## On-Line Supplementary Material to accompany

### "The effects of metamorphism on O and Fe isotope compositions in the Biwabik Iron Formation, northern, Minnesota"

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from Valaas (2004)

**Table S1.** Modal abundances (%) and grain size for Biwabik banded iron formation.

| Sample 03-BIW- | Mt size (μm) | Magnetite | Fe Silicate | Carbonate | Quartz |
|---|---|---|---|---|---|
| 39C | 1210 | 19 | 15 | 0 | 66 |
| 40B * | | 13 | 47 | 0 | 40 |
| 43E | | 28 | 40 | 0 | 32 |
| 43D | 394 | | | | |
| 18E | | 28 | 15 | 0 | 57 |
| 18C | 410 | 24 | 26 | 0 | 51 |
| 17E | | 22 | 46 | 0 | 32 |
| 17D | | 19 | 65 | 0 | 16 |
| 17B | 454 | | | | |
| 12C | 468 | 18 | 45 | 0 | 37 |
| 12D | | 15 | 30 | 0 | 55 |
| 6A | | 17 | 22 | 0 | 61 |
| 8D | | 25 | 37 | 0 | 38 |
| 3E | 448 | 27 | 21 | 0 | 52 |
| 3B * | | 30 | 45 | 0 | 25 |
| 22C | | 20 | 45 | 0 | 35 |
| 22B | 870 | 23 | 30 | 0 | 47 |
| 22E | | 20 | 52 | 0 | 28 |
| 23B-1 | 1100 | | | | |
| 23B-2 | 840 | | | | |
| 31D | 1100 | 18 | 55 | 0 | 27 |
| 31C | | 20 | 65 | 0 | 15 |
| 31A | 900 | | | | |
| 44B-1 * | | 25 | 22 | 0 | 53 |
| 44D | | 33 | 35 | 0 | 32 |
| 44C | | 35 | 30 | 0 | 35 |
| 44A * | 150 | 35 | 50 | 0 | 15 |
| 34A | | 25 | 55 | 0 | 20 |
| 34C | 10 | 45 | 35 | 1 | 19 |
| 34B | 10 | | | | |
| 34D | 10 | | | | |
| 34E | 10 | | | | |
| 35B-1 | | 13 | 40 | 5 | 42 |
| 35E | | 37 | 7 | 6 | 50 |
| 36M | | 40 | 5 | 8 | 47 |

Modal (volume) abundances determined by image analysis. Data obtained on thin sections, except where noted "*", where data were obtained on thick sections. Quartz component determined by difference, and includes additional minor phases.

## APPENDIX 1

### Correction of $\delta^{18}O$ (Mt)

To correct the $\delta^{18}O$ of sawed magnetite pieces for silicate contamination, the $\delta^{18}O$ (of silicates) was estimated from the weight of residue after dissolution of magnetite in HCl. These minerals, identified in thin section, include quartz, greenalite, minnesotaite, and stilpnomelane in low grade rocks; and quartz, grunerite, hedenbergite, and fayalite at higher grade. The percentages of quartz vs. other silicates were estimated from grain mounts of the residue in refractive index oil (RI = 1.558) using a petrographic microscope. The other silicates were approximated as diopside. Quartz contamination was based on measured $\delta^{18}O$ (Qt). Minerals other than quartz were assigned $\delta^{18}O$ diopside values calculated from $\Delta^{18}O$ (Qt-Di) (Table S2; Clayton and Kieffer, 1991):

$$1000 \ln\alpha \text{ (Qt-Di)} = (2.75*10^6)/(T)^2 \qquad \text{T in °K} \qquad \textbf{(A1)}$$

using the measured $\delta^{18}O$ (Qt) and apparent temperature from the $\Delta^{18}O$ (Qt-Mt) thermometer (Clayton and Kieffer, 1991):

$$1000 \ln\alpha \text{ (Qt-Mt)} = (6.29*10^6)/(T)^2 \qquad \text{T in °K} \qquad \textbf{(A2)}$$

calculated with measured $\delta^{18}O$ (Mt) (Table S2). The values of $\delta^{18}O$ of quartz and diopside were subtracted from $\delta^{18}O$ (Mt) in proportion to their percentage of contamination to find corrected $\delta^{18}O$ (Mt) values (Table S2). Iteration using the corrected $\delta^{18}O$ (Mt) value when solving for $\delta^{18}O$ diopside changed the final apparent temperature by at most 12°C, with differences of 0-5°C more common.

**Table S2.** Correction for silicate impurity of $\delta^{18}O$ of 1 $mm^3$ pieces of magnetite cut from thick microscope sections (see text). Measured and calculated $\delta^{18}O$ values, starting mass and mass after HCl dissolution, Wt % of magnetite, diopside and quartz, mol fraction oxygen, and corrected magnetite $\delta^{18}O$ values. Qt = quartz, Mt = magnetite, Di = diopside, and VSMOW = Vienna standard mean ocean water.

| Sample # 03-BIW- | Measured $\delta^{18}O$ (Qt) ‰ VSMOW | Measured $\delta^{18}O$ (Mt) ‰ VSMOW | Calculated* $\delta^{18}O$ (Di) ‰ VSMOW | Start mass (mg) | End mass (mg) | Wt% Mt | Wt% Di | Wt% Qt | Mol fraction Oxygen (Mt) | Corrected $\delta^{18}O$(Mt)‰ |
|---|---|---|---|---|---|---|---|---|---|---|
| 22B | 14.51 | 7.78 | 11.57 | 2.95 | 0.10 | 96.65 | 2.35 | 1.01 | 0.93 | 7.46 |
| | 14.51 | 7.86 | 11.61 | 2.95 | 0.10 | 96.65 | 2.35 | 1.01 | 0.93 | 7.54 |
| 22C | 13.88 | 7.68 | 11.17 | 14.99 | 0.14 | 99.08 | 0.92 | 0.00 | 0.98 | 7.62 |
| | 13.88 | 7.68 | 11.17 | 14.99 | 0.14 | 99.08 | 0.92 | 0.00 | 0.98 | 7.62 |
| 22D | 14.36 | 7.86 | 11.52 | 4.29 | 0.02 | 99.63 | 0.37 | 0.00 | 0.99 | 7.83 |
| | 14.36 | 7.51 | 11.36 | 4.29 | 0.02 | 99.63 | 0.37 | 0.00 | 0.99 | 7.48 |
| 22E | 14.42 | 7.60 | 11.44 | 12.78 | 0.04 | 99.66 | 0.20 | 0.00 | 1.00 | 7.59 |
| | 14.42 | 7.58 | 11.43 | 12.78 | 0.04 | 99.66 | 0.20 | 0.00 | 1.00 | 7.57 |
| 23A | 14.60 | 7.68 | 11.57 | 23.57 | 0.02 | 99.92 | 0.08 | 0.00 | 1.00 | 7.68 |
| | 14.60 | 7.69 | 11.58 | 23.57 | 0.02 | 99.92 | 0.08 | 0.00 | 1.00 | 7.69 |
| 23B-1 | 14.45 | 8.11 | 11.68 | 17.93 | 0.27 | 98.51 | 1.49 | 0.00 | 0.97 | 8.00 |
| | 14.45 | 7.97 | 11.62 | 17.93 | 0.27 | 98.51 | 1.49 | 0.00 | 0.97 | 7.86 |
| | 14.45 | 7.87 | 11.57 | 17.93 | 0.27 | 98.51 | 1.49 | 0.00 | 0.97 | 7.75 |
| 23B-2 | 14.53 | 7.54 | 11.48 | 8.51 | 0.04 | 99.54 | 0.46 | 0.00 | 0.99 | 7.51 |
| | 14.53 | 7.45 | 11.44 | 8.51 | 0.04 | 99.54 | 0.46 | 0.00 | 0.99 | 7.41 |
| 23E | 14.33 | 7.41 | 11.30 | 10.18 | 0.06 | 99.46 | 0.32 | 0.22 | 0.99 | 7.36 |
| | 14.33 | 7.71 | 11.44 | 10.18 | 0.06 | 99.46 | 0.32 | 0.22 | 0.99 | 7.66 |
| 27A | 14.63 | 8.42 | 11.91 | 2.90 | 0.24 | 91.91 | 8.09 | 0.00 | 0.85 | 7.79 |
| | 14.63 | 8.62 | 12.00 | 2.90 | 0.24 | 91.91 | 8.09 | 0.00 | 0.85 | 8.01 |
| 27B | 15.14 | 7.00 | 11.58 | 3.66 | 0.19 | 94.83 | 5.17 | 0.00 | 0.90 | 6.49 |
| | 15.14 | 7.07 | 11.61 | 3.66 | 0.19 | 94.80 | 5.20 | 0.00 | 0.90 | 6.56 |
| 30D | 13.25 | 5.65 | 9.93 | 4.67 | 0.10 | 97.95 | 1.23 | 0.82 | 0.96 | 5.42 |
| | 13.25 | 5.85 | 10.02 | 4.67 | 0.10 | 97.95 | 1.23 | 0.82 | 0.96 | 5.62 |
| 31A | 14.65 | 7.73 | 11.63 | 3.34 | 0.02 | 99.52 | 0.34 | 0.34 | 0.99 | 7.66 |
| | 14.65 | 7.97 | 11.73 | 3.34 | 0.02 | 99.52 | 0.34 | 0.34 | 0.99 | 7.90 |
| 31C | 14.77 | 9.97 | 12.67 | 6.87 | 1.08 | 84.23 | 11.04 | 4.73 | 0.73 | 8.72 |
| | 14.77 | 8.67 | 12.10 | 6.87 | 1.08 | 84.23 | 11.04 | 4.73 | 0.73 | 7.08 |
| 31D | 14.97 | 8.39 | 12.09 | 4.70 | 0.07 | 98.55 | 1.45 | 0.00 | 0.97 | 8.28 |
| | 14.97 | 8.34 | 12.07 | 4.70 | 0.07 | 98.55 | 1.45 | 0.00 | 0.97 | 8.23 |
| | 14.97 | 8.55 | 12.16 | 4.70 | 0.07 | 98.55 | 1.45 | 0.00 | 0.97 | 8.44 |
| | 14.97 | 8.22 | 12.02 | 4.70 | 0.07 | 98.55 | 1.45 | 0.00 | 0.97 | 8.12 |
| 32B | 14.20 | 6.57 | 10.86 | 11.73 | 0.61 | 94.79 | 5.21 | 0.00 | 0.90 | 6.08 |
| | 14.20 | 6.33 | 10.76 | 11.73 | 0.61 | 94.79 | 5.21 | 0.00 | 0.90 | 5.83 |
| 44A | 17.23 | 7.23 | 12.86 | 6.13 | 0.35 | 94.22 | 5.78 | 0.00 | 0.89 | 6.52 |
| | 17.23 | 7.11 | 12.81 | 6.13 | 0.35 | 94.22 | 5.78 | 0.00 | 0.89 | 6.39 |
| 44B-1 | 16.08 | 6.01 | 11.68 | 2.64 | 0.16 | 93.79 | 4.34 | 1.86 | 0.88 | 5.08 |
| | 16.08 | 5.94 | 11.65 | 2.64 | 0.16 | 93.79 | 4.34 | 1.86 | 0.88 | 5.01 |

* Calculated using measured $\delta^{18}O$ and apparent temperatures calculated from the uncorrected $\Delta^{18}O$ (Qt-Mt)

## Table S2 Continued

| Sample # 03-BIW- | Measured $\delta^{18}O$ (Qt) ‰ VSMOW | Measured $\delta^{18}O$ (Mt) ‰ VSMOW | Calculated* $\delta^{18}O$ (Di) ‰ VSMOW | Start mass (mg) | End mass (mg) | Wt% Mt | Wt% Di | Wt% Qt | Mol fraction Oxygen (Mt) | Corrected $\delta^{18}O$(Mt)‰ |
|---|---|---|---|---|---|---|---|---|---|---|
| 44C | 16.75 | 6.90 | 12.45 | 7.77 | 0.22 | 97.19 | 2.81 | 0.00 | 0.94 | 6.57 |
| | 16.75 | 6.98 | 12.48 | 7.77 | 0.22 | 97.19 | 2.81 | 0.00 | 0.94 | 6.66 |
| | 16.75 | 6.70 | 12.36 | 13.99 | 0.72 | 94.86 | 5.14 | 0.00 | 0.90 | 6.07 |
| | 16.75 | 8.29 | 13.05 | 13.99 | 0.72 | 94.86 | 5.14 | 0.00 | 0.90 | 7.76 |
| | 16.75 | 7.46 | 12.69 | 6.34 | 0.47 | 92.65 | 7.35 | 0.00 | 0.86 | 6.61 |
| | 16.75 | 7.48 | 12.70 | 6.34 | 0.47 | 92.65 | 7.35 | 0.00 | 0.86 | 6.63 |
| 44D | 16.76 | 6.52 | 12.29 | 7.79 | 0.29 | 96.33 | 3.67 | 0.00 | 0.93 | 6.07 |
| 34A | 17.00 | 4.38 | 11.49 | 9.06 | 1.37 | 84.85 | 15.15 | 0.00 | 0.73 | 1.77 |
| | 17.00 | 4.23 | 11.42 | 9.06 | 1.37 | 84.85 | 15.15 | 0.00 | 0.73 | 1.59 |
| | 17.00 | 3.77 | 11.22 | 3.41 | 0.41 | 87.88 | 12.12 | 0.00 | 0.78 | 1.65 |
| | 17.00 | 3.51 | 11.10 | 3.41 | 0.41 | 87.88 | 12.12 | 0.00 | 0.78 | 1.35 |
| 34B | 17.27 | 2.49 | 10.81 | 6.93 | 0.35 | 94.98 | 5.02 | 0.00 | 0.90 | 1.59 |
| | 17.27 | 2.49 | 10.81 | 6.93 | 0.35 | 94.98 | 5.02 | 0.00 | 0.90 | 1.59 |
| 34C | 16.87 | 5.09 | 11.72 | 5.31 | 0.73 | 86.19 | 13.81 | 0.00 | 0.75 | 2.90 |
| | 16.87 | 4.64 | 11.52 | 5.31 | 0.73 | 86.19 | 13.81 | 0.00 | 0.75 | 2.37 |
| 34D | 17.38 | 4.74 | 11.85 | 3.79 | 0.59 | 84.50 | 15.50 | 0.00 | 0.73 | 2.05 |
| | 17.38 | 4.33 | 11.67 | 3.79 | 0.59 | 84.50 | 15.50 | 0.00 | 0.73 | 1.54 |
| 34E | 17.11 | 4.63 | 11.66 | 18.35 | 2.88 | 84.31 | 15.69 | 0.00 | 0.72 | 1.94 |
| | 17.11 | 4.64 | 11.66 | 18.35 | 2.88 | 84.31 | 15.69 | 0.00 | 0.72 | 1.95 |
| 35A-1 | 18.83 | 7.17 | 13.73 | 3.66 | 0.29 | 92.09 | 7.12 | 0.79 | 0.85 | 5.93 |
| | 18.83 | 7.90 | 14.05 | 3.66 | 0.29 | 92.09 | 7.12 | 0.79 | 0.85 | 6.74 |
| 35A-2 | 18.26 | 4.60 | 12.29 | 13.57 | 1.07 | 92.09 | 7.91 | 0.00 | 0.85 | 3.24 |
| | 18.26 | 3.77 | 11.93 | 13.57 | 1.07 | 92.09 | 7.91 | 0.00 | 0.85 | 2.32 |
| 35B-1 | 19.19 | 0.08 | 10.83 | 8.58 | 0.56 | 93.46 | 6.54 | 0.00 | 0.87 | -1.47 |
| | 19.19 | -1.12 | 10.31 | 8.58 | 0.56 | 93.46 | 6.54 | 0.00 | 0.87 | -2.76 |
| 35B-2 | 19.00 | -2.43 | 9.63 | 4.53 | 0.36 | 91.96 | 5.63 | 2.41 | 0.85 | -5.95 |
| | 19.00 | -1.37 | 10.10 | 4.53 | 0.36 | 91.96 | 5.63 | 2.41 | 0.85 | -4.90 |
| | 19.00 | -3.25 | 9.27 | 4.53 | 0.36 | 91.96 | 5.63 | 2.41 | 0.85 | -5.03 |
| | 19.00 | -2.31 | 9.69 | 4.53 | 0.36 | 91.96 | 5.63 | 2.41 | 0.85 | -3.85 |
| | 19.00 | -3.44 | 9.19 | 9.42 | 0.42 | 95.54 | 4.46 | 0.00 | 0.91 | -4.65 |
| | 19.00 | -2.88 | 9.44 | 9.42 | 0.42 | 95.54 | 4.46 | 0.00 | 0.91 | -4.06 |
| | 19.00 | -2.67 | 9.53 | 3.28 | 0.36 | 88.99 | 8.81 | 2.20 | 0.80 | -6.19 |
| | 19.00 | -1.44 | 10.07 | 3.28 | 0.36 | 88.99 | 8.81 | 2.20 | 0.80 | -4.76 |
| | 19.00 | -3.46 | 9.18 | 4.67 | 0.19 | 96.03 | 3.17 | 0.79 | 0.92 | -4.68 |
| | 19.00 | -2.55 | 9.58 | 4.67 | 0.19 | 96.03 | 3.17 | 0.79 | 0.92 | -3.72 |
| 35E | 18.93 | -4.18 | 8.83 | 5.86 | 0.29 | 95.05 | 1.48 | 3.46 | 0.91 | -6.22 |
| | 18.93 | -4.25 | 8.80 | 5.86 | 0.29 | 95.05 | 1.48 | 3.46 | 0.91 | -6.30 |
| | 18.93 | -5.28 | 8.35 | 4.23 | 0.09 | 97.94 | 1.85 | 0.21 | 0.96 | -5.91 |
| | 18.93 | -3.84 | 8.97 | 3.45 | 0.43 | 87.49 | 10.01 | 2.50 | 0.77 | -8.11 |
| | 18.93 | -2.94 | 9.37 | 3.45 | 0.43 | 87.49 | 10.01 | 2.50 | 0.77 | -7.04 |
| | 18.93 | -3.35 | 9.19 | 14.02 | 0.25 | 98.22 | 1.60 | 0.18 | 0.96 | -3.85 |
| | 18.93 | -3.07 | 9.31 | 14.02 | 0.25 | 98.22 | 1.60 | 0.18 | 0.96 | -3.56 |

* Calculated using measured $\delta^{18}O$ and apparent temperatures calculated from the uncorrected $\Delta^{18}O$ (Qt-Mt)

**Table S2 Continued**

| Sample # 03-BIW- | Measured $\delta^{18}O$ (Qt) ‰ VSMOW | Measured $\delta^{18}O$ (Mt) ‰ VSMOW | Calculated* $\delta^{18}O$ (Di) ‰ VSMOW | Start mass (mg) | End mass (mg) | Wt% Mt | Wt% Di | Wt% Qt | Mol Fraction Oxygen (Mt) | Corrected $\delta^{18}O$ (Mt)‰ |
|---|---|---|---|---|---|---|---|---|---|---|
| 36M | 18.79 | -2.50 | 9.48 | 9.11 | 0.07 | 99.19 | 0.81 | 0.00 | 0.98 | -2.70 |
| | 18.79 | -2.89 | 9.31 | 9.11 | 0.07 | 99.19 | 0.81 | 0.00 | 0.98 | -3.10 |
| | 18.79 | 0.05 | 10.60 | 0.99 | 0.06 | 93.82 | 5.56 | 0.62 | 0.88 | -1.48 |
| | 18.79 | -1.28 | 10.02 | 0.99 | 0.06 | 93.82 | 5.56 | 0.62 | 0.88 | -2.91 |
| | 18.79 | -1.64 | 9.86 | 13.42 | 0.05 | 99.66 | 0.34 | 0.00 | 0.99 | -1.72 |
| | 18.79 | -1.06 | 10.11 | 13.42 | 0.05 | 99.66 | 0.34 | 0.00 | 0.99 | -1.14 |
| | 18.79 | -2.49 | 9.49 | 9.02 | 0.04 | 99.55 | 0.45 | 0.00 | 0.99 | -2.60 |
| | 18.79 | -1.89 | 9.75 | 9.02 | 0.04 | 99.55 | 0.45 | 0.00 | 0.99 | -2.00 |

* Calculated using measured $\delta^{18}O$ and apparent temperatures calculated from the uncorrected $\Delta^{18}O$ (Qt-Mt)

## APPENDIX 2

Calculation of whole rock (WR) values for O and Fe isotope ratios: $\delta^{18}O$, estimated percentage of quartz and magnetite, and moles of oxygen in quartz and magnetite used to calculate the whole rock $\delta^{18}O$ values (equation 3). For simplification, silicate minerals other than magnetite and quartz were calculated as quartz. The quartz and magnetite volumes were divided by their respective molar volumes to get moles/liter. The result for magnetite was multiplied by two because the mineral has twice as many oxygen atoms per formula unit as quartz. Then, the analyzed $\delta^{18}O$ (Qt) and $\delta^{18}O$ (Mt) were multiplied by their respective molar oxygen fraction, and added together, to estimate a whole rock $\delta^{18}O$ value. Whole rock $\delta^{56}Fe$ values calculated in the same manner using the modes listed in Table S1, converted to molar Fe proportions.

**Table S3.** Calculated whole-rock $\delta^{18}O$ values.

| Sample 03-BIW- | $\delta^{18}O$ Qt ‰VSMOW | $\delta^{18}O$ Mt ‰VSMOW | Estimated % Qt | Estimated % Mt | Mol/l Oxygen (Qt) | Mol/l Oxygen (Mt) | $\delta^{18}O$ Whole Rock |
|---|---|---|---|---|---|---|---|
| 39C | 13.26 | 8.82 | 80.6 | 19.4 | 35.53 | 8.71 | 12.38 |
| 43B | 13.13 | 6.51 | 76.8 | 23.2 | 33.85 | 10.42 | 11.58 |
| 18C | 13.95 | 6.48 | 76.5 | 23.5 | 33.70 | 10.58 | 12.16 |
| 17B | 12.42 | 4.47 | 86.4 | 13.6 | 38.10 | 6.09 | 11.32 |
| 12C | 13.73 | 7.38 | 83.6 | 16.4 | 36.85 | 7.37 | 12.67 |
| 3E | 13.15 | 6.13 | 72.9 | 27.1 | 32.13 | 12.18 | 11.22 |
| 22B | 14.51 | 7.50 | 77.1 | 22.9 | 34.00 | 10.27 | 12.89 |
| 23B-1 | 14.45 | 7.75 | 69.6 | 30.4 | 30.67 | 13.66 | 12.38 |
| 23B-2 | 14.53 | 7.46 | 83.3 | 16.7 | 36.72 | 7.50 | 13.33 |
| 31A | 14.65 | 7.78 | 84.8 | 15.2 | 37.40 | 6.81 | 13.59 |
| 31D | 14.97 | 8.26 | 81.6 | 18.4 | 35.96 | 8.27 | 13.72 |
| 44A | 17.23 | 6.46 | 65.2 | 34.8 | 28.75 | 15.62 | 13.44 |
| 34B | 17.27 | 1.59 | 71.1 | 28.9 | 31.33 | 12.99 | 12.68 |
| 34C | 16.87 | 2.64 | 55.1 | 44.9 | 24.30 | 20.16 | 10.41 |
| 34D | 17.38 | 1.80 | 66.2 | 33.8 | 29.17 | 15.19 | 12.04 |
| 34E | 17.11 | 1.95 | 65.0 | 35.0 | 28.65 | 15.72 | 11.74 |
| 35A-2 | 18.26 | 2.79 | 79.9 | 20.1 | 35.22 | 9.03 | 15.11 |
| 35B-1 | 19.19 | -2.11 | 80.4 | 19.6 | 35.44 | 8.80 | 14.95 |
| 35B-2 | 19.00 | -4.78 | 80.4 | 19.6 | 35.44 | 8.80 | 14.27 |
| 35E | 18.93 | -5.19 | 63.0 | 37.0 | 27.77 | 16.62 | 9.90 |
| 36M | 18.79 | -2.21 | 60.3 | 39.7 | 26.58 | 17.83 | 10.36 |

**Table S4.** Calculated whole-rock $\delta^{56}$Fe values.

| Sample # 03-BIW- | $\delta^{56}$Fe Mt | $\delta^{56}$Fe Fe Sil | Estimated % Mt | Estimated % Fe Sil | Estimated % Carb | Mol/l Iron (Mt) | Mol/l Iron (FeSil) | Mol/l Iron (Carb) | $\delta^{56}$Fe Whole rock |
|---|---|---|---|---|---|---|---|---|---|
| 40B | 0.33 | 0.16 | 13.0 | 47.0 | 0.0 | 14.54 | 21.97 | 0.00 | 0.23 |
| 6A | 0.19 | 0.03 | 17.0 | 22.0 | 0.0 | 29.26 | 15.82 | 0.00 | 0.13 |
| 8D | 0.23 | 0.06 | 25.0 | 37.0 | 0.0 | 27.06 | 16.74 | 0.00 | 0.17 |
| 3E | -0.01 | -0.26 | 27.1 | 21.0 | 0.0 | 37.81 | 12.24 | 0.00 | -0.07 |
| 22C | 0.30 | 0.05 | 20.0 | 45.0 | 0.0 | 20.65 | 19.42 | 0.00 | 0.18 |
| 31D | 0.39 | 0.20 | 18.0 | 55.0 | 0.0 | 16.55 | 21.13 | 0.00 | 0.28 |
| 31C | 0.36 | 0.25 | 20.0 | 65.0 | 0.0 | 15.79 | 21.45 | 0.00 | 0.30 |
| 44A | 0.65 | 0.26 | 34.8 | 50.0 | 0.0 | 27.54 | 16.54 | 0.00 | 0.50 |
| 34A | 0.01 | -0.26 | 25.0 | 55.0 | 0.0 | 20.97 | 19.28 | 0.00 | -0.12 |
| 34C | 0.09 | -0.39 | 45.0 | 35.0 | 1.0 | 37.29 | 12.12 | 0.35 | -0.03 |
| 35B-1 | 0.73 | 0.16 | 13.0 | 40.0 | 5.0 | 15.04 | 19.34 | 2.42 | 0.38 |

## APPENDIX 3

**Calculation of the Jaeger curve for the Duluth Complex and Biwabik Iron Formation**

The contact temperature of the Duluth Complex and the Biwabik Iron Formation was calculated two ways. Assuming only thermal conduction (Jaeger, 1959):

$$T_{contact} = \sigma\, T_1/(1 + \sigma) + 250°C + T_i \text{ country rock} = 668°C \qquad \textbf{(A1)}$$

Where $T_1$ is $\Delta T$ (melting temperature of the Duluth Complex vs. pre-metamorphic country rock temperature) = (1150 – 250°C) (French, 1973; Chalokwu et al., 1993; Koptev-Dornikov et al., 1995). Also, $\sigma$:

$$\sigma = (K_1 k_o^{0.5})/ (K_o k_1^{0.5}) = 0.865 \qquad \textbf{(A2)}$$

$K_1$ = thermal conductivity of gabbro = 0.0043
$k_1$ = diffusivity of gabbro = 0.008
$K_o$ = thermal conductivity of quartzite and shale = (0.0128 + 0.0019)/2 = 0.00735
$k_o$ = diffusivity of quartzite and shale = (0.031 + 0.004)/2 = 0.0175

Assuming a latent heat of fusion of 418 J/gm, the estimated temperature at the contact is raised to 768°C, which is ~70°C higher than the $\Delta^{18}O$ (Qt-Mt) apparent temperature at the contact in Fig. 9. To make the predicted contact metamorphic thermal profile, temperatures were calculated of $T_m/T_{contact}$ vs. X/D where $T_m$ = maximum temperature at distance X from the contact, and D is the thickness of the intrusion; Jaeger's curve 5: assumes equal thermal properties for the country rock and magma, latent heat of fusion = 418 J/gm and $T_1$ = (1100-800°C). The thickness is estimated at 3 km for the Duluth Complex by averaging known thicknesses to the south, (2 km; Hauck et al., 1997), and to the north, (4 km; Miller, 1999), of the study area. The assumption of equal thermal properties for the country rock and magma is a reasonable simplification; because the thermal properties of gabbro and the layered quartzite-shale BIF are similar (see above). The change in the estimated thermal profile of the Biwabik Iron Formation would be minimal if the country rock and magma were not assumed equal in thermal properties.

The contact temperature = 768°C calculated with these assumptions is slightly lower than the estimate from metamorphic pigeonite (T >825°C). The curve in Fig. 6 is adjusted upwards by 60°C to be consistent with the stability of pigeonite.

**Table S5.** Chemical analyses by electron microprobe of pyroxenes.

| | 39C; 9 | 39C; 11 | 39C; 12 | 39C; 12 | 39C; 12 | 39C; 13 | 39C; 14 | 39C; 14 | 39C; 14 |
|---|---|---|---|---|---|---|---|---|---|
| Si | 1.959 | 1.963 | 1.958 | 1.948 | 1.957 | 1.953 | 1.969 | 1.965 | 1.968 |
| Al | 0.013 | 0.014 | 0.008 | 0.014 | 0.009 | 0.007 | 0.008 | 0.012 | 0.009 |
| Ti | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| $Fe^{3+}$ | 0.042 | 0.039 | 0.038 | 0.053 | 0.039 | 0.044 | 0.027 | 0.036 | 0.029 |
| Mg | 0.637 | 0.642 | 0.857 | 0.651 | 0.840 | 0.846 | 0.836 | 0.647 | 0.794 |
| $Fe^{2+}$ | 0.454 | 0.466 | 1.018 | 0.446 | 0.969 | 1.027 | 1.044 | 0.457 | 0.910 |
| Mn | 0.030 | 0.034 | 0.068 | 0.030 | 0.064 | 0.077 | 0.083 | 0.033 | 0.072 |
| Ca | 0.848 | 0.825 | 0.053 | 0.839 | 0.120 | 0.044 | 0.032 | 0.835 | 0.214 |
| Na | 0.016 | 0.017 | 0.000 | 0.018 | 0.002 | 0.001 | 0.001 | 0.014 | 0.004 |
| Name | Aug | Aug | Hst | Lm | Pg | Opx | Hst | Lm | Pg |

| | 43B; 6 | 43B; 7 | 43B; 8 | 18C; 17 | 18C; 17 | 18C; 17 | 18C; 20 | 18C; 20 | 18C; 20 |
|---|---|---|---|---|---|---|---|---|---|
| Si | 1.968 | 2.107 | 1.967 | 1.949 | 1.934 | 1.947 | 1.941 | 1.958 | 1.943 |
| Al | 0.034 | 0.049 | 0.039 | 0.004 | 0.007 | 0.005 | 0.005 | 0.009 | 0.005 |
| Ti | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 |
| $Fe^{3+}$ | 0.015 | 0.000 | 0.014 | 0.050 | 0.075 | 0.053 | 0.058 | 0.052 | 0.057 |
| Mg | 0.987 | 1.014 | 0.985 | 0.746 | 0.584 | 0.727 | 0.744 | 0.574 | 0.726 |
| $Fe^{2+}$ | 0.958 | 0.784 | 0.953 | 1.147 | 0.588 | 1.081 | 1.150 | 0.531 | 1.082 |
| Mn | 0.008 | 0.007 | 0.009 | 0.042 | 0.023 | 0.040 | 0.049 | 0.021 | 0.046 |
| Ca | 0.030 | 0.036 | 0.031 | 0.060 | 0.760 | 0.143 | 0.052 | 0.825 | 0.137 |
| Na | 0.000 | 0.003 | 0.002 | 0.002 | 0.027 | 0.005 | 0.002 | 0.030 | 0.005 |
| Name | Opx | Opx | Opx | Hst | Lm | Pg | Hst | Lm | Pg |

| | 18C; 22 | 18C; 22 | 18C; 22 | 18C; 26 | 18C; 26 | 18C; 26 | 18C; 28 | 18C; 28 | 18C; 28 |
|---|---|---|---|---|---|---|---|---|---|
| Si | 1.934 | 1.945 | 1.935 | 1.953 | 1.957 | 1.953 | 1.963 | 1.957 | 1.962 |
| Al | 0.004 | 0.009 | 0.004 | 0.004 | 0.008 | 0.005 | 0.003 | 0.008 | 0.004 |
| Ti | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.001 | 0.000 |
| $Fe^{3+}$ | 0.065 | 0.065 | 0.065 | 0.045 | 0.054 | 0.046 | 0.036 | 0.053 | 0.039 |
| Mg | 0.744 | 0.582 | 0.726 | 0.750 | 0.580 | 0.727 | 0.744 | 0.591 | 0.721 |
| $Fe^{2+}$ | 1.150 | 0.544 | 1.080 | 1.154 | 0.527 | 1.070 | 1.151 | 0.584 | 1.065 |
| Mn | 0.045 | 0.021 | 0.043 | 0.043 | 0.020 | 0.040 | 0.045 | 0.021 | 0.041 |
| Ca | 0.056 | 0.803 | 0.141 | 0.050 | 0.824 | 0.154 | 0.055 | 0.756 | 0.162 |
| Na | 0.002 | 0.030 | 0.005 | 0.000 | 0.030 | 0.004 | 0.002 | 0.029 | 0.006 |
| Name | Hst | Lm | Pg | Hst | Lm | Pg | Hst | Lm | Pg |

| | 18C; 24 | 17C; 30 | 12C; 1 | 12C; 2 | 12C; 4 |
|---|---|---|---|---|---|
| Si | 2.036 | 1.949 | 1.983 | 1.980 | 1.961 |
| Al | 0.006 | 0.008 | 0.014 | 0.015 | 0.015 |
| Ti | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| $Fe^{3+}$ | 0.021 | 0.047 | 0.011 | 0.012 | 0.031 |
| Mg | 0.748 | 0.472 | 0.488 | 0.463 | 0.454 |
| $Fe^{2+}$ | 1.090 | 1.458 | 1.409 | 1.448 | 1.450 |
| Mn | 0.043 | 0.011 | 0.035 | 0.034 | 0.041 |
| Ca | 0.053 | 0.055 | 0.060 | 0.047 | 0.046 |
| Na | 0.003 | 0.001 | 0.001 | 0.000 | 0.001 |
| Name | Opx | Opx | Opx | Opx | Opx |

Host (Hst) and lamellae (Lm) of reintegrated pigeonite (Pg), and augite (Aug) and orthopyroxene (Opx) in the Biwabik Iron Formation near the contact with the Duluth Complex. Pigeonites were reintegrated using *NIH image*, ImageJ, to estimate % of lamellae and host from BSE images. $Fe^{3+}$ calculated based on charge balance.

**Table S6.** Oxygen isotope compositions of quartz and magnetite (outside Dunka Pit, magnetite values are corrected for small amounts of silicate impurity, see Appendix 1), $\Delta^{18}O$ (Qt-Mt), and respective standard deviations; temperatures; and isograd zones for samples collected in this study from the Biwabik Iron Formation of Minnesota.

| Sample # 03-BIW- | Distance from contact (m, map) | Distance from contact (m, 3-D) | $\delta^{18}O$ (Qt) ‰VSMOW | ±1 St D | Ave | $\delta^{18}O$ (Mt) ‰VSMOW | ±1 St D | Ave | $\Delta^{18}O$ (Qt-Mt) ‰VSMOW | ±1 St D | T, °C * | Isograd zone ‡ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 39C | 0 | 0 | 13.23 | 0.03 | 13.26 | 8.79 | 0.04 | 8.82 | 4.44 | 0.05 | 917 | 8 |
| | | | 13.29 | | | 8.86 | | | | | | |
| 40B | 1 | 0.5 | 14.87 | 0.00 | 14.87 | 9.26 | 0.05 | 9.32 | 5.56 | 0.05 | 791 | 8 |
| | | | 14.87 | | | 9.37 | | | | | | |
| 40A | 1 | 0.5 | 15.06 | 0.02 | 15.05 | 9.08 | 0.03 | 9.06 | 5.99 | 0.03 | 752 | 8 |
| | | | 15.03 | | | 9.03 | | | | | | |
| 40C | 1 | 0.5 | 15.22 | 0.05 | 15.17 | 8.88 | 0.01 | 8.90 | 6.28 | 0.05 | 728 | 8 |
| | | | 15.12 | | | 8.91 | | | | | | |
| 39E | 8 | 4 | 13.51 | 0.23 | 13.66 | 7.21 | 0.16 | 7.26 | 6.40 | 0.28 | 719 | 8 |
| | | | 13.62 | | | 7.07 | | | | | | |
| | | | 14.00 | | | 7.39 | | | | | | |
| | | | 13.51 | | | 7.39 | | | | | | |
| 39D | 8 | 4 | 14.55 | 0.06 | 14.61 | 8.24 | 0.00 | 8.25 | 6.37 | 0.06 | 721 | 8 |
| | | | 14.67 | | | 8.25 | | | | | | |
| 43E | 10 | 5 | 12.67 | 0.11 | 12.78 | 6.93 | 0.06 | 6.99 | 5.79 | 0.13 | 769 | 8 |
| | | | 12.89 | | | 7.05 | | | | | | |
| 43B | 10 | 5 | 12.96 | 0.17 | 13.13 | 6.58 | 0.07 | 6.51 | 6.62 | 0.18 | 702 | 8 |
| | | | 13.30 | | | 6.44 | | | | | | |
| 43A | 10 | 5 | 13.64 | 0.09 | 13.55 | 6.90 | 0.02 | 6.92 | 6.63 | 0.09 | 701 | 8 |
| | | | 13.46 | | | 6.95 | | | | | | |
| 43D | 10 | 5 | 14.40 | -- | -- | 6.72 | 0.05 | 6.67 | 7.73 | 0.05 | 629 | 8 |
| | | | | | | 6.62 | | | | | | |
| 18E | 15 | 8 | 15.18 | 0.09 | 15.09 | 8.06 | 0.09 | 8.15 | 6.95 | 0.12 | 679 | 8 |
| | | | 15.00 | | | 8.23 | | | | | | |
| 18C | 15 | 8 | 13.95 | 0.00 | 13.95 | 6.58 | 0.11 | 6.48 | 7.47 | 0.11 | 644 | 8 |
| | | | 13.94 | | | 6.37 | | | | | | |
| 18B | 15 | 8 | 13.76 | 0.02 | 13.78 | 7.31 | 0.24 | 7.02 | 6.76 | 0.25 | 691 | 8 |
| | | | 13.80 | | | 6.75 | | | | | | |
| | | | | | | 7.11 | | | | | | |
| | | | | | | 6.90 | | | | | | |
| 17E | 20 | 10 | 12.51 | 0.29 | 12.80 | 7.17 | 0.17 | 7.00 | 5.80 | 0.34 | 768 | 8 |
| | | | 13.09 | | | 6.83 | | | | | | |
| 17D | 20 | 10 | 13.94 | -- | -- | 6.94 | 0.02 | 6.95 | 6.99 | 0.02 | 676 | 8 |
| | | | | | | 6.97 | | | | | | |
| 17B | 20 | 10 | 12.45 | 0.03 | 12.42 | 4.47 | 0.00 | 4.47 | 7.96 | 0.03 | 616 | 8 |
| | | | 12.39 | | | 4.46 | | | | | | |
| 17C | 20 | 10 | 12.32 | 0.00 | 12.32 | 6.18 | 0.05 | 6.13 | 6.19 | 0.05 | 735 | 8 |
| | | | 12.32 | | | 6.08 | | | | | | |
| 2B | 16 | 9 | 12.10 | 0.30 | 12.40 | 4.92 | -- | -- | 7.48 | 0.30 | 644 | 8 |
| | | | 12.70 | | | | | | | | | |

## Table S6 Continued

| Sample # 03-BIW- | Distance from contact (m, map) | Distance from contact (m, 3-D) | $\delta^{18}O$ (Qt) ‰VSMOW | ±1 St D | Ave | $\delta^{18}O$ (Mt) ‰VSMOW | ±1 St D | Ave | $\Delta^{18}O$(Qt-Mt) ‰VSMOW | ±1 St D | T, °C * | Isograd zone ‡ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12C | 40 | 20 | 13.69 | 0.04 | 13.73 | 7.34 | 0.04 | 7.38 | 6.35 | 0.06 | 722 | 8 |
| | | | 13.77 | | | 7.42 | | | | | | |
| 12D | 40 | 20 | 13.42 | 0.17 | 13.59 | 7.13 | 0.21 | 6.92 | 6.67 | 0.27 | 698 | 8 |
| | | 20 | 13.75 | | | 6.71 | | | | | | |
| 12B | 40 | 20 | 13.30 | 0.01 | 13.30 | 7.10 | 0.04 | 7.14 | 6.16 | 0.04 | 737 | 8 |
| | | | 13.29 | | | 7.17 | | | | | | |
| 6A | 60 | 30 | 14.59 | 0.00 | 14.59 | 6.62 | 0.07 | 6.56 | 8.04 | 0.07 | 612 | 8 |
| | | | 14.59 | | | 6.49 | | | | | | |
| 6D | 60 | 30 | 14.12 | 0.03 | 14.09 | 7.06 | 0.05 | 7.01 | 7.09 | 0.06 | 669 | 8 |
| | | | 14.06 | | | 6.95 | | | | | | |
| 6C | 60 | 30 | 14.43 | 0.07 | 14.49 | 6.93 | 0.02 | 6.90 | 7.59 | 0.07 | 637 | 8 |
| | | | 14.56 | | | 6.88 | | | | | | |
| 6B | 60 | 30 | 14.43 | 0.12 | 14.33 | 6.20 | 0.16 | 6.37 | 7.96 | 0.20 | 616 | 8 |
| | | | 14.20 | | | 6.51 | | | | | | |
| | | | 14.36 | | | 6.40 | | | | | | |
| 8D | 55 | 28 | 14.23 | 0.05 | 14.28 | 6.77 | 0.08 | 6.85 | 7.44 | 0.09 | 647 | 8 |
| | | | 14.33 | | | 6.92 | | | | | | |
| 8C | 55 | 28 | 14.66 | 0.01 | 14.68 | 7.17 | 0.04 | 7.14 | 7.54 | 0.04 | 640 | 8 |
| | | | 14.69 | | | 7.10 | | | | | | |
| 3E | 65 | 33 | 13.13 | 0.02 | 13.15 | 6.32 | 0.20 | 6.13 | 7.03 | 0.20 | 673 | 8 |
| | | | 13.17 | | | 5.93 | | | | | | |
| 3A | 65 | 33 | 11.15 | -- | -- | 3.68 | 0.02 | 3.70 | 7.46 | 0.02 | 645 | 8 |
| | | | | | | 3.71 | | | | | | |
| 3B | 65 | 33 | 11.51 | -- | -- | 5.11 | 0.05 | 5.06 | 6.45 | 0.05 | 714 | 8 |
| | | | | | | 5.01 | | | | | | |
| 3C | 65 | 33 | 14.81 | 0.17 | 14.98 | 7.33 | 0.03 | 7.30 | 7.68 | 0.17 | 632 | 8 |
| | | | 15.15 | | | 7.27 | | | | | | |
| 10A | 35 | 18 | 12.43 | 0.01 | 12.44 | 5.88 | 0.01 | 5.87 | 6.58 | 0.02 | 705 | 8 |
| | | | 12.46 | | | 5.86 | | | | | | |
| 10C | 35 | 18 | 13.41 | 0.04 | 13.36 | 6.47 | 0.03 | 6.50 | 6.87 | 0.05 | 684 | 8 |
| | | | 13.32 | | | 6.53 | | | | | | |
| 22C | 200 | 100 | 13.85 | 0.02 | 13.88 | 7.62 | 0.00 | 7.62 | 6.26 | 0.02 | 729 | 8 |
| | | | 13.90 | | | 7.62 | | | | | | |
| 22B | 200 | 100 | 14.50 | 0.01 | 14.51 | 7.46 | 0.04 | 7.50 | 7.01 | 0.04 | 674 | 8 |
| | | | 14.52 | | | 7.54 | | | | | | |
| 22E | 200 | 100 | 14.47 | -- | -- | 7.59 | 0.01 | 7.58 | 6.89 | 0.01 | 682 | 8 |
| | | | | | | 7.57 | | | | | | |
| 22D | 200 | 100 | 14.21 | 0.15 | 14.36 | 7.83 | 0.18 | 7.66 | 6.70 | 0.23 | 696 | 8 |
| | | | 14.50 | | | 7.48 | | | | | | |
| 23B-1 | 210 | 105 | 14.37 | 0.08 | 14.45 | 7.75 | 0.13 | 7.87 | 6.58 | 0.15 | 705 | 8 |
| | | | 14.53 | | | 8.00 | | | | | | |
| | | | | | | 7.86 | | | | | | |
| 23E | 210 | 105 | 14.40 | 0.07 | 14.33 | 7.36 | 0.15 | 7.51 | 6.82 | 0.17 | 687 | 8 |
| | | | 14.26 | | | 7.66 | | | | | | |
| 23A | 210 | 105 | 14.77 | 0.18 | 14.60 | 7.68 | 0.01 | 7.69 | 6.91 | 0.18 | 681 | 8 |
| | | | 14.42 | | | 7.69 | | | | | | |

## Table S6 Continued

| Sample # 03-BIW- | Distance from contact (m, map) | Distance from contact (m, 3-D) | δ$^{18}$O (Qt) ‰VSMOW | ±1 St D | Ave | δ$^{18}$O (Mt) ‰VSMOW | ±1 St D | Ave | Δ$^{18}$O (Qt-Mt) ‰VSMOW | ±1 St D | T, $^{o}$C * | Isograd zone ‡ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 23B-1 | 210 | 105 | 14.37 | 0.08 | 14.45 | 7.75 | 0.13 | 7.87 | 6.58 | 0.15 | 705 | 8 |
| | | | 14.53 | | | 8.00 | | | | | | |
| | | | | | | 7.86 | | | | | | |
| 23E | 210 | 105 | 14.40 | 0.07 | 14.33 | 7.36 | 0.15 | 7.51 | 6.82 | 0.17 | 687 | 8 |
| | | | 14.26 | | | 7.66 | | | | | | |
| 23A | 210 | 105 | 14.77 | 0.18 | 14.60 | 7.68 | 0.01 | 7.69 | 6.91 | 0.18 | 681 | 8 |
| | | | 14.42 | | | 7.69 | | | | | | |
| 23B-2 | 210 | 105 | 14.61 | 0.05 | 14.57 | 7.51 | 0.05 | 7.46 | 7.11 | 0.07 | 668 | 8 |
| | | | 14.52 | | | 7.41 | | | | | | |
| 27A | 300 | 150 | 14.69 | 0.06 | 14.63 | 7.79 | 0.11 | 7.90 | 6.73 | 0.13 | 694 | 8 |
| | | | 14.56 | | | 8.01 | | | | | | |
| 27B | 300 | 150 | 15.17 | 0.03 | 15.14 | 6.49 | 0.03 | 6.53 | 8.62 | 0.05 | 581 | 8 |
| | | | 15.11 | | | 6.56 | | | | | | |
| 30D | 325 | 163 | 13.16 | 0.09 | 13.25 | 5.42 | 0.10 | 5.52 | 7.73 | 0.13 | 629 | 8 |
| | | | 13.34 | | | 5.62 | | | | | | |
| 31D | 220 | 110 | 14.97 | -- | -- | 8.28 | 0.13 | 8.27 | 6.70 | 0.13 | 696 | 8 |
| | | | | | | 8.23 | | | | | | |
| | | | | | | 8.44 | | | | | | |
| | | | | | | 8.12 | | | | | | |
| 31A | 220 | 110 | 14.66 | 0.01 | 14.65 | 7.66 | 0.12 | 7.78 | 6.87 | 0.12 | 684 | 8 |
| | | | 14.64 | | | 7.90 | | | | | | |
| 31C | 220 | 110 | 14.45 | 0.32 | 14.77 | 8.72 | 0.82 | 7.90 | 6.87 | 0.88 | 684 | 8 |
| | | | 15.09 | | | 7.08 | | | | | | |
| 32B | 330 | 170 | 14.12 | 0.08 | 14.20 | 6.08 | 0.13 | 5.96 | 8.24 | 0.15 | 601 | 7 |
| | | | 14.27 | | | 5.83 | | | | | | |
| 44B-1 | 2500 | 1250 | 16.25 | 0.17 | 16.08 | 5.08 | 0.04 | 5.05 | 11.04 | 0.17 | 482 | 7 |
| | | | 15.91 | | | 5.01 | | | | | | |
| 44D | 2500 | 1250 | 16.72 | 0.04 | 16.76 | 6.07 | -- | -- | 10.69 | 0.04 | 494 | 7 |
| | | | 16.80 | | | | | | | | | |
| 44C | 2500 | 1250 | 16.58 | 0.17 | 16.75 | 6.57 | 0.56 | 6.71 | 10.04 | 0.58 | 518 | 7 |
| | | | 16.92 | | | 6.66 | | | | | | |
| 44C; M1 | | | | | | 6.07 | | | | | | |
| 44C; M1 | | | | | | 7.76 | | | | | | |
| 44C; M2 | | | | | | 6.61 | | | | | | |
| 44C; M2 | | | | | | 6.63 | | | | | | |
| 44A | 2500 | 1250 | 17.38 | 0.15 | 17.23 | 6.52 | 0.06 | 6.46 | 10.77 | 0.17 | 491 | 7 |
| | | | 17.07 | | | 6.39 | | | | | | |
| 34B | 3000 | 2598 | 17.18 | 0.09 | 17.27 | 1.59 | 0.00 | 1.59 | 15.68 | 0.09 | 360 | 3 |
| | | | 17.36 | | | 1.59 | | | | | | |
| 34A | 3000 | 2598 | 17.01 | 0.01 | 17.00 | 1.77 | 0.18 | 1.59 | 15.41 | 0.18 | 366 | 3 |
| | | | 16.99 | | | 1.59 | | | | | | |
| | | | | | | 1.65 | | | | | | |
| | | | | | | 1.35 | | | | | | |
| 34E | 3000 | 2598 | 17.11 | -- | -- | 1.94 | 0.01 | 1.95 | 15.17 | 0.01 | 371 | 3 |
| | | | | | | 1.95 | | | | | | |
| 34D | 3000 | 2598 | 17.34 | 0.04 | 17.38 | 2.05 | 0.26 | 1.80 | 15.59 | 0.26 | 362 | 3 |
| | | | 17.43 | | | 1.54 | | | | | | |

## Table S6 Continued

| Sample # 03-BIW- | Distance from contact (m, map) | Distance from contact (m, 3-D) | $\delta^{18}O$ (Qt) ‰VSMOW | ±1 St D | Ave | $\delta^{18}O$ (Mt) ‰VSMOW | ±1 St D | Ave | $\Delta^{18}O$ (Qt-Mt) ‰VSMOW | ±1 St D | T, °C * | Isograd zone ‡ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 34C | 3000 | 2598 | 16.91 | 0.04 | 16.87 | 2.90 | 0.27 | 2.64 | 14.23 | 0.27 | 392 | 3 |
| | | | 16.82 | | | 2.37 | | | | | | |
| 35A-1 | 3100 | 2685 | 18.86 | 0.03 | 18.83 | 5.93 | 0.41 | 6.34 | 12.50 | 0.41 | 436 | 3 |
| | | | 18.80 | | | 6.74 | | | | | | |
| 35A-2 | 3100 | 2685 | 18.09 | 0.17 | 18.26 | 3.24 | 0.46 | 2.78 | 15.48 | 0.49 | 364 | 2 |
| | | | 18.43 | | | 2.32 | | | | | | |
| 35B-1 | 3100 | 2685 | 19.12 | 0.07 | 19.19 | -1.47 | 0.65 | -2.12 | 21.30 | 0.65 | 270 | 2 |
| | | | 19.26 | | | -2.76 | | | | | | |
| 35E | 3100 | 2685 | 18.86 | 0.07 | 18.93 | -6.22 | 1.64 | -5.86 | 24.79 | 1.64 | 231 | 2 |
| | | | 19.00 | | | -6.30 | | | | | | |
| 35E; M1 | | | | | | -5.91 | | | | | | |
| 35E; M2 | | | | | | -8.11 | | | | | | |
| 35E; M2 | | | | | | -7.04 | | | | | | |
| 35E; M3 | | | | | | -3.85 | | | | | | |
| 35E; M3 | | | | | | -3.56 | | | | | | |
| 35B-2 | 3100 | 2685 | 19.00 | 0.00 | 19.00 | -5.95 | 0.82 | -4.78 | 23.78 | 0.82 | 241 | 2 |
| | | | 19.00 | | | -4.90 | | | | | | |
| | | | | | | -5.03 | | | | | | |
| | | | | | | -3.85 | | | | | | |
| 35B2;M1 | | | | | | -4.65 | | | | | | |
| 35B2;M1 | | | | | | -4.06 | | | | | | |
| 35B2;M2 | | | | | | -6.19 | | | | | | |
| 35B2;M2 | | | | | | -4.76 | | | | | | |
| 35B2;M3 | | | | | | -4.68 | | | | | | |
| 35B2;M3 | | | | | | -3.72 | | | | | | |
| 36M | 3150 | 2728 | 18.86 | 0.07 | 18.79 | -2.70 | 0.72 | -2.21 | 21.00 | 0.73 | 274 | 2 |
| | | | 18.72 | | | -3.10 | | | | | | |
| 36M;M1 | | | | | | -1.48 | | | | | | |
| 36M;M1 | | | | | | -2.91 | | | | | | |
| 36M;M2 | | | | | | -1.72 | | | | | | |
| 36M;M2 | | | | | | -1.14 | | | | | | |
| 36M;M3 | | | | | | -2.60 | | | | | | |
| 36M;M3 | | | | | | -2.00 | | | | | | |

*Clayton and Kieffer (1991); ‡ French (1968), Frost et al. (2007); ** Values of $\delta^{18}O$ (Mt) are corrected for small amounts of silicate impurities, see text and Appendix 1.

**Table S7.** Partial dissolution tests of magnetite, siderite, and Fe silicate.

| | Initial wt (mg) | Time (h) | Temp. | Acid | Supernatant Fe(II)/Fe-T | $\delta^{56}$Fe | Residue Fe(II)/Fe-T | $\delta^{56}$Fe | % Dissolved |
|---|---|---|---|---|---|---|---|---|---|
| **Acid treatment of magnetite powder, Experiment 1** | | | | | | | | | |
| Mag-1 | 0.70 | 1.00 | 21 °C | 0.75M HCl | 0.32 | | 0.32 | | 0.6 |
| Mag-2 | 0.74 | 3.25 | " | " | 0.34 | | 0.29 | | 1.9 |
| Mag-3 | 0.74 | 5.00 | " | " | 0.29 | | 0.30 | | 2.8 |
| Mag-4 | 0.81 | 9.25 | " | " | 0.27 | | 0.30 | | 5.3 |
| Mag-5 | 0.81 | 20.00 | " | " | 0.32 | | 0.30 | | 13.6 |
| Mag-6 | 1.06 | 31.50 | " | " | 0.33 | | 0.25 | | 13.2 |
| **Acid treatment of magnetite powder, Experiment 2** | | | | | | | | | |
| Mag-1 | 1.12 | 5.00 | 21 °C | 1.0M HCl | 0.31 | 0.40 | 0.31 | 0.31 | 3.4 |
| Mag-2 | 1.14 | 9.00 | " | " | 0.30 | 0.31 | 0.30 | 0.30 | 7.4 |
| Mag-3 | 1.08 | 20.00 | " | " | 0.29 | 0.30 | 0.32 | 0.34 | 21.4 |
| Mag-4 | 1.07 | 30.00 | " | " | 0.28 | 0.34 | 0.33 | 0.31 | 32.5 |
| **Acid treatment of magnetite powder, Experiment 3** | | | | | | | | | |
| Mag-1 | 0.97 | 5.00 | 40 °C | 20% HAc | 0.66 | -0.16 | 0.28 | 0.32 | 3.4 |
| Mag-2 | 1.28 | 9.00 | " | " | 0.50 | -0.09 | 0.29 | 0.41 | 4.5 |
| Mag-3 | 1.09 | 20.00 | " | " | 0.54 | -0.03 | 0.28 | 0.28 | 8.2 |
| Mag-4 | 1.09 | 30.00 | " | " | 0.24 | | 0.27 | | 6.8 |
| **Acid treatment of siderite powder, Experiment 1** | | | | | | | | | |
| Sid-1 | 1.03 | 1.50 | 21 °C | 0.75M HCl | | | | | 8.2 |
| Sid-2 | 1.00 | 3.00 | " | " | | | | | 13.1 |
| Sid-3 | 0.97 | 5.00 | " | " | | | | | 26.9 |
| Sid-4 | 0.78 | 8.25 | " | " | | | | | 44.8 |
| Sid-5 | 0.98 | 20.00 | " | " | | | | | 84.0 |
| Sid-6 | 0.97 | 43.00 | " | " | | | | | 99.6 |
| **Acid treatment of siderite powder, Experiment 2** | | | | | | | | | |
| Sid-1 | 0.83 | 24.00 | 40 °C | 20% HAc | | | | | 61.5 |
| **Acid treatment of orthopyroxene mineral separate, Experiment 1** | | | | | | | | | |
| Opx-1 | 1.5 | 24.0 | 27 °C | 0.5M HCl | | | | | 0.8 |
| Opx-1 | 1.5 | 96.0 | " | " | | | | | 1.9 |
| **Acid treatment of orthopyroxene mineral separate, Experiment 2** | | | | | | | | | |
| Opx-1 | 20.7 | 3.0 | 20 °C | 12M HCl | | | | | 2.0 |
| Opx-2 | 20.0 | 3.0 | " | " | | | | | 0.4 |
| Opx-3 | 20.3 | 3.0 | " | " | | | | | 0.4 |

$\delta^{56}$Fe of magnetite starting material =+0.34. Fe(II) and total Fe contents determined by *Ferrozine* assay. Opx-1 contains 8.3 wt. % FeO and consists of 0.2 to 0.7 mm-size crystals. Opx-2 contains 10.5 wt. % FeO and consists of 0.5 to 1.5 mm crystals. Opx-3 is same material as Opx-2 but consists of 1 to 2 mm crystals.

**Table S8.** Fe isotope data for magnetite and Fe silicates from Biwabik Iron Formation.

| Sample: 03-BIW- | Fe Silicate Mineralogy | Dist. (m) | | $\delta^{56}Fe$ | $\delta^{57}Fe$ |
|---|---|---|---|---|---|
| 39C-Magnetite | | 0.5 | | 0.23±0.03 | 0.44±0.02 |
| repeat | | | | 0.28±0.04 | 0.46±0.03 |
| repeat | | | | 0.31±0.07 | 0.44±0.03 |
| | | | Avg: | 0.28±0.04 | 0.44±0.01 |
| 40B-Magnetite | | 0.5 | | | |
| aliquot A | | | | 0.38±0.04 | 0.58±0.04 |
| aliquot B | | | | 0.19±0.02 | 0.33±0.03 |
| aliquot C | | | | 0.43±0.03 | 0.67±0.02 |
| | | | Avg: | 0.33±0.13 | 0.53±0.18 |
| 40B-Fe Silicate | primarily Fe-opx, minor fayalite | | | 0.16±0.05 | 0.29±0.05 |
| 43E-Magnetite | | 5 | | 0.01±0.04 | 0.06±0.03 |
| 18E-Magnetite | | 8 | | 0.36±0.03 | 0.51±0.02 |
| 18C-Magnetite | | 8 | | 0.35±0.03 | 0.58±0.03 |
| 17E-Magnetite | | 10 | | 0.35±0.02 | 0.48±0.03 |
| 17D-Magnetite | | 10 | | 0.13±0.03 | 0.18±0.04 |
| 12C-Magnetite | | 20 | | | |
| aliquot A | | | | 0.11±0.04 | 0.20±0.03 |
| aliquot B | | | | 0.12±0.04 | 0.06±0.03 |
| | | | Avg: | 0.11±0.01 | 0.13±0.10 |
| 12D-Magnetite | | 20 | | | |
| aliquot A | | | | -0.20±0.04 | -0.32±0.03 |
| repeat | | | | -0.23±0.03 | -0.33±0.02 |
| aliquot B | | | | -0.28±0.03 | -0.42±0.03 |
| | | | Avg: | -0.24±0.04 | -0.36±0.05 |
| 6A-Magnetite | | 30 | | 0.19±0.03 | 0.30±0.03 |
| 6A-Fe Silicate | primarily Fe-opx, minor fayalite | | | 0.05±0.04 | 0.02±0.05 |
| repeat | | | | 0.01±0.03 | 0.03±0.03 |
| | | | Avg: | 0.03±0.03 | 0.03±0.01 |
| 8D-Magnetite | | 55 | | 0.23±0.03 | 0.35±0.02 |
| 8D-Fe Silicate | primarily Fe-opx, minor fayalite | | | 0.06±0.03 | 0.02±0.05 |
| 3E-Magnetite | | 65 | | -0.01±0.05 | 0.04±0.02 |
| 3E-Fe Silicate | primarily Fe-opx, minor fayalite | | | -0.26±0.03 | -0.41±0.05 |
| 3B-Magnetite | | 65 | | 0.00±0.03 | 0.09±0.03 |
| 22C-Magnetite | | 100 | | 0.30±0.03 | 0.48±0.03 |
| 22C-Fe Silicate | primarily Fe-opx, minor fayalite | | | 0.05±0.03 | 0.11±0.04 |
| 22B-Magnetite | | 100 | | 0.27±0.04 | 0.42±0.04 |
| 22E-Magnetite | | 100 | | 0.20±0.06 | 0.36±0.04 |
| 31D-Magnetite | | 110 | | 0.39±0.02 | 0.57±0.03 |
| repeat | | | | 0.39±0.05 | 0.60±0.05 |
| | | | Avg: | 0.39±0.00 | 0.59±0.02 |

## Table S8 Continued

| Sample: 03-BIW- | Fe Silicate Mineralogy | Dist. (m) | | $\delta^{56}Fe$ | $\delta^{57}Fe$ |
|---|---|---|---|---|---|
| 31D-Fe Silicate | primarily Fe-opx, minor fayalite | | | 0.20±0.06 | 0.31±0.04 |
| 31C-Magnetite | | 110 | | 0.36±0.03 | 0.64±0.03 |
| 31C-Fe Silicate | primarily Fe-opx, minor fayalite | | | 0.27±0.03 | 0.38±0.05 |
| repeat | | | | 0.23±0.04 | 0.30±0.05 |
| | | Avg: | | 0.25±0.03 | 0.34±0.06 |
| 44B-1-Magnetite | | 1250 | | 0.60±0.05 | 0.86±0.03 |
| 44D-Magnetite | | 1250 | | 0.58±0.07 | 0.80±0.03 |
| 44C-Magnetite | | 1250 | | 0.45±0.04 | 0.69±0.03 |
| 44A-Magnetite | | 1250 | | 0.65±0.07 | 0.97±0.04 |
| 44A-Fe Silicate | primarily hedenbergite, minor fayalite | | | 0.25±0.04 | 0.46±0.06 |
| repeat | | | | 0.28±0.06 | 0.39±0.04 |
| | | | Avg: | 0.27±0.02 | 0.43±0.05 |
| 34A-Magnetite | | 2598 | | 0.06±0.07 | 0.14±0.03 |
| repeat | | | | -0.04±0.03 | 0.00±0.03 |
| | | | Avg: | 0.01±0.07 | 0.07±0.10 |
| 34A-Fe Silicate | primarily grunerite | | | -0.26±0.05 | -0.43±0.06 |
| 34C-Magnetite | | 2598 | | 0.09±0.05 | 0.17±0.05 |
| 34C-Fe Silicate | primarily grunerite | | | -0.39±0.04 | -0.51±0.05 |
| repeat | | | | -0.38±0.03 | -0.48±0.04 |
| | | | Avg: | -0.39±0.01 | -0.50±0.02 |
| 35B-1-Magnetite | | 2685 | | 0.73±0.07 | 1.16±0.03 |
| 35B-1-Fe Silicate | primarily minnesotaite, minor greenalite | | | 0.11±0.04 | 0.14±0.05 |
| repeat | | | | 0.21±0.04 | 0.30±0.04 |
| | | | Avg: | 0.16±0.07 | 0.22±0.11 |
| 35E-Magnetite | | 2685 | | 0.50±0.06 | 0.81±0.08 |
| 36M-Magnetite | | 2728 | | 0.23±0.03 | 0.44±0.03 |
| repeat | | | | 0.28±0.04 | 0.46±0.04 |
| repeat | | | | 0.31±0.07 | 0.44±0.03 |
| | | | Avg: | 0.28±0.04 | 0.44±0.01 |

"repeat" notes re-analysis of same solution from ion exchange separation.  Different aliquots taken from same mineral separate noted.

**Table S9.** Measured grain size of magnetite from thin sections and closure temperatures ($T_C$). Input data for the Dodson equation (7) for magnetite 1 kb, hydrothermal conditions. Linear cooling rate was estimated at 5.6°C/kyr. Closure temperatures (°C) were calculated based on the measured grain diameters and diffusion characteristics, $D_o$, E, A, and a (below).

| Sample # | Distance (m, 3-D) | Grain radii (μm) | Tc (°C) |
|---|---|---|---|
| 03 BIW 39C | 0 | 605 | 700 |
| 03 BIW 43B | 5 | 197 | 620 |
| 03 BIW 18C | 8 | 205 | 623 |
| 03 BIW 17B | 10 | 227 | 630 |
| 03 BIW 12C | 20 | 234 | 631 |
| 03 BIW 3E | 33 | 224 | 629 |
| 03 BIW 22B | 100 | 435 | 675 |
| 03 BIW 23B-1 | 105 | 550 | 693 |
| 03 BIW 23B-2 | 105 | 420 | 673 |
| 03 BIW 31A | 110 | 450 | 678 |
| 03 BIW 31D | 110 | 550 | 693 |
| 03 BIW 44A | 1250 | 75 | 561 |
| 03 BIW 34B | 2598 | 5 | 429 |
| 03 BIW 34C | 2598 | 5 | 433 |
| 03 BIW 34D | 2598 | 5 | 430 |
| 03 BIW 34E | 2598 | 5 | 428 |

*Giletti and Hess, 1988

Input data for the Dodson equation (7) for magnetite 1 kb, hydrothermal conditions: the diffusion characteristics are $D_o = 3.5 \times 10^{-6}$ cm$^2$/s, E = 188000 J/mol, and A = 55 is the diffusional anisotropy parameter (Giletti and Hess, 1988). Linear cooling rate was estimated at 5600°C/Ma and a = radius of mineral grain. Closure temperatures (°C) were calculated based on the measured grain diameters.

**Table S10.** Values of $\delta^{18}O$ measured for hand-picked single magnetite crystals from samples 03BIW-43B and 03BIW-18C at Dunka Pit: 500-350 µm in diameter and 150-105 µm in diameter. Note that the apparent temperatures for bulk unsieved magnetite concentrates are bracketed by the temperatures of the two sieved grain sizes.

| Sample # | Diameter µm | $\delta^{18}O$(Qt) ‰VSMOW | $\delta^{18}O$(Mt) ‰VSMOW | Ave. $\delta^{18}O$(Mt) ‰VSMOW | Mt St D | T °C |
|---|---|---|---|---|---|---|
| 03BIW43B | 105-150 µm | 13.13 | 6.09 | 6.05 | 0.04 | 669 |
| 03BIW43B | 105-150 µm | | 6.01 | | | |
| 03BIW43B | 300-500 µm | 13.13 | 6.81 | 6.70 | 0.11 | 716 |
| 03BIW43B | 300-500 µm | | 6.59 | | | |
| 03BIW43B | bulk | 13.13 | 6.58 | 6.51 | 0.07 | 702 |
| 03BIW43B | bulk | | 6.44 | | | |
| | | | | | | |
| 03BIW18C | 105-150 µm | 13.95 | 5.75 | 5.71 | 0.04 | 601 |
| 03BIW18C | 105-150 µm | | 5.66 | | | |
| 03BIW18C | 300-500 µm | 13.95 | 7.74 | 7.72 | 0.02 | 732 |
| 03BIW18C | 300-500 µm | | 7.70 | | | |
| 03BIW18C | 300-500 µm | | 7.71 | | | |
| 03BIW18C | bulk | 13.95 | 6.58 | 6.48 | 0.11 | 644 |
| 03BIW18C | bulk | | 6.37 | | | |

**Table S11.** Perry and Bonnichsen (1966) data of the Biwabik Iron Formation showing distances from the contact (3-D) with the Duluth Complex, $\delta^{18}O$ values of magnetite and quartz, $\Delta^{18}O$ (Qt-Mt), and the recalculated temperatures based on equation 2.

| Sample # | Distance to contact (m, 3-D) | $\delta^{18}O$(Qt) ‰ VSMOW | $\delta^{18}O$(Mt) ‰ VSMOW | $\Delta^{18}O$(Qt-Mt) ‰ | T°C * |
|---|---|---|---|---|---|
| M12056 | 15 | 15.21 | 7.43 | 7.7 | 631 |
| M12022 | 52 | 12.91 | 4.69 | 8.2 | 603 |
| M12133 | 63 | 12.45 | 4.95 | 7.4 | 649 |
| M12067 | 71 | 12.64 | 4.49 | 8.1 | 608 |
| M12167 | 102 | 13.09 | 4.22 | 8.8 | 572 |
| M12232 | 128 | 13.98 | 5.49 | 8.4 | 592 |
| 36-64 | 154 | 18.90 | 9.28 | 9.5 | 541 |
| 37-64 | 171 | 12.53 | 2.49 | 10.0 | 520 |
| 38-64 | 210 | 14.10 | 2.53 | 11.5 | 466 |
| 32-64 | 480 | 13.63 | 6.43 | 7.1 | 668 |
| 6-64 | 1850 | 17.25 | 5.13 | 12.0 | 451 |
| 5-64 | 2250 | 12.11 | 2.21 | 9.8 | 528 |
| 7-64 | 2810 | 16.31 | 0.62 | 15.6 | 362 |
| 2-64 | 2970 | 17.03 | -2.10 | 19.0 | 302 |

*Clayton and Kieffer, 1991.

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