# SUPPORTING INFORMATION (SI)

**Synthesis and stability of some members of the pharmacosiderite group, *A*Fe4(OH)4(AsO4)3·*n*H2O (*A* = K, Na, 0.5Ba, 0.5Sr)**

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Table S1. Electron microprobe analyses of the pharmacosiderite samples. All data in weight %. Note that because of extreme sensitivity of these samples to the electron beam and the dependence of the analytical results on the sample current, these analyses can be regarded only as semiquantitative.

K-pharmacosiderite

Na2O As2O5 SrO BaO K2O SO3 Fe2O3 Total

0.79 42.38 0.00 0.00 5.00 2.03 38.21 88.40

1.24 38.96 0.80 0.00 4.41 1.91 39.09 86.42

0.99 42.28 0.38 0.11 4.48 1.68 38.28 88.21

1.13 42.25 0.00 0.00 5.34 1.76 38.19 88.68

0.65 42.80 0.16 0.00 5.49 1.78 38.65 89.53

0.08 41.89 0.00 0.05 8.16 1.74 36.62 88.53

0.34 40.86 0.15 0.00 6.99 1.53 36.29 86.16

0.28 41.59 0.00 0.07 7.27 1.65 38.15 89.01

0.69 41.89 0.44 0.03 5.94 1.91 37.57 88.46

0.75 40.07 0.00 0.28 5.73 1.55 37.46 85.85

0.55 42.29 0.43 0.19 7.22 1.88 37.80 90.37

0.69 41.37 0.00 0.01 6.39 2.08 37.23 87.76

0.07 42.26 0.00 0.00 8.13 1.53 38.16 90.14

0.72 41.84 0.64 0.00 4.41 1.85 36.81 86.27

Ba-pharmacosiderite

Na2O As2O5 SrO BaO K2O SO3 Fe2O3 Total

0.04 38.93 0.04 11.64 0.00 1.73 35.89 88.27

0.04 39.62 0.10 10.18 0.00 1.87 34.18 85.99

0.06 38.71 0.18 10.35 0.01 2.02 33.67 84.99

0.04 37.16 0.00 12.64 0.01 1.81 36.36 88.03

0.05 37.19 0.00 12.32 0.02 1.95 34.75 86.27

0.07 38.60 0.12 10.83 0.00 1.79 34.27 85.68

0.05 37.60 0.10 10.63 0.02 1.84 34.09 84.33

0.00 37.76 0.21 11.75 0.00 1.84 35.40 86.95

0.00 38.00 0.26 11.16 0.00 1.87 35.30 86.60

0.03 37.87 0.00 9.85 0.01 1.75 35.37 84.88

Sr-pharmacosiderite

Na2O As2O5 SrO BaO K2O SO3 Fe2O3 Total

0.03 38.90 9.78 0.07 0.00 1.20 30.82 80.80

0.00 40.12 9.93 0.17 0.02 1.39 30.57 82.19

0.01 39.40 10.13 0.08 0.05 1.34 29.50 80.51

0.00 39.88 9.73 0.10 0.02 1.45 29.70 80.88

0.00 39.49 9.68 0.28 0.01 1.34 28.99 79.79

0.00 41.65 8.23 0.40 0.01 1.44 30.91 82.64

0.00 41.89 9.30 0.34 0.00 1.38 29.92 82.83

0.01 41.34 8.10 0.30 0.02 1.32 28.95 80.04

Na-pharmacosiderite

Na2O As2O5 SrO BaO K2O SO3 Fe2O3 Total

7.46 38.65 0.00 0.00 0.81 0.24 29.27 76.42

Table S2. Measured heat capacity for K-pharmacosiderite (composition K1.086Fe4[(AsO4)0.953(SO4)0.047]3 (OH)3.772O0.228·4.432H2O), molecular mass 824.2076 g·mol–1. Temperature (*T*) in K, heat capacity (*C*p) in J·mol–1·K–1.

*T* *C*p *T* *C*p *T* *C*p

2.2204 4.4038 11.550 24.868 63.706 178.31

2.3263 4.8008 12.146 25.468 66.992 189.77

2.4368 5.2217 12.774 26.070 70.453 201.62

2.5538 5.6727 13.432 26.688 74.075 215.14

2.6775 6.1630 14.120 27.626 77.896 228.23

2.8061 6.6813 14.850 28.596 81.904 241.48

2.9424 7.2681 15.609 29.689 86.127 255.14

3.0843 7.8872 16.413 30.949 90.577 268.75

3.2350 8.6167 17.263 32.383 95.258 282.86

3.3966 9.3992 18.123 33.939 100.15 299.56

3.5613 10.248 19.070 35.613 105.32 315.63

3.7340 11.175 20.060 38.158 110.76 333.66

3.9154 12.171 21.104 39.795 116.47 350.45

4.1074 13.253 22.194 43.116 122.47 367.83

4.3098 14.418 23.316 45.254 128.79 385.53

4.5216 15.642 24.521 47.279 135.46 404.14

4.7453 16.815 25.781 50.383 142.44 422.36

4.9796 17.814 27.096 54.558 149.78 440.94

5.2271 18.426 28.500 58.701 157.51 458.92

5.4886 18.801 29.969 62.742 165.67 479.01

5.7648 19.128 31.513 67.513 174.22 500.25

6.0550 19.550 33.136 72.522 183.21 523.36

6.3600 19.958 34.840 77.919 192.66 547.47

6.6920 20.284 36.640 83.673 202.60 573.09

7.0362 20.636 38.527 90.122 213.06 599.83

7.3748 20.985 40.514 96.890 224.05 627.23

7.7499 21.301 42.598 104.02 235.60 650.55

8.1449 21.678 44.799 111.37 247.76 674.67

8.5603 22.030 47.115 119.20 260.54 699.72

8.9986 22.427 49.545 127.73 273.97 727.75

9.4579 22.838 52.098 136.98 288.02 763.61

9.9418 23.320 54.786 146.47 302.66 796.67

10.452 23.788 57.607 156.60

10.987 24.289 60.578 167.21

Table S3. Measured heat capacity for Ba-pharmacosiderite (composition Ba0.702Fe4[(AsO4)0.953(SO4)0.047]3(OH)3.455O0.545·5.647H2O), molecular mass 899.7194 g·mol–1. Temperature (*T*) in K, heat capacity (*C*p) in J·mol–1·K–1.

*T* *C*p *T* *C*p *T* *C*p

2.2208 1.4848 12.779 37.876 31.512 66.448

2.3268 1.6413 12.958 38.992 33.130 71.138

2.4374 1.8083 13.210 40.431 34.836 76.108

2.5547 1.9894 13.437 41.642 36.632 81.493

2.6785 2.1869 13.463 41.971 38.522 87.447

2.8076 2.3973 13.715 43.640 40.508 93.788

2.9427 2.6315 13.966 45.100 42.594 100.58

3.0852 2.8823 14.124 46.038 44.790 107.88

3.2359 3.1755 14.216 46.761 47.104 115.73

3.3986 3.4919 14.474 48.196 49.530 124.07

3.5626 3.8285 14.731 49.706 52.085 133.10

3.7354 4.2012 14.841 50.727 54.766 142.74

3.9175 4.6020 14.984 51.417 57.597 152.49

4.1090 5.0337 15.231 52.087 60.567 163.07

4.3116 5.4985 15.482 51.546 63.692 174.17

4.5254 6.0048 15.590 51.240 66.981 186.04

4.7492 6.5475 15.729 50.282 70.437 197.64

4.9855 7.1631 15.978 48.133 74.067 210.28

5.2344 7.8141 16.221 46.456 77.888 223.23

5.4964 8.5292 16.397 44.820 81.902 235.55

5.7732 9.2907 16.494 44.198 86.126 250.79

6.0641 10.147 16.743 43.897 90.574 265.70

6.3719 11.031 16.996 43.084 95.236 282.44

6.7033 12.078 17.242 42.468 100.16 297.39

7.0507 13.187 17.243 42.549 105.31 316.95

7.3835 14.309 17.494 42.212 110.75 334.45

7.7594 15.613 17.754 41.541 116.46 352.66

8.1562 17.026 18.009 41.154 122.47 370.11

8.5719 18.568 18.119 41.896 128.79 390.25

9.0106 20.275 18.249 41.523 135.44 410.79

9.4700 22.127 18.507 41.638 142.43 430.08

9.9543 24.167 18.769 41.472 149.77 449.17

10.181 25.181 19.015 41.772 157.46 472.47

10.434 26.285 19.046 41.925 165.63 493.08

10.461 26.451 19.269 41.872 174.19 515.16

10.686 27.444 19.524 41.993 183.17 538.15

10.938 28.619 19.777 42.227 192.63 561.54

10.999 28.916 20.028 42.692 202.57 584.04

11.190 29.829 20.052 42.512 213.03 606.30

11.443 31.028 21.087 43.791 224.03 630.28

11.564 31.613 22.175 44.425 235.58 651.16

11.695 32.283 23.306 47.030 247.74 673.78

11.944 33.634 24.508 48.827 260.51 697.08

12.156 34.624 25.765 52.179 273.90 722.71

12.196 34.950 27.095 55.513 287.90 750.87

12.449 36.299 28.494 58.560 302.45 772.65

12.703 37.688 29.963 62.269

Table S4. Smoothed thermodynamic functions for K-pharmacosiderite (composition K1.086Fe4[(AsO4)0.953(SO4)0.047]3 (OH)3.772O0.228·4.432H2O), molecular mass 824.2076 g·mol–1., calculated from the measured heat capacity (see Table S2).

*T* *C*p H*T*-H0 *S* G*T*-G0

K J·mol–1·K–1 J·mol–1 J·mol–1·K–1 J·mol–1

0 0 0 0 0

5.0 17.72 34.02 11.35 -22.73

10.0 23.39 138.8 25.67 -117.9

15.0 28.78 268.2 36.09 -273.2

20.0 37.47 432.6 45.49 -477.2

25.0 49.67 649.6 55.12 -728.5

30.0 63.37 931.8 65.38 -1030

35.0 77.97 1285 76.23 -1383

40.0 93.82 1714 87.66 -1793

45.0 111.3 2226 99.7 -2261

50.0 130.1 2829 112.4 -2791

55.0 148.9 3527 125.7 -3386

60.0 166.5 4316 139.4 -4048

65.0 182.8 5189 153.4 -4780

70.0 200.6 6147 167.6 -5583

75.0 218.0 7194 182.0 -6456

80.0 234.8 8326 196.6 -7403

85.0 251.3 9542 211.3 -8423

90.0 267.3 10840 226.2 -9516

95.0 283.2 12210 241.0 -10680

100.0 299.0 13670 256.0 -11930

110.0 330.2 16820 285.9 -14640

120.0 360.6 20270 316.0 -17650

130.0 389.4 24020 346.0 -20960

140.0 416.2 28050 375.8 -24570

150.0 441.3 32340 405.4 -28470

160.0 465.4 36880 434.7 -32670

170.0 489.6 41650 463.6 -37160

180.0 514.5 46670 492.3 -41940

190.0 540.3 51940 520.8 -47010

200.0 566.8 57480 549.2 -52360

210.0 592.7 63280 577.5 -57990

220.0 617.2 69330 605.6 -63910

230.0 639.5 75610 633.6 -70110

240.0 659.7 82110 661.2 -76580

250.0 678.6 88800 688.5 -83330

260.0 698.0 95690 715.5 -90350

270.0 719.4 102800 742.3 -97640

273.15 726.7 105000 750.6 -99990

280.0 743.2 110100 768.8 -105200

290.0 768.0 117600 795.4 -113000

298.15 787.1 124000 816.9 -119600

300.0 791.1 125400 821.8 -121100

Table S5. Fitting functions used to integrate heat capacity of K-pharmacosiderite (see Table S2 for the data and Table S4 for the result of integration). All functions are polynomials of the form *C*p =  *anT n*. The exponents *n* and coefficients *an* are listed in the Table.

**fit 1: polynomial from *T* = 0.0 to *T* = 4.9 K**

exponent *n* coefficient *an*

1.0 1.24623055153

3.0 0.165991131938

5.0 -0.00287207020945

**fit 2: polynomial from *T* = 4.9 to *T* = 19.0 K**

exponent *n* coefficient *an*

0.0 -138.705292068

1.0 101.85993035

2.0 -27.8200457497

3.0 4.14474858941

4.0 -0.360308880387

5.0 0.0182720609325

6.0 -0.000500602950073

7.0 5.72425797346e-06

**fit 3: polynomial from *T* = 19.0 to *T* = 63.47 K**

exponent *n* coefficient *an*

0.0 -16.4374675729

1.0 12.70863738

2.0 -1.70908648216

3.0 0.121392446586

4.0 -0.00466811234888

5.0 0.000104523454143

6.0 -1.3540917529e-06

7.0 9.37874484995e-09

8.0 -2.68178441905e-11

**fit 4: polynomial from *T* = 63.47 to *T* = 305.0 K**

exponent *n* coefficient *an*

0.0 3656.49027305

1.0 -287.672494133

2.0 9.86368504281

3.0 -0.189437648297

4.0 0.00228574206678

5.0 -1.8124284516e-05

6.0 9.57618106365e-08

7.0 -3.33529353403e-10

8.0 7.34556581939e-13

9.0 -9.26132951976e-16

10.0 5.08958501261e-19

Table S6. Smoothed thermodynamic functions for Ba-pharmacosiderite (composition Ba0.702Fe4[(AsO4)0.953(SO4)0.047]3(OH)3.455O0.545·5.647H2O), molecular mass 899.7194 g·mol–1., calculated from the measured heat capacity (see Table S3).

*T* *C*p H*T*-H0 *S* G*T*-G0

K J·mol–1·K–1 J·mol–1 J·mol–1·K–1 J·mol–1

0 0 0 0 0

5.0 7.107 12.57 3.887 -6.871

10.0 24.44 87.77 13.63 -48.55

15.0 51.46 272.8 28.27 -151.3

20.0 41.83 494.2 41.09 -327.5

25.0 50.97 723.6 51.29 -558.5

30.0 62.51 1007 61.59 -840.6

35.0 75.81 1352 72.18 -1175

40.0 92.06 1770 83.34 -1563

45.0 109.6 2274 95.2 -2009

50.0 126.1 2864 107.6 -2516

55.0 142.0 3534 120.4 -3086

60.0 161.2 4290 133.5 -3721

65.0 178.6 5139 147.1 -4422

70.0 195.9 6076 161.0 -5192

75.0 213.0 7098 175.1 -6032

80.0 230.2 8206 189.4 -6943

85.0 247.3 9400 203.8 -7926

90.0 264.3 10680 218.4 -8982

95.0 281.2 12040 233.2 -10110

100.0 298.1 13490 248.0 -11310

110.0 331.1 16640 278.0 -13940

120.0 363.2 20110 308.2 -16870

130.0 394.0 23900 338.5 -20110

140.0 423.4 27980 368.8 -23640

150.0 451.5 32360 399.0 -27480

160.0 478.5 37010 429.0 -31620

170.0 504.6 41930 458.8 -36060

180.0 529.9 47100 488.3 -40800

190.0 554.4 52520 517.6 -45830

200.0 578.0 58190 546.7 -51150

210.0 600.5 64080 575.4 -56760

220.0 621.7 70190 603.9 -62660

230.0 641.5 76510 631.9 -68840

240.0 660.0 83020 659.6 -75290

250.0 677.8 89710 686.9 -82030

260.0 695.7 96570 713.9 -89030

270.0 714.6 103600 740.5 -96300

273.15 720.9 105900 748.8 -98650

280.0 735.0 110900 766.8 -103800

290.0 755.4 118300 793.0 -111600

298.15 768.7 124500 814.1 -118200

300.0 770.7 126000 818.9 -119700

Table S7. Fitting functions used to integrate heat capacity of Ba-pharmacosiderite (see Table S3 for the data and Table S6 for the result of integration). All functions are polynomials of the form *C*p =  *anT n*. The exponents *n* and coefficients *an* are listed in the Table.

**fit 1: polynomial from T = 0.0 to T = 15.18 K**

exponent *n* coefficient *an*

1.0 0.0492843666889

2.0 0.330221604706

3.0 -0.0132451069419

4.0 0.000417148183755

**fit 2: polynomial from T = 15.18 to T = 60.0 K**

exponent *n* coefficient *an*

0.0 1534.41817363

1.0 -302.396566391

2.0 25.2646807292

3.0 -1.13500568926

4.0 0.0297492917765

5.0 -0.000454180483929

6.0 3.74152309564e-06

7.0 -1.28479216135e-08

**fit 3: polynomial from T = 60.0 to T = 305.0 K**

exponent *n* coefficient *an*

0.0 -99.8250082674

1.0 4.83846584516

2.0 0.0421913146894

3.0 -0.0023166606727

4.0 4.26061322896e-05

5.0 -4.15307441163e-07

6.0 2.34506337849e-09

7.0 -7.70407961485e-12

8.0 1.36717874219e-14

9.0 -1.01313790912e-17