

**a**

| Sample ID                                                      | DIG-1A |       |       |       |       | DIG-1B |       | TER-1A |       | TER-1B |       |       | NAG-3B |       |
|----------------------------------------------------------------|--------|-------|-------|-------|-------|--------|-------|--------|-------|--------|-------|-------|--------|-------|
| Target                                                         | 1      | 2     | 4     | 5     | 6     | 2      | 3     | 1      | 2     | 1      | 2     | 3     | 2      | 3     |
|                                                                | C      | C     | C     | C     | C     | C      | C     | C      | C     | C      | C     | C     | C      | C     |
| Mn                                                             | 55.44  | 59.04 | 58.57 | 60.12 | 59.66 | 59.13  | 56.54 | 57.47  | 57.67 | 60.94  | 58.14 | 58.48 | 57.16  | 58.44 |
| Al                                                             | 2.10   | 0.75  | 0.89  | 0.32  | 0.38  | 0.50   | 1.50  | 1.29   | 1.26  | 0.42   | 1.05  | 0.60  | 0.72   | 0.75  |
| Fe                                                             | 0.36   | 0.01  | 0.06  | 0.00  | 0.18  | 0.00   | 0.00  | 0.03   | 0.21  | 0.00   | 0.36  | 0.00  | 0.00   | 0.07  |
| K                                                              | 2.61   | 2.36  | 2.38  | 1.99  | 2.19  | 1.34   | 2.05  | 3.00   | 2.62  | 1.06   | 3.22  | 2.52  | 2.45   | 2.49  |
| Na                                                             | 0.27   | 0.25  | 0.27  | 0.30  | 0.27  | 0.19   | 0.24  | 0.25   | 0.33  | 0.16   | 0.22  | 0.46  | 0.08   | 0.03  |
| Zn                                                             | 0.04   | 0.02  | 0.03  | 0.02  | 0.03  | 0.023  | 0.027 | 0.029  | 0.020 | 0.030  | 0.020 | 0.029 | 0.021  | 0.036 |
| Co                                                             | 0.06   | 0.05  | 0.05  | 0.12  | 0.05  | 0.036  | 0.046 | 0.098  | 0.120 | 0.120  | 0.060 | 0.268 | 0.023  | 0.029 |
| Ba                                                             | 1.36   | 0.40  | 0.52  | 0.03  | 0.06  | 0.804  | 1.480 | 0.108  | 0.290 | 0.110  | 0.050 | 0.228 | 2.215  | 0.332 |
| Ni                                                             | 0.01   | 0     | 0     | 0     | 0     | 0      | 0.006 | 0.068  | 0.040 | 0.010  | 0.030 | 0.031 | 0.010  | 0.006 |
| Ti                                                             | 0.01   | 0     | 0     | 0     | 0     | 0.005  | 0.006 | 0      | 0.001 | 0      | 0.003 | 0     | 0.013  | 0.001 |
| Mg                                                             | 0.01   | 0     | 0     | 0     | 0     | 0.002  | 0.004 | 0.009  | 0.020 | 0.010  | 0.010 | 0.024 | 0.012  | 0.007 |
| Si                                                             | 0.25   | 0.20  | 0.08  | 0.05  | 0.05  | 0.08   | 0.17  | 0.11   | 0.12  | 0.08   | 0.13  | 0.07  | 0.10   | 0.10  |
| Ca                                                             | 0.05   | 0.04  | 0.04  | 0.04  | 0.02  | 0.03   | 0.03  | 0.06   | 0.07  | 0.07   | 0.05  | 0.17  | 0.21   | 0.13  |
| O                                                              | 35.39  | 35.95 | 35.70 | 35.93 | 35.78 | 35.50  | 35.19 | 35.55  | 35.68 | 36.32  | 35.85 | 35.55 | 34.95  | 35.48 |
| Total                                                          | 97.96  | 99.08 | 98.58 | 98.93 | 98.67 | 97.93  | 97.29 | 98.08  | 98.45 | 99.33  | 99.19 | 98.43 | 97.97  | 97.92 |
| Stoichiometric composition of cryptomelane based on 16 oxygens |        |       |       |       |       |        |       |        |       |        |       |       |        |       |
| K                                                              | 0.48   | 0.43  | 0.44  | 0.36  | 0.40  | 0.25   | 0.38  | 0.55   | 0.48  | 0.19   | 0.59  | 0.46  | 0.46   | 0.46  |
| Mn <sup>IV</sup>                                               | 7.52   | 7.57  | 7.56  | 7.64  | 7.60  | 7.75   | 7.62  | 7.45   | 7.52  | 7.81   | 7.41  | 7.54  | 7.54   | 7.54  |
| Mn <sup>III</sup>                                              | 0.48   | 0.43  | 0.44  | 0.36  | 0.40  | 0.25   | 0.38  | 0.55   | 0.48  | 0.19   | 0.59  | 0.46  | 0.46   | 0.46  |

C = Cryptomelane; C-Fe =Cryptomelane and iron  
oxy-hydroxide

TABLE DR4

b

| Sample ID                                                      | ILV-1B |       |       |       | ILV-2C |       | ILV-3A |       | ILV-3C |       |       |       | ILV-6A |       |       |       |       | ILV-6B |       |       |
|----------------------------------------------------------------|--------|-------|-------|-------|--------|-------|--------|-------|--------|-------|-------|-------|--------|-------|-------|-------|-------|--------|-------|-------|
| Target                                                         | 1      | 3     | 4     | 5     | 1      | 4     | 1      | 2     | 1      | 2     | 3     | 4     | 1      | 2     | 3     | 4     | 5     | 3      | 4     | 6     |
|                                                                | C      | C     | C     | C     | C      | C     | C      | C     | C      | C     | C     | C     | C      | C     | C     | C     | C     | C      | C     | C     |
| Mn                                                             | 57.98  | 58.99 | 57.57 | 56.82 | 57.54  | 57.57 | 58.43  | 59.21 | 59.43  | 59.17 | 58.59 | 59.03 | 58.97  | 58.35 | 58.27 | 51.37 | 57.69 | 57.36  | 58.70 | 59.00 |
| Al                                                             | 0.45   | 0.18  | 0.77  | 1.02  | 1.15   | 1.15  | 0.63   | 0.40  | 0.35   | 0.43  | 0.45  | 0.50  | 0.32   | 0.29  | 0.26  | 1.94  | 0.38  | 0.96   | 0.42  | 0.23  |
| Fe                                                             | 0.14   | 0.12  | 0.28  | 0.55  | 0.00   | 0.04  | 0.00   | 0.00  | 0.00   | 0.04  | 0.27  | 0.18  | 0.00   | 0.00  | 0.00  | 0.00  | 0.00  | 0.03   | 0.00  | 0.00  |
| K                                                              | 3.05   | 2.89  | 2.72  | 2.17  | 3.43   | 3.19  | 2.67   | 2.37  | 2.37   | 2.36  | 2.70  | 2.74  | 2.59   | 2.13  | 3.03  | 2.70  | 3.29  | 3.12   | 2.59  | 2.31  |
| Na                                                             | 0.39   | 0.33  | 0.20  | 0.21  | 0.41   | 0.03  | 0.22   | 0.29  | 0.20   | 0.25  | 0.25  | 0.20  | 0.34   | 0.26  | 0.41  | 0.26  | 0.35  | 0.19   | 0.33  | 0.35  |
| Zn                                                             | 0.030  | 0.010 | 0.025 | 0.017 | 0.030  | 0.028 | 0.018  | 0.014 | 0.020  | 0.010 | 0.010 | 0.016 | 0.041  | 0.050 | 0.041 | 0.050 | 0.070 | 0.030  | 0.050 | 0.050 |
| Co                                                             | 0.020  | 0.010 | 0.026 | 0.020 | 0.060  | 0.087 | 0.007  | 0.008 | 0.005  | 0.003 | 0.003 | 0.003 | 0.119  | 0.070 | 0.093 | 0.090 | 0.320 | 0.079  | 0.120 | 0.090 |
| Ba                                                             | 0.002  | 0.007 | 0.123 | 0.168 | 0.010  | 0.086 | 0.276  | 0.164 | 0.190  | 0.120 | 0.110 | 0.153 | 0.038  | 0.190 | 0.075 | 0.900 | 0.190 | 0.620  | 0.330 | 0.200 |
| Ni                                                             | 0.010  | 0.005 | 0.020 | 0.018 | 0.100  | 0.096 | 0.010  | 0.008 | 0.009  | 0.001 | 0.017 | 0.012 | 0.007  | 0.010 | 0.006 | 0.030 | 0.030 | 0.011  | 0.010 | 0.010 |
| Ti                                                             | 0.001  | 0.001 | 0.003 | 0     | 0      | 0     | 0.003  | 0.002 | 0.001  | 0.002 | 0.001 | 0.001 | 0      | 0     | 0.001 | 0.004 | 0     | 0.002  | 0.004 | 0.002 |
| Mg                                                             | 0.010  | 0.010 | 0.089 | 0.109 | 0.020  | 0.022 | 0.007  | 0.008 | 0.007  | 0.004 | 0.010 | 0.009 | 0.010  | 0.007 | 0.005 | 0.010 | 0.010 | 0.007  | 0.010 | 0.007 |
| Si                                                             | 0.13   | 0.14  | 0.14  | 0.15  | 0.10   | 0.07  | 0.13   | 0.08  | 0.14   | 0.14  | 0.14  | 0.08  | 0.69   | 0.20  | 0.19  | 0.24  | 0.06  | 0.21   | 0.07  | 0.06  |
| Ca                                                             | 0.07   | 0.06  | 0.20  | 0.23  | 0.12   | 0.14  | 0.08   | 0.08  | 0.07   | 0.07  | 0.11  | 0.08  | 0.14   | 0.18  | 0.10  | 0.18  | 0.18  | 0.18   | 0.17  | 0.18  |
| O                                                              | 35.17  | 35.48 | 35.25 | 35.04 | 35.61  | 35.55 | 35.45  | 35.59 | 35.71  | 35.63 | 35.47 | 35.66 | 35.47  | 35.13 | 35.23 | 32.79 | 35.02 | 35.40  | 35.45 | 35.38 |
| Total                                                          | 97.45  | 98.23 | 97.41 | 97.41 | 98.58  | 98.06 | 97.93  | 98.23 | 98.50  | 98.23 | 98.13 | 98.67 | 98.74  | 96.87 | 97.72 | 90.56 | 97.59 | 98.21  | 98.25 | 97.87 |
| Stoichiometric composition of cryptomelane based on 16 oxygens |        |       |       |       |        |       |        |       |        |       |       |       |        |       |       |       |       |        |       |       |
| K                                                              | 0.57   | 0.53  | 0.51  | 0.41  | 0.63   | 0.59  | 0.50   | 0.44  | 0.44   | 0.43  | 0.50  | 0.50  | 0.48   | 0.40  | 0.56  | 0.54  | 0.62  | 0.58   | 0.48  | 0.43  |
| Mn <sup>IV</sup>                                               | 7.43   | 7.47  | 7.49  | 7.59  | 7.37   | 7.41  | 7.50   | 7.56  | 7.56   | 7.57  | 7.50  | 7.50  | 7.52   | 7.60  | 7.44  | 7.46  | 7.38  | 7.42   | 7.52  | 7.57  |
| Mn <sup>III</sup>                                              | 0.57   | 0.53  | 0.51  | 0.41  | 0.63   | 0.59  | 0.50   | 0.44  | 0.44   | 0.43  | 0.50  | 0.50  | 0.48   | 0.40  | 0.56  | 0.54  | 0.62  | 0.58   | 0.48  | 0.43  |

C = Cryptomelane; C-Fe =Cryptomelane and iron oxy-hydroxide

TABLE DR4

**C**

| Sample ID                                                      | PRA-1B |       |       |       | PRA-2A |       |       | PRA-2B |       |       |       |       | PRA-3B |
|----------------------------------------------------------------|--------|-------|-------|-------|--------|-------|-------|--------|-------|-------|-------|-------|--------|
| Target                                                         | 1      | 2     | 3     | 4     | 1      | 2     | 3     | 1      | 2     | 3     | 4     | 5     | 2      |
|                                                                | C-Fe   | C     | C-Fe  | C-Fe  | C      | C     | C     | C      | C-Fe  | C     | C-Fe  | C     | C      |
| Mn                                                             | 44.89  | 59.56 | 37.62 | 42.15 | 57.86  | 57.21 | 57.26 | 57.18  | 41.76 | 57.26 | 52.19 | 46.41 | 58.37  |
| Al                                                             | 4.04   | 0.26  | 1.85  | 4.23  | 1.13   | 1.40  | 1.33  | 1.15   | 1.84  | 1.33  | 2.43  | 1.17  | 0.87   |
| Fe                                                             | 9.82   | 0.06  | 19.12 | 11.95 | 0.39   | 0.30  | 0.41  | 0.35   | 15.19 | 0.41  | 3.48  | 1.30  | 0.00   |
| K                                                              | 1.86   | 3.71  | 2.19  | 1.55  | 4.25   | 4.03  | 4.02  | 4.01   | 2.00  | 4.02  | 2.50  | 3.12  | 2.23   |
| Na                                                             | 0.21   | 0.35  | 0.24  | 0.17  | 0.30   | 0.31  | 0.38  | 0.32   | 0.21  | 0.38  | 0.23  | 0.20  | 0.74   |
| Zn                                                             | 0      | 0.007 | 0.010 | 0.010 | 0.001  | 0.005 | 0     | 0      | 0.007 | 0     | 0.003 | 0.001 | 0.004  |
| Co                                                             | 0      | 0.012 | 0     | 0     | 0.009  | 0.007 | 0.009 | 0.003  | 0     | 0.010 | 0.001 | 0.010 | 0.009  |
| Ba                                                             | 0.041  | 0     | 0     | 0.070 | 0      | 0     | 0     | 0      | 0.012 | 0     | 0.050 | 0     | 0      |
| Ni                                                             | 0      | 0.001 | 0     | 0.001 | 0      | 0     | 0.004 | 0      | 0.021 | 0.004 | 0.030 | 0.002 | 0.004  |
| Ti                                                             | 0.066  | 0.003 | 0.120 | 0.100 | 0.001  | 0.003 | 0.003 | 0.002  | 0.008 | 0.002 | 0.010 | 0.003 | 0.004  |
| Mg                                                             | 0.018  | 0.003 | 0.070 | 0.020 | 0.002  | 0.003 | 0.004 | 0      | 0.068 | 0.004 | 0.080 | 0.003 | 0.012  |
| Si                                                             | 0.42   | 0.07  | 0.60  | 0.52  | 0.16   | 0.21  | 0.19  | 0.14   | 0.33  | 0.19  | 0.27  | 0.23  | 0.07   |
| Ca                                                             | 0.06   | 0.02  | 0.04  | 0.07  | 0.02   | 0.02  | 0.02  | 0.02   | 0.04  | 0.02  | 0.06  | 0.02  | 0.11   |
| O                                                              | 33.56  | 35.92 | 30.40 | 32.83 | 35.99  | 35.83 | 35.84 | 35.52  | 31.25 | 35.84 | 34.55 | 29.43 | 35.63  |
| Total                                                          | 94.98  | 99.97 | 92.26 | 93.67 | 100.13 | 99.33 | 99.47 | 98.69  | 92.74 | 99.47 | 95.88 | 81.90 | 98.06  |
| Stoichiometric composition of cryptomelane based on 16 oxygens |        |       |       |       |        |       |       |        |       |       |       |       |        |
| K                                                              | 0.36   | 0.68  | 0.47  | 0.31  | 0.78   | 0.74  | 0.74  | 0.74   | 0.42  | 0.74  | 0.47  | 0.70  | 0.41   |
| Mn <sup>IV</sup>                                               | 7.64   | 7.32  | 7.53  | 7.69  | 7.22   | 7.26  | 7.26  | 7.26   | 7.58  | 7.26  | 7.53  | 7.30  | 7.59   |
| Mn <sup>III</sup>                                              | 0.36   | 0.68  | 0.47  | 0.31  | 0.78   | 0.74  | 0.74  | 0.74   | 0.42  | 0.74  | 0.47  | 0.70  | 0.41   |

C = Cryptomelane; C-Fe =Cryptomelane and iron oxy-hydroxide

TABLE DR4