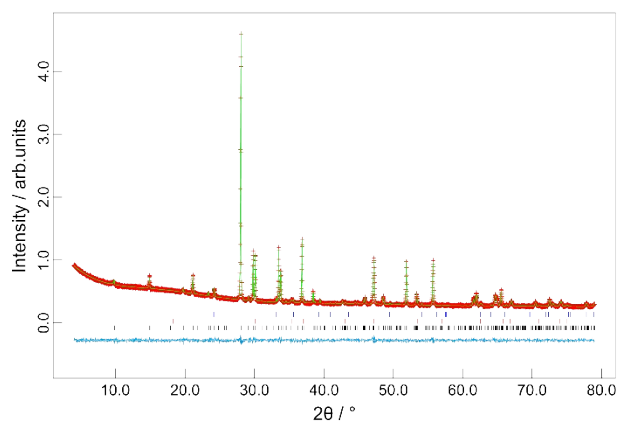
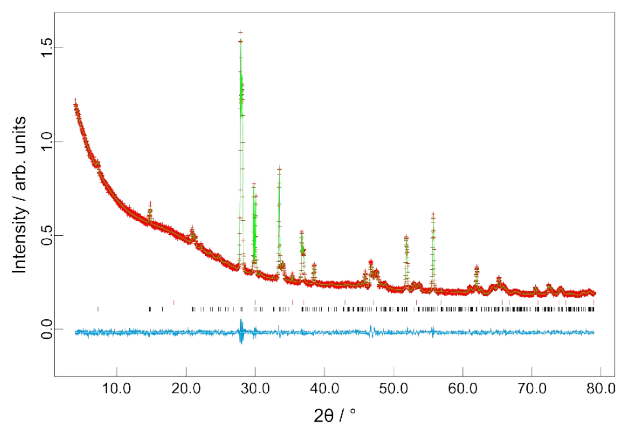


## Supplementary Information

### XRPD Refinement Plots

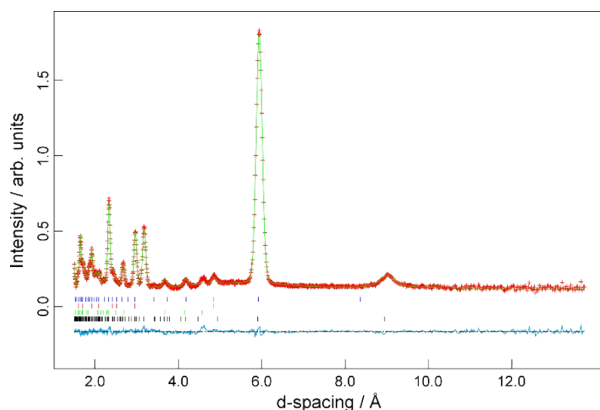


**Figure S1:** Apuanite XRPD refinement at 298 K (Bruker D8). Black ticks-main phase; red ticks-Fe<sub>3</sub>O<sub>4</sub> phase; blue ticks-Fe<sub>2</sub>O<sub>3</sub> phase.

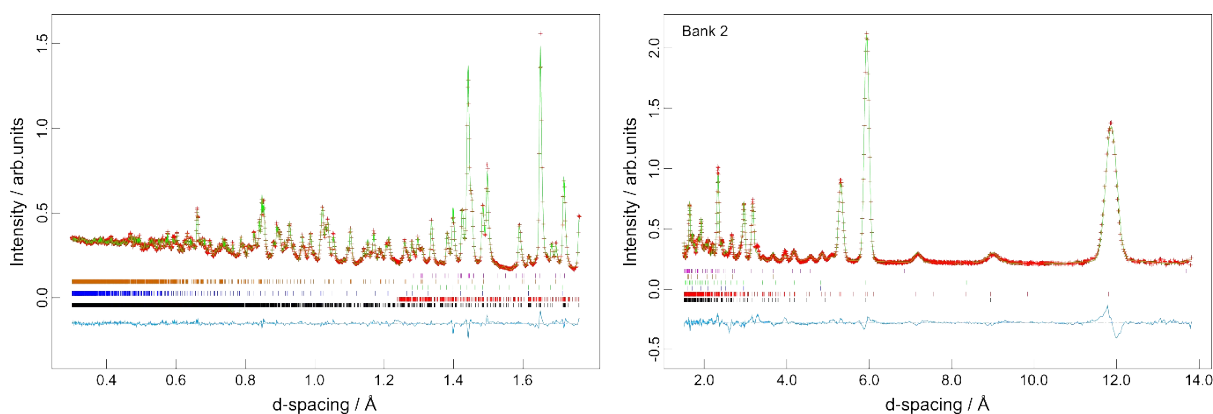


**Figure S2:** Versiliaite XRPD refinement at 298 K (Bruker D8). Black ticks-main phase; red ticks-Fe<sub>3</sub>O<sub>4</sub> phase.

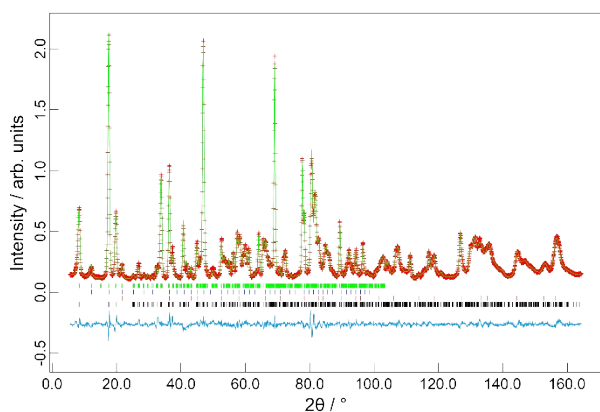
## NPD Refinement Plots



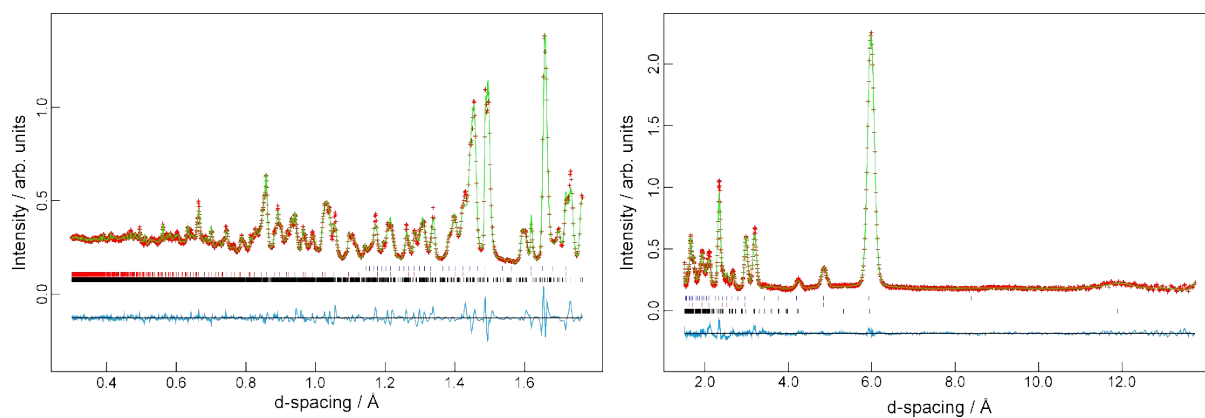
**Figure S3:** Apuanite NPD refinement at 298 K (GEM@ISIS, bank 2). Black ticks-main phase; red (blue) ticks- $\text{Fe}_3\text{O}_4$  nuclear (magnetic) phases; green ticks- $\text{Fe}_2\text{O}_3$  nuclear and magnetic phase.



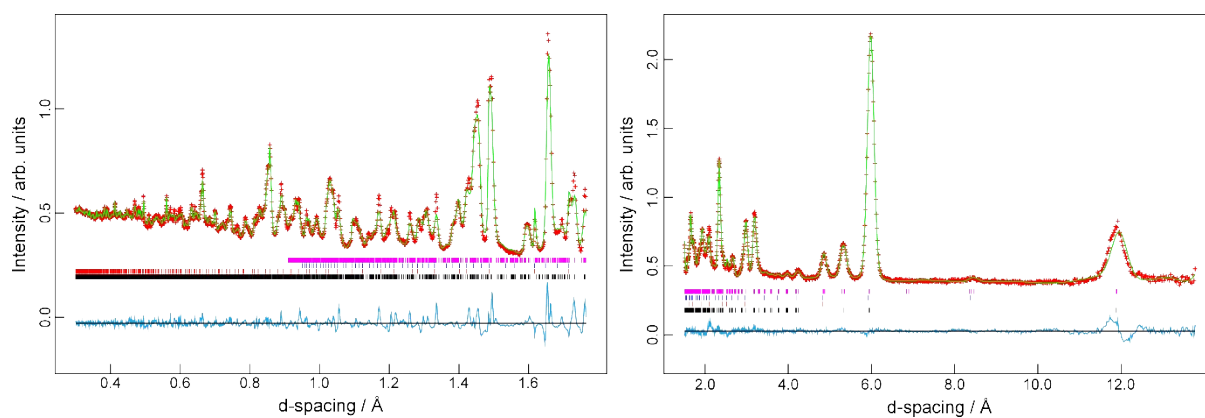
**Figure S4:** Apuanite NPD refinement at 5 K (GEM@ISIS) from bank 6 (left) and bank 2 (right). Black (red) ticks-main nuclear (magnetic) phases; blue (green) ticks- $\text{Fe}_3\text{O}_4$  nuclear (magnetic) phases; green (magenta) ticks- $\text{Fe}_2\text{O}_3$  nuclear (magnetic) phases.



**Figure S5:** Versiliaite NPD refinement (HRPT@PSI) at 1.5 K. Black (green) ticks-main nuclear (magnetic) phases; red (blue) ticks- $\text{Fe}_3\text{O}_4$  nuclear (magnetic) phases.



**Figure S6:** Mg-substituted versiliaite  $\text{Mg}_4\text{Fe}_8\text{Sb}_{12}\text{O}_{32}\text{S}_2$  refinement plot at 298 K (GEM@ISIS, banks 2 [right] and 6 [left]). Black ticks-main phase; red (blue) ticks- $\text{Fe}_3\text{O}_4$  nuclear (magnetic) phases.



**Figure S7:** Mg-substituted versiliaite  $\text{Mg}_4\text{Fe}_8\text{Sb}_{12}\text{O}_{32}\text{S}_2$  refinement plot at 5 K (GEM@ISIS, banks 2 [right] and 6 [left]). Black (magenta) ticks-main nuclear (magnetic) phase; red (blue) ticks- $\text{Fe}_3\text{O}_4$  nuclear (magnetic) phases.

## Structural Parameters from NPD refinement

† HRPT,  $\lambda = 1.4880 \text{ \AA}$

‡ D2B,  $\lambda = 1.5943 \text{ \AA}$

§ HRPT,  $\lambda = 1.8852 \text{ \AA}$

- Uiso constrained to 0 due to small, negative refined value

### Versiliaite

|                         |                                     | 298 K†     | 150 K‡     | 50 K‡      | 20 K‡      | 1.5 K§     |
|-------------------------|-------------------------------------|------------|------------|------------|------------|------------|
| $a / \text{\AA}$        |                                     | 8.4460(4)  | 8.4561(4)  | 8.4548(5)  | 8.4552(4)  | 8.4563(3)  |
| $b / \text{\AA}$        |                                     | 8.3155(3)  | 8.3111(5)  | 8.3083(5)  | 8.3085(5)  | 8.3199(3)  |
| $c / \text{\AA}$        |                                     | 11.9281(4) | 11.9454(3) | 11.9354(3) | 11.9343(3) | 11.9392(3) |
| Volume / $\text{\AA}^3$ |                                     | 837.74(7)  | 839.52(8)  | 838.41(8)  | 838.39(8)  | 839.98(6)  |
| Fe1 (4g)                | $x$                                 | 0.3115(7)  | 0.3112(8)  | 0.3103(8)  | 0.3102(8)  | 0.3113(6)  |
|                         | $y$                                 | 0.3204(6)  | 0.3225(8)  | 0.3204(8)  | 0.3208(7)  | 0.3174(7)  |
|                         | $100 \times U_{iso} / \text{\AA}^2$ | 1.6(1)     | 0.9(1)     | 0.6(1)     | 0.4(1)     | 1.2(1)     |
| Fe2 (4f)                | $z$                                 | 0.3766(5)  | 0.3799(6)  | 0.3778(7)  | 0.3789(6)  | 0.3755(6)  |
|                         | $100 \times U_{iso} / \text{\AA}^2$ | 0.9(1)     | 0.8(1)     | 0.9(2)     | 0.8(1)     | 0.4(1)     |
| Fe3 (4f)                | $z$                                 | 0.1261(6)  | 0.1282(7)  | 0.1280(7)  | 0.1293(7)  | 0.1237(7)  |
|                         | $100 \times U_{iso} / \text{\AA}^2$ | 0.5(1)     | -0.1(1)    | -0.3(1)    | -0.4(1)    | 0.5(1)     |
| Sb1 (8i)                | $x$                                 | 0.1705(5)  | 0.1691(6)  | 0.1689(6)  | 0.1681(6)  | 0.1694(5)  |
|                         | $y$                                 | 0.1677(5)  | 0.1658(6)  | 0.1659(6)  | 0.1663(6)  | 0.1670(4)  |
|                         | $z$                                 | 0.2472(6)  | 0.2460(6)  | 0.2450(7)  | 0.2456(7)  | 0.2455(6)  |
|                         | $100 \times U_{iso} / \text{\AA}^2$ | 0.85(8)    | 0.8(1)     | 0.4(1)     | 0.5(1)     | 0.18(8)    |
| Sb2 (4h)                | $x$                                 | 0.330(1)   | 0.331(1)   | 0.332(1)   | 0.333(1)   | 0.334(1)   |
|                         | $y$                                 | 0.3267(9)  | 0.327(1)   | 0.330(1)   | 0.329(1)   | 0.332(1)   |

|         |                                     |           |           |           |           |           |
|---------|-------------------------------------|-----------|-----------|-----------|-----------|-----------|
|         | $100 \times U_{iso} / \text{\AA}^2$ | 0.2(2)    | 0.4(3)    | 0.7(3)    | 0.8(3)    | 1.4(2)    |
| S (2a)  | $100 \times U_{iso} / \text{\AA}^2$ | 2.4(5)    | 4.3(8)    | 2.9(7)    | 3.4(7)    | 0.6(4)    |
| O1 (4h) | $x$                                 | 0.3591(9) | 0.359(1)  | 0.359(1)  | 0.360(1)  | 0.3597(9) |
|         | $y$                                 | 0.094(1)  | 0.093(1)  | 0.092(1)  | 0.091(1)  | 0.095(1)  |
|         | $100 \times U_{iso} / \text{\AA}^2$ | 1.2(2)    | 0.8(2)    | 0.7(2)    | 0.7(2)    | 1.3(2)    |
| O2 (8i) | $x$                                 | 0.4015(5) | 0.4015(5) | 0.4012(5) | 0.4009(5) | 0.3995(4) |
|         | $y$                                 | 0.1358(4) | 0.1360(5) | 0.1363(5) | 0.1359(5) | 0.1358(4) |
|         | $z$                                 | 0.2482(7) | 0.2476(7) | 0.2470(8) | 0.2464(7) | 0.2483(7) |
|         | $100 \times U_{iso} / \text{\AA}^2$ | 1.08(8)   | 0.4(1)    | 0.2(1)    | 0.1(1)    | 0.9(1)    |
| O3 (8i) | $x$                                 | 0.3254(7) | 0.3265(9) | 0.3264(9) | 0.3262(8) | 0.3292(6) |
|         | $y$                                 | 0.8189(7) | 0.820(1)  | 0.8183(9) | 0.8186(9) | 0.8198(7) |
|         | $z$                                 | 0.3775(5) | 0.3769(7) | 0.3763(7) | 0.3762(7) | 0.3764(5) |
|         | $100 \times U_{iso} / \text{\AA}^2$ | 1.4(1)    | 1.7(2)    | 1.4(2)    | 1.3(2)    | 1.0(1)    |
| O4 (8i) | $x$                                 | 0.1880(6) | 0.1824(8) | 0.1821(8) | 0.1812(8) | 0.1868(6) |
|         | $y$                                 | 0.3419(7) | 0.339(1)  | 0.3412(9) | 0.3407(9) | 0.3426(7) |
|         | $z$                                 | 0.1330(4) | 0.1306(6) | 0.1303(7) | 0.1303(6) | 0.1320(5) |
|         | $100 \times U_{iso} / \text{\AA}^2$ | 0.5(1)    | 0.7(2)    | 0.6(2)    | 0.6(2)    | 0.9(2)    |
| O5 (4g) | $x$                                 | 0.614(1)  | 0.611(1)  | 0.613(1)  | 0.613(1)  | 0.612(1)  |
|         | $y$                                 | 0.886(1)  | 0.880(1)  | 0.878(1)  | 0.878(1)  | 0.884(1)  |
|         | $100 \times U_{iso} / \text{\AA}^2$ | 1.1(2)    | 0.8(3)    | 1.0(3)    | 1.0(3)    | 0.7(3)    |

**Apuanite (GEM)**

|                         |                                     | 298 K      | 210 K      | 170 K      | 150 K      | 130 K      | 120 K      | 100 K      | 80 K       | 40 K       | 5 K        |
|-------------------------|-------------------------------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|
| $a / \text{\AA}$        |                                     | 8.3825(3)  | 8.3821(4)  | 8.3817(4)  | 8.3816(4)  | 8.3816(3)  | 8.3811(4)  | 8.3814(4)  | 8.3812(4)  | 8.3804(3)  | 8.3806(3)  |
| $c / \text{\AA}$        |                                     | 17.9787(7) | 17.9678(9) | 17.9601(9) | 17.9569(9) | 17.9550(8) | 17.9521(9) | 17.9500(9) | 17.9476(9) | 17.9444(8) | 17.9440(8) |
| Volume / $\text{\AA}^3$ |                                     | 1263.3(1)  | 1262.4(2)  | 1261.8(2)  | 1261.5(2)  | 1261.4(1)  | 1261.0(2)  | 1261.0(2)  | 1260.7(2)  | 1260.2(1)  | 1260.3(1)  |
| Fe1 (8h)                | $x$                                 | 0.3129(5)  | 0.3141(6)  | 0.3114(6)  | 0.3115(5)  | 0.3117(4)  | 0.3123(5)  | 0.3122(5)  | 0.3117(5)  | 0.3115(5)  | 0.3113(5)  |
|                         | $y$                                 | 0.3194(5)  | 0.3188(6)  | 0.3192(5)  | 0.3194(5)  | 0.3188(4)  | 0.3179(5)  | 0.3184(5)  | 0.3176(5)  | 0.3179(5)  | 0.3178(5)  |
|                         | $100 \times U_{iso} / \text{\AA}^2$ | 1.08(8)    | 0.75(7)    | 0.55(7)    | 0.55(6)    | 0.48(5)    | 0.52(6)    | 0.40(6)    | 0.44(6)    | 0.32(5)    | 0.31(5)    |
| Fe2 (4d)                | $100 \times U_{iso} / \text{\AA}^2$ | 1.0(1)     | 0.7(1)     | 0.7(1)     | 0.5(1)     | 0.57(9)    | 0.44(9)    | 0.39(9)    | 0.41(9)    | 0.34(8)    | 0.33(8)    |
| Fe3 (8f)                | $z$                                 | 0.0838(2)  | 0.0840(3)  | 0.0835(3)  | 0.0839(3)  | 0.0837(3)  | 0.0836(3)  | 0.0837(3)  | 0.0835(3)  | 0.0836(3)  | 0.0836(3)  |
|                         | $100 \times U_{iso} / \text{\AA}^2$ | 0.22(4)    | 0.14(5)    | 0.05(5)    | 0.04(4)    | 0.03(4)    | 0.04(4)    | 0.00(4)    | 0.01(4)    | -0.03(4)   | -0.03(4)   |
| Sb (16i)                | $x$                                 | 0.1696(4)  | 0.1696(5)  | 0.1698(6)  | 0.1689(5)  | 0.1693(5)  | 0.1687(5)  | 0.1688(5)  | 0.1686(5)  | 0.1686(5)  | 0.1686(5)  |
|                         | $y$                                 | 0.1703(5)  | 0.1704(6)  | 0.1688(6)  | 0.1702(5)  | 0.1693(5)  | 0.1703(5)  | 0.1691(5)  | 0.1701(5)  | 0.1692(5)  | 0.1695(5)  |
|                         | $z$                                 | 0.1652(3)  | 0.1643(3)  | 0.1653(4)  | 0.1649(3)  | 0.1651(3)  | 0.1649(3)  | 0.1649(4)  | 0.1647(3)  | 0.1652(3)  | 0.1651(3)  |
|                         | $100 \times U_{iso} / \text{\AA}^2$ | 0.67(6)    | 0.50(7)    | 0.40(6)    | 0.37(6)    | 0.39(5)    | 0.34(6)    | 0.38(6)    | 0.27(5)    | 0.28(5)    | 0.29(5)    |
| S (2a)                  | $100 \times U_{iso} / \text{\AA}^2$ | 4.5(4)     | 4.3(5)     | 3.0(5)     | 2.0(3)     | 2.5(3)     | 3.0(4)     | 2.3(4)     | 1.6(3)     | 1.8(3)     | 1.6(3)     |
| O1 (16i)                | $x$                                 | 0.9023(4)  | 0.9023(5)  | 0.9024(5)  | 0.9030(4)  | 0.9032(4)  | 0.9031(4)  | 0.9034(4)  | 0.9029(5)  | 0.9028(4)  | 0.9031(4)  |
|                         | $y$                                 | 0.3639(4)  | 0.3636(4)  | 0.3609(4)  | 0.3615(4)  | 0.3612(4)  | 0.3614(4)  | 0.3609(4)  | 0.3611(4)  | 0.3609(4)  | 0.3605(4)  |
|                         | $z$                                 | 0.1653(3)  | 0.1646(4)  | 0.1653(4)  | 0.1649(4)  | 0.1652(3)  | 0.1650(4)  | 0.1654(4)  | 0.1648(4)  | 0.1652(3)  | 0.1649(3)  |
|                         | $100 \times U_{iso} / \text{\AA}^2$ | 0.71(6)    | 0.53(6)    | 0.37(6)    | 0.44(6)    | 0.44(5)    | 0.42(6)    | 0.36(5)    | 0.28(5)    | 0.35(5)    | 0.34(5)    |
| O2 (8h)                 | $x$                                 | 0.8884(8)  | 0.8900(9)  | 0.8901(9)  | 0.8896(8)  | 0.8887(7)  | 0.8883(8)  | 0.8883(8)  | 0.8895(8)  | 0.8883(7)  | 0.8886(7)  |
|                         | $y$                                 | 0.3893(8)  | 0.3874(8)  | 0.3874(9)  | 0.3875(8)  | 0.3874(7)  | 0.3876(8)  | 0.3882(8)  | 0.3864(8)  | 0.3876(7)  | 0.3872(7)  |
|                         | $100 \times U_{iso} / \text{\AA}^2$ | 1.1(1)     | 0.8(1)     | 0.6(1)     | 0.5(1)     | 0.44(8)    | 0.6(1)     | 0.42(9)    | 0.6(1)     | 0.42(8)    | 0.40(8)    |
| O3 (16i)                | $x$                                 | 0.8147(4)  | 0.8157(5)  | 0.8145(5)  | 0.8145(5)  | 0.8149(4)  | 0.8149(5)  | 0.8151(5)  | 0.8153(5)  | 0.8153(4)  | 0.8152(4)  |
|                         | $y$                                 | 0.6566(4)  | 0.6568(5)  | 0.6570(5)  | 0.6563(4)  | 0.6568(4)  | 0.6573(5)  | 0.6575(5)  | 0.6575(5)  | 0.6574(4)  | 0.6571(4)  |
|                         | $z$                                 | 0.0889(2)  | 0.0881(3)  | 0.0877(3)  | 0.0877(3)  | 0.0878(2)  | 0.0877(3)  | 0.0880(3)  | 0.0878(3)  | 0.0876(3)  | 0.0876(3)  |

|         |     |                                     |           |           |           |           |           |           |           |           |           |           |
|---------|-----|-------------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
|         |     | $100 \times U_{iso} / \text{\AA}^2$ | 0.88(8)   | 0.67(8)   | 0.49(8)   | 0.54(7)   | 0.50(6)   | 0.51(7)   | 0.52(8)   | 0.46(7)   | 0.44(6)   | 0.44(6)   |
| O4 (8g) | $x$ |                                     | 0.8214(5) | 0.8214(6) | 0.8219(6) | 0.8223(5) | 0.8223(5) | 0.8224(5) | 0.8228(5) | 0.8226(6) | 0.8226(5) | 0.8227(5) |
|         |     | $100 \times U_{iso} / \text{\AA}^2$ | 0.41(8)   | 0.4(1)    | 0.19(9)   | 0.21(8)   | 0.18(7)   | 0.17(8)   | 0.16(8)   | 0.25(9)   | 0.07(7)   | 0.10(7)   |

## Mg Versiliaite (GEM)

|                         |                                     | 298 K       | 5 K        |
|-------------------------|-------------------------------------|-------------|------------|
| $a / \text{\AA}$        |                                     | 8.4933(12)  | 8.4976(13) |
| $b / \text{\AA}$        |                                     | 8.3897(12)  | 8.3869(14) |
| $c / \text{\AA}$        |                                     | 11.9525(13) | 11.927(2)  |
| Volume / $\text{\AA}^3$ |                                     | 851.69(19)  | 850.0(3)   |
| Fe1 / Mg1 (4g)          | $x$                                 | 0.3161(13)  | 0.319(2)   |
|                         | $y$                                 | 0.3223(10)  | 0.3269(16) |
|                         | $100 \times U_{iso} / \text{\AA}^2$ | 0.56(14)    | 0.2(2)     |
|                         | Fe Occupancy                        | 0.51(3)     | 0.51       |
| Fe2 (4f)                | $z$                                 | 0.3781(19)  | 0.3764(16) |
|                         | $100 \times U_{iso} / \text{\AA}^2$ | 3.5(4)      | 0.6(2)     |
|                         | Fe Occupancy                        | 0.78(5)     | 0.78       |
| Fe3 (4f)                | $z$                                 | 0.1278(8)   | 0.1304(12) |
|                         | $100 \times U_{iso} / \text{\AA}^2$ | 0•          | 0.0(1)     |
|                         | Fe Occupancy                        | 0.71(5)     | 0.71       |
| Sb1 (8i)                | $x$                                 | 0.1680(10)  | 0.1711(11) |
|                         | $y$                                 | 0.1673(10)  | 0.1717(12) |
|                         | $z$                                 | 0.2462(10)  | 0.2481(15) |
|                         | $100 \times U_{iso} / \text{\AA}^2$ | 1.11(15)    | 0.4(1)     |
| Sb2 (4h)                | $x$                                 | 0.331(2)    | 0.328(3)   |

|         |                                                             |                                              |            |
|---------|-------------------------------------------------------------|----------------------------------------------|------------|
|         | $y$                                                         | 0.3239(18)                                   | 0.324(3)   |
|         | $100 \times U_{iso} / \text{\AA}^2$                         | 1.30(3)                                      | 0.4(3)     |
| S (2a)  | $100 \times U_{iso} / \text{\AA}^2$                         | 28.19                                        | 71(42)     |
|         | $100 \times U_{11}, U_{22}, U_{33}, U_{12}, U_{13}, U_{23}$ | 52.(26), 31.(14), 2.1(35), 38.(18), 0.0, 0.0 |            |
| O1 (4h) | $x$                                                         | 0.3558(17)                                   | 0.355(2)   |
|         | $y$                                                         | 0.099(2)                                     | 0.090(2)   |
|         | $100 \times U_{iso} / \text{\AA}^2$                         | 1.5(3)                                       | 0.5(3)     |
| O2 (8i) | $x$                                                         | 0.4001(9)                                    | 0.3993(10) |
|         | $y$                                                         | 0.1318(9)                                    | 0.1373(9)  |
|         | $z$                                                         | 0.2474(13)                                   | 0.2463(17) |
|         | $100 \times U_{iso} / \text{\AA}^2$                         | 1.90(21)                                     | 0.7(2)     |
| O3 (8i) | $x$                                                         | 0.1770(12)                                   | 0.180(2)   |
|         | $y$                                                         | 0.3169(11)                                   | 0.3210(16) |
|         | $z$                                                         | 0.3698(10)                                   | 0.3726(17) |
|         | $100 \times U_{iso} / \text{\AA}^2$                         | 1.32(17)                                     | 0.9(2)     |
| O4 (8i) | $x$                                                         | 0.1864(11)                                   | 0.1781(15) |
|         | $y$                                                         | 0.3455(10)                                   | 0.3373(15) |
|         | $z$                                                         | 0.1269(10)                                   | 0.1257(14) |
|         | $100 \times U_{iso} / \text{\AA}^2$                         | 1.14(18)                                     | 0.29(15)   |
| O5 (4g) | $x$                                                         | 0.3881(23)                                   | 0.385(3)   |
|         | $y$                                                         | 0.1187(22)                                   | 0.117(2)   |
|         | $100 \times U_{iso} / \text{\AA}^2$                         | 3.24(48)                                     | 2.1(5)     |