Supplementary Materials

A Synchrotron Mössbauer Spectroscopy Study of a Hydrated Iron-Sulfate at High Pressures

Table S1. Lattice parameters of szomolnokite at ambient pressure and temperature conditions.

a (Å)	b (Å)	c (Å)	β (degrees)	Volume (Å³)	ref.
7.0823(2)	7.5525(2)	7.7786(5)	118.631(3)	365.226(30)	Meusberger et al. (2019)
7.084	7.550	7.779	118.63	395.16	Giester et al. (1994)
7.078(3)	7.549(3)	7.773(3)	118.65(2)	364.48	Wildner and Giester (1991)
7.123(9)	7.469(9)	7.837(9)	118.65(2)	364.48	Pistorius (1960)
7.09	7.55	7.78	118.65(2)	365.2(1)	This study

Table S2. Best fit hyperfine parameters for szomolnokite according to Model 1.

Pressure (GPa)	0[a]	0	0.40(4)	1.6(3)	2.9(4)	6.4(9)	12(1)	19(1)	45(3)	56(1)	62(1)	73.4(1)	95(4)
QS (mm/s)													
Site 1	2.670(3)	2.642(3)	2.64	2.79	2.79	2.834(2)	2.795(2)	2.838(6)	2.96(4)	2.843(9)	2.89(2)	3.08(3)	3.05(2)
Site 2	2.07(3)	2.306(13)	1.95	1.51	1.51	2.178(8)	2.01(7)	2.187(4)	2.41(3)	2.10(2)	2.18(4)	2.23(2)	2.24(2)
Site 3	-	-	1.16	1.27	1.27	1.06(19)	1.216(32)	2.76(3)	1.78(2)	1.841(5)	1.88(1)	1.80(2)	1.718(7)
Site 4	-	-	-	-	-	-	-	0.34(1)	-	-	-	-	-
IS[a], *Δ*IS1 (mm/s)													
Site 1	1.231(7)	-	-	-	-	-	-	-	-	-	-	-	-
Site 2	0.98(2)	-0.339(12)	-0.16	-0.16	-0.16	-0.069(6)	0.02(1)	-0.061(6)	0.048(1)	-0.054(4)	-0.071(5)	-0.042(7)	-0.102(6)
Site 3	-	-	-0.35	-0.4	-0.4	-0.241(5)	0.32(1)	-0.1(1)	-0.72(2)	-0.796(3)	-0.794(4)	-0.74(2)	-0.84(1)
Site 4	-	-	-	-	-	-	-	-0.135(9)	-	-	-	-	-
Weight Fraction													
Site 1	0.83(6)	0.91(66)	0.647(9)	0.625(7)	0.612(5)	0.643	0.643	0.51	0.463	0.522	0.475	0.409	0.368
Site 2	0.17	0.09	0.144	0.153	0.159	0.2	0.2	0.27	0.21(4)	0.15(1)	0.21(2)	0.30(2)	0.28(2)
Site 3	-	-	0.209	0.221	0.229	0.157	0.157	0.16	0.24(1)	0.242(6)	0.2(1)	0.223(7)	0.29(7)
Site 4	-	-	-	-	-	-	-	0.06	-	-	-	-	-
FWHM (mm/s)													
Site 1	0.116(4)	0.061(2)	0.085(3)	0.093(4)	0.119(4)	0.095	0.095	0.15	0.4	0.4	0.4	0.4	0.4
Site 2	0.008(4)	0.03(4)	0.16(1)	0.27(2)	0.18(2)	0.05	0.05	0.05	0.3	0.3	0.3	0.3	0.3
Site 3	-	-	0.5	0.5	0.5	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3
Site 4	-	-	-	-	-	-	-	0.1	-	-	-	-	-
χ^2	1.52	1.25	1.44	1.23	1.60	1.42	1.42	1.04	1.62	1.48	1.36	1.25	1.64

Notes: Best-fit values using CONUSS version 2.2.0 (Sturhahn, 2000; www.nrixs.com). Uncertainties are given at the 68% level. Values without reported errors were fixed. Pressures were determined using ruby fluorescence and the Dewaele et al. 2008 scale. Thickness was fixed at 3 μm and the Lamb-Mössbauer factor was fixed at 0.6 at all compression points. The isomer shifts of Sites 2 to 4 are given relative to Site 1 (see text for details), with the exception of the values for 0[a] GPa. [a]Values from ambient pressure determined from a dual fit with a 10 μm thick naturally enriched stainless steel foil in the x-ray beam path with the sample, and isomer shift values are relative to α-iron.

Table S3. Best fit hyperfine parameters for szomolnokite according to Model 2.

Pressure (GPa)	0[a]	0	0.40(4)	1.6(3)	2.9(4)	6.4(9)	12(1)	19(1)	45(3)	56(1)	62(1)	73.4(1)	95(4)
QS (mm/s)													
Site 1	2.670(3)	2.642(3)	2.64	2.79	2.79	2.834(2)	2.795(2)	2.838(7)	3.125(5)	3.152(6)	3.177(5)	3.223(9)	3.179(6)
Site 2	2.07(3)	2.31(1)	1.95	1.51	1.51	2.177(8)	2.009(7)	2.187(4)	2.64(5)	2.508(6)	2.451(8)	2.548(8)	2.519(9)
Site 3	-	-	1.16	1.27	1.27	1.06(2)	1.22(3)	2.76(3)	0	0	0	0	0
Site 4	-	-	-	-	-	-	-	0.34(1)	1.12(1)	0.983(9)	1.12(1)	1.086(8)	1
IS [a], ΔIS1 (mm/s)													
Site 1	1.231(7)	-	-	-	-	-	-	-	-	-	-	-	-
Site 2	0.98(2)	-0.34	-0.16	-0.16	-0.16	-0.069(5)	0.03(1)	-0.061(6)	-0.07(5)	-0.066(6)	0.02(6)	0.042(6)	-0.13
Site 3	-	-	-0.35	-0.4	-0.4	-0.241(5)	-0.32(1)	-0.13(2)	-0.449(5)	-0.456(4)	-0.429(8)	-0.473(5)	-0.435(4)
Site 4	-	-	-	-	-	-	-	-0.135(9)	-0.52(1)	-0.53(8)	-0.47(1)	-0.51(1)	-0.463(7)
Weight Fraction													
Site 1	0.83(6)	0.91(7)	0.64(8)	0.62(7)	0.61(5)	0.643	0.643	0.51	0.387	0.387	0.387	0.387	0.371
Site 2	0.17	0.090	0.144	0.153	0.159	0.2	0.2	0.27	0.258	0.258	0.258	0.258	0.222
Site 3	-	-	0.208	0.221	0.230	0.157	0.157	0.16	0.29	0.29	0.29	0.29	0.30(6)
Site 4	-	-	-	-	-	-	-	0.06	0.065	0.065	0.065	0.065	0.111
FWHM (mm/s)													
Site 1	0.116(4)	0.061(1)	0.085(3)	0.093(3)	0.119(4)	0.095	0.095	0.15	0.4	0.4	0.4	0.5	0.5
Site 2	0.008(4)	0.02(4)	0.16(1)	0.27(2)	0.18(2)	0.05	0.05	0.05	0.3	0.3	0.3	0.3	0.3
Site 3	-	-	0.5	0.5	0.5	0.2	0.2	0.2	0.6	0.6	0.6	0.6	0.47(6)
Site 4	-	-	-	-	-	-	-	0.1	0.05	0.05	0.05	0.05	0.1
χ^2	1.52	1.25	1.44	1.23	1.60	1.42	1.41	1.04	1.75	1.65	1.69	1.59	1.18

Notes: Best-fit values using CONUSS version 2.2.0 (Sturhahn, 2000; www.nrixs.com). Uncertainties are given at the 68% level. Values without reported errors were fixed. Pressures were determined using ruby fluorescence and the Dewaele et al. 2008 scale. Thickness was fixed at 3 μm and the Lamb-Mössbauer factor was fixed at 0.6 at all compression points. The isomer shift of Sites 2 to 4 are given relative to Site 1 (see text for details), with the exception of the values for 0[a] GPa. [a]Values from ambient pressure determined from a dual fit with a 10 μm thick naturally enriched stainless steel foil in the x-ray beam path with the sample, and isomer shift values are relative to α-iron.

Table S4. Best fit hyperfine parameters for szomolnokite according to Model 3.

Pressure (GPa)	0[a]	0	0.40(4)	1.6(3)	2.9(4)	6.4(9)	12(1)	19(1)	45(3)	56(1)	62(1)	73.4(1)	95(4)
QS (mm/s)													
Site 1	2.670(3)	2.642(3)	2.64	2.79	2.79	2.834(2)	2.795(2)	2.838(6)	3.0(1)	3.058(9)	3.057(2)	3.175(8)	3.21(1)
Site 2	2.07(3)	2.31(1)	1.95	1.51	1.51	2.177(8)	2.009(7)	2.187(4)	2.69(2)	2.521(7)	2.482(2)	2.40(2)	2.35(1)
Site 3	-	-	1.16	1.27	1.27	1.06(2)	1.22(3)	2.76(3)	2.71(2)	2.73(2)	2.75(3)	2.64(3)	2.50(5)
Site 4	-	-	-	-	-	-	-	0.34(1)	0.388(7)	0.41(2)	0.39(2)	0.40(1)	0.32(8)
Site 5	-	-	-	-	-	-	-	-	0	0	0	0	0
IS [a], ΔIS1 (mm/s)													
Site 1	1.231(7)	-	-	-	-	-	-	-	-	-	-	-	-
Site 2	0.98(2)	-0.34	-0.16	-0.16	-0.16	-0.069(5)	0.025(10)	-0.061(6)	-0.07(1)	-0.019(7)	0.01(1)	-0.03	-0.029
Site 3	-		-0.35	-0.4	-0.4	-0.241(5)	-0.32(1)	-0.13(1)	0.32(1)	0.37(1)	0.41(2)	0.32	0.29
Site 4	-							-0.135(9)	-0.13(3)	-0.393(7)	-0.42(4)	-0.59	-0.603
Site 5	-								-0.245(5)	-0.02(1)	-0.03(2)	-0.074	-0.078
Weight Fraction													
Site 1	0.83(6)	0.91(7)	0.64(8)	0.62(7)	0.61(5)	0.643	0.643	0.51	0.406	0.406	0.401	0.406	0.406
Site 2	0.17	0.090	0.144	0.153	0.159	0.2	0.2	0.27	0.297	0.297	0.293	0.297	0.297
Site 3	-	-	0.208	0.221	0.230	0.157	0.157	0.16	0.158	0.129	0.12(9)	0.099	0.05
Site 4	-	-	-	-	-	-	-	0.06	0.099	0.099	0.098	0.099	0.099
Site 5	-	-	-	-	-	-	-	-	0.04	0.069	0.088	0.099	0.149
FWHM (mm/s)													
Site 1	0.116(4)	0.061(1)	0.085(3)	0.093(3)	0.119(4)	0.095	0.095	0.15	0.4	0.4	0.4	0.4	0.42
Site 2	0.008(4)	0.02(4)	0.16(1)	0.27(2)	0.18(2)	0.05	0.05	0.05	0.3	0.3	0.3	0.3	0.32
Site 3	-	-	0.5	0.5	0.5	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.22
Site 4	-	-	-	-	-	-	-	0.1	0.1	0.1	0.1	0.1	0.12
Site 5	-	-	-	-	-	-	-	-	0.2	0.2	0.2	0.2	0.22
χ^2	1.52	1.25	1.44	1.23	1.60	1.42	1.41	1.04	1.38	1.48	1.43	1.49	1.28

Notes: Best-fit values using CONUSS version 2.2.0 (Sturhahn, 2000; www.nrixs.com). Uncertainties are given at the 68% level. Values without reported errors were fixed. Pressures were determined using ruby fluorescence and the Dewaele et al. 2008 scale. Thickness was fixed at 3 μm and the Lamb-Mössbauer factor was fixed at 0.6 at all compression points. The isomer shift of sites 2 to 5 are given relative to site 1 (see text for details), with the exception of the values for 0[a] GPa. [a]Values from ambient pressure determined from a dual fit with a 10 μm thick naturally enriched stainless steel foil in the x-ray beam path with the sample, and isomer shift values are relative to α-iron.

Table S5. Hydrated iron-bearing sulfates and their experimentally determined quadrupole and isomer shift values at ambient pressure and temperature.

Mineral	Formula	Number (Fig. 2)	Sample	IS (mm/s)	QS (mm/s)	Weight %
Szomolnokite	$FeSO_4 \cdot H_2O$	1a	This study	1.23	2.64	91
Szomolnokite	$FeSO_4 \cdot H_2O$	1b	This study	0.89	2.31	9
Szomolnokite	$FeSO_4 \cdot H_2O$	Blue Square	Alboom et al. 2009	1.263	2.231	100
Szomolnokite	$FeSO_4 \cdot H_2O$	Orange Square	Giester et al. 1994	1.26	2.71	100
Szomolnokite	$FeSO_4 \cdot H_2O$	Pink Square	Russel & Montano 1978	1.18	2.69	100
Szomolnokite	$FeSO_4 \cdot H_2O$	2	ML-S77	1.26	2.73	94
Szomolnokite	$FeSO_4 \cdot H_2O$	3	92942	1.26	2.73	96
Szomolnokite	$FeSO_4 \cdot H_2O$	4a	136685-2	1.29	2.74	82
Szomolnokite	$FeSO_4 \cdot H_2O$	4b	136685-2	0.23	0.69	12
Szomolnokite	$FeSO_4 \cdot H_2O$	4c	136685-2	0.54	0.14	7
Szomolnokite	$FeSO_4 \cdot H_2O$	5	104276	1.28	2.76	100
Szomolnokite	$FeSO_4 \cdot H_2O$	6a	ML-S60	1.31	2.89	57
Szomolnokite	$FeSO_4 \cdot H_2O$	6b	ML-S60	1.31	3.42	31
Szomolnokite	$FeSO_4 \cdot H_2O$	6c	159098	1.24	2.78	43
Szomolnokite	$FeSO_4 \cdot H_2O$	7a	159098	1.31	2.69	42
Szomolnokite	$FeSO_4 \cdot H_2O$	7b	159098	0.49	0.18	12
Szomolnokite	$FeSO_4 \cdot H_2O$	8a	ML-S103	1.27	2.74	93
Szomolnokite	$FeSO_4 \cdot H_2O$	8b	ML-S103	0.43	0.42	7
Szomolnokite	$FeSO_4 \cdot H_2O$	9a	159266	0.46	0.36	72
Szomolnokite	$FeSO_4 \cdot H_2O$	9b	159266	0.14	0.56	28
Szmikite	$MnSO_4 \cdot H_2O$	10a	159189	0.52	0.93	18
Szmikite	$MnSO_4 \cdot H_2O$	10b	159189	1.24	2.59	82
Gunningite	$ZnSO_4 \cdot H_2O$	11a	56925	0.26	0.4	32
Gunningite	$ZnSO_4 \cdot H_2O$	11b	56925	0.37	1.26	10
Gunningite	$ZnSO_4 \cdot H_2O$	11c	56925	1.25	2.74	58
Chalcanthite	$CuSO_4 \cdot 5H_2O$	12a	DD100	0.1	0.51	29
Chalcanthite	$CuSO_4 \cdot 5H_2O$	12b	DD100	0.26	0.76	30
Chalcanthite	$CuSO_4 \cdot 5H_2O$	12c	DD100	1.26	2.32	22
Chalcanthite	$CuSO_4 \cdot 5H_2O$	12d	DD100	1.3	2.88	19
Pentahydrite	$MgSO_4 \cdot 5H_2O$	13a	VZO121	0.5	0.83	8
Pentahydrite	$MgSO_4 \cdot 5H_2O$	13b	VZO121	1.26	3	53
Pentahydrite	$MgSO_4 \cdot 5H_2O$	13c	VZO121	1.27	3.68	38
Jokokuite	$MnSO_4 \cdot 5H_2O$	14a	G3536	0.15	0.56	26

Jokokuite	$MnSO_4{\cdot}5H_2O$	14b	G3536	1.13	2.63	6
Jokokuite	$MnSO_4{\cdot}5H_2O$	14c	G3536	1.26	2.51	65
Halotrichite	$FeAl_2(SO_4)_4{\cdot}22H_2O$	15a	G1616	1.27	3.29	92
Halotrichite	$FeAl_2(SO_4)_4{\cdot}22H_2O$	16a	VZO128	0.13	0.49	10
Halotrichite	$FeAl_2(SO_4)_4{\cdot}22H_2O$	16b	VZO128	0.36	0.31	14
Halotrichite	$FeAl_2(SO_4)_4{\cdot}22H_2O$	16c	VZO128	1.45	1.56	13
Halotrichite	$FeAl_2(SO_4)_4{\cdot}22H_2O$	16d	VZO128	1.28	2.76	43
Halotrichite	$FeAl_2(SO_4)_4{\cdot}22H_2O$	16e	VZO128	1.3	3.29	20
Melanterite	$Fe^{2+}(H_2O)_6SO_4{\cdot}H_2O$	16	2070	1.27	3.21	100
Rozenite	$FeSO_4{\cdot}4H_2O$	17a	JB626B	1.33	2.97	59
Rozenite	$FeSO_4{\cdot}4H_2O$	17b	JB626B	1.33	3.39	34
Rozenite	$FeSO_4{\cdot}4H_2O$	18a	SPT130	0.39	0.95	8
Rozenite	$FeSO_4{\cdot}4H_2O$	18b	SPT130	1.27	3.21	92
Starkeyite	$MgSO_4{\cdot}4H_2O$	19a	137725	0	0.57	9
Starkeyite	$MgSO_4{\cdot}4H_2O$	19b	137725	1.14	2.65	91

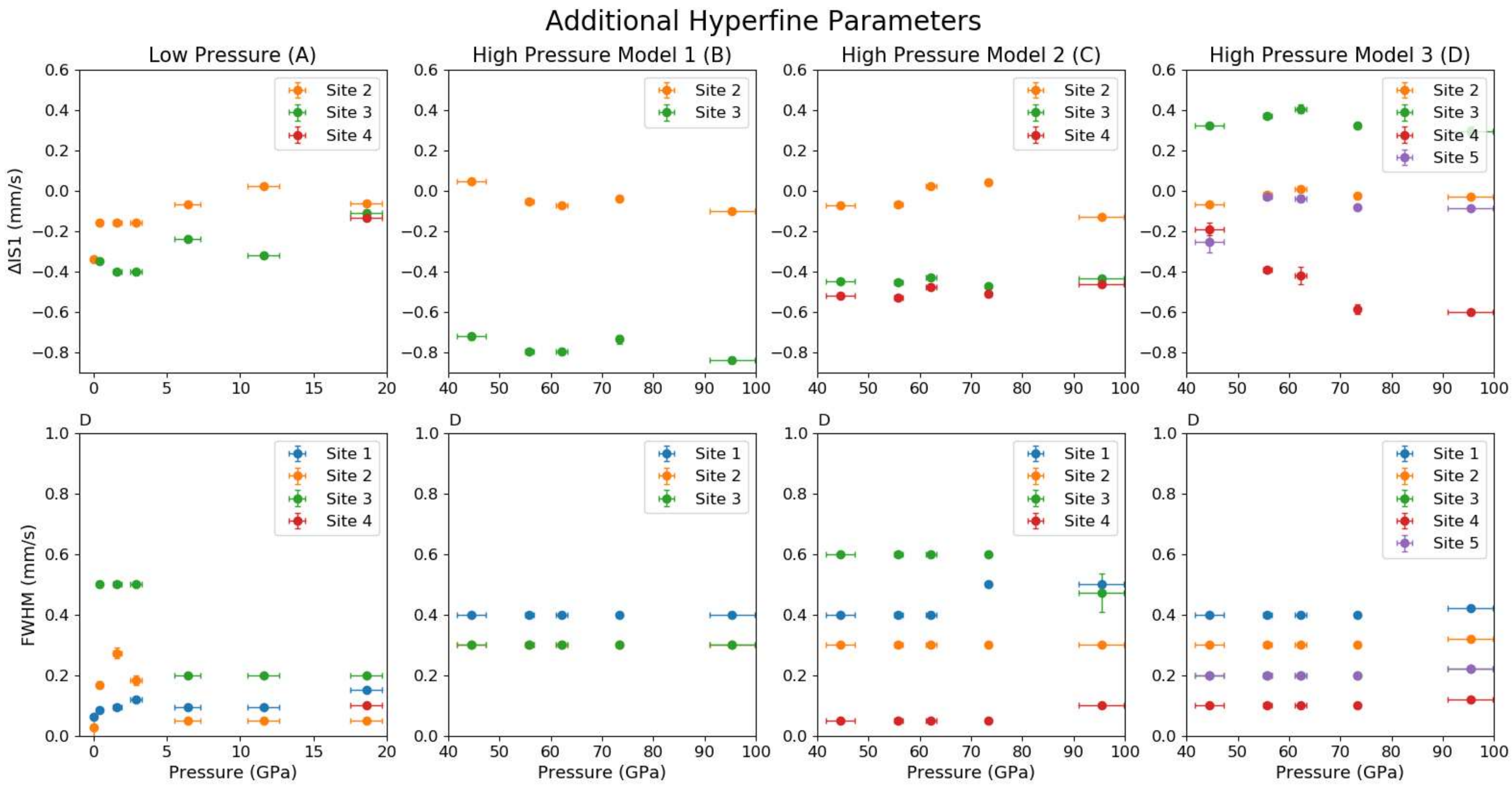

Figure S1. Fitted hyperfine parameters determined using CONUSS: The relative isomer shift values of sites 2 to 5 are given with respect to site 1 (ΔIS1), and the full width at half maximum (FWHM) describes the distribution of field gradients in mm/s for a particular site. (**A**) Low pressure values, as all models are identical from 0 to 19 GPa. (**B**) Values from Model 1 applied to 19-95 GPa. Sites 2 and 3 have FWHM fixed to the same value so they overlap completely in the figure. (**C**) Values from Model 2 applied to 19-95 GPa. In this model, site 3 (green) undergoes a high to low spin transition between 19 and 45 GPa. (**D**) Values from Model 3 (gradual spin transition) applied to 19-95 GPa. Sites 3 and 5 have FWHM fixed to the same value so they overlap completely in the figure. See text for more details on Models 1, 2, and 3. Values, including the χ^2 for each fit, are reported in Tables S2, S3, and S4.