**Fe-, Fe,Mn- and Fe,Mg-chlorite: a genetic linkage to W, (Cu,Mo)-mineralization in the magmatic-hydrothermal system at Borralha, northern Portugal**

I. BOBOS1,\*, F. NORONHA1 AND A. MATEUS2

1Instituto de Ciências da Terra – Polo Porto, Departamento de Geociências, Ambiente e Ordenamento do Território, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal

2 Departamento de Geologia e IDL, Faculdade de Ciências, Universidade de Lisboa, C6, Campo Grande, 1746-016 Lisboa, Portugal

Supplementary material

**FIGURE S1.** XRD patterns (oriented specimens) of the <2 μm grain fractions of Fe,Mg-chlorite and Fe,Mn-chlorite.

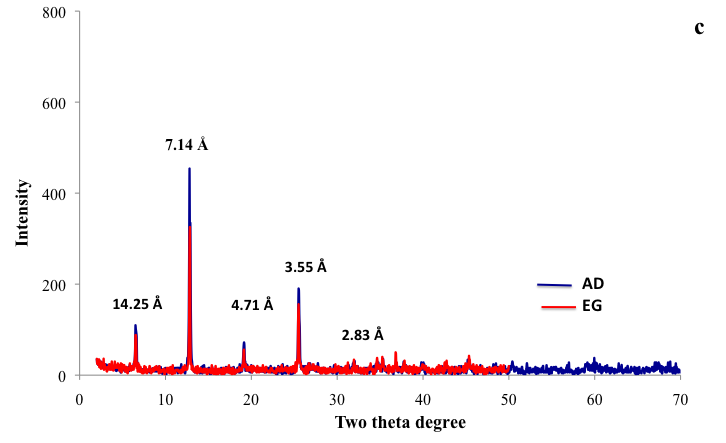
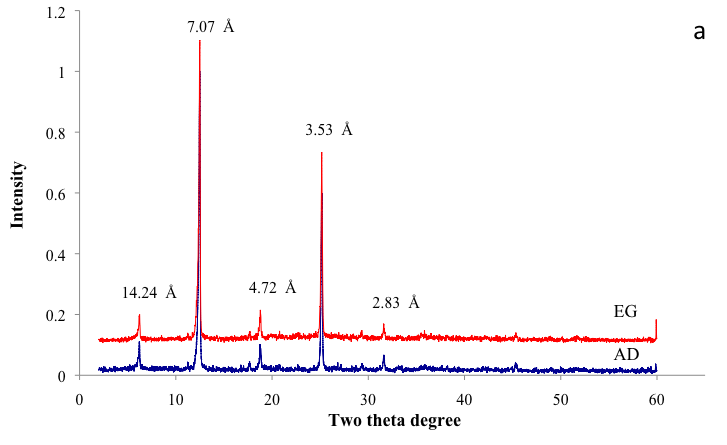
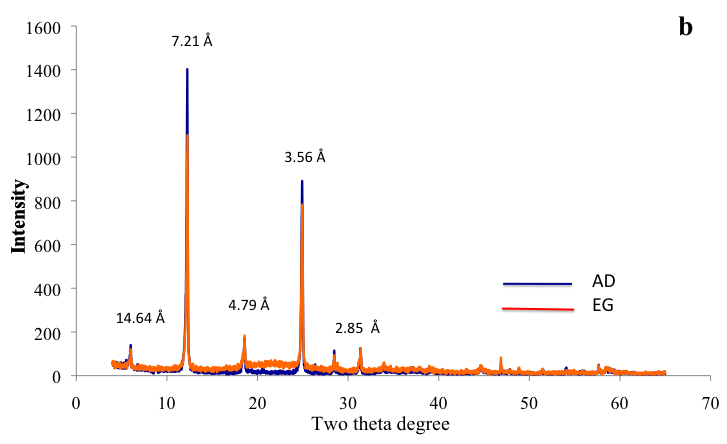


Table S1. EMPA results of Fe,Mn-chlorite (around scheelite crystals) and calculated structural formula based on 28 oxygens (Fe2+/Fe3+ and OH– calculated assuming full site occupancy)

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Element | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| SiO2 | 23.18 | 22.7 | 23.2 | 23.13 | 23.06 | 23.66 | 23.32 | 23.73 | 22.46 | 23.16 | 22.71 | 23.11 |
| TiO2 | 0.08 | 0.00 | 0.02 | 0.03 | 0.01 | 0.03 | 0.02 | 0.04 | 0.04 | 0.03 | 0.03 | 0.01 |
| Al2O3 | 19.88 | 19.95 | 19.82 | 20.44 | 21.26 | 18.62 | 19.12 | 20.14 | 20.86 | 18.71 | 19.32 | 19.82 |
| FeO | 39.52 | 39.86 | 39.53 | 39.26 | 38.39 | 39.48 | 39.83 | 39.55 | 38.59 | 39.19 | 38.78 | 39.13 |
| MnO | 6.23 | 5.03 | 5.82 | 4.2 | 3.92 | 6.07 | 6.12 | 5.28 | 5.81 | 6.35 | 5.83 | 6.21 |
| MgO | 1.87 | 1.44 | 1.88 | 2.7 | 3.01 | 1.82 | 1.58 | 1.75 | 1.01 | 1.61 | 1.282 | 1.67 |
| CaO | 0.04 | 0.01 | 0.03 | 0.05 | 0.05 | 0.03 | 0.05 | 0.05 | 0.06 | 0.04 | 0.03 | 0.05 |
| Na2O | 0.03 | 0.03 | - | - | 0.01 | - | 0.01 | - | 0.01 | - | - | 0.01 |
| K2O | 0.01 | - | - | - | 0.01 | - | - | - | 0.01 | - | - | - |
| ZnO | 0.11 | 0.29 | 0.06 | 0.08 | 0.06 | 0.19 | 0.04 | 0.08 | 0.06 | 0.18 | 0.19 | 0.04 |
| F | - | - | - | - | - | - | - | - | - | - | - | - |
| Cl | - | - | - | - | - | - | 0.01 | - | - | - | - | 0.01 |
| Cr2O3 | - | - | 0.04 | - | - | - | 0.05 | - | - | - | - | 0.05 |
| P2O5 | - | - | 0.01 | 0.01 | - | - | 0.01 | 0.02 | - | - | - | 0.01 |
| Total | 90.95 | 89.31 | 90.41 | 89.90 | 89.78 | 89.90 | 90.16 | 90.68 | 88.92 | 89.27 | 88.17 | 90.14 |
| Si | 5.27 | 5.26 | 5.31 | 5.26 | 5.21 | 5.45 | 5.37 | 5.37 | 5.20 | 5.39 | 5.34 | 5.30 |
| Al(IV) | 2.73 | 2.73 | 2.69 | 2.73 | 2.79 | 2.54 | 2.63 | 2.62 | 2.79 | 2.61 | 2.66 | 2.69 |
| Al(VI) | 2.61 | 2.72 | 2.65 | 2.75 | 2.88 | 2.52 | 2.56 | 2.76 | 2.90 | 2.53 | 2.69 | 2.67 |
| Ti | 0.01 | - | - | 0.01 | - | - | - | 0.01 | 0.01 | - | - | - |
| Cr | - | - | 0.01 | - | - | - | 0.01 | - | - | - | - | 0.01 |
| Fe3+ | - | - | - | 0.01 | 0.05 | - | - | 0.08 | 0.06 | - | 0.02 | - |
| Fe2+ | 7.56 | 7.74 | 7.57 | 7.46 | 7.20 | 7.62 | 7.69 | 7.41 | 7.41 | 7.66 | 7.60 | 7.51 |
| Mn | 1.20 | 0.99 | 1.13 | 0.81 | 0.75 | 1.19 | 1.19 | 1.01 | 1.14 | 1.25 | 1.16 | 1.21 |
| Mg | 0.63 | 0.50 | 0.64 | 0.92 | 1.01 | 0.63 | 0.54 | 0.59 | 0.35 | 0.56 | 0.45 | 0.57 |
| Zn | 0.02 | 0.05 | 0.01 | 0.01 | 0.01 | 0.03 | 0.01 | 0.01 | 0.01 | 0.03 | 0.03 | 0.01 |
| Ca | 0.01 | - | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Na | 0.02 | 0.02 | - | - | - | - | 0.01 | 0 | - | - | - | 0.01 |
| F | - | - | - | - | - | - | - | - | - | - | - | - |
| Cl | - | - | - | - | - | - | 0.01 | - | - | - | - | 0.01 |
| OH | 16.00 | 16.00 | 15.99 | 16.00 | 16.00 | 16.00 | 15.99 | 16.00 | 16.00 | 16.00 | 16.00 | 15.99 |

Table S2. Calculation of the oxidation state of Fe,Mn-chlorite

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Element | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Oxidized | Yes | yes | yes | yes | yes | yes | Yes | yes | yes | yes | Yes | yes |
| Fe/(Fe+Mg) | 0.92 | 0.94 | 0.92 | 0.89 | 0.87 | 0.92 | 0.93 | 0.93 | 0.95 | 0.93 | 0.94 | 0.93 |
| Variety | daphnite | daphnite | daphnite | daphnite | daphnite | daphnite | daphnite | daphnite | daphnite | daphnite | daphnite | daphnite |

Table S3. EMPA results of Fe-chlorite (around intergrowth of wolframite and scheelite) and calculated structural formula based on 28 oxygens (Fe2+/Fe3+ and OH– calculated assuming full site occupancy).

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Element | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
| SiO2 | 22.74 | 22.92 | 23 | 23.25 | 22.84 | 23.59 | 23.3 | 23.39 | 23.6 | 23.47 | 22.95 | 23.47 | 23.23 | 23.04 |
| TiO2 | 0.02 | - | 0.07 | 0.02 | 0.07 | 0.02 | - | 0.06 | - | - | - | - | - | 0.04 |
| Al2O3 | 20.27 | 20.64 | 20.37 | 20.07 | 20.39 | 19.81 | 20.31 | 20.08 | 20.56 | 21.12 | 20.51 | 18.98 | 19.98 | 18.26 |
| FeO | 42.2 | 42.54 | 41.47 | 42.51 | 41.37 | 42.25 | 42.4 | 41.61 | 40.78 | 40.2 | 39.98 | 43.34 | 42.75 | 41.51 |
| MnO | 1.21 | 1.33 | 1.46 | 1.48 | 1.88 | 1.64 | 1.77 | 1.92 | 1.49 | 1.09 | - | 0.65 | 1.57 | 0.76 |
| MgO | 0.52 | 0.45 | 0.51 | 0.66 | 0.81 | 0.45 | 0.43 | 0.46 | 0.54 | 0.58 | 0.40 | 0.67 | 0.42 | 0.61 |
| CaO | 0.05 | - | 0.02 | 0.06 | 0.09 | - | 0.01 | - | 0.01 | 0.06 | 0.02 | 0.02 | 0.05 | 0.09 |
| Na2O | 0.06 | - | 0.06 | 0.02 | - | 0.04 | 0.02 | 0.09 | 0.02 | - | 0.03 | 0.10 | 0.02 | 0.06 |
| K2O | - | - | - | - | - | 0.04 | - | - | - | 0.01 | - | 0.02 | 0.01 | - |
| F | - | - | - | - | - | 0.0 | - | - | - | - | - | - | - | - |
| Cl | 0.01 | - | 0.01 | - | 0.01 | 0.01 | - | - | 0.01 | - | - | - | - | - |
| Cr2O3 | 0.02 | - | - | 0.02 | 0.06 | - | 0.01 | 0.01 | - | - | - | - | - | - |
| CoO | 0.01 | 0.11 | - | - | - | - | - | - | - | - | - | - | - | - |
| Total | 87.12 | 87.9 | 86.9 | 88.0 | 87.51 | 87.85 | 88.25 | 87.61 | 87.01 | 86.52 | 83.92 | 87.25 | 88.03 | 84.37 |
| Si | 5.35 | 5.34 | 5.39 | 5.41 | 5.34 | 5.49 | 5.41 | 5.45 | 5.48 | 5.45 | 5.48 | 5.53 | 5.42 | 5.59 |
| Al(IV) | 2.65 | 2.65 | 2.61 | 2.59 | 2.66 | 2.51 | 2.59 | 2.55 | 2.52 | 2.55 | 2.52 | 2.47 | 2.58 | 2.41 |
| Al(VI) | 2.99 | 3.03 | 3.04 | 2.93 | 2.97 | 2.95 | 2.99 | 2.99 | 3.15 | 3.27 | 3.31 | 2.82 | 2.93 | 2.83 |
| Ti | - | - | 0.01 | - | 0.01 | - | - | 0.01 | - | - | - | - | - | 0.01 |
| Cr | - | - | - | - | 0.01 | - | - | - | - | - | - | - | - | - |
| Fe3+ | 0.18 | 0.21 | 0.24 | 0.19 | 0.19 | 0.24 | 0.21 | 0.24 | 0.35 | 0.39 | 0.43 | 0.17 | 0.19 | 0.23 |
| Fe2+ | 8.19 | 8.08 | 7.88 | 8.08 | 7.89 | 7.99 | 8.01 | 7.87 | 7.58 | 7.41 | 7.56 | 8.37 | 8.15 | 8.19 |
| Mn | 0.24 | 0.26 | 0.29 | 0.29 | 0.37 | 0.32 | 0.34 | 0.38 | 0.29 | 0.21 | - | 0.13 | 0.31 | 0.16 |
| Mg | 0.18 | 0.15 | 0.18 | 0.23 | 0.28 | 0.16 | 0.15 | 0.16 | 0.19 | 0.20 | 0.14 | 0.23 | 0.15 | 0.22 |
| Ca | 0.01 | - | 0.01 | 0.01 | 0.02 | - | - | - | - | 0.01 | 0.01 | 0.01 | 0.01 | 0.02 |
| Na | 0.05 | - | 0.05 | 0.02 | - | 0.04 | 0.02 | 0.08 | 0.02 | - | 0.03 | 0.09 | 0.02 | 0.06 |
| K | - | - | - | - | - | 0.02 | - | - | - | 0.01 | - | 0.01 | 0.01 | - |
| F | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Cl | 0.01 | - | 0.01 | - | 0.01 | 0.01 | - | - | 0.01 | - | - | - | - | - |
| OH | 15.99 | 16.00 | 15.99 | 16.00 | 15.99 | 15.99 | 16.00 | 16.00 | 15.99 | 16.00 | 16.00 | 16.00 | 16.00 | 16.00 |

Table S4. Calculation of oxidation state of Fe-chlorite.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Element | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| Oxidized | yes | yes | yes | yes | yes | yes | yes | yes | yes | yes | yes | yes |
| Fe/(Fe+Mg) | 0.98 | 0.98 | 0.98 | 0.97 | 0.97 | 0.98 | 0.98 | 0.98 | 0.98 | 0.97 | 0.98 | 0.97 |
| Variety | daphnite | daphnite | daphnite | daphnite | daphnite | daphnite | daphnite | daphnite | daphnite | daphnite | daphnite | daphnite |

Table S5. EMPA analyses of Mg,Fe-chlorite and calculated structural formula based on 28 oxygens (Fe2+/Fe3+ and OH– calculated assuming full site occupancy).

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Element | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| SiO2 | 30.19 | 29.19 | 28.93 | 29.86 | 28.62 | 29.37 | 28.85 | 30.46 |
| TiO2 | 0.02 | 0.06 | 0.03 | 0.01 | 0.01 | 0.03 | 0.04 | - |
| Al2O3 | 20.47 | 20.09 | 20.18 | 19.79 | 18.19 | 17.97 | 17.58 | 17.67 |
| FeO | 12.21 | 13.99 | 12.72 | 13.47 | 13.25 | 12.63 | 12.82 | 12.44 |
| MnO | 0.04 | 0.03 | 0.08 | 0.03 | 0.05 | 0.04 | 0.06 | 0.04 |
| MgO | 21.33 | 19.48 | 20.81 | 21.29 | 20.36 | 21.68 | 20.84 | 22.09 |
| CaO | 1.21 | 0.96 | 0.85 | 1.01 | 1.14 | 1.32 | 1.58 | 0.51 |
| Na2O | - | - | 0.01 | - | 0.02 | 0.04 | 0.06 | 0.09 |
| K2O | - | - | - | - | - | 0.02 | 0.07 | 0.05 |
| F | - | - | - | - | - | - | - | - |
| Cl | 0.03 | - | - | 0.04 | 0.03 | - | 0.02 | 0.03 |
| Total | 85.50 | 83.80 | 83.61 | 85.50 | 81.67 | 83.1 | 81.90 | 83.35 |
| Si | 5.99 | 5.97 | 5.90 | 5.98 | 6.03 | 6.06 | 6.06 | 6.21 |
| Al(IV) | 2.01 | 2.03 | 2.10 | 2.02 | 1.97 | 1.94 | 1.94 | 1.79 |
| Al(VI) | 2.82 | 2.85 | 2.79 | 2.68 | 2.57 | 2.45 | 2.44 | 2.49 |
| Ti | - | 0.01 | - | - | - | - | 0.01 | - |
| Fe3+ | 0.46 | 0.47 | 0.39 | 0.38 | 0.34 | 0.28 | 0.27 | 0.38 |
| Fe2+ | 1.57 | 1.93 | 1.78 | 1.88 | 2.00 | 1.89 | 1.98 | 1.74 |
| Mn | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Mg | 6.31 | 5.94 | 6.33 | 6.35 | 6.39 | 6.67 | 6.53 | 6.72 |
| Ca | 0.26 | 0.21 | 0.19 | 0.22 | 0.26 | 0.29 | 0.36 | 0.11 |
| Na | - | - | 0.01 | - | 0.02 | 0.03 | 0.05 | 0.07 |
| K | - | - | - | - | - | 0.01 | 0.04 | 0.03 |
| Cl | 0.02 | - | - | 0.03 | 0.02 | - | 0.01 | 0.02 |
| OH | 15.98 | 15.99 | 16 | 15.97 | 15.98 | 15.99 | 15.99 | 15.98 |

Table S6. Calculation of oxidation state of Mg,Fe-chlorite.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Elements | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Oxidized | yes | yes | yes | yes | yes | Yes | yes | yes |
| Fe/(Fe+Mg) | 0.24 | 0.29 | 0.25 | 0.26 | 0.27 | 0.25 | 0.26 | 0.24 |
| Variety | pycnochlorite | pycnochlorite | pycnochlorite | pycnochlorite | pycnochlorite | pycnochlorite | pycnochlorite | diabantite |

Table S7. EMPA results of Fe,Mg chlorite and calculated structural formula based on 28 oxygens (Fe2+/Fe3+ and OH– calculated assuming full site occupancy).

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Element | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| SiO2 | 23.28 | 23.83 | 23.00 | 23.42 | 23.6 | 23.37 | 23.02 | 23.89 | 24.19 | 22.93 | 24.02 |
| TiO2 | 0.01 | 0.01 | 0.03 | - | - | 0.03 | - | 0.02 | - | - | - |
| Al2O3 | 21.02 | 21.14 | 20.54 | 20.66 | 20.29 | 19.97 | 21.36 | 20.47 | 20.09 | 20.18 | 20.79 |
| FeO | 35.57 | 34.43 | 35.68 | 35.57 | 33.85 | 35.63 | 34.41 | 35.21 | 33.99 | 35.72 | 33.97 |
| MnO | 1.06 | 1.07 | 1.11 | 1.32 | 1.15 | 1.14 | 0.96 | 1.14 | 1.30 | 1.18 | 0.89 |
| MgO | 5.9 | 6.42 | 6 | 6.32 | 6.36 | 6.13 | 5.85 | 6.33 | 6.48 | 5.96 | 6.29 |
| CaO | 0.01 | 0.01 | - | 0.01 | - | - | 0.02 | 0.01 | - | - | 0.01 |
| Na2O | - | 0.01 | - | - | 0.02 | - | 0.08 | - | - | 0.01 | - |
| K2O | - | - | - | - | - | - | 0.02 | - | - | - | - |
| BaO | - | 0.08 | - | 0.06 | - | 0.17 | 0.03 | 0.08 | - | - | 0.11 |
| Rb2O | - | 0.03 | - | 0.01 | 0.02 | 0.02 | 0.01 | - | - | 0.01 | 0.03 |
| ZnO | 0.05 | - | 0.17 | 0.06 | 0.11 | - | 0.16 | - | 0.16 | - | 0.02 |
| F | 0.25 | 0.15 | 0.19 | 0.13 | 0.20 | 0.18 | 0.24 | 0.25 | 0.30 | 0.31 | 0.249 |
| Cl | - | - | - | 0.02 | 0.01 | - | 0.01 | - | - | - | - |
| Total | 87.21 | 87.24 | 86.72 | 87.62 | 85.68 | 86.74 | 86.25 | 87.41 | 86.57 | 86.37 | 86.46 |
| Si | 5.24 | 5.32 | 5.23 | 5.27 | 5.37 | 5.32 | 5.21 | 5.35 | 5.43 | 5.24 | 5.39 |
| Al(iv) | 2.76 | 2.68 | 2.77 | 2.73 | 2.63 | 2.68 | 2.79 | 2.65 | 2.57 | 2.76 | 2.61 |
| Al(vi) | 2.85 | 2.92 | 2.77 | 2.77 | 2.85 | 2.71 | 2.95 | 2.78 | 2.79 | 2.71 | 2.93 |
| Ti | - | - | 0.01 | - | - | - | - | - | - | - | - |
| Fe3+ | 0.17 | 0.20 | 0.09 | 0.09 | 0.21 | 0.11 | 0.19 | 0.19 | 0.26 | 0.11 | 0.29 |
| Fe2+ | 6.53 | 6.23 | 6.70 | 6.61 | 6.23 | 6.68 | 6.33 | 6.40 | 6.12 | 6.71 | 6.08 |
| Mn | 0.20 | 0.20 | 0.21 | 0.25 | 0.22 | 0.22 | 0.18 | 0.22 | 0.25 | 0.23 | 0.19 |
| Mg | 1.98 | 2.14 | 2.03 | 2.12 | 2.16 | 2.08 | 1.97 | 2.11 | 2.17 | 2.03 | 2.10 |
| Zn | 0.01 | - | 0.03 | 0.01 | 0.02 | - | 0.03 | - | 0.03 | - | - |
| Ca | - | - | - | - | - | - | 0.01 | - | - | - | - |
| Na | - | 0.01 | - | - | 0.02 | - | 0.07 | - | - | 0.01 | - |
| K | - | - | - | - | - | - | 0.01 | - | - | - | - |
| Ba | - | 0.01 | - | 0.01 | - | 0.03 | 0.01 | 0.01 | - | - | 0.02 |
| Na | - | 0.01 | - | - | 0.02 | - | 0.07 | - | - | 0.01 | - |
| Rb | - | 0.01 | - | - | 0.01 | 0.01 | - | - | - | - | 0.01 |
| F | 0.36 | 0.21 | 0.27 | 0.18 | 0.28 | 0.26 | 0.34 | 0.36 | 0.43 | 0.44 | 0.30 |
| Cl | - | - | - | 0.01 | 0.01 | - | 0.01 | - | - | - | - |
| OH | 15.64 | 15.79 | 15.73 | 15.80 | 15.71 | 15.73 | 15.64 | 15.64 | 15.57 | 15.56 | 15.64 |

Table S8. Calculation of oxidation state of Fe,Mg-chlorite.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Element | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| Oxidized | Yes | Yes | Yes | Yes | Yes | Yes | Yes | Yes | Yes | Yes | Yes |
| Fe/(Fe+Mg) | 0.77 | 0.75 | 0.77 | 0.76 | 0.75 | 0.76 | 0.78 | 0.76 | 0.75 | 0.77 | 0.75 |
| Variety | ripidolite | ripidolite | ripidolite | ripidolite | ripidolite | ripidolite | ripidolite | Ripidolite | ripidolite | ripidolite | ripidolite |

Table S9. EMPA results of scheelite and calculated structural formula based on 4 oxygens.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Element | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 |
| WO3 | 80.51 | 80.77 | 79.2 | 81.02 | 81.63 | 81.39 | 81.04 | 80.98 | 79.66 | 81.18 | 79.78 | 80.92 | 81.17 |
| CaO | 17.89 | 18.15 | 18 | 18.19 | 18.35 | 18.78 | 18.16 | 18.55 | 18.8 | 18.08 | 18.08 | 18.18 | 18.12 |
| TiO2 | - | - | - | 1.82 | - | - | - | - | - | - | - | - | - |
| FeO | 0.06 | 0.02 | - | 0.03 | - | - | - | 0.10 | - | 0.2019 | 0.2 | - | 0.04 |
| SnO2 | 0.03 | - | - | - | - | - | - | - | 0.07 | - | - | - | 0.08 |
| PbO | 0.14 | - | 0.05 | - | 0.08 | - | 0.03 | - | 0.22 | - | 0.05 | - | - |
| MnO | - | - | - | 0.02 | - | 0.08 | - | - | - | - | - | - | - |
| Bi2O3 | - | - | - | 0.06 | 0.01 | - | - | 0.03 | 0.04 | - | - | - | - |
| MoO3 | - | - | - | 0.10 | 0.05 | 0.08 | 0.062 | - | 0.24 | - | 0.07 | 0.11 | - |
| Total | 98.63 | 98.94 | 97.25 | 101.24 | 100.12 | 100.33 | 99.29 | 99.67 | 99.04 | 99.46 | 98.15 | 99.21 | 99.41 |
| W | 1.090 | 1.089 | 1.086 | 1.088 | 1.088 | 1.083 | 1.089 | 1.083 | 1.078 | 1.088 | 1.085 | 1.089 | 1.09 |
| Ca | 0.727 | 0.734 | 0.741 | 0.733 | 0.734 | 0.749 | 0.732 | 0.744 | 0.763 | 0.727 | 0.738 | 0.734 | 0.729 |
| Ti | - | - | - | 0.001 | - | - | - | 0.001 | 0.001 | - | - | - | - |
| Fe | 0.003 | 0.001 | - | 0.001 | - | - | - | 0.004 | - | 0.008 | 0.007 | - | 0.002 |
| Sn | 0.001 | - | - | - | - | - | - | - | 0.001 | - | - | - | 0.002 |
| Pb | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Mn | - | - | - | 0.001 | - | 0.003 | - | - | - | - | - | - | - |
| Bi | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Mo | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Total | 1.820 | 1.823 | 1.827 | 1.823 | 1.823 | 1.835 | 1.822 | 1.833 | 1.843 | 1.823 | 1.830 | 1.823 | 1.821 |

Table S10. EMPA results of wolframite and calculated structural formula based on 4 oxygens.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Elements | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
| WO3 | 74.68 | 74.91 | 74.41 | 73.86 | 73.99 | 73.81 | 73.45 | 73.57 | 73.36 | 74.69 | 74.09 |
| FeO | 11.35 | 9.99 | 10.69 | 9.14 | 10.17 | 10.75 | 12.39 | 10.74 | 11.01 | 10.28 | 10.81 |
| MnO | 13.50 | 14.66 | 14.31 | 16.29 | 15.33 | 14.95 | 13.71 | 15.23 | 15.14 | 14.50 | 14.58 |
| Nb2O5 | 0.36 | 0.32 | 0.38 | 0.40 | 0.41 | 0.35 | 0.37 | 0.33 | 0.38 | 0.42 | 0.39 |
| TiO2 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| SnO2 | 0.02 | 0.02 | 0.03 | 0.01 | 0.01 | 0.02 | 0.01 | 0.03 | 0.01 | 0.01 | 0.03 |
| Ta2O5 | 0.05 | 0.05 | 0.05 | 0.06 | 0.04 | 0.06 | 0.05 | 0.05 | 0.05 | 0.06 | 0.06 |
| Sc2O3 | - | - | - | - | - | - | - | - | - | - | - |
| ThO2 | - | - | - | - | - | - | - | - | - | - | - |
| UO2 | - | - | - | - | - | - | - | - | - | - | - |
| CaO | 0.03 | 0.04 | 0.01 | 0.02 | 0.04 | 0.05 | 0.01 | 0.04 | 0.04 | 0.03 | 0.03 |
| Total | 100.00 | 100.00 | 99.89 | 99.79 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |
| W | 0.974 | 0.977 | 0.971 | 0.964 | 0.964 | 0.962 | 0.957 | 0.958 | 0.955 | 0.974 | 0.966 |
| Fe | 0.478 | 0.420 | 0.450 | 0.385 | 0.428 | 0.452 | 0.521 | 0.452 | 0.463 | 0.432 | 0.455 |
| Mn | 0.575 | 0.625 | 0.610 | 0.695 | 0.653 | 0.637 | 0.584 | 0.648 | 0.644 | 0.618 | 0.621 |
| Nb | 0.008 | 0.007 | 0.009 | 0.009 | 0.009 | 0.008 | 0.008 | 0.007 | 0.009 | 0.010 | 0.009 |
| Ti | - | - | - | - | - | - | - | - | - | - | - |
| Sn | - | - | 0.001 | - | - | - | - | 0.001 | - | - | 0.001 |
| Ta | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 |
| Sc | - | - | - | - | - | - | - | - | - | - | - |
| Th | - | - | - | - | - | - | - | - | - | - | - |
| U | - | - | - | - | - | - | - | - | - | - | - |
| Ca | 0.002 | 0.002 | 0.001 | 0.001 | 0.002 | 0.003 | 0.001 | 0.002 | 0.002 | 0.002 | 0.002 |
| Total | 2.038 | 2.023 | 2.043 | 2.055 | 2.057 | 2.063 | 2.072 | 2.069 | 2.074 | 2.034 | 2.055 |