minerals

Supplementary Materials: Sources of Hydrothermal Fluids Inferred from Oxygen and Carbon Isotope Composition of Calcite, Keweenaw Peninsula Native Copper District, Michigan, USA

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Table S1. Main-stage stable isotope bulk calcite data from the Kearsarge deposit, collected by Bornhorst and Woodruff [1] but previously unpublished. All of these were determined to be within the temperature zone of pumpellyite = 212.5 °C or pumpellyite/epidote = 245 °C. Bornhorst and Woodruff [1] sample numbers are ###CL# (example: 221CL2). The first three numbers differentiate the samples, the ending number is 1–3, to indicate when there is more than one sample from the same source. Example number 221CL2, the 2 after CL is the 2nd of the 221CL# samples. All of these samples were collected from surface rock piles. Estimated analytical error is 0.2‰.

Sample Number	Sample Location	Temperatures (°C)	Measured $\delta^{18}O_{SMOW}$	Calculated $\delta^{18}O_{H2O}$	Measured $\delta^{13}C_{PDB}$	Calculated $\delta^{13}C_{CO2}$
227CL2	LaSalle #3–4	212.5	19.3	10.4	−3.0	−0.7
218CL1	LaSalle #3–4	212.5	15.3	6.4	−2.9	−0.6
228CL2	Centennial #1	212.5	13.1	4.2	−2.8	−0.4
214CL3	Centennial #1	212.5	12.7	3.8	−2.4	0.0
214CL2	South Kearsarge #1	245.0	13.6	6.1	−2.9	0.0
215CL2	South Kearsarge #1	245.0	13.9	6.5	−2.3	0.6
226CL1	Wolverine #3	245.0	14.1	6.6	−2.2	0.7
219CL1	Wolverine #3	245.0	12.7	5.2	−2.9	0.0
216CL1	Wolverine #2	245.0	14.1	6.6	−2.5	0.4
216CL3	Wolverine #2	245.0	13.7	6.2	−2.7	0.2
216CL2	Wolverine #2	245.0	14.2	6.8	−3.2	−0.3
222CL1	North Kearsarge #1	245.0	16.5	9.0	−3.1	−0.2
223CL1	North Kearsarge #3	245.0	13.0	5.5	−2.8	0.1
229CL1	North Kearsarge #3	245.0	17.0	9.5	−2.7	0.2
221CL2	North Kearsarge #3	245.0	13.6	6.2	−1.7	1.2
230CL1	North Kearsarge #4	245.0	18.3	10.8	−3.2	−0.3
228CL1	North Kearsarge #4	245.0	13.0	5.5	−3.0	−0.1
218CL3	Ahmeek #1	245.0	17.8	10.3	−3.4	−0.5
217CL2	Ahmeek #1	245.0	13.8	6.3	−3.1	−0.2
219CL3	Ahmeek #1	245.0	18.1	10.7	−3.2	−0.3
225CL2	Ahmeek #2	245.0	13.8	6.3	−2.8	0.1
225CL1	Ahmeek #2	245.0	19.1	11.7	−3.9	−1.0
220CL2	Mohawk#6	245.0	18.1	10.6	−3.1	−0.2
224CL3	Mohawk#5	245.0	17.6	10.1	−2.8	0.1
224CL2	Mohawk#5	245.0	13.2	5.7	−3.2	−0.3
221CL3	Mohawk#4	245.0	12.6	5.2	−3.4	−0.5
218CL2	Mohawk#4	245.0	14.0	6.5	−2.9	−0.1
219CL2	Mohawk#4	245.0	13.7	6.2	−2.4	0.5
215CL3	Mohawk#4	245.0	13.8	6.3	−3.4	−0.5
215CL1	Mohawk#4	245.0	14.2	6.7	−2.1	0.8
223CL2	Mohawk#3	245.0	16.7	9.2	−2.7	0.2
220CL3	Mohawk#3	245.0	15.3	7.8	−2.2	0.7
228CL3	Mohawk#2	245.0	16.6	9.2	−4.4	−1.5
222CL3	Mohawk#2	245.0	18.7	11.2	−3.5	−0.6
224CL1	Mohawk#2	245.0	13.9	6.4	−3.7	−0.8
225CL3	Seneca # 2	245.0	14.8	7.3	−3.4	−0.5
221CL1	Seneca # 2	245.0	13.8	6.4	−2.5	0.3
222CL2	Seneca #3	245.0	13.8	6.3	−2.9	0.0
226CL3	Seneca #3	245.0	13.2	5.7	−3.0	−0.1

223CL3	Central #58	245.0	16.0	8.5	−3.2	−0.3
227CL3	Central #32	245.0	17.9	10.4	−2.6	0.3

Table S2. Main-stage stable isotope SIMS calcite data for sample TB-293. TB-293 was collected underground from the Quincy mine in vicinity of the intersection of the horizontal adit and the #5 shaft, more than 70 m from the portal and 100 m vertically below the surface. The sample is from a vuggy flow top with mineralogy of calcite, quartz, prehnite, and epidote. The analyzed sample is a vug-filling calcite crystal. This sample was assigned a formation temperature of 212.5 °C (zone of pumpellyite). XMn discussed in text. Measurement error is 2SE. Spot locations provided in Figure S1.

Sample Number	Spot Location	Analysis Location	Measured $\delta^{18}O_{SMOW}$	$\delta^{18}O$ Measurement Error	Calculated $\delta^{18}O_{H2O}$	Measured $\delta^{13}C_{PDB}$	$\delta^{13}C$ Measurement Error	Calculated $\delta^{13}C_{CO2}$	XMn
TB-293	A1	Quincy Mine	18.2	0.31	9.3	−2.5	0.62	−0.2	0.00000
TB-293	A2	Quincy Mine	21.3	0.33	12.4	−5.0	0.62	−2.7	0.00000
TB-293	A3	Quincy Mine	15.9	0.32	7.0	−3.2	0.61	−0.9	0.00044
TB-293	A4	Quincy Mine	16.1	0.26	7.2	−5.0	0.54	−2.7	0.00089
TB-293	A5	Quincy Mine	16.0	0.34	7.1	−9.3	0.63	−7.0	0.00070
TB-293	A6	Quincy Mine	15.7	0.31	6.8	−2.7	0.66	−0.4	0.00000
TB-293	A7	Quincy Mine	16.1	0.31	7.2	not analyzed	not analyzed	not analyzed	0.00096
TB-293	A8	Quincy Mine	16.3	0.31	7.4	−3.6	0.61	−1.3	0.00106
TB-293	A9	Quincy Mine	16.1	0.33	7.2	−4.3	0.61	−2.0	0.00106
TB-293	A10	Quincy Mine	21.1	0.29	12.2	−3.8	0.62	−1.5	0.00182
TB-293	A11	Quincy Mine	16.2	0.29	7.3	−2.9	0.62	−0.6	0.00139
TB-293	A12	Quincy Mine	21.6	0.29	12.7	−6.6	0.70	−4.3	0.00000
TB-293	A13	Quincy Mine	21.7	0.28	12.8	−7.4	0.62	−5.1	0.00000
TB-293	A14	Quincy Mine	20.8	0.21	11.9	−7.2	0.61	−4.9	0.00000
TB-293	A15	Quincy Mine	20.6	0.34	11.7	−6.2	0.62	−3.9	0.00070
TB-293	A16	Quincy Mine	21.1	0.41	12.2	−7.0	0.62	−4.7	0.00000
TB-293	A17	Quincy Mine	22.1	0.25	13.2	−6.2	0.61	−3.9	0.00116
TB-293	A18	Quincy Mine	20.7	0.23	11.8	−4.9	0.62	−2.6	0.00036
TB-293	A19	Quincy Mine	22.0	0.30	13.1	−6.0	0.68	−3.7	0.00000
TB-293	A20	Quincy Mine	18.5	0.26	9.6	−2.1	0.62	0.2	0.00070
TB-293	A21	Quincy Mine	18.1	0.41	9.2	−2.5	0.62	−0.2	0.00000
TB-293	A22	Quincy Mine	14.6	0.31	5.7	−2.9	0.57	−0.6	0.00034
TB-293	A23	Quincy Mine	17.1	0.23	8.2	−5.8	0.40	−3.5	0.00061
TB-293	A24	Quincy Mine	15.6	0.30	6.7	not analyzed	not analyzed	not analyzed	0.00000
TB-293	A25	Quincy Mine	16.0	0.25	7.1	−2.8	0.67	−0.5	0.00097
TB-293	A26	Quincy Mine	17.3	0.33	8.4	−2.1	0.62	0.2	0.00035
TB-293	A27	Quincy Mine	16.6	0.24	7.7	−3.4	0.77	−1.1	0.00000
TB-293	A28	Quincy Mine	15.8	0.25	6.9	−3.0	0.67	−0.7	0.00052
TB-293	A29	Quincy Mine	16.0	0.28	7.1	−1.9	0.60	0.4	0.00053
TB-293	A30	Quincy Mine	21.6	0.30	12.7	−6.2	0.62	−3.9	0.00572
TB-293	A31	Quincy Mine	22.1	0.29	13.2	−7.5	0.60	−5.2	0.00579
TB-293	A32	Quincy Mine	22.2	0.28	13.3	−7.3	0.65	−5.0	0.00062
TB-293	A33	Quincy Mine	21.7	0.33	12.8	−10.1	0.72	−7.8	0.00176
TB-293	A34	Quincy Mine	21.5	0.33	12.6	−9.0	0.63	−6.7	0.00321
TB-293	A35	Quincy Mine	21.4	0.33	12.5	not analyzed	not analyzed	not analyzed	0.00027
TB-293	A36	Quincy Mine	23.4	0.31	14.5	−9.3	0.63	−7.0	0.00563
TB-293	A37	Quincy Mine	22.6	0.30	13.7	−7.4	0.63	−5.1	0.00192
TB-293	A38	Quincy Mine	21.4	0.35	12.5	−5.1	0.63	−2.8	0.00009
TB-293	A39	Quincy Mine	21.9	0.24	13.0	−7.8	0.55	−5.5	0.01067
TB-293	A40	Quincy Mine	20.5	0.28	11.6	−4.0	0.63	−1.7	0.00000
TB-293	A41	Quincy Mine	21.1	0.39	12.2	−7.2	0.62	−4.9	0.00207
TB-293	A42	Quincy Mine	21.9	0.20	13.0	not analyzed	not analyzed	not analyzed	-
TB-293	A43	Quincy Mine	23.5	0.28	14.6	not analyzed	not analyzed	not analyzed	-
TB-293	A44	Quincy Mine	21.1	0.26	12.2	−4.1	0.77	−1.8	0.00314
TB-293	A45	Quincy Mine	22.8	0.26	13.9	−6.3	0.63	−4.0	0.00532

Table S3. Late-stage stable isotope SIMS calcite data for sample WAS-121. WAS-121 is part of the A. E. Seaman Mineral Museum Research Collection. It was collected underground by W. A. Seaman from the Seneca #2 mine, Kearsarge flow top deposit. The sample is part of a late-stage vein with the minerals calcite, laumontite and natrolite. It was assigned a formation temperature of 150 °C. XMn discussed in text. Measurement error is 2SE. Spot locations provided in Figure S2.

Sample Number	Spot Location	Analysis Location	Measured $\delta^{18}O_{SMOW}$	$\delta^{18}O$ Measurement Error	Calculated $\delta^{18}O_{H2O}$	Measured $\delta^{13}C_{PDB}$	$\delta^{13}C$ Measurement Error	Calculated $\delta^{13}C_{CO2}$	XMn
WAS-121	B1	Kearsarge Seneca Mine Lake Vein	14.1	0.28	−0.5	−4.6	0.63	−5.1	0.00000
WAS-121	B2	Kearsarge Seneca Mine Lake Vein	16.1	0.32	1.4	−9.7	0.66	−10.2	0.00000
WAS-121	B3	Kearsarge Seneca Mine Lake Vein	15.6	0.24	1.0	−7.6	0.67	−8.1	0.00061
WAS-121	B4	Kearsarge Seneca Mine Lake Vein	15.7	0.28	1.0	−6.4	0.64	−6.9	0.00000
WAS-121	B5	Kearsarge Seneca Mine Lake Vein	16.0	0.23	1.4	−8.3	0.63	−8.8	0.00000
WAS-121	B6	Kearsarge Seneca Mine Lake Vein	14.5	0.36	−0.1	−7.4	0.63	−7.9	0.00096
WAS-121	B7	Kearsarge Seneca Mine Lake Vein	14.4	0.30	−0.3	−5.9	0.64	−6.4	0.00000
WAS-121	B8	Kearsarge Seneca Mine Lake Vein	14.8	0.29	0.2	−9.7	0.63	−10.2	0.00000
WAS-121	B9	Kearsarge Seneca Mine Lake Vein	19.0	0.25	4.3	−4.6	0.63	−5.1	0.00000
WAS-121	B10	Kearsarge Seneca Mine Lake Vein	20.2	0.27	5.6	−3.6	0.63	−4.1	0.00000
WAS-121	B11	Kearsarge Seneca Mine Lake Vein	19.1	0.29	4.5	−3.4	0.64	−3.9	0.00071
WAS-121	B12	Kearsarge Seneca Mine Lake Vein	19.2	0.23	4.5	−1.4	0.64	−1.9	0.00000
WAS-121	B13	Kearsarge Seneca Mine Lake Vein	19.0	0.31	4.3	−2.9	0.64	−3.4	0.00000
WAS-121	B14	Kearsarge Seneca Mine Lake Vein	18.8	0.36	4.2	−1.4	0.64	−1.9	0.00000
WAS-121	B15	Kearsarge Seneca Mine Lake Vein	18.3	0.35	3.7	−2.1	0.64	−2.6	0.00000
WAS-121	B16	Kearsarge Seneca Mine Lake Vein	19.6	0.25	5.0	−2.4	0.64	−2.9	0.00061
WAS-121	B17	Kearsarge Seneca Mine Lake Vein	19.1	0.26	4.5	−2.0	0.64	−2.5	0.00000
WAS-121	B18	Kearsarge Seneca Mine Lake Vein	18.7	0.30	4.0	−1.7	0.64	−2.2	0.00000
WAS-121	B19	Kearsarge Seneca Mine Lake Vein	17.6	0.31	3.0	−2.9	0.64	−3.4	0.00043
WAS-121	B20	Kearsarge Seneca Mine Lake Vein	18.2	0.28	3.5	−2.3	0.64	−2.8	0.00105
WAS-121	B21	Kearsarge Seneca Mine Lake Vein	19.4	0.31	4.8	−0.5	0.66	−1.0	0.00000
WAS-121	B22	Kearsarge Seneca Mine Lake Vein	18.0	0.25	3.4	−2.3	0.64	−2.8	0.00017
WAS-121	B23	Kearsarge Seneca Mine Lake Vein	17.9	0.29	3.2	−3.7	0.64	−4.2	0.00000
WAS-121	B24	Kearsarge Seneca Mine Lake Vein	18.6	0.26	3.9	−2.1	0.64	−2.6	0.00026
WAS-121	B25	Kearsarge Seneca Mine Lake Vein	18.6	0.34	3.9	−3.2	0.65	−3.7	0.00026
WAS-121	B26	Kearsarge Seneca Mine Lake Vein	18.6	0.23	4.0	−3.4	0.66	−3.9	0.00000
WAS-121	B27	Kearsarge Seneca Mine Lake Vein	18.3	0.32	3.6	−4.4	0.64	−4.9	0.00017

WAS-121	B28	Kearsarge Seneca Mine Lake Vein	17.6	0.34	2.9	−3.7	0.65	−4.2	0.00000
WAS-121	B29	Kearsarge Seneca Mine Lake Vein	12.7	0.26	−2.0	−5.2	0.64	−5.7	0.00009
WAS-121	B30	Kearsarge Seneca Mine Lake Vein	14.3	0.28	−0.3	−5.5	0.73	−6.0	0.00035

Table S4. Main-stage stable isotope SIMS calcite data sample WAS752. WAS752 was collected from the Kearsarge Wolverine mine with the minerals calcite, copper, prehnite, and epidote. This sample was assigned a temperature zone of pumpellyite/epidote at 245 °C. XMn discussed in text. Measurement error is 2SE. Spot locations provided in Figure S3.

Sample Number	Spot Location	Analysis Location	Measured $\delta^{18}O_{SMOW}$	$\delta^{18}O$ Measurement Error	Calculated $\delta^{18}O_{H2O}$	Measured $\delta^{13}C_{PDB}$	$\delta^{13}C$ Measurement Error	Calculated $\delta^{13}C_{CO2}$	XMn
WAS-752a	C1	Kearsarge Wolverine Mine	13.7	0.29	6.3	−6.0	0.61	−3.1	0.00105
WAS-752a	C2	Kearsarge Wolverine Mine	13.9	0.31	6.5	−2.7	0.67	0.2	0.00000
WAS-752a	C3	Kearsarge Wolverine Mine	13.9	0.31	6.5	−8.7	0.95	−5.8	0.00216
WAS-752a	C4	Kearsarge Wolverine Mine	14.0	0.25	6.6	−2.4	0.82	0.5	0.00044
WAS-752a	C5	Kearsarge Wolverine Mine	13.1	0.29	5.7	−2.2	0.65	0.7	0.00000
WAS-752a	C6	Kearsarge Wolverine Mine	13.9	0.32	6.4	−4.6	0.63	−1.7	0.00026
WAS-752a	C7	Kearsarge Wolverine Mine	14.2	0.30	6.8	−6.1	0.57	−3.2	0.00111
WAS-752a	C8	Kearsarge Wolverine Mine	13.7	0.28	6.2	−0.2	0.64	2.7	0.00044
WAS-752b	C9	Kearsarge Wolverine Mine	13.2	0.20	5.7	−7.3	0.54	−4.4	0.00131
WAS-752b	C10	Kearsarge Wolverine Mine	14.1	0.33	6.6	−2.1	0.65	0.8	0.00036
WAS-752b	C11	Kearsarge Wolverine Mine	13.6	0.30	6.2	−2.2	0.65	0.7	0.00000
WAS-752b	C12	Kearsarge Wolverine Mine	14.3	0.30	6.9	−1.0	0.97	1.9	0.00069
WAS-752b	C13	Kearsarge Wolverine Mine	14.1	0.30	6.6	−2.0	0.65	0.9	0.00087
WAS-752b	C14	Kearsarge Wolverine Mine	13.9	0.34	6.5	−1.3	0.74	1.6	0.00000
WAS-752b	C15	Kearsarge Wolverine Mine	13.8	0.29	6.4	−5.9	0.57	−3.0	0.00105
WAS-752b	C16	Kearsarge Wolverine Mine	14.0	0.28	6.6	−2.3	0.74	0.6	0.00000
WAS-752b	C17	Kearsarge Wolverine Mine	13.3	0.25	5.9	−1.6	0.82	1.3	0.00156
WAS-752b	C18	Kearsarge Wolverine Mine	13.6	0.32	6.1	−3.4	0.65	−0.5	0.00018
WAS-752b	C19	Kearsarge Wolverine Mine	13.8	0.33	6.3	−1.3	0.65	1.6	0.00018
WAS-752b	C20	Kearsarge Wolverine Mine	13.7	0.28	6.3	−1.8	0.67	1.1	0.00018
WAS-752b	C21	Kearsarge Wolverine Mine	13.6	0.26	6.1	−3.2	0.63	−0.3	0.00000
WAS-752b	C22	Kearsarge Wolverine Mine	13.6	0.29	6.1	−4.3	0.64	−1.4	0.00069
WAS-752b	C23	Kearsarge Wolverine Mine	13.6	0.34	6.1	−1.8	0.81	1.1	0.00000
WAS-752b	C24	Kearsarge Wolverine Mine	13.6	0.26	6.1	−1.7	0.65	1.2	0.00000

WAS-752b	C25	Kearsarge Wolverine Mine	13.7	0.28	6.3	−2.8	0.65	0.1	0.00000
WAS-752b	C26	Kearsarge Wolverine Mine	13.4	0.26	5.9	−1.6	0.65	1.3	0.00000
WAS-752b	C27	Kearsarge Wolverine Mine	14.0	0.29	6.5	−1.5	0.63	1.4	0.00000
WAS-752b	C28	Kearsarge Wolverine Mine	14.0	0.32	6.5	not analyzed	not analyzed	not analyzed	-

Table S5. Main-stage stable isotope SIMS calcite data for sample WAS-505. WAS503 is part of the A. E. Seaman Mineral Museum Research Collection. It was collected underground by W. A. Seaman from the Quincy mine, Pewabic flow top deposit. The sample is from the 260 m level of the #6 shaft about 75 m south of the main "spar crossing" from a transverse vein dipping 70°. Calcite, quartz and epidote are associated with native copper. This sample was assigned a formation temperature of 212.5 °C (pumpellyite zone). XMn discussed in text. Measurement error is 2SE. Spot locations provided in Figure S4.

Sample Number	Spot Location	Analysis Location	Measured $\delta^{18}O_{SMOW}$	$\delta^{18}O$ Measurement Error	Calculated $\delta^{18}O_{H2O}$	Measured $\delta^{13}C_{PDB}$	$\delta^{13}C$ Measurement Error	Calculated $\delta^{13}C_{CO2}$	XMn
WAS-505	D1	Quincy Mine	18.9	0.29	10.0	not analyzed	not analyzed	not analyzed	0.01707
WAS-505	D2	Quincy Mine	19.5	0.32	10.6	−5.4	0.73	−3.1	0.01608
WAS-505	D3	Quincy Mine	18.8	0.53	9.9	−5.4	0.73	−3.1	0.01650
WAS-505	D4	Quincy Mine	17.7	0.32	8.8	−4.1	0.76	−1.7	0.00000
WAS-505	D5	Quincy Mine	16.2	0.33	7.3	−3.9	0.73	−1.6	0.00048
WAS-505	D6	Quincy Mine	14.4	0.33	5.5	−3.0	0.74	−0.7	0.00042
WAS-505	D7	Quincy Mine	13.5	0.43	4.6	−2.4	0.85	−0.1	0.00191
WAS-505	D8	Quincy Mine	13.8	0.36	4.9	−3.5	0.96	−1.1	0.00066
WAS-505	D9	Quincy Mine	14.5	0.32	5.6	−2.9	0.74	−0.6	0.00048
WAS-505	D10	Quincy Mine	14.6	0.36	5.7	−2.5	0.73	−0.1	0.00243
WAS-505	D11	Quincy Mine	14.6	0.34	5.8	−2.4	0.79	0.0	0.00089
WAS-505	D12	Quincy Mine	14.4	0.35	5.5	−3.4	0.74	−1.1	0.00000
WAS-505	D13	Quincy Mine	14.2	0.30	5.3	−3.6	0.73	−1.3	0.00165
WAS-505	D14	Quincy Mine	12.9	0.40	4.0	not analyzed	not analyzed	not analyzed	0.00148
WAS-505	D15	Quincy Mine	15.2	0.37	6.3	−2.4	0.73	0.0	0.00000
WAS-505	D16	Quincy Mine	14.9	0.44	6.1	−1.7	0.84	0.7	0.00134
WAS-505	D17	Quincy Mine	15.8	0.38	6.9	−2.2	0.73	0.2	0.00166
WAS-505	D18	Quincy Mine	18.4	0.34	9.5	−1.2	0.73	1.1	0.00118
WAS-505	D19	Quincy Mine	18.8	0.36	9.9	−2.0	0.73	0.3	0.00000
WAS-505	D20	Quincy Mine	19.1	0.36	10.2	−2.4	0.82	−0.1	0.00083
WAS-505	D21	Quincy Mine	17.5	0.30	8.6	−3.3	0.73	−1.0	0.00181

WAS-505	D22	Quincy Mine	18.7	0.36	9.8	−3.3	0.74	−0.9	0.00000
WAS-505	D23	Quincy Mine	17.2	0.33	8.3	−2.6	0.79	−0.3	0.00036
WAS-505	D24	Quincy Mine	18.1	0.36	9.2	−2.7	1.05	−0.4	0.00000
WAS-505	D25	Quincy Mine	18.1	0.50	9.2	not analyzed	not analyzed	not analyzed	-
WAS-505	D26	Quincy Mine	17.5	0.30	8.6	not analyzed	not analyzed	not analyzed	0.00388
WAS-505	D27	Quincy Mine	18.2	0.27	9.3	not analyzed	not analyzed	not analyzed	0.00265
WAS-505	D28	Quincy Mine	17.7	0.30	8.8	not analyzed	not analyzed	not analyzed	0.00047
WAS-505	D29	Quincy Mine	17.4	0.33	8.5	not analyzed	not analyzed	not analyzed	0.00112
WAS-505	D30	Quincy Mine	14.7	0.35	5.8	−2.5	0.76	−0.2	0.00012
WAS-505	D31	Quincy Mine	14.2	0.33	5.3	−2.3	0.78	0.1	0.00118
WAS-505	D32	Quincy Mine	18.5	0.31	9.6	−1.1	0.75	1.2	0.00099
WAS-505	D33	Quincy Mine	18.6	0.33	9.7	−1.5	0.80	0.8	0.01273
WAS-505	D34	Quincy Mine	20.0	0.32	11.1	−2.1	0.82	0.2	0.01801
WAS-505	D35	Quincy Mine	19.3	0.36	10.4	−1.3	0.73	1.0	0.00111
WAS-505	D36	Quincy Mine	17.0	0.39	8.1	not analyzed	not analyzed	not analyzed	0.00035
WAS-505	D37	Quincy Mine	15.9	0.25	7.0	not analyzed	not analyzed	not analyzed	0.00738

Table S6. Main-stage stable isotope SIMS calcite data for sample CAL-94-29. CAL-94-29 is part of the A. E. Seaman Mineral Museum Research Collection. It was collected underground by T. J. Bornhorst from a freshly blasted mineralized pocket at the base of the Knowlton flow top about 15 m up dip from the horizontal adit of the Caledonia Mine, which is parallel to the strike of the flow top, at about the 220 m marker along the adit. The pocket appears to be fracture controlled with strike of pocket parallel to strike of the flow top but dip of pocket steeper than the dip of the flow top [2]. Calcite, quartz, and epidote are associated with native copper. It was assigned a formation temperature of 245 °C (pumpellyite/epidote zone). XMn discussed in text. Measurement error is 2SE. Spot locations provided in Figure S5.

Sample Number	Spot Location	Analysis Location	Measured $\delta^{18}O_{SMOW}$	$\delta^{18}O$ Measurement Error	Calculated $\delta^{18}O_{H2O}$	Measured $\delta^{13}C_{PDB}$	$\delta^{13}C$ Measurement Error	Calculated $\delta^{13}C_{CO2}$	XMn
CAL-94-29	E1	Caledonia Mine	12.7	0.32	5.2	−4.7	0.68	−1.8	0.00080
CAL-94-29	E2	Caledonia Mine	12.9	0.34	5.4	−3.4	0.72	−0.6	0.00030
CAL-94-29	E3	Caledonia Mine	12.2	0.40	4.7	−2.9	0.80	0.0	0.00128
CAL-94-29	E4	Caledonia Mine	12.6	0.34	5.1	−3.1	0.70	−0.3	0.00055
CAL-94-29	E5	Caledonia Mine	12.2	0.37	4.7	−4.0	0.77	−1.1	0.00018
CAL-94-29	E6	Caledonia Mine	12.6	0.35	5.1	−3.5	0.67	−0.6	0.00036
CAL-94-29	E7	Caledonia Mine	12.2	0.40	4.7	−4.1	0.67	−1.2	0.00079
CAL-94-29	E8	Caledonia Mine	11.6	0.40	4.2	−3.7	0.71	−0.8	0.00230

CAL-94-29	E9	Caledonia Mine	11.9	0.41	4.4	not analyzed	not analyzed	not analyzed	0.00171
CAL-94-29	E10	Caledonia Mine	12.3	0.47	4.8	not analyzed	not analyzed	not analyzed	0.00036
CAL-94-29	E11	Caledonia Mine	12.3	0.48	4.8	−1.9	0.73	1.0	0.00030
CAL-94-29	E12	Caledonia Mine	12.3	0.47	4.9	−3.7	0.67	−0.8	0.00145

Table S7. Main-stage stable isotope SIMS calcite data for sample MOR-1. MOR-1 is part of the A. E. Seaman Mineral Museum Research Collection. It was from the collection of Arthur Moretta and is from the Quincy Mine in vicinity of the #5 or #6 shaft and likely above the 10th level or 150 m vertically below the surface (Pewabic flow top deposit. This sample is a single vug-filling transparent calcite crystal about 3 cm tall. There are many inclusions of native copper. It was assigned a formation temperature of 215.5 °C (pumpellyite zone). XMn discussed in text. Measurement error is 2SE. Spot locations provided in Figure S6.

Sample Number	Spot Location	Analysis Location	Measured $\delta^{18}O_{SMOW}$	$\delta^{18}O$ Measurement Error	Calculated $\delta^{18}O_{H2O}$	Measured $\delta^{13}C_{PDB}$	$\delta^{13}C$ Measurement Error	Calculated $\delta^{13}C_{CO2}$	XMn
MOR-1	F1	Quincy Mine	18.4	0.43	9.5	−5.0	0.63	−2.6	0.00000
MOR-1	F2	Quincy Mine	18.0	0.52	9.1	−4.5	0.63	−2.2	0.00000
MOR-1	F3	Quincy Mine	18.7	0.47	9.8	−3.7	0.69	−1.4	0.00029
MOR-1	F4	Quincy Mine	17.9	0.43	9.0	−2.6	0.64	−0.3	0.00012
MOR-1	F5	Quincy Mine	18.5	0.45	9.6	−1.3	0.66	1.0	0.00152
MOR-1	F6	Quincy Mine	16.9	0.54	8.0	−2.9	0.64	−0.6	0.00053
MOR-1	F7	Quincy Mine	16.5	0.36	7.6	−2.0	0.67	0.3	0.00053
MOR-1	F8	Quincy Mine	18.2	0.44	9.3	−2.9	0.70	−0.6	0.00199

Table S8. Main-stage stable isotope SIMS calcite data for sample DK-1. DK-1 is part of the A. E. Seaman Mineral Museum Research Collection. It was collected by D. Kelly from the Seneca #1 mine surface rock pile, Kearsarge flow top deposit. Calcite is associated with native copper. It was assigned a formation temperature of at 245 °C (pumpellyite/epidote zone). XMn discussed in text. Measurement error is 2SE. Spot locations provided in Figure S7.

Sample Number	Spot Location	Analysis Location	Measured $\delta^{18}O_{SMOW}$	$\delta^{18}O$ Measurement Error	Calculated $\delta^{18}O_{H2O}$	Measured $\delta^{13}C_{PDB}$	$\delta^{13}C$ Measurement Error	Calculated $\delta^{13}C_{CO2}$	XMn
DK-1a	G1	Kearsarge deposit/Seneca Mine	20.0	0.48	12.6	−4.3	0.66	−1.4	0.00000
DK-1a	G2	Kearsarge deposit/Seneca Mine	20.1	0.44	12.6	−4.4	0.74	−1.5	0.00000
DK-1a	G3	Kearsarge deposit/Seneca Mine	20.7	0.46	13.2	−1.9	0.64	0.9	0.00134
DK-1a	G4	Kearsarge deposit/Seneca Mine	20.1	0.48	12.7	−3.1	0.66	−0.2	0.00180
DK-1a	G5	Kearsarge deposit/Seneca Mine	20.6	0.43	13.2	−3.9	0.64	−1.0	0.00000
DK-1a	G6	Kearsarge deposit/Seneca Mine	20.8	0.49	13.3	−3.6	0.63	−0.7	0.00053
DK-1a	G7	Kearsarge deposit/Seneca Mine	20.2	0.47	12.7	−4.3	0.64	−1.4	0.00088
DK-1a	G8	Kearsarge deposit/Seneca Mine	19.3	0.56	11.8	−4.1	0.64	−1.2	0.00029
DK-1a	G9	Kearsarge deposit/Seneca Mine	17.9	0.42	10.5	not analyzed	not analyzed	not analyzed	0.00222
DK-1a	G10	Kearsarge deposit/Seneca Mine	17.0	0.48	9.5	−4.3	0.63	−1.5	0.00342
DK-1a	G11	Kearsarge deposit/Seneca Mine	15.9	0.42	8.5	−7.6	0.62	−4.7	0.00449
DK-1a	G12	Kearsarge deposit/Seneca Mine	20.8	0.44	13.3	−5.2	0.74	−2.3	0.00000

DK-1a	G13	Kearsarge deposit/Seneca Mine	19.3	0.36	11.8	−2.7	0.67	0.2	0.00006
DK-1a	G14	Kearsarge deposit/Seneca Mine	19.9	0.42	12.4	not analyzed	not analyzed	not analyzed	0.00017
DK-1a	G15	Kearsarge deposit/Seneca Mine	20.1	0.39	12.6	−4.6	0.82	−1.7	0.00012
DK-1a	G16	Kearsarge deposit/Seneca Mine	20.0	0.32	12.5	−8.2	0.70	−5.3	0.00730
DK-1a	G17	Kearsarge deposit/Seneca Mine	17.7	0.41	10.3	−5.3	0.63	−2.4	0.00255
DK-1a	G18	Kearsarge deposit/Seneca Mine	17.0	0.36	9.6	−10.2	0.63	−7.3	0.00320
DK-1a	G19	Kearsarge deposit/Seneca Mine	17.0	0.41	9.5	−6.4	0.63	−3.5	0.00000
DK-1a	G20	Kearsarge deposit/Seneca Mine	19.0	0.34	11.5	−6.1	0.63	−3.3	0.00245
DK-1a	G21	Kearsarge deposit/Seneca Mine	18.6	0.52	11.2	−4.8	0.71	−1.9	0.00477
DK-1a	G22	Kearsarge deposit/Seneca Mine	14.5	0.41	7.1	−8.7	0.63	−5.8	0.00029
DK-1b	G23	Kearsarge deposit/Seneca Mine	18.7	0.47	11.3	−1.8	0.64	1.1	0.00053
DK-1b	G24	Kearsarge deposit/Seneca Mine	17.9	0.43	10.5	−1.7	0.64	1.2	0.00098
DK-1b	G25	Kearsarge deposit/Seneca Mine	17.5	0.36	10.1	−2.5	0.80	0.4	0.00000
DK-1b	G26	Kearsarge deposit/Seneca Mine	18.4	0.42	10.9	−3.0	0.64	−0.1	0.00058
DK-1b	G27	Kearsarge deposit/Seneca Mine	17.9	0.51	10.5	−1.8	0.65	1.1	0.00100
DK-1b	G28	Kearsarge deposit/Seneca Mine	18.2	0.42	10.8	−1.4	0.73	1.5	0.00055
DK-1b	G29	Kearsarge deposit/Seneca Mine	18.1	0.37	10.6	−1.1	0.69	1.8	0.00064
DK-1b	G30	Kearsarge deposit/Seneca Mine	18.5	0.35	11.0	−2.7	0.64	0.2	0.00000
DK-1b	G31	Kearsarge deposit/Seneca Mine	17.3	0.50	9.8	−3.1	0.64	−0.2	0.00064
DK-1b	G32	Kearsarge deposit/Seneca Mine	17.2	0.51	9.8	−5.1	0.73	−2.2	0.00006
DK-1b	G33	Kearsarge deposit/Seneca Mine	17.4	0.41	10.0	−2.1	0.64	0.8	0.00000

Table S9. Late-stage stable isotope SIMS calcite data for sample CM-1. CM-1 is part of the A. E. Seaman Mineral Museum Research Collection, also labeled CAL 94-7. It was collected underground by T. Bornhorst at the 195 m marker along the main adit which is parallel to the strike of the Knowlton flow top at the Caledonia Mine. An approximately 10 cm wide vein with strike perpendicular to the flow top deposit and near vertical dip. The barren vein clearly cross cuts the native copper mineralized Knowlton flow top deposit. This is a late-stage vein with calcite and laumontite and lacking native copper [2]. It was assigned formation temperature of 150 °C. XMn discussed in text. Measurement error is 2SE. Spot locations provided in Figure S8.

Sample Number	Spot Location	Analysis Location	Measured $\delta^{18}O_{SMOW}$	$\delta^{18}O$ Measurement Error	Calculated $\delta^{18}O_{H2O}$	Measured $\delta^{13}C_{PDB}$	$\delta^{13}C$ Measurement Error	Calculated $\delta^{13}C_{CO2}$	XMn
CM-1a	H1	Caledonia Mine	17.5	0.44	2.9	not analyzed	not analyzed	not analyzed	0.00000
CM-1a	H2	Caledonia Mine	17.2	0.39	2.5	−8.5	0.88	−8.9	0.00088
CM-1a	H3	Caledonia Mine	16.1	0.42	1.4	−7.1	0.68	−7.6	0.00000

CM-1a	H4	Caledonia Mine	16.1	0.41	1.4	−10.4	0.88	−10.9	0.00059
CM-1a	H5	Caledonia Mine	16.4	0.48	1.7	−9.9	0.64	−10.4	0.00053
CM-1a	H6	Caledonia Mine	16.6	0.38	1.9	−9.8	0.65	−10.3	0.00000
CM-1a	H7	Caledonia Mine	16.7	0.39	2.0	−9.1	0.72	−9.6	0.00000
CM-1a	H8	Caledonia Mine	17.2	0.51	2.6	−8.3	0.68	−8.8	0.00047
CM-1a	H9	Caledonia Mine	16.9	0.31	2.2	−9.0	0.72	−9.5	0.00012
CM-1a	H10	Caledonia Mine	17.3	0.43	2.7	−7.8	0.64	−8.2	0.00000
CM-1a	H11	Caledonia Mine	17.1	0.58	2.4	−9.0	0.64	−9.5	0.00000
CM-1a	H12	Caledonia Mine	17.0	0.48	2.4	−9.8	0.64	−10.2	0.00029
CM-1a	H13	Caledonia Mine	17.3	0.48	2.6	−8.5	0.64	−9.0	0.00081
CM-1a	H14	Caledonia Mine	17.5	0.41	2.8	−8.4	0.90	−8.9	0.00041
CM-1a	H15	Caledonia Mine	17.4	0.47	2.8	−8.3	0.70	−8.8	0.00023
CM-1a	H16	Caledonia Mine	17.8	0.44	3.2	−8.5	0.67	−9.0	0.00000
CM-1b	H17	Caledonia Mine	16.5	0.40	1.8	−10.7	0.64	−11.2	0.00081
CM-1b	H18	Caledonia Mine	16.8	0.53	2.2	−9.5	0.73	−10.0	0.00023
CM-1b	H19	Caledonia Mine	16.4	0.45	1.8	−9.3	0.73	−9.8	0.00029
CM-1b	H20	Caledonia Mine	18.2	0.33	3.5	−10.5	0.62	−11.0	0.00023
CM-1b	H21	Caledonia Mine	15.4	0.42	0.8	−10.2	0.63	−10.7	0.00000
CM-1b	H22	Caledonia Mine	16.4	0.42	1.7	−10.5	0.70	−10.9	0.00047
CM-1b	H23	Caledonia Mine	16.9	0.52	2.2	−9.5	0.78	−10.0	0.00052
CM-1b	H24	Caledonia Mine	16.8	0.45	2.2	−8.8	0.64	−9.3	0.00012
CM-1b	H25	Caledonia Mine	16.7	0.46	2.0	−10.1	0.64	−10.6	0.00000
CM-1b	H26	Caledonia Mine	17.2	0.37	2.6	−9.1	0.64	−9.5	0.00140
CM-1b	H27	Caledonia Mine	16.9	0.57	2.2	−9.2	0.74	−9.7	0.00000
CM-1b	H28	Caledonia Mine	16.4	0.50	1.8	−11.4	0.62	−11.9	0.00000
CM-1c	H29	Caledonia Mine	16.7	0.46	2.0	−8.5	0.64	−9.0	0.00134
CM-1c	H30	Caledonia Mine	16.9	0.42	2.2	−9.7	0.64	−10.2	0.00111
CM-1c	H31	Caledonia Mine	16.9	0.43	2.2	−11.1	0.64	−11.6	0.00000
CM-1c	H32	Caledonia Mine	17.6	0.43	2.9	−10.1	0.65	−10.6	0.00000
CM-1c	H33	Caledonia Mine	17.7	0.44	3.1	−9.2	0.64	−9.7	0.00000
CM-1c	H34	Caledonia Mine	16.7	0.46	2.1	−9.9	0.72	−10.4	0.00000

CM-1c	H35	Caledonia Mine	18.3	0.49	3.7	−9.5	0.68	−10.0	0.00111
CM-1c	H36	Caledonia Mine	16.3	0.54	1.7	−11.6	0.65	−12.1	0.00081
CM-1c	H37	Caledonia Mine	16.1	0.46	1.5	−9.5	0.64	−10.0	0.00000
CM-1c	H38	Caledonia Mine	17.1	0.48	2.5	−9.3	0.64	−9.8	0.00000
CM-1c	H39	Caledonia Mine	17.5	0.50	2.8	−8.7	0.64	−9.2	0.00023
CM-1c	H40	Caledonia Mine	17.4	0.49	2.8	−10.0	0.74	−10.5	0.00133
CM-1c	H41	Caledonia Mine	17.4	0.38	2.8	−8.5	0.64	−9.0	0.00070
CM-1c	H42	Caledonia Mine	20.7	0.59	6.0	−9.1	0.64	−9.6	0.00000
CM-1c	H43	Caledonia Mine	17.8	0.37	3.1	−8.5	0.71	−9.0	0.00000
CM-1c	H44	Caledonia Mine	not analyzed	not analyzed	not analyzed	−9.6	0.64	−10.0	0.00000

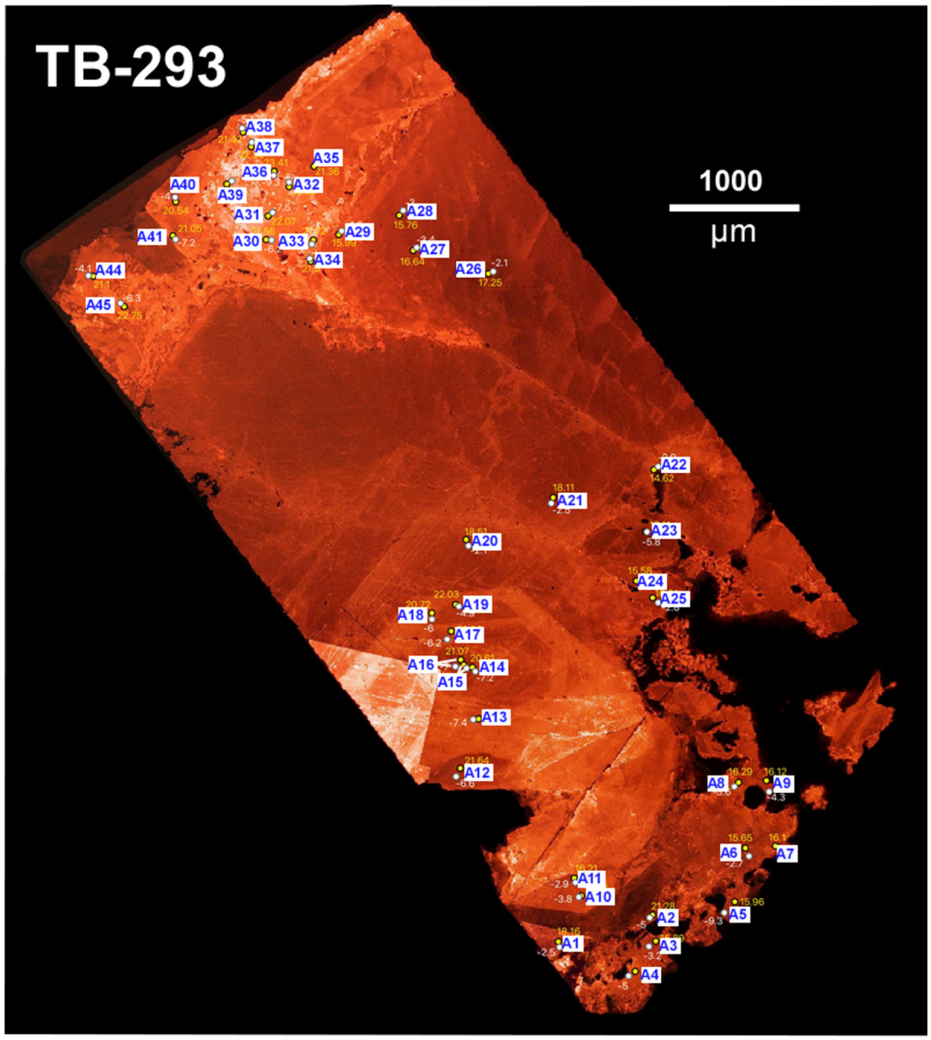

Figure S1. Spot Analysis Cathodoluminescence image of TB-293. This sample is from the Quincy mine. Small circles represent spot location for oxygen and carbon isotopic determinations, the labels are the spot locations referenced in Table S2.

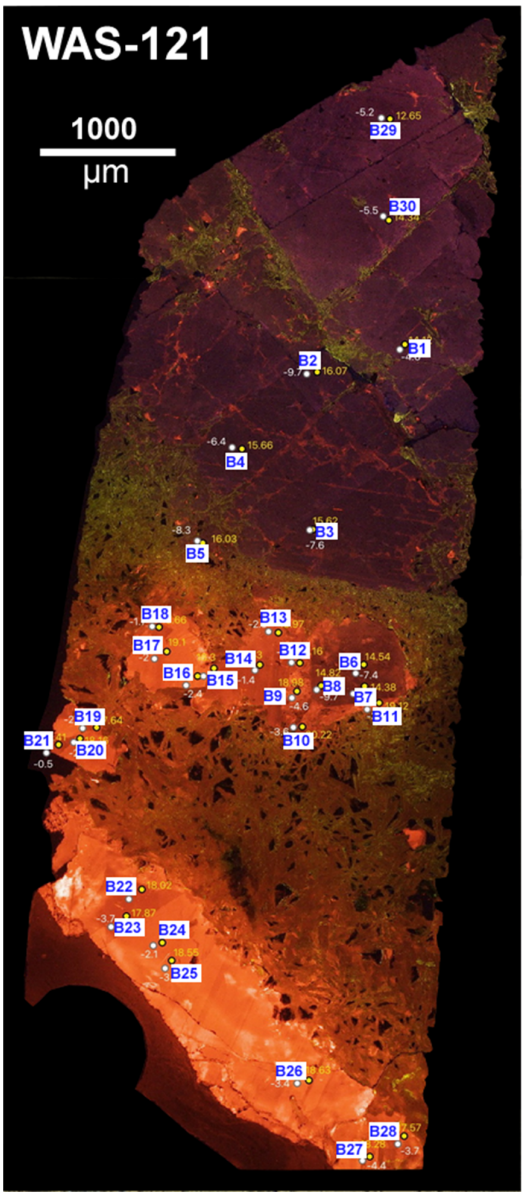

Figure S2. Spot Analysis Cathodoluminescence image of WAS-121. This sample is from the Kearsarge Seneca mine. Small circles represent spot location for oxygen and carbon isotopic determinations, the labels are the spot locations referenced in Table S3.

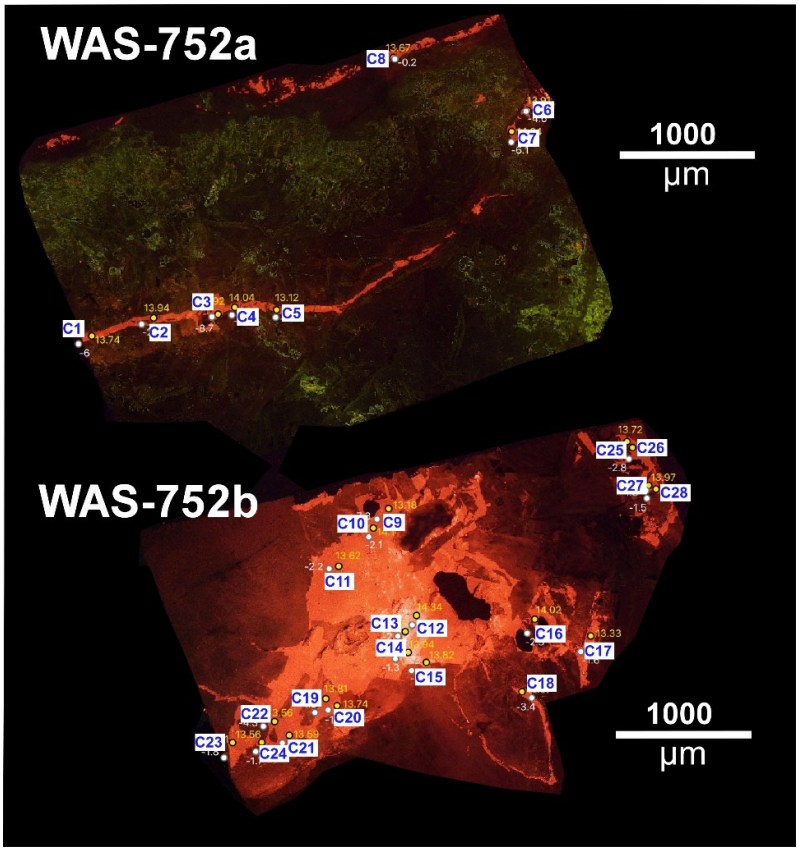

Figure S3. Spot Analysis Cathodoluminescence image of WAS-752. This sample is from the Kearsarge Wolverine mine. Small circles represent spot location for oxygen and carbon isotopic determinations, the labels are the spot locations referenced in Table S4.

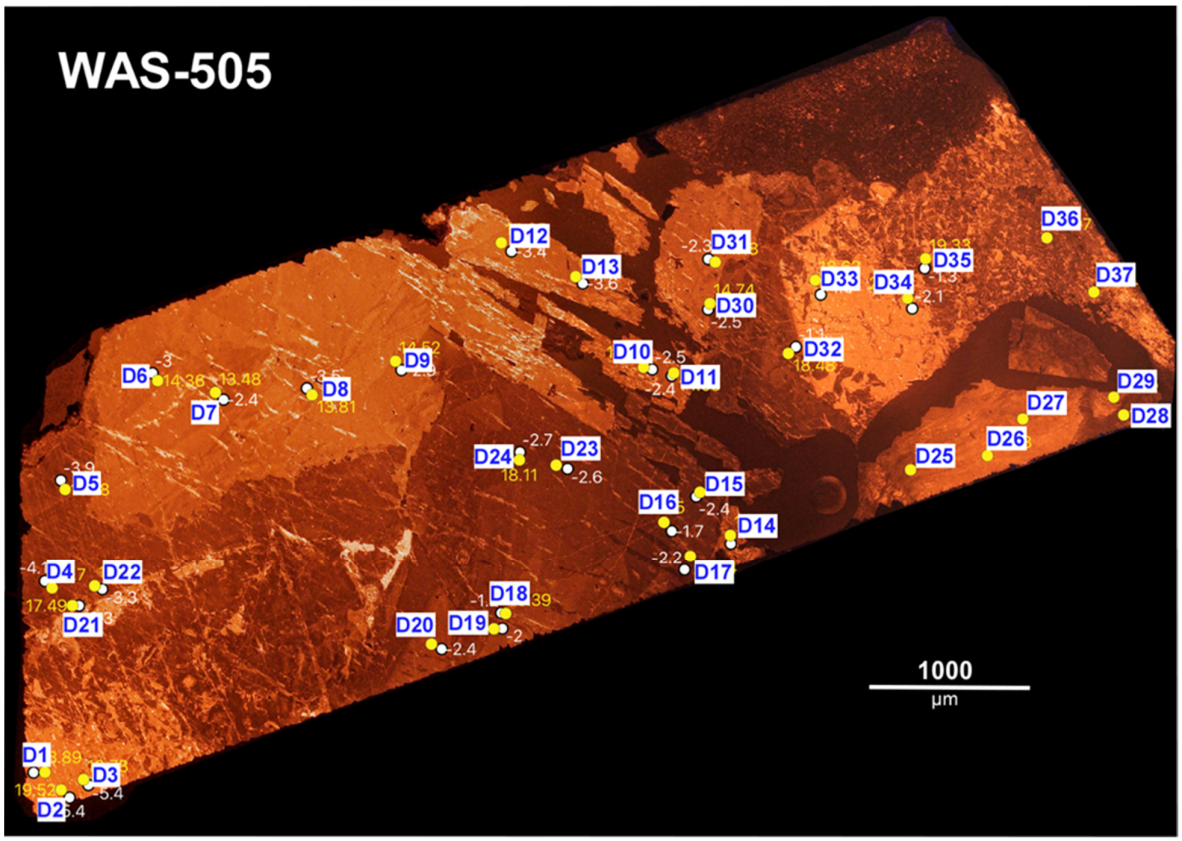

Figure S4. Spot analysis cathodoluminescence image of WAS-505. This sample is from the Quincy mine. Small circles represent spot location for oxygen and carbon isotopic determinations, the labels are the spot locations referenced in Table S5.

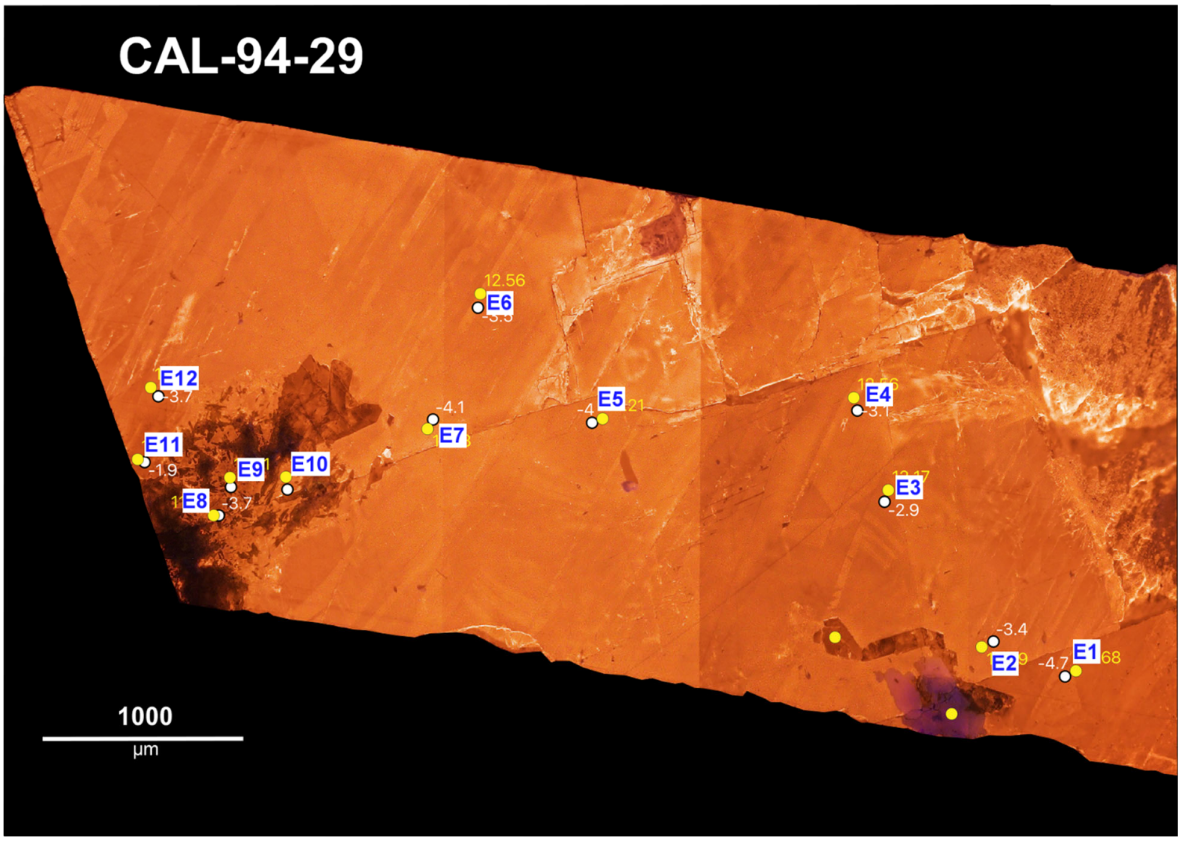

Figure S5. Spot analysis cathodoluminescence image of CAL-94-29. This sample is from the Caledonia mine. Small circles represent spot location for oxygen and carbon isotopic determinations, the labels are the spot locations referenced in Table S6.

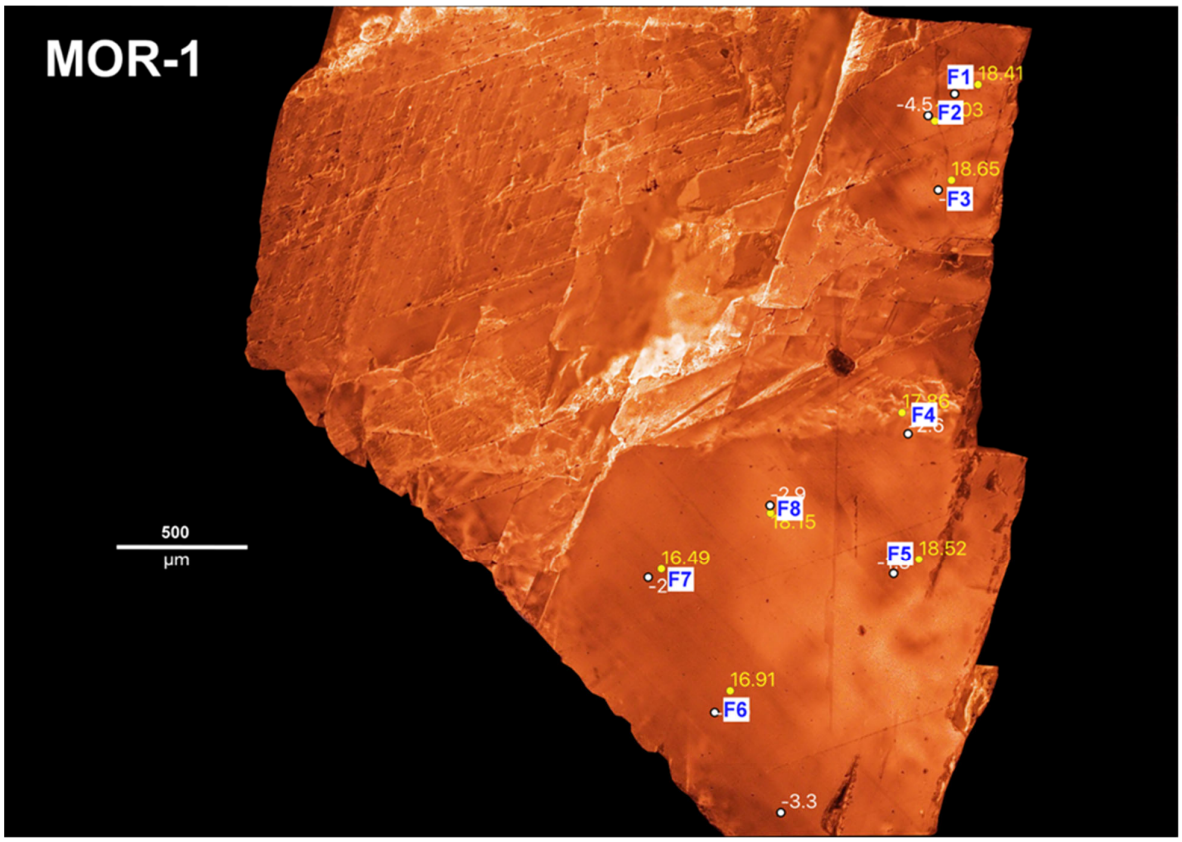

Figure S6. Spot analysis cathodoluminescence image of MOR-1. This sample is from the Quincy mine. Small circles represent spot location for oxygen and carbon isotopic determinations, the labels are the spot locations referenced in Table S7.

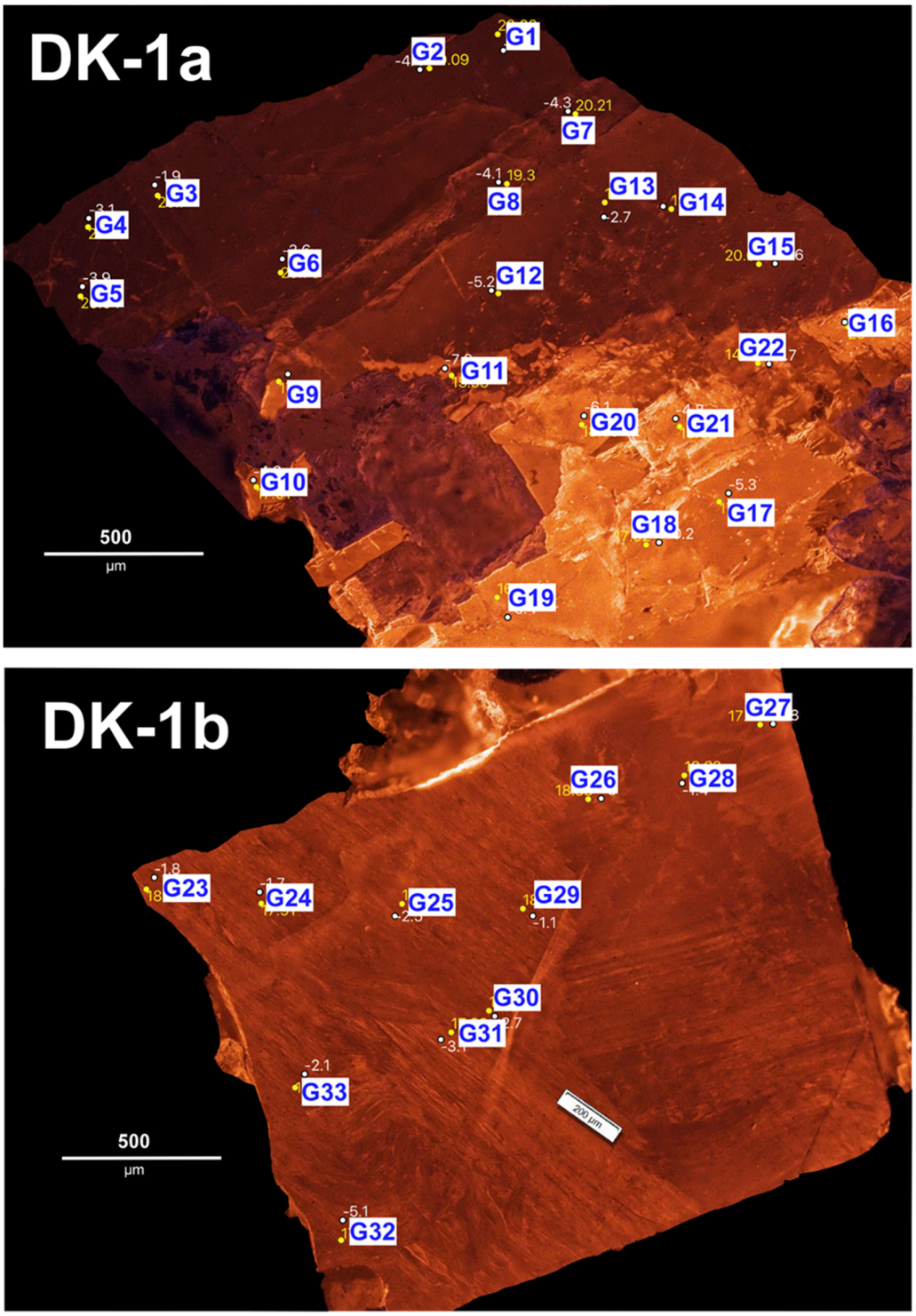

Figure S7. Spot analysis cathodoluminescence images of DK-1a and DK-1b. These samples are from the Kearsarge Seneca mine. Small circles represent spot location for oxygen and carbon isotopic determinations, the labels are the spot locations referenced in Table S8.

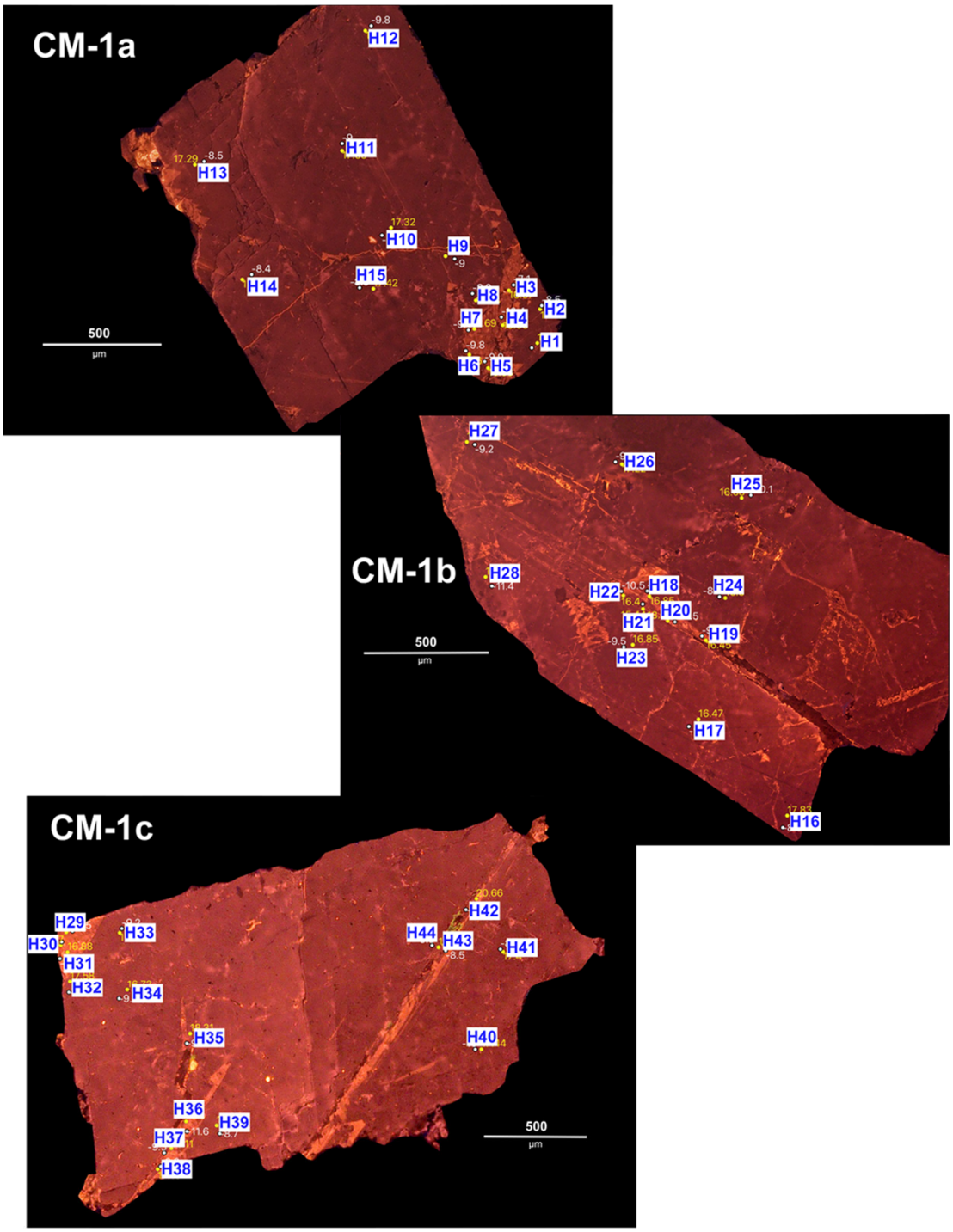

Figure S8. Spot Analysis Cathodoluminescence images of CM-1a, CM-1b, and CM-1c. These samples are from the Caledonia mine. Small circles represent spot location for oxygen and carbon isotopic determinations, the labels are the spot locations referenced in Table S9.

References

1. Bornhorst, T.J.; Woodruff, L.G. Native copper precipitation by fluid-mixing Keweenaw Peninsula, Michigan. *Inst. Lake Super. Geol. Proc.* **1997**, *43 part 1*, 9–10.
2. Bornhorst, T.J.; Barron, R.J.; and Whiteman, R.C. Caledonia Mine, Keweenaw Peninsula Native Copper District, Ontonagon County, Michigan. *Inst. Lake Super. Geol. Proc.* **2013**, *59 part 2*, 43–57.