|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Table S1.** Assigned site populations (ASP) for the crystallographic sites of tourmalines from Minas Gerais. These populations were calculated to reach the best fits between the refined site-scattering (RSS) and the calculated site scattering values (CSS), between the bond-valence sums (BVS) and the theoretical valence sums (TV), between the mean bond lengths (MBL) and the calculated bond lengths (CBM), and between the chemical formulae obtained from the crystal structure (STR) and from the electron microprobe data (EMP). | | | | | | | |
| **WR037** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.82 Na + 0.15 □ + 0.02 Ca + 0.01 K | 10.30 | 9.66 | 2.612 | 2.675 | 0.97 | 1.03 |
| *Y* | 0.36 Al + 0.33 Li + 0.24 Fe2+ + 0.06 Mn2+ + 0.02 Mg | 13.60 | 13.64 | 2.048 | 2.036 | 1.98 | 2.04 |
| *Z* | 1.00 Al | 13.00 | 13.00 | 1.905 | 1.907 | 3.03 | 3.00 |
| *T* | 0.99 Si + 0.01 B | 14.00 | 13.96 | 1.619 | 1.619 | 4.05 | 4.00 |
| *B* | 1.00 B | 5.00 | 5.00 | 1.380 | 1.371 | 3.00 | 3.00 |
| EMP | (Na0.82□0.15Ca0.02K0.01)(Al1.01Li0.98Fe0.79Mn0.16Mg0.05)Al6.02B2.72O9[(Si5.98)O18](OH)3.00(F0.68OH0.32) | | | | | | |
| STR | (Na0.82□0.15Ca0.02K0.01)(Al1.07Li0.98Fe2+0.73Mn0.17Mg0.05)Al6.00B3.00O9[(Si5.97B0.03)O18](OH)3.00(F0.68OH0.32) | | | | | | |
| **WR044** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.64 Na + 0.29 □ + 0.06 Ca + 0.01 K | 8.82 | 8.31 | 2.608 | 2.671 | 1.00 | 1.08 |
| *Y* | 0.52 Al + 0.37 Li + 0.06 Mn2+ + 0.05 Fe2+ + 0.01 Mg | 10.79 | 10.69 | 2.017 | 2.017 | 1.95 | 2.15 |
| *Z* | 1.00 Al | 13.00 | 13.00 | 1.905 | 1.906 | 3.02 | 3.00 |
| *T* | 0.97 Si + 0.03 B | 14.00 | 13.78 | 1.617 | 1.617 | 4.01 | 3.98 |
| *B* | 1.00 B | 4.57 | 5.00 | 1.380 | 1.372 | 2.99 | 3.00 |
| EMP | (Na0.64□0.30Ca0.06K0.01)(Al1.52Li1.10Mn0.16Fe0.16Mg0.02)Al6.00B2.74O9[Si6.00O18](OH)3.00(F0.49OH0.26O0.25) | | | | | | |
| STR | (Na0.64□0.30Ca0.06K0.01)(Al1.55Li1.10Mn0.16Fe2+0.16Mg0.02)Al6.00B3.00O9[(Si5.85B0.15)O18](OH)3.00(F0.49OH0.27O0.24) | | | | | | |
| **WR065** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.57 Na + 0.40 □ + 0.02 Ca + 0.01 K | 7.26 | 6.80 | 2.610 | 2.670 | 0.97 | 1.04 |
| *Y* | 0.50 Li + 0.49 Al + 0.01 Mn2+ | 7.76 | 8.18 | 2.010 | 2.007 | 1.82 | 1.99 |
| *Z* | 1.00 Al | 12.47 | 13.00 | 1.905 | 1.906 | 3.03 | 3.00 |
| *T* | 0.98 Si + 0.02 B | 14.00 | 13.87 | 1.618 | 1.618 | 4.03 | 3.99 |
| *B* | 1.00 B | 5.00 | 5.00 | 1.380 | 1.375 | 2.97 | 3.00 |
| EMP | (Na0.57□0.41Ca0.02K0.01)(Li1.49Al1.44Mn0.03Fe0.01)Al6.00B2.75O9[Si6.00O18](OH)3.00(OH0.57F0.43) | | | | | | |
| STR | (Na0.57□0.41Ca0.02K0.01)(Li1.49Al1.47Mn0.03)Al6.00B3.00O9[(Si5.91B0.09)O18](OH)3.00(OH0.57F0.43) | | | | | | |
| **KM058-R** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.61 Na + 0.32 □ + 0.06 Ca + 0.01 K | 7.11 | 8.00 | 2.608 | 2.676 | 0.98 | 1.09 |
| *Y* | 0.45 Al + 0.45 Li + 0.07 Fe2+ + 0.02 Mn2+ + 0.01 Mg | 8.79 | 9.80 | 2.021 | 2.000 | 1.95 | 2.01 |
| *Z* | 1.00 Al | 13.00 | 13.00 | 1.905 | 1.908 | 3.01 | 3.00 |
| *T* | 0.99 Si + 0.01 B | 14.00 | 13.94 | 1.619 | 1.619 | 4.04 | 3.99 |
| *B* | 1.00 B | 5.00 | 5.00 | 1.380 | 1.374 | 2.98 | 3.00 |
| EMP | (Na0.61□0.33Ca0.06K0.01)(Al1.35Li1.34Fe0.22Mn0.08Mg0.02)Al6.04B2.81O9[(Si5.96)O18](OH)3.00(F0.51OH0.49) | | | | | | |
| STR | (Na0.61□0.33Ca0.06K0.01)(Al1.35Li1.34Fe2+0.22Mn0.08Mg0.02)Al6.00B3.00O9[(Si5.96B0.04)O18](OH)3.00(F0.51OH0.49) | | | | | | |
| **KM058-V** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.61 Na + 0.32 □ + 0.06 Ca + 0.01 K | 7.90 | 8.00 | 2.608 | 2.671 | 1.00 | 1.09 |
| *Y* | 0.46 Al + 0.44 Li + 0.07 Fe2+ + 0.02 Mn2+ + 0.01 Mg | 8.89 | 9.89 | 2.019 | 2.012 | 1.89 | 2.02 |
| *Z* | 1.00 Al | 11.49 | 13.00 | 1.905 | 1.908 | 3.02 | 3.00 |
| *T* | 0.97 Si + 0.03 B | 14.00 | 13.78 | 1.617 | 1.617 | 4.01 | 3.98 |
| *B* | 1.00 B | 5.00 | 5.00 | 1.380 | 1.374 | 2.98 | 3.00 |
| EMP | (Na0.61□0.33Ca0.06K0.01)(Al1.36Li1.34Fe0.22Mn0.08Mg0.02)Al6.04B2.81O9[(Si5.96)O18](OH)3.00(F0.51OH0.49) | | | | | | |
| STR | (Na0.61□0.33Ca0.06K0.01)(Al1.38Li1.31Fe2+0.22Mn0.08Mg0.02)Al6.00B3.00O9[(Si5.85B0.15)O18](OH)3.00(F0.51OH0.49) | | | | | | |
| **KM066** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.71 Na + 0.22 □ + 0.06 Ca + 0.01 K | 7.24 | 9.18 | 2.607 | 2.674 | 0.97 | 1.08 |
| *Y* | 0.40 Al + 0.42 Li + 0.10 Mn2+ + 0.06 Fe2+ + 0.01 Ti | 9.33 | 10.64 | 2.069 | 2.003 | 1.90 | 1.97 |
| *Z* | 1.00 Al | 13.00 | 13.00 | 1.905 | 1.906 | 3.03 | 3.00 |
| *T* | 0.98 Si + 0.02 B | 14.00 | 13.82 | 1.618 | 1.618 | 4.02 | 3.98 |
| *B* | 1.00 B | 5.00 | 5.00 | 1.380 | 1.369 | 3.02 | 3.00 |
| EMP | (Na0.71□0.22Ca0.06K0.01)(Li1.26Al1.19Mn0.29Fe0.18Ti0.02Mg0.01)Al6.00B2.83O9[Si6.00O18](OH)3.00(F0.62OH0.38) | | | | | | |
| STR | (Na0.71□0.22Ca0.06K0.01)(Li1.26Al1.20Mn0.29Fe2+0.18Ti0.02Mg0.01)Al6.00B3.00O9[(Si5.88B0.12)O18](OH)3.00(F0.62OH0.38) | | | | | | |
| **KM076** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.77 Na + 0.16 □ + 0.06 Ca + 0.01 K | 10.07 | 9.79 | 2.609 | 2.675 | 0.98 | 1.07 |
| *Y* | 0.39 Al + 0.37 Li + 0.10 Fe2+ + 0.09 Mn2+ + 0.05 Zn | 12.27 | 12.64 | 2.039 | 2.026 | 1.96 | 2.03 |
| *Z* | 1.00 Al | 13.00 | 13.00 | 1.905 | 1.908 | 3.01 | 3.00 |
| *T* | 0.98 Si + 0.02 B | 14.00 | 13.82 | 1.618 | 1.618 | 4.01 | 3.98 |
| *B* | 1.00 B | 5.00 | 5.00 | 1.380 | 1.372 | 2.99 | 3.00 |
| EMP | (Na0.78□0.16Ca0.06K0.01)(Al1.11Li1.10Fe0.32Mn0.28Zn0.18)Al6.00B2.80O9[Si6.00O18](OH)3.00(F0.69OH0.31) | | | | | | |
| STR | (Na0.78□0.16Ca0.06K0.01)(Al1.17Li1.10Fe2+0.30Mn0.26Zn0.17)Al6.00B3.00O9[(Si5.88B0.12)O18](OH)3.00(F0.69OH0.31) | | | | | | |
| **KM117** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.61 Na + 0.32 □ + 0.06 Ca + 0.01 K | 9.28 | 8.01 | 2.607 | 2.674 | 0.99 | 1.09 |
| *Y* | 0.51 Al + 0.40 Li + 0.05 Fe2+ + 0.04 Mn2+ | 10.58 | 10.24 | 2.010 | 2.012 | 1.93 | 2.11 |
| *Z* | 1.00 Al | 13.00 | 13.00 | 1.905 | 1.908 | 3.01 | 3.00 |
| *T* | 0.99 Si + 0.01 B | 14.00 | 13.91 | 1.619 | 1.619 | 4.03 | 3.99 |
| *B* | 1.00 B | 5.00 | 5.00 | 1.380 | 1.376 | 2.96 | 3.00 |
| EMP | (Na0.61□0.33Ca0.06K0.01)(Al1.52Li1.19Fe0.16Mn0.13)Al6.03B2.70O9[(Si5.97)O18](OH)3.00(F0.56OH0.40O0.04) | | | | | | |
| STR | (Na0.61□0.33Ca0.06K0.01)(Al1.52Li1.19Fe2+0.16Mn0.13)Al6.00B3.00O9[(Si5.94B0.06)O18](OH)3.00(F0.57OH0.40O0.03) | | | | | | |
| **KM118** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.54 Na + 0.42 □ + 0.03 Ca + 0.01 K | 7.48 | 6.58 | 2.610 | 2.666 | 0.99 | 1.04 |
| *Y* | 0.53 Al + 0.45 Li + 0.01 Mn2+ | 8.22 | 8.67 | 2.041 | 2.004 | 1.88 | 2.08 |
| *Z* | 1.00 Al | 13.00 | 13.00 | 1.905 | 1.906 | 3.02 | 3.00 |
| *T* | 0.95 Si + 0.05 B | 14.00 | 13.55 | 1.614 | 1.614 | 3.97 | 3.95 |
| *B* | 1.00 B | 5.00 | 5.00 | 1.380 | 1.376 | 2.96 | 3.00 |
| EMP | (Na0.54□0.43Ca0.03K0.01)(Al1.58Li1.35Mn0.04)Al6.00B2.78O9[Si6.00O18](OH)3.00(OH0.54F0.46) | | | | | | |
| STR | (Na0.54□0.43Ca0.03K0.01)(Al1.60Li1.35Mn0.04)Al6.00B3.00O9[(Si5.70B0.30)O18](OH)3.00(OH0.54F0.46) | | | | | | |
| **KM119** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.55 Na + 0.44 □ + 0.01 Ca | 7.47 | 6.25 | 2.611 | 2.677 | 0.95 | 1.02 |
| *Y* | 0.54 Al + 0.44 Li + 0.01 Mn2+ + 0.01 Fe2+ | 9.22 | 8.72 | 2.000 | 1.997 | 1.92 | 2.09 |
| *Z* | 1.00 Al | 12.90 | 13.00 | 1.905 | 1.908 | 3.01 | 3.00 |
| *T* | 0.99 Si + 0.01 B | 14.00 | 13.97 | 1.620 | 1.620 | 4.04 | 4.00 |
| *B* | 1.00 B | 5.00 | 5.00 | 1.380 | 1.375 | 2.97 | 3.00 |
| EMP | (Na0.55□0.44Ca0.01)(Al1.61Li1.34Mn0.03Fe0.02)Al6.04B2.74O9[(Si5.96)O18](OH)3.00(OH0.59F0.41) | | | | | | |
| STR | (Na0.55□0.44Ca0.01)(Al1.61Li1.34Mn0.03Fe2+0.02)Al6.00B3.00O9[(Si5.98B0.02)O18](OH)3.00(OH0.59F0.41) | | | | | | |
| **KM120** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.51 Na + 0.29 □ + 0.15 Ca + 0.05 Li | 7.50 | 8.81 | 2.629 | 2.672 | 0.98 | 1.21 |
| *Y* | 0.47 Al + 0.47 Li + 0.03 Ca + 0.02 Mn2+ + 0.01 Fe2+ | 8.63 | 8.59 | 2.061 | 2.002 | 1.90 | 1.98 |
| *Z* | 1.00 Al | 12.90 | 13.00 | 1.905 | 1.907 | 3.02 | 3.00 |
| *T* | 0.98 Si + 0.02 B | 14.00 | 13.87 | 1.618 | 1.618 | 4.02 | 3.99 |
| *B* | 1.00 B | 5.00 | 5.00 | 1.380 | 1.376 | 2.96 | 3.00 |
| EMP | (Na0.51□0.28Ca0.20K0.01)(Li1.52Al1.40Mn0.06Fe0.02)Al6.00B2.79O9[Si6.00O18](OH)3.00(F0.63OH0.37) | | | | | | |
| STR | (Na0.51□0.29Ca0.15Li0.05)(Li1.52Al1.40Ca0.10Mn0.06Fe2+0.02)Al6.00B3.00O9[(Si5.91B0.09)O18](OH)3.00(F0.63OH0.37) | | | | | | |
| **KM132** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.59 □ + 0.41 Na + 0.01 K | 4.62 | 4.54 | 2.613 | 2.712 | 0.84 | 1.00 |
| *Y* | 0.46 Fe2+ + 0.44 Al + 0.05 Li + 0.04 Zn + 0.01 Mn2+ | 19.06 | 19.28 | 2.030 | 2.033 | 2.37 | 2.39 |
| *Z* | 0.95Al + 0.05 Fe3+ | 13.00 | 13.65 | 1.911 | 1.913 | 3.01 | 3.00 |
| *T* | 0.99 Si + 0.01 B | 14.00 | 13.91 | 1.619 | 1.619 | 4.03 | 3.99 |
| *B* | 1.00 B | 5.00 | 5.00 | 1.380 | 1.373 | 2.98 | 3.00 |
| EMP | (□0.59Na0.40K0.01)(Fe1.62Al1.06Li0.15Zn0.12Mn0.04Mg0.01)Al6.00B2.81O9[Si6.00O18](OH)3.00(OH0.52O0.37F0.11) | | | | | | |
| STR | (□0.59Na0.41) (Fe2+1.38Al1.32Li0.15Zn0.12Mn0.04Mg0.01)(Al5.70Fe3+0.30)B3.00O9[(Si5.94B0.06)O18](OH)3.00(OH0.52O0.37F0.11) | | | | | | |
| **KF081** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.51 Na + 0.48 □ + 0.01 Ca | 6.80 | 5.84 | 2.610 | 2.675 | 0.94 | 1.02 |
| *Y* | 0.64 Al + 0.35 Li | 8.92 | 9.52 | 2.016 | 1.990 | 2.04 | 2.29 |
| *Z* | 1.00 Al | 12.82 | 13.00 | 1.905 | 1.906 | 3.03 | 3.00 |
| *T* | 0.99 Si + 0.01 B | 14.00 | 13.91 | 1.619 | 1.619 | 4.03 | 3.99 |
| *B* | 1.00 B | 5.00 | 5.00 | 1.380 | 1.376 | 2.96 | 3.00 |
| EMP | (Na0.51□0.48Ca0.01)(Al1.93Li1.06Mn0.01)Al6.04B2.72O9[(Si5.96)O18](OH)3.00(OH0.42O0.36F0.23) | | | | | | |
| STR | (Na0.51□0.48Ca0.01)(Al1.93Li1.06Mn0.01)Al6.00B3.00O9[(Si5.94B0.06)O18](OH)3.00(OH0.42O0.36F0.23) | | | | | | |
| **WR045** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.58 Na + 0.22 Ca + 0.20 Li + 0.01 K | 10.68 | 11.39 | 2.585 | 2.669 | 0.88 | 1.22 |
| *Y* | 0.31 Al + 0.39 Li + 0.18 Fe2+ + 0.06 Mn2+ + 0.04 Ca + 0.02 Mg + 0.01 Ti | 13.81 | 12.51 | 2.108 | 2.040 | 1.93 | 1.93 |
| *Z* | 1.00 Al | 12.84 | 13.00 | 1.905 | 1.909 | 3.00 | 3.00 |
| *T* | 0.99 Si + 0.01 B | 14.00 | 13.91 | 1.619 | 1.619 | 4.03 | 3.99 |
| *B* | 1.00 B | 5.00 | 5.00 | 1.380 | 1.371 | 3.01 | 3.00 |
| EMP | (Na0.58Ca0.32□0.09K0.01)(Li1.37Al0.82Fe0.56Mn0.17Mg0.05Ti0.03)Al6.09B2.80O9[(Si5.91)O18](OH)3.00(F0.66OH0.34) | | | | | | |
| STR | (Na0.58Ca0.17Li0.15□0.09K0.01)(Li1.17Al0.92Fe2+0.56Mn0.17Ca0.10Mg0.05Ti0.03)Al6.00B3.00O9[(Si5.94B0.06)O18](OH)3.00(F0.66OH0.34) | | | | | | |
| **KM075** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.82 Na + 0.14 □ + 0.03 Ca + 0.01 K | 10.53 | 9.75 | 2.611 | 2.675 | 0.97 | 1.03 |
| *Y* | 0.33 Al + 0.32 Li + 0.28 Fe2+ + 0.04 Mn2+ + 0.02 Mg + 0.01 Ti | 13.29 | 13.65 | 2.037 | 2.026 | 1.84 | 1.98 |
| *Z* | 1.00 Al | 13.00 | 13.00 | 1.905 | 1.908 | 3.01 | 3.00 |
| *T* | 0.98 Si + 0.02 B | 14.00 | 13.87 | 1.618 | 1.618 | 4.02 | 3.99 |
| *B* | 1.00 B | 5.00 | 5.00 | 1.380 | 1.372 | 2.99 | 3.00 |
| EMP | (Na0.82□0.14Ca0.03K0.01)(Al0.98Li0.95Fe0.83Mn0.11Mg0.05Ti0.01)Al6.00B2.84O9[Si6.00O18](OH)3.00(F0.69OH0.23O0.09) | | | | | | |
| STR | (Na0.82□0.14Ca0.03K0.01)(Al0.98Li0.95Fe2+0.83Mn0.11Mg0.05Ti0.02)Al6.00B3.00O9[(Si5.91B0.09)O18](OH)3.00(F0.69OH0.23O0.09) | | | | | | |
| **U13757** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.56 Na + 0.41 □ + 0.02 Ca + 0.01 K | 7.74 | 6.73 | 2.612 | 2.667 | 0.99 | 1.03 |
| *Y* | 0.51 Al + 0.46 Li + 0.02 Mn2+ | 8.48 | 8.67 | 2.006 | 2.001 | 1.90 | 2.05 |
| *Z* | 1.00 Al | 13.00 | 13.00 | 1.905 | 1.904 | 3.04 | 3.00 |
| *T* | 0.95 Si + 0.05 B | 14.00 | 13.55 | 1.614 | 1.614 | 3.97 | 3.95 |
| *B* | 1.00 B | 5.00 | 5.00 | 1.380 | 1.374 | 2.98 | 3.00 |
| EMP | (Na0.56□0.41Ca0.02K0.01)(Al1.54Li1.38Mn0.07)Al6.00B2.74O9[(Si5.96Al0.04)O18](OH)3.00(OH0.57F0.43) | | | | | | |
| STR | (Na0.56□0.41Ca0.02K0.01)(Al1.54Li1.39Mn0.07)Al6.00B3.00O9[(Si5.70B0.30)O18](OH)3.00(OH0.57F0.43) | | | | | | |
| **U20662** | | | | | | | |
| Site | ASP | RSS | CSS | CBL | MBL | BVS | TV |
| *X* | 0.67 Na + 0.26 □ + 0.06 Ca + 0.01 K | 9.12 | 8.64 | 2.607 | 2.672 | 1.00 | 1.08 |
| *Y* | 0.43 Al + 0.41 Li + 0.09 Fe2+ + 0.07 Mn2+ | 11.18 | 10.99 | 2.029 | 2.022 | 1.91 | 2.03 |
| *Z* | 1.00 Al | 12.26 | 13.00 | 1.905 | 1.907 | 3.02 | 3.00 |
| *T* | 0.99 Si + 0.01 B | 14.00 | 13.91 | 1.619 | 1.619 | 4.03 | 3.99 |
| *B* | 1.00 B | 5.00 | 5.00 | 1.380 | 1.372 | 2.99 | 3.00 |
| EMP | (Na0.67□0.27Ca0.06K0.01)(Al1.30Li1.21Fe0.26Mn0.22)Al6.07B2.79O9[(Si5.93)O18](OH)3.00(F0.62OH0.38) | | | | | | |
| STR | (Na0.67□0.27Ca0.06K0.01)(Al1.30Li1.21Fe2+0.26Mn0.22)Al6.00B3.00O9[(Si5.94B0.06)O18](OH)3.00(F0.62OH0.38) | | | | | | |