

Table S1

Summary of minerals and their formulas cited in the text.

Mineral	Discredited name	Formula
alunogen		$\text{Al}_2(\text{SO}_4)_3(\text{H}_2\text{O})_{12} \cdot 5\text{H}_2\text{O}$
anglesite		$\text{Pb}(\text{SO}_4)$
anhydrite		$\text{Ca}(\text{SO}_4)$
antlerite		$\text{Cu}^{2+} \cdot (\text{SO}_4)(\text{OH})_4$
aphthalite		$\text{K}_3\text{Na}(\text{SO}_4)_2$
atacamite		$\text{Cu}_2\text{Cl}(\text{OH})_3$
azurite		$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
bannermanite		$(\text{Na}, \text{K})x\text{V}_4+x\text{V}^{5+} \cdot {}_{6-x}\text{O}_{15} \quad (0.5 < x < 0.9)$
blossite		$\text{Cu}_2\text{V}^{5+} \cdot 2\text{O}_7$
botallackite		$\text{Cu}_2\text{Cl}(\text{OH})_3$
cerussite		$\text{Pb}(\text{CO}_3)$
chrysocolla		$(\text{Cu}_{2-x}\text{Al}_x)\text{H}_{2-x}\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$
clinoatacamite		$\text{Cu}_2\text{Cl}(\text{OH})_3$
colimaite		K_3VS_4
cuprite		Cu_2O
descloizite		$\text{PbZn}(\text{VO}_4)(\text{OH})$
dioptase		$\text{CuSiO}_3 \cdot \text{H}_2\text{O}$
euchlorine		$\text{KNaCu}_3\text{O}(\text{SO}_4)_3$
fingerite		$\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$
gypsum		$\text{Ca}(\text{SO}_4) \cdot 2\text{H}_2\text{O}$
halite		NaCl
hausmannite		$\text{Mn}^{2+} \text{Mn}^{3+} \cdot 2\text{O}_4$
hollandite		$\text{Ba}(\text{Mn}^{4+} \cdot {}_6\text{Mn}^{3+})\text{O}_{16}$
hydrokenoralstonite	ralstonite	$\square_2\text{Al}_2\text{F}_6(\text{H}_2\text{O})$
leningradite		$\text{PbCu}_3(\text{VO}_4)_2\text{Cl}_2$
malachite		$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$
mcbirneyite		$\text{Cu}_3(\text{VO}_4)_2$
mottramite		$\text{PbCu}(\text{VO}_4)(\text{OH})$
opal		$\text{SiO}_2 \cdot n\text{H}_2\text{O}$
paratacamite	atelina	$\text{Cu}_3(\text{Cu}, \text{Zn})\text{Cl}_2(\text{OH})_6$
pyromorphite		$\text{Pb}_5(\text{PO}_4)_3\text{Cl}$
realgar		AsS
romanèchite		$(\text{Ba}, \text{H}_2\text{O})_2(\text{Mn}^{4+}, \text{Mn}^{3+})_5\text{O}_{10}$
salammoniac		$(\text{NH}_4)\text{Cl}$
sassolite		$\text{B}(\text{OH})_3$
shcherbinaita		V_2O_5
starovaite		$\text{KCu}_5\text{O}(\text{VO}_4)_3$
stoiberite		$\text{Cu}_5\text{O}_2(\text{VO}_4)_2$
stolzite		$\text{Pb}(\text{WO}_4)$
sylvite		KCl
tenorite		CuO
thenardite		$\text{Na}_2(\text{SO}_4)$
vanadinite		$\text{Pb}_5(\text{VO}_4)_3\text{Cl}$
vesignieite		$\text{Cu}_3\text{Ba}(\text{VO}_4)_2(\text{OH})_2$
volborthite		$\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$
wulfenite		PbMoO_4

Table S3

Selected compositions of mottramite from the studied samples (EDS). Sample in bold Italics were analyzed by WDS.

Group I	Group I	Group I	Group I	Group I	Group I	Group I	Group I	Group I	Group I	Group I	Group I	Group II	Group II	Group II	Group II	Group II	Group II	Group II	Group II	Group II						
911R-g	911R-g	911R-g	911R-g	911R-g	911R-g	911R-g	911R-g	911R-g	911R-b	911R-b	911R-b	P18	P18	P18	P18	911R-T	998R	1002R	1002R	1002R						
SiO ₂	0.54	2.22	4.83	5.42	5.58	5.66	2.22	2.22	1.70	0.00	0.00	0.00	0.00	0.87	0.00	1.12	0.00	4.30	4.08	0.00	1.66	1.65				
Al ₂ O ₃	0.00	1.10	3.71	4.19	3.89	4.42	1.10	1.10	0.76	0.65	0.00	0.88	0.00	0.00	0.00	0.00	3.83	0.70	0.00	0.68	0.77					
FeO	0.78	0.05	0.07	0.08	0.12	0.11	0.05	0.05	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.00	0.00	0.00	0.00					
MnO	0.00	0.23	0.00	0.00	0.00	0.00	0.23	0.23	0.20	0.00	0.00	0.00	0.97	1.54	1.64	0.90	0.83	0.00	0.00	1.03	0.00					
MgO	0.22	0.00	0.27	0.26	0.28	0.27	0.07	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00					
CaO	0.00	0.05	1.96	2.01	2.12	1.98	0.33	0.33	0.18	0.00	0.00	0.00	0.00	1.56	1.50	0.00	0.00	0.50	0.76	0.58	0.56					
K ₂ O	0.00	0.24	0.00	0.00	0.00	0.00	0.24	0.24	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.73	0.00	0.00					
CuO	15.66	18.72	16.73	16.60	16.20	15.98	18.72	18.72	16.80	21.03	21.20	17.91	18.00	22.26	21.32	18.22	16.09	17.19	20.64	20.06	22.04	22.28				
ZnO	0.00	0.00	0.70	0.74	0.70	0.72	0.00	0.00	0.00	0.00	0.00	0.00	1.62	0.00	0.00	1.62	0.00	0.00	0.00	0.00	0.00	0.00				
PbO	60.13	54.70	45.96	43.88	45.94	47.88	54.70	54.70	54.56	50.23	51.46	53.15	54.37	44.25	48.76	49.84	55.01	47.92	50.09	48.54	51.05	49.52				
As ₂ O ₅	0.84	0.63	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.07	1.49	1.47	0.00	0.00	0.97	0.00	0.59	0.07	0.00				
V ₂ O ₅	15.30	16.34	20.19	19.63	20.74	20.00	18.09	18.56	17.75	21.08	21.72	18.17	20.76	19.71	21.18	22.12	20.42	16.56	19.55	23.07	19.08	18.87				
P ₂ O ₅	0.00	0.60	0.13	0.12	0.16	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.70	0.00	0.00	0.00	0.00				
SO ₃	0.00	0.00	0.13	0.13	0.15	0.11	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.78	0.00	0.73	0.00	0.00				
OH*	1.88	2.16	2.61	2.62	2.69	2.69	2.20	2.22	2.06	2.18	2.19	1.98	2.20	2.26	2.25	2.30	2.09	2.40	2.42	2.36	2.24	2.22				
sum	95.35	97.07	97.29	95.69	98.57	99.97	97.95	98.44	94.05	95.17	96.57	92.02	5 anions pfu. O ₄ (OH)				98.99	93.94	98.12	94.90	96.06	94.42	98.68	97.87	97.40	95.87
Si	0.04	0.15	0.28	0.31	0.31	0.32	0.15	0.15	0.12	0.00	0.00	0.00	0.00	0.06	0.00	0.07	0.00	0.27	0.25	0.00	0.10	0.10				
Al	0.00	0.09	0.25	0.28	0.26	0.29	0.09	0.09	0.07	0.05	0.00	0.08	0.00	0.00	0.00	0.00	0.28	0.05	0.00	0.05	0.06					
Fe	0.05	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00					
Mn	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.06	0.09	0.09	0.05	0.05	0.00	0.05	0.00	0.00					
Mg	0.03	0.00	0.02	0.02	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00					
Ca	0.00	0.00	0.12	0.12	0.13	0.12	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.11	0.10	0.00	0.00	0.03	0.05	0.04	0.04					
K	0.00	0.02	0.00	0.00	0.00	0.00	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.05	0.00	0.00					
Cu	0.94	0.98	0.73	0.72	0.68	0.67	0.96	0.95	0.92	1.09	1.10	1.02	0.93	1.11	1.05	0.92	0.87	0.81	0.96	0.87	1.00	1.02				
Zn	0.00	0.00	0.03	0.03	0.03	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.08	0.00	0.00	0.09	0.00	0.00	0.00	0.00	0.00					
Pb	1.29	1.02	0.71	0.68	0.69	0.72	1.00	0.99	1.07	0.93	0.95	1.08	1.00	0.79	0.86	0.90	1.06	0.81	0.83	0.75	0.83	0.81				
As	0.03	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.05	0.05	0.00	0.03	0.00	0.02	0.00	0.00					
V	0.81	0.75	0.77	0.74	0.76	0.74	0.82	0.83	0.85	0.96	0.98	0.91	0.94	0.86	0.91	0.98	0.97	0.68	0.80	0.87	0.76	0.76				
P	0.00	0.04	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.04	0.00	0.00	0.00					
SO ₂	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00	0.00					
OH	0.97	1.00	1.02	1.02	1.02	1.00	1.00	1.00	1.00	1.00	1.00	0.99	1.00	1.00	0.98	1.03	1.00	1.00	0.90	0.90	1.00					

* Calculated from stoichiometry. pfu. per formula unit.

Table S4

Selected compositions of vanadinite (EDS).

	Group I	Group I	Group I	Group II												
	P2	911R-g	911R-g	P18	P18	P18	P18	911R-T	911R-T	912R	990R	990R	998R	998R	998R*	
SiO ₂	0.64	3.12	0.74	0.00	0.00	0.00	0.00	1.24	0.00	0.00	0.19	1.22	0.94	0.66	1.54	0.00
Al ₂ O ₃	0.00	1.86	0.79	0.00	0.00	0.00	0.00	0.27	0.00	0.00	0.47	0.89	0.15	0.00	0.00	0.00
FeO	0.46	0.00	0.17	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.76	0.21	0.00	0.00	0.00
MnO	0.00	0.00	0.6	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.22	0.34	0.18	0.00	0.00	0.00
MgO	0.19	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.18	0.37	0.05	0.00	0.00	0.00
CaO	0.00	0.00	0.57	0.00	0.00	0.00	0.00	0.00	0.00	0.10	2.75	2.37	0.00	0.00	0.57	
K ₂ O	1.16	0.35	0.34	2.00	1.39	1.29	2.09	0.00	0.00	1.01	0.57	0.44	0.00	0.48	0.00	
CuO	1.22	1.13	1.31	1.69	1.60	1.79	2.14	3.85	2.50	2.90	3.73	3.36	3.70	5.74	5.70	5.41
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PbO	77.95	73.42	76.33	76.37	76.44	76.25	77.13	74.60	76.91	75.99	76.15	71.05	73.12	73.99	72.43	75.18
As ₂ O ₅	0.00	1.19	1.14	0.00	1.39	1.18	0.00	0.91	0.00	0.00	0.00	0.09	0.44	0.00	0.00	0.00
V ₂ O ₅	15.74	14.68	15.99	17.85	17.72	17.73	16.70	15.84	17.76	16.53	15.13	16.72	16.16	15.62	16.54	9.80
MoO ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
WO ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P ₂ O ₅	0.00	0.67	0.02	0.00	0.00	0.00	0.00	0.43	0.00	0.00	0.00	0.25	0.00	1.53	0.90	6.48
SO ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.66	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cl	3.30	2.22	2.00	2.75	2.32	2.19	2.76	3.11	3.06	3.13	3.33	2.69	3.00	3.06	2.88	3.14
O=Cl	0.75	0.50	0.45	0.62	0.52	0.49	0.62	0.70	0.69	0.71	0.75	0.61	0.68	0.69	0.65	0.71
sum	99.93	98.53	99.57	100.04	100.34	99.93	100.19	100.89	99.54	97.84	99.81	100.45	100.07	99.91	99.83	99.87
16 cations (M+B)																
Si	0.29	1.34	0.32	0.00	0.00	0.00	0.00	0.54	0.00	0.00	0.08	0.48	0.39	0.29	0.65	0.00
Al	0.00	0.94	0.40	0.00	0.00	0.00	0.00	0.14	0.00	0.00	0.24	0.42	0.07	0.00	0.00	0.00
Fe	0.18	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.25	0.07	0.00	0.00	0.00
Mn	0.00	0.00	0.22	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.08	0.12	0.06	0.00	0.00	0.00
Mg	0.13	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.12	0.22	0.03	0.00	0.00	0.00
Ca	0.00	0.00	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	1.16	1.06	0.00	0.00	0.26
K	0.67	0.19	0.19	1.13	0.79	0.74	1.18	0.00	0.00	0.00	0.55	0.29	0.24	0.00	0.26	0.00
Cu	0.42	0.37	0.43	0.56	0.54	0.60	0.72	1.27	0.88	1.04	1.21	1.00	1.17	1.90	1.83	1.77
Zn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Pb	9.57	8.47	8.98	9.09	9.15	9.16	9.21	8.77	9.65	9.75	8.82	7.54	8.22	8.72	8.29	8.87
As	0.00	0.27	0.26	0.00	0.32	0.27	0.00	0.21	0.00	0.00	0.00	0.02	0.10	0.00	0.00	0.00
V	4.74	4.16	4.62	5.22	5.2	5.23	4.89	4.57	5.47	5.21	4.30	4.35	4.46	4.52	4.64	2.81
Mo	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
W	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P	0.00	0.24	0.01	0.00	0.00	0.00	0.00	0.16	0.00	0.00	0.00	0.08	0.00	0.57	0.33	2.31
SO ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cl	2.55	1.61	1.48	2.06	1.75	1.66	2.07	2.30	2.42	2.53	2.43	1.80	2.13	2.27	2.07	2.31

* Solid solution with pyromorphite.

Table S7

Selected compositions of azurite and malachite from the studied samples (EDS).

	Group II	Group II	Group II	Group II	Group II	Group II	Group II	Group II					
	azurite					malachite							
	c26	c26	911R-T	911R-T	911R-T	912R	912R	912R	912R	998R	998R	998R	998R
SiO ₂	1.36	0.58	0.00	0.00	0.00	0.00	0.08	0.04	0.00	0.00	0.00	0.00	0.00
Al ₂ O ₃	0.00	0.80	0.00	0.00	0.00	0.00	0.00	0.51	0.00	0.00	0.00	0.00	0.00
FeO	0.00	0.13	0.00	0.22	0.16	0.00	0.25	0.00	0.00	0.00	0.00	0.00	0.00
MnO	0.22	0.27	0.00	0.87	0.35	0.18	0.00	0.15	0.12	0.00	0.00	0.00	0.00
MgO	0.30	0.00	0.00	0.00	0.00	0.00	0.20	0.02	0.00	0.00	0.00	0.00	0.00
CaO	0.00	0.17	0.00	0.00	0.00	0.18	0.20	0.16	0.10	0.00	0.00	0.00	0.00
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.23	0.02	0.00	0.00	0.00	0.00	0.00	0.00
CuO	66.02	65.38	68.23	67.38	67.12	70.30	70.03	70.28	69.75	70.92	70.21	70.36	71.02
ZnO	0.00	1.23	0.00	0.00	0.00	0.00	0.28	0.09	0.00	0.00	0.00	0.00	0.00
PbO	0.32	0.00	0.00	0.00	0.25	1.06	0.65	0.50	0.73	0.99	1.13	0.89	0.62
As ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.06	0.00	0.00	0.00	0.00
V ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.43	0.54	0.54	0.98	0.73
P ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0.04	0.27	0.22	0.58	0.00	0.00	0.00	0.00
CO ₂ *	23.93	24.69	24.33	24.16	24.08	20.32	20.58	20.45	19.91	20.21	20.04	20.03	20.16
H ₂ O*	5.02	4.99	5.15	5.21	5.14	8.03	7.99	8.00	7.95	8.07	8.00	8.01	8.07
sum	97.17	98.24	97.71	97.84	98.81	100.46	100.54	100.41	99.62	100.73	100.35	100.02	100.41
8 anions pfu							5 anions pfu						
Si	0.00	0.05	0.00	0.00	0.00	0.00	0.01	0.02	0.03	0.00	0.00	0.00	0.00
Al	0.09	0.04	0.00	0.00	0.00	0.00	0.03	0.04	0.00	0.00	0.00	0.00	0.00
Fe	0.00	0.01	0.00	0.01	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.01	0.01	0.00	0.04	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mg	0.03	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cu	2.95	3.00	3.05	3.01	3.02	1.95	1.92	1.93	1.94	1.96	1.94	1.95	1.96
Zn	0.00	0.05	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Pb	0.01	0.00	0.00	0.00	0.00	0.01	0.02	0.01	0.01	0.03	0.05	0.05	0.00
As	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
V	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.02	0.02	0.01
P	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.02	0.00	0.00	0.00	0.00
C	1.93	1.96	1.97	1.95	1.96	1.02	1.02	1.01	1.00	1.01	1.00	1.01	1.01
OH	1.98	1.94	2.03	2.06	2.05	1.96	1.94	1.94	1.95	1.97	1.96	1.96	1.97

* Calculated from stoichiometry; pfu. per formula unit.