

Table S1 Separation scheme of Cu

Separation stage	Reagent	Volume (mL)
Resin: 2 mL AG-MP-1M, 100-200 mesh		
Cleaning resin	0.5 mol/L HNO ₃	30
Cleaning resin	deionized water	30
Conditioning	6 mol/L HCl + 0.001% H ₂ O ₂	10
Sample loading	6 mol/L HCl + 0.001% H ₂ O ₂	1
Elution of matrix,	6 mol/L HCl + 0.001% H ₂ O ₂	5
Elution of Cu	6 mol/L HCl + 0.001% H ₂ O ₂	26
Cleaning resin	6 mol/L HCl + 0.001% H ₂ O ₂	1
Cleaning resin	0.5 mol/L HNO ₃	10
Cleaning resin	deionized water	10

Table S2 Element concentrations (wt%) of the TQ-Ccp chalcopyrite measured by EPMA

Spot No.	Fragment ID	Element concentrations (wt%)						Total
		Cu	Fe	S	Pb	Co	Ni	
1	TQ-Ccp -1	34.05	30.40	34.89	0.00	0.03	0.00	99.36
2		34.29	30.43	34.59	0.00	0.05	0.00	99.36
3		34.44	29.98	34.72	0.00	0.04	0.00	99.17
4	TQ-Ccp-2	34.74	30.14	34.72	0.05	0.07	0.00	99.70
5		34.90	30.04	34.43	0.00	0.04	0.00	99.42
6		34.54	30.61	34.60	0.00	0.04	0.00	99.80
7	TQ-Ccp-3	33.35	30.89	34.85	0.00	0.04	0.02	99.15
8		34.72	30.83	34.59	0.05	0.07	0.02	100.28
9		33.95	30.09	34.71	0.00	0.07	0.00	98.81
10	TQ-Ccp-4	34.40	30.49	34.45	0.00	0.05	0.00	99.38
11		33.78	30.52	34.50	0.00	0.03	0.01	98.83
12		33.79	31.08	34.21	0.00	0.06	0.00	99.15
13	TQ-Ccp-5	34.26	29.88	34.58	0.07	0.01	0.00	98.80
14		34.02	30.17	35.20	0.03	0.03	0.00	99.45
15		33.18	31.17	34.61	0.03	0.03	0.00	99.03
16	TQ-Ccp-6	35.06	29.68	34.65	0.02	0.04	0.00	99.44
17		34.47	30.51	34.50	0.00	0.06	0.02	99.55
18		34.77	29.61	34.49	0.01	0.06	0.01	98.94
19	TQ-Ccp-7	34.30	29.82	34.75	0.08	0.06	0.00	99.00
20		33.81	31.02	34.93	0.00	0.04	0.00	99.81
21		34.09	31.00	34.41	0.00	0.02	0.00	99.52
22	TQ-Ccp-8	33.94	30.81	34.29	0.00	0.02	0.00	99.06
23		34.22	30.76	34.94	0.00	0.03	0.00	99.95
24		34.35	30.77	34.70	0.00	0.02	0.01	99.84
25	TQ-Ccp-9	33.87	30.27	34.87	0.00	0.05	0.00	99.06
26		34.20	30.31	34.71	0.00	0.04	0.00	99.26
27		34.44	31.12	34.23	0.00	0.06	0.00	99.84
28	TQ-Ccp-10	34.47	29.81	35.23	0.00	0.03	0.00	99.53
29		33.33	30.99	34.78	0.00	0.08	0.01	99.20
30		34.03	30.67	34.78	0.06	0.05	0.03	99.62
31	TQ-Ccp-11	35.39	29.77	34.77	0.03	0.04	0.00	99.99
32		34.57	29.85	34.54	0.01	0.04	0.00	99.01
33		33.64	30.54	34.62	0.00	0.07	0.03	98.90
34	TQ-Ccp-12	33.89	30.81	34.73	0.00	0.07	0.00	99.51
35		34.34	29.73	34.58	0.00	0.05	0.00	98.69
36		34.36	30.43	34.10	0.07	0.04	0.00	98.99
37	TQ-Ccp-13	34.58	29.88	34.59	0.08	0.02	0.00	99.16
38		33.02	30.97	34.75	0.00	0.06	0.02	98.82
39		34.72	30.49	34.60	0.00	0.12	0.00	99.93
40	TQ-Ccp-14	34.25	30.32	34.86	0.00	0.08	0.00	99.51

Table S2 continued

41		34.23	29.90	34.76	0.00	0.03	0.00	98.92
42		34.61	30.22	34.71	0.04	0.01	0.00	99.59
43	TQ-Ccp-15	34.92	30.46	34.83	0.01	0.06	0.00	100.28
44		34.79	30.24	34.81	0.00	0.07	0.05	99.96
45		33.36	31.18	34.15	0.00	0.02	0.00	98.71
46	TQ-Ccp-16	34.86	29.76	34.50	0.09	0.05	0.00	99.25
47		34.80	30.10	34.38	0.00	0.02	0.00	99.30
48		34.27	30.11	34.46	0.05	0.05	0.02	98.96
49	TQ-Ccp-17	33.72	30.30	34.91	0.06	0.00	0.00	99.00
50		34.98	30.71	34.85	0.00	0.10	0.00	100.64
51		33.27	31.57	34.83	0.00	0.06	0.00	99.72
52	TQ-Ccp-18	34.55	30.43	34.89	0.03	0.06	0.00	99.95
53		34.95	30.19	34.29	0.00	0.03	0.00	99.45
54		33.58	31.44	34.25	0.08	0.07	0.00	99.42
55	TQ-Ccp-19	34.19	29.35	34.94	0.15	0.07	0.00	98.70
56		34.29	30.59	34.93	0.00	0.05	0.00	99.87
57		34.55	30.90	34.83	0.07	0.12	0.04	100.51
58	TQ-Ccp-20	35.43	29.98	34.45	0.00	0.04	0.05	99.93
59		35.07	29.73	34.56	0.00	0.02	0.00	99.37
60		34.29	30.50	34.72	0.01	0.00	0.00	99.52
61	TQ-Ccp-21	35.18	30.31	34.39	0.00	0.04	0.00	99.92
62		34.72	30.19	34.64	0.09	0.09	0.00	99.73
63		33.62	31.27	34.16	0.00	0.03	0.00	99.08
64	TQ-Ccp-22	34.50	30.03	34.88	0.01	0.06	0.01	99.50
65		34.35	29.91	34.74	0.03	0.03	0.00	99.06
66		34.53	29.97	34.85	0.00	0.01	0.01	99.37
67	TQ-Ccp-23	33.83	30.61	34.49	0.00	0.06	0.00	98.99
68		34.42	29.75	34.56	0.00	0.03	0.00	98.75
69		33.93	30.84	34.54	0.00	0.02	0.00	99.34
70	TQ-Ccp-24	34.54	30.37	34.19	0.05	0.02	0.00	99.16
71		34.08	30.29	34.64	0.00	0.06	0.00	99.07
72		34.78	30.08	34.75	0.00	0.06	0.00	99.67
73	TQ-Ccp-25	34.97	30.53	34.72	0.01	0.04	0.02	100.30
74		33.86	30.78	35.03	0.01	0.03	0.00	99.71
75		33.58	30.07	34.96	0.04	0.04	0.00	98.68
76	TQ-Ccp-26	34.12	30.77	34.75	0.02	0.00	0.08	99.73
77		34.71	30.33	34.74	0.02	0.05	0.00	99.85
78		34.63	30.55	34.61	0.07	0.00	0.00	99.86
79	TQ-Ccp-27	33.89	30.20	34.44	0.00	0.05	0.00	98.58
80		34.13	29.78	34.72	0.00	0.03	0.00	98.66
81		34.10	30.95	34.22	0.00	0.03	0.00	99.29
82	TQ-Ccp-28	34.49	30.57	34.65	0.00	0.06	0.01	99.78
83		34.20	30.18	34.80	0.01	0.01	0.06	99.26

Table S2 continued

84		34.34	30.51	34.67	0.17	0.01	0.00	99.71
85	TQ-Ccp-29	34.34	30.29	34.86	0.00	0.04	0.00	99.52
86		34.67	30.67	34.75	0.00	0.10	0.02	100.22
87		34.97	30.48	34.27	0.01	0.05	0.00	99.78
88	TQ-Ccp-30	34.53	29.99	34.92	0.01	0.06	0.02	99.55
89		34.76	31.02	34.73	0.01	0.00	0.00	100.52
90		34.71	31.25	33.94	0.00	0.03	0.00	99.94
91	TQ-Ccp-31	34.98	30.91	34.78	0.00	0.02	0.00	100.69
92		35.37	30.25	34.37	0.09	0.03	0.00	100.10
93		33.70	31.24	34.27	0.00	0.07	0.00	99.28
94	TQ-Ccp-32	34.73	30.94	34.80	0.08	0.11	0.00	100.66
95		34.63	30.07	34.51	0.00	0.01	0.00	99.22
96		34.00	30.81	34.12	0.07	0.04	0.03	99.06
97	TQ-Ccp-33	34.09	30.31	34.44	0.00	0.02	0.02	98.89
98		34.04	31.09	34.69	0.00	0.06	0.00	99.87
99		33.96	30.26	34.59	0.00	0.08	0.00	98.89
100	TQ-Ccp-34	34.20	30.59	34.86	0.00	0.06	0.00	99.71
101		34.68	30.37	35.05	0.00	0.04	0.00	100.15
102		34.54	30.96	34.79	0.00	0.04	0.05	100.37
103	TQ-Ccp-35	33.98	29.66	35.03	0.00	0.03	0.02	98.73
104		34.74	30.17	34.88	0.00	0.07	0.00	99.86
105		35.55	30.28	34.68	0.01	0.01	0.00	100.53
106	TQ-Ccp-36	34.51	29.91	34.97	0.04	0.05	0.01	99.49
107		33.93	30.24	34.70	0.01	0.06	0.00	98.94
108		35.10	30.33	35.06	0.02	0.02	0.01	100.53
109	TQ-Ccp-37	33.95	30.80	34.86	0.02	0.05	0.00	99.67
110		34.11	30.87	34.68	0.00	0.02	0.00	99.66
111		34.27	30.96	34.63	0.00	0.09	0.00	99.95
112	TQ-Ccp-38	33.84	31.18	34.79	0.00	0.02	0.00	99.82
113		34.34	30.77	34.68	0.09	0.05	0.01	99.93
114		34.18	30.66	34.47	0.09	0.05	0.00	99.45
115	TQ-Ccp-39	34.51	30.37	34.49	0.00	0.07	0.00	99.43
116		34.68	30.32	34.62	0.00	0.02	0.00	99.63
117		34.71	29.44	34.76	0.06	0.04	0.00	99.01
118	TQ-Ccp-40	35.56	30.64	34.80	0.09	0.00	0.00	101.10
119		33.78	30.38	34.56	0.00	0.03	0.00	98.74
120		33.96	31.04	34.37	0.00	0.04	0.00	99.41
121	TQ-Ccp-41	34.70	30.21	34.80	0.00	0.04	0.00	99.75
122		33.98	30.64	34.79	0.03	0.02	0.00	99.45
123		33.68	31.37	34.33	0.00	0.06	0.00	99.44
124	TQ-Ccp-42	33.48	31.28	35.22	0.00	0.05	0.02	100.04
125		33.70	31.42	35.41	0.01	0.01	0.00	100.54
126		35.01	31.02	34.93	0.00	0.08	0.00	101.05

Table S2 continued

127	TQ-Ccp-43	35.14	30.34	35.06	0.00	0.04	0.00	100.58
128		34.65	29.92	34.86	0.00	0.06	0.01	99.50
129		34.86	30.51	34.68	0.03	0.07	0.01	100.17
130	TQ-Ccp-44	35.36	29.51	34.85	0.00	0.01	0.02	99.75
131		34.99	30.39	34.87	0.00	0.04	0.00	100.29
132		34.68	30.30	34.60	0.00	0.01	0.02	99.60
133	TQ-Ccp-45	34.24	30.29	34.76	0.00	0.06	0.00	99.35
134		33.41	30.96	34.84	0.00	0.05	0.00	99.27
135		34.97	30.72	34.85	0.03	0.08	0.00	100.66
136	TQ-Ccp-46	34.92	30.72	34.64	0.00	0.07	0.00	100.36
137		34.18	30.41	34.81	0.05	0.05	0.00	99.51
138		34.16	30.27	35.01	0.15	0.10	0.00	99.68
139	TQ-Ccp-47	34.45	30.50	34.87	0.08	0.04	0.00	99.94
140		35.30	30.09	34.61	0.00	0.04	0.00	100.04
141		34.97	30.47	35.34	0.00	0.05	0.00	100.82
142	TQ-Ccp-48	35.27	30.84	35.20	0.00	0.05	0.04	101.39
143		34.95	30.34	34.83	0.03	0.03	0.00	100.18
144		33.55	31.08	34.33	0.04	0.02	0.00	99.02
145	TQ-Ccp-49	34.33	30.05	34.66	0.02	0.03	0.02	99.11
146		34.75	31.23	34.83	0.00	0.06	0.00	100.87
147		33.84	30.02	34.90	0.06	0.06	0.00	98.87
148	TQ-Ccp-50	34.52	30.59	34.97	0.00	0.03	0.00	100.11
149		34.23	29.71	35.16	0.00	0.03	0.00	99.13
150		33.49	31.10	34.71	0.02	0.01	0.00	99.32
151	TQ-Ccp-51	33.90	30.75	34.61	0.00	0.05	0.00	99.32
152		34.00	31.41	34.17	0.03	0.03	0.00	99.64
153		33.26	31.34	34.33	0.00	0.07	0.00	99.01
154	TQ-Ccp-52	34.63	30.75	34.57	0.01	0.04	0.00	99.99
155		34.79	30.01	34.77	0.00	0.06	0.00	99.62
156		34.56	30.54	34.94	0.00	0.01	0.00	100.05
157	TQ-Ccp-53	34.85	30.98	34.75	0.00	0.04	0.01	100.63
158		35.36	30.51	34.93	0.03	0.05	0.00	100.87
159		34.86	30.56	34.66	0.06	0.06	0.00	100.20
160	TQ-Ccp-54	33.87	30.77	34.75	0.04	0.04	0.00	99.46
161		34.61	30.74	34.58	0.00	0.02	0.00	99.94
162		33.51	31.64	34.21	0.01	0.04	0.00	99.40
163	TQ-Ccp-55	34.83	30.06	35.21	0.03	0.03	0.00	100.16
164		35.20	30.13	34.79	0.00	0.05	0.01	100.19
165		34.94	30.37	34.98	0.00	0.06	0.00	100.35
166	TQ-Ccp-56	33.83	30.77	34.80	0.00	0.03	0.00	99.44
167		35.89	29.95	34.79	0.00	0.02	0.00	100.65
168		34.48	30.64	34.94	0.00	0.04	0.00	100.10
169	TQ-Ccp-57	34.95	31.04	34.68	0.01	0.06	0.00	100.73

Table S2 continued

170		35.12	31.10	34.64	0.04	0.00	0.03	100.93
171		34.29	30.92	34.49	0.01	0.02	0.00	99.74
172	TQ-Ccp-58	34.55	30.05	34.55	0.03	0.08	0.00	99.25
173		33.78	30.55	34.29	0.00	0.04	0.00	98.66
174		34.31	30.05	34.65	0.00	0.02	0.01	99.04
175	TQ-Ccp-59	34.41	30.32	34.83	0.00	0.09	0.02	99.66
176		34.57	30.59	34.70	0.00	0.01	0.00	99.86
177		34.59	30.73	34.89	0.00	0.01	0.01	100.22
178	TQ-Ccp-60	35.02	30.58	35.28	0.00	0.02	0.00	100.89
179		34.87	30.44	34.48	0.00	0.06	0.00	99.85
180		35.81	30.14	35.08	0.00	0.02	0.01	101.07
181	TQ-Ccp-61	34.62	29.78	34.43	0.00	0.00	0.00	98.84
182		33.58	30.96	34.08	0.04	0.01	0.00	98.67
183		33.64	31.39	34.39	0.00	0.02	0.01	99.45
184	TQ-Ccp-62	33.37	31.25	34.42	0.00	0.04	0.00	99.08
185		34.12	30.61	34.25	0.05	0.06	0.00	99.09
186		33.26	31.54	34.55	0.00	0.07	0.00	99.42
187	TQ-Ccp-63	34.20	31.35	34.54	0.00	0.02	0.00	100.11
188		33.91	31.38	34.50	0.05	0.04	0.00	99.88
189		34.45	30.21	34.43	0.00	0.05	0.02	99.16
190	TQ-Ccp-64	33.89	31.47	34.65	0.01	0.00	0.00	100.02
191		34.44	31.71	34.30	0.01	0.04	0.00	100.50
192		34.48	30.60	34.47	0.04	0.04	0.04	99.66
193	TQ-Ccp-65	33.91	31.29	34.26	0.00	0.05	0.02	99.53
194		33.83	31.23	34.23	0.00	0.03	0.00	99.33
195		33.74	30.99	34.26	0.00	0.06	0.00	99.05
196	TQ-Ccp-66	33.33	31.32	34.41	0.00	0.07	0.00	99.12
197		34.38	30.98	34.25	0.00	0.03	0.00	99.65
198		34.17	31.12	34.16	0.00	0.05	0.00	99.50
199	TQ-Ccp-67	33.91	31.13	34.15	0.05	0.04	0.03	99.29
200		34.32	31.40	34.23	0.00	0.04	0.01	100.00
201		34.18	31.36	34.34	0.00	0.06	0.00	99.94
202	TQ-Ccp-68	34.30	31.15	34.73	0.00	0.08	0.00	100.26
203		33.64	31.11	34.25	0.00	0.02	0.00	99.01
204		33.87	31.12	34.42	0.00	0.07	0.00	99.47
205	TQ-Ccp-69	33.85	30.50	34.66	0.00	0.04	0.00	99.04
206		33.36	31.27	34.56	0.01	0.07	0.00	99.26
207		34.05	31.34	34.50	0.00	0.06	0.00	99.95
208	TQ-Ccp-70	33.78	31.11	34.73	0.00	0.04	0.00	99.65
209		33.89	30.84	34.07	0.00	0.02	0.00	98.83
210		33.60	31.27	34.38	0.00	0.06	0.00	99.31
211	TQ-Ccp-71	33.47	31.44	34.41	0.01	0.04	0.00	99.36
212	TQ-Ccp-72	33.67	31.20	34.46	0.04	0.04	0.04	99.44

Table S2 continued

213	TQ-Ccp-73	34.28	30.00	34.69	0.00	0.01	0.00	98.98
214	TQ-Ccp-74	34.57	29.87	34.47	0.00	0.03	0.05	98.99
215	TQ-Ccp-75	34.99	30.53	34.05	0.00	0.03	0.00	99.59
216	TQ-Ccp-76	34.78	30.40	34.23	0.00	0.08	0.00	99.48
217	TQ-Ccp-77	35.05	30.06	34.25	0.00	0.03	0.06	99.45
218	TQ-Ccp-78	34.45	29.90	34.59	0.00	0.08	0.00	99.02
219	TQ-Ccp-79	34.45	30.37	34.36	0.03	0.02	0.01	99.25
220	TQ-Ccp-80	34.33	29.92	34.55	0.00	0.02	0.00	98.82
221	TQ-Ccp-81	35.11	29.82	34.06	0.07	0.07	0.00	99.13
222	TQ-Ccp-82	33.80	31.18	34.33	0.07	0.03	0.00	99.40
223	TQ-Ccp-83	34.65	29.97	34.33	0.18	0.07	0.00	99.20
224	TQ-Ccp-84	34.70	29.69	34.74	0.00	0.06	0.03	99.22
225	TQ-Ccp-85	34.54	30.01	34.48	0.00	0.04	0.00	99.06
226	TQ-Ccp-86	35.13	30.96	34.27	0.00	0.05	0.00	100.40
227	TQ-Ccp-87	34.68	29.92	34.08	0.01	0.05	0.00	98.73
228	TQ-Ccp-88	34.15	30.69	34.62	0.00	0.03	0.03	99.52
229	TQ-Ccp-89	33.75	30.69	34.39	0.01	0.08	0.04	98.96
230	TQ-Ccp-90	34.57	29.85	34.46	0.00	0.08	0.03	98.99
231	TQ-Ccp-91	35.40	30.27	34.07	0.00	0.02	0.03	99.79
232	TQ-Ccp-92	35.08	29.01	34.44	0.05	0.05	0.00	98.63
233	TQ-Ccp-93	34.99	30.36	34.14	0.08	0.04	0.00	99.61
234	TQ-Ccp-94	33.83	31.11	34.37	0.00	0.05	0.00	99.36
	Mean	34.35	30.54	34.62	0.02	0.04	0.01	99.59
	SD	0.55	0.52	0.28	0.03	0.02	0.01	
	RSD (%)	0.80	0.84	0.40				

Table S3 Copper isotope compositions of the doping solutions analyzed by MC-ICP-MS^a

Molar element ratio	$\delta^{65}\text{Cu}_{\text{ERM-647}}$ (‰)	2SD (n=3)
Fe:Cu = 2:3	-0.04	0.05
Fe:Cu = 1:1	0.00	0.05
Fe:Cu = 2:1	-0.03	0.03
Fe:Cu = 5:1	0.01	0.04
Fe:Cu = 10:1	0.00	0.02
As:Cu = 1:20	-0.03	0.02
As:Cu = 1:10	-0.02	0.03
As:Cu = 1:5	-0.01	0.01
As:Cu = 1:2	0.00	0.01
As:Cu = 1:1	0.00	0.01
Fe:As:Cu = 2:1:2	-0.05	0.03
Fe:As:Cu = 1:1:1	-0.03	0.02
Fe:As:Cu = 1:2:1	-0.03	0.04
Fe:S:Cu = 2:1:2	0.01	0.04
Fe:S:Cu = 1:1:1	0.00	0.01
Fe:S:Cu = 1:2:1	-0.01	0.03
Fe:S:As:Cu = 2:2:1:2	0.00	0.00
Fe:S:As:Cu = 1:1:1:1	-0.01	0.01
Fe:S:As:Cu = 1:1:2:1	-0.02	0.04

^a $\delta^{65}\text{Cu}_{\text{ERM-647}} = [({}^{65}\text{Cu}/{}^{63}\text{Cu})_{\text{ERM-647 with doping elements}} / ({}^{65}\text{Cu}/{}^{63}\text{Cu})_{\text{ERM-647}} - 1] \times 1000\text{‰}$.

Fig. S1

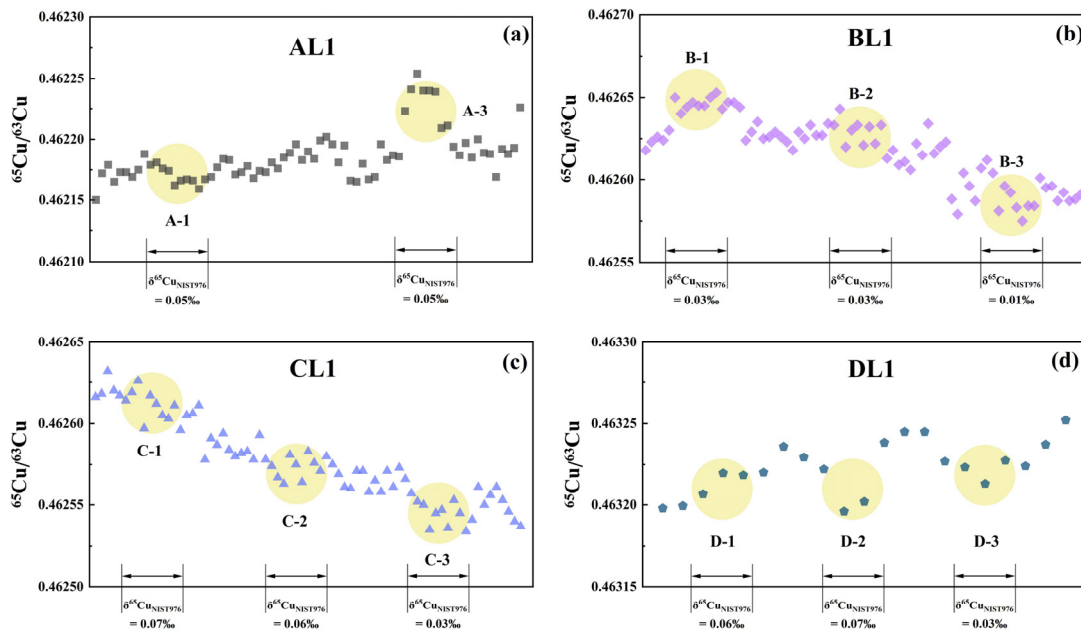


Fig. S1 The raw $^{65}\text{Cu}/^{63}\text{Cu}$ of the ablation spots in the lines AL1 (a), BL1 (b), CL1 (c), and DL1 (d) on the four large chalcopyrite fragments in the mount III. The yellow circles show the corresponding positions of the micro-drilled samples along the lines (X axis), and their $\delta^{65}\text{Cu}_{\text{NIST976}}$ were analyzed by solution MC-ICP-MS (not related with Y axis). The detailed positions of the lines and the micro-drill sampling areas on the fragments are shown in Fig. 1c.