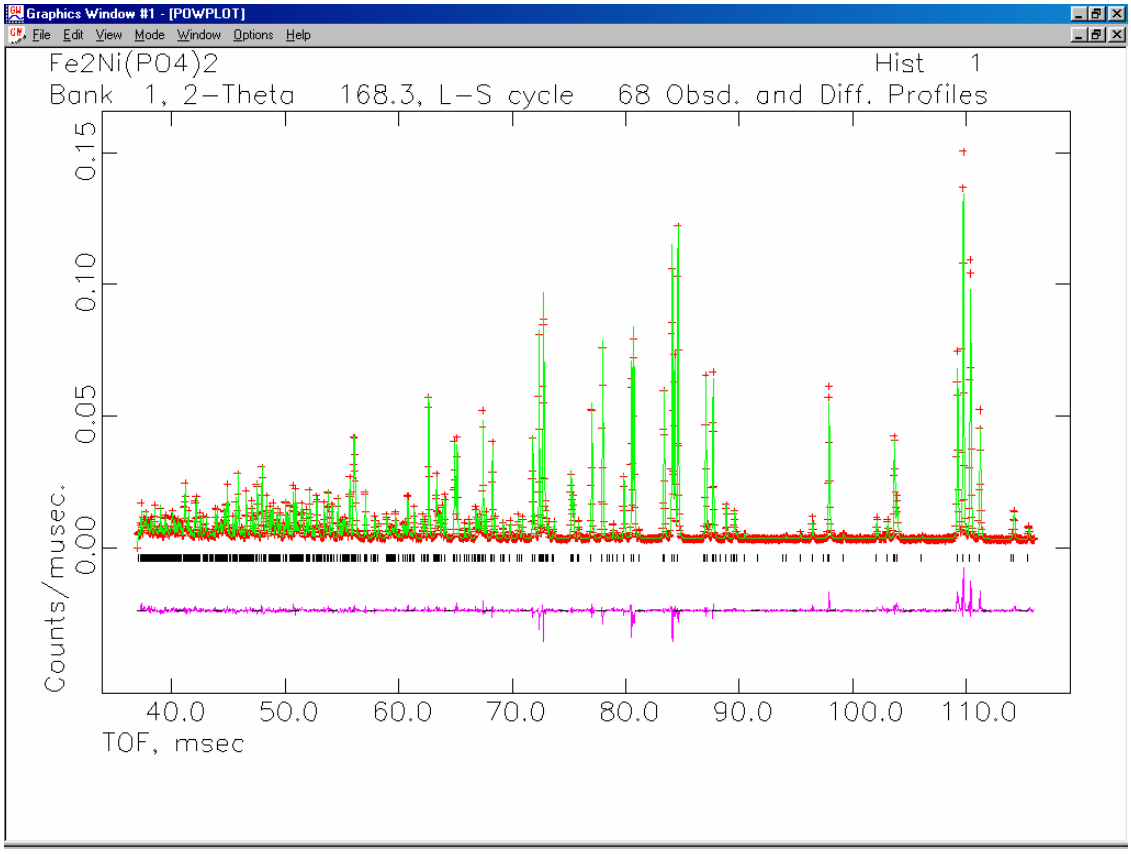

Figure S6 Profile fit from the neutron single data-set Rietveld refinement of $Fe_2{}^{Nat}Ni(PO_4)_2$.