Rock glaciers in the Central Eastern Alps – How permafrost degradation can cause acid rock drainage, mobilization of toxic elements and formation of basaluminite

Electronic Appendix

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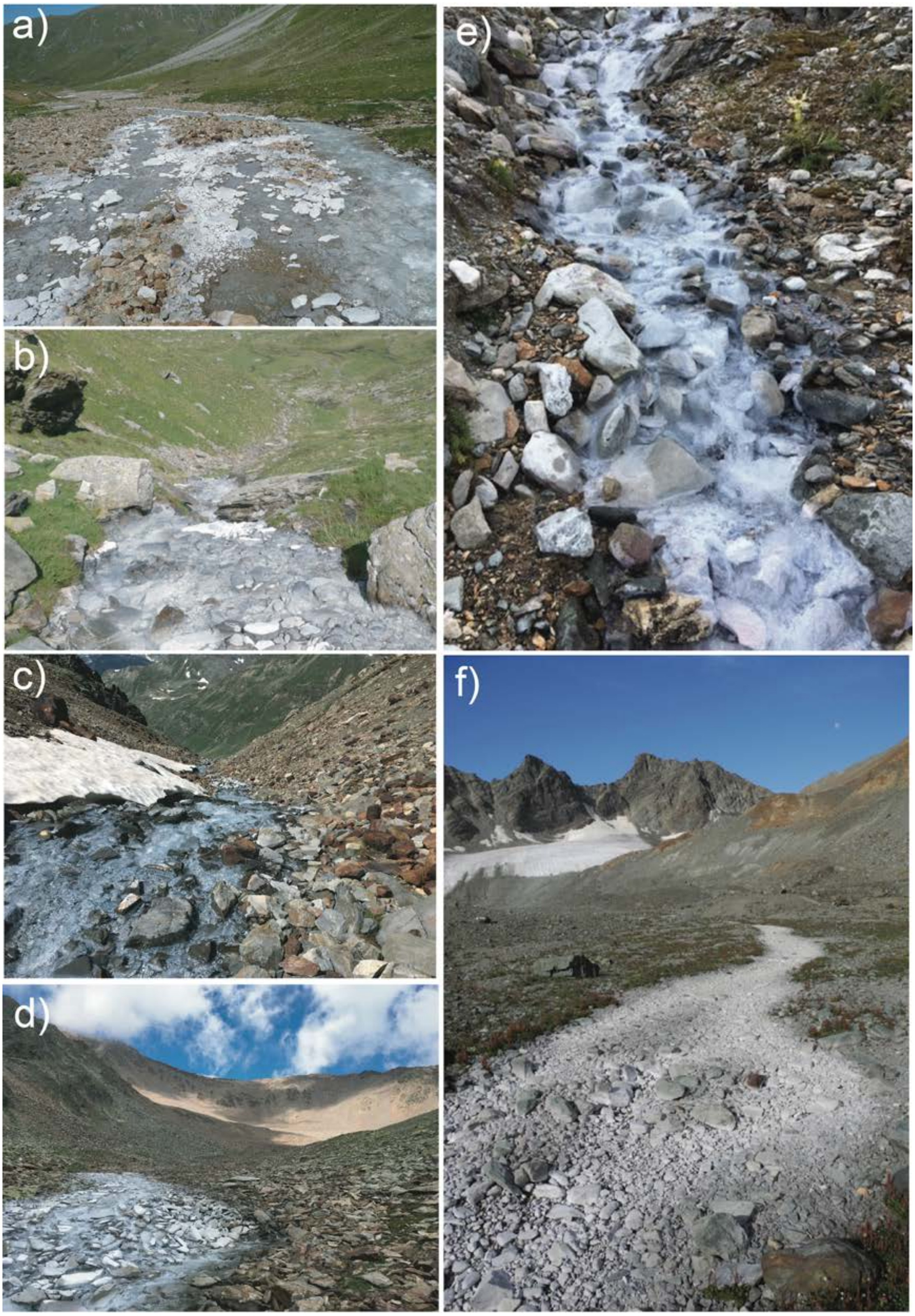

Figure S1: Photographs of the sampled high-alpine stream systems with white-colored streambeds inherited from basaluminite precipitation. **a)** Val Costainas. **b)** Val Poschiavo. **c)** Lago Vago. **d)** Schlandraun. **e)** Traunter Ovas 1. **f)** Vadret Agnel. The geographic location of the streams is shown on Figures 1 and S2, while the exact coordinates of the streamwater and precipitated samples are provided in Table 2.

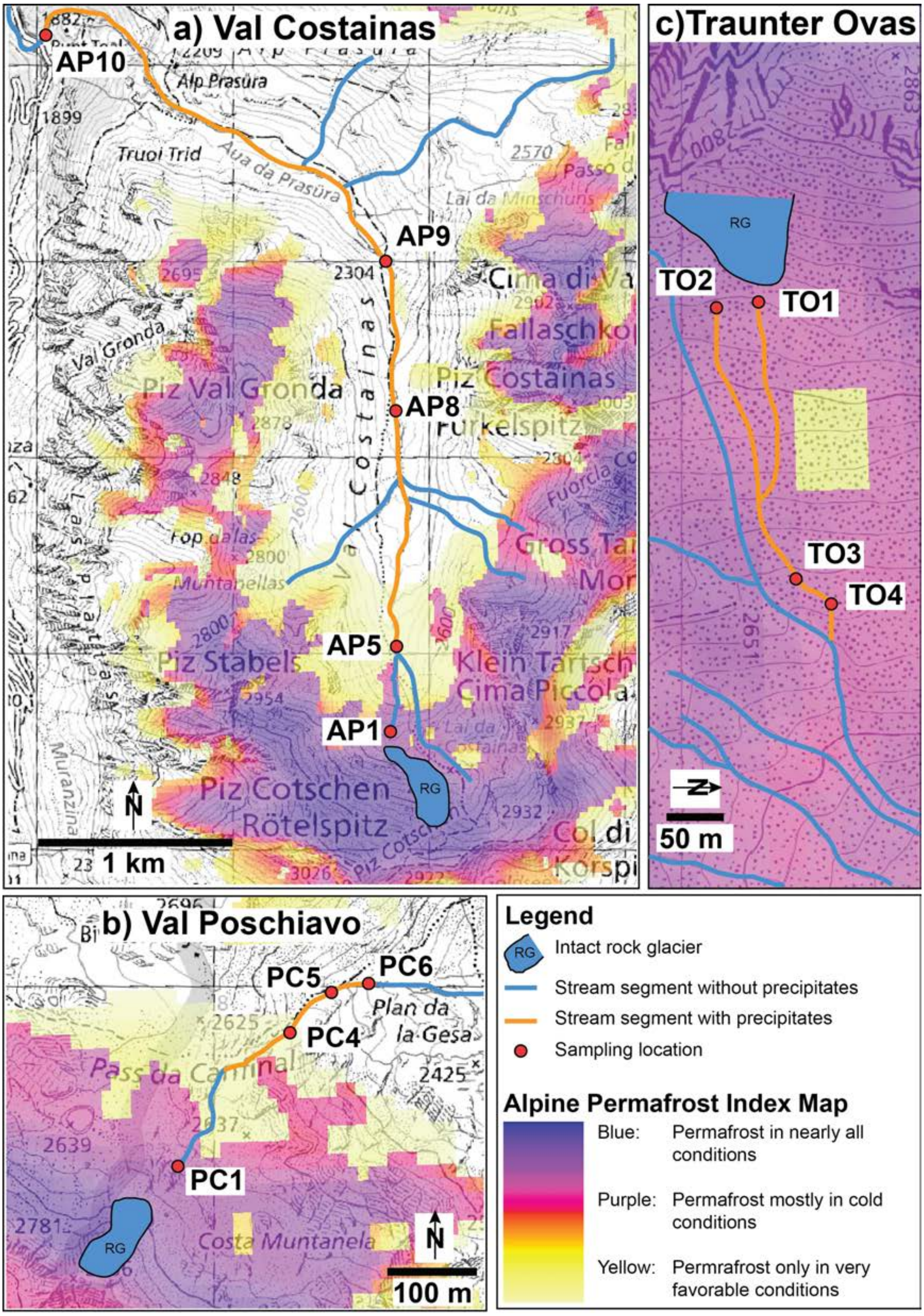

Figure S2: Overview maps of the six high-alpine systems, from which streamwater and white precipitate samples were collected. The maps show sampling locations, the approximate extents of the rock glaciers at the origin of the streams, and the white colored segment of the acidic streams. Moreover, the Alpine Permafrost Index Map (APIM, Boeckli et al., 2012) was added to illustrate that only streams originating from intact rock glaciers are affected by the strong mobilization of toxic elements.

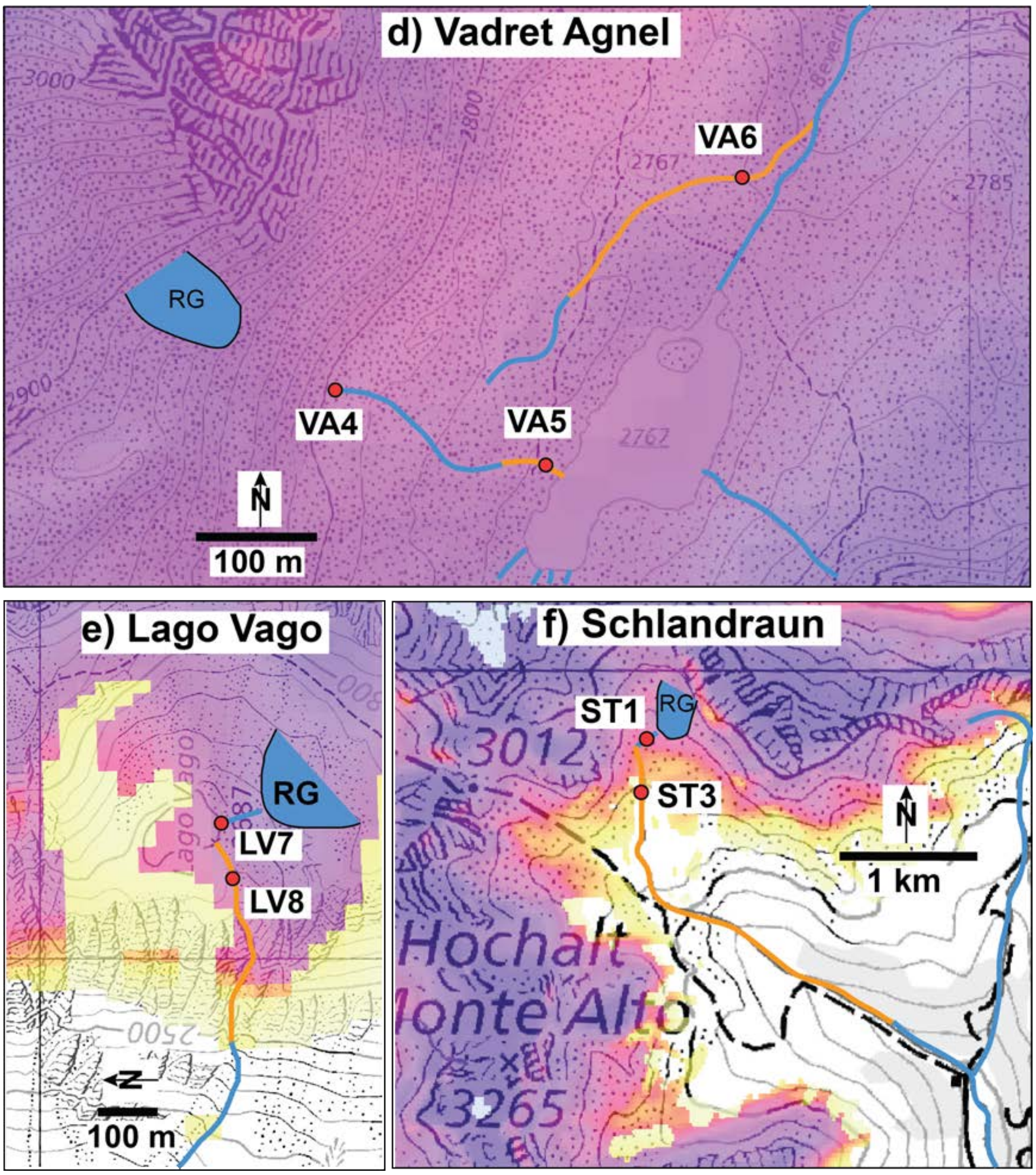

Fig. S2 continued

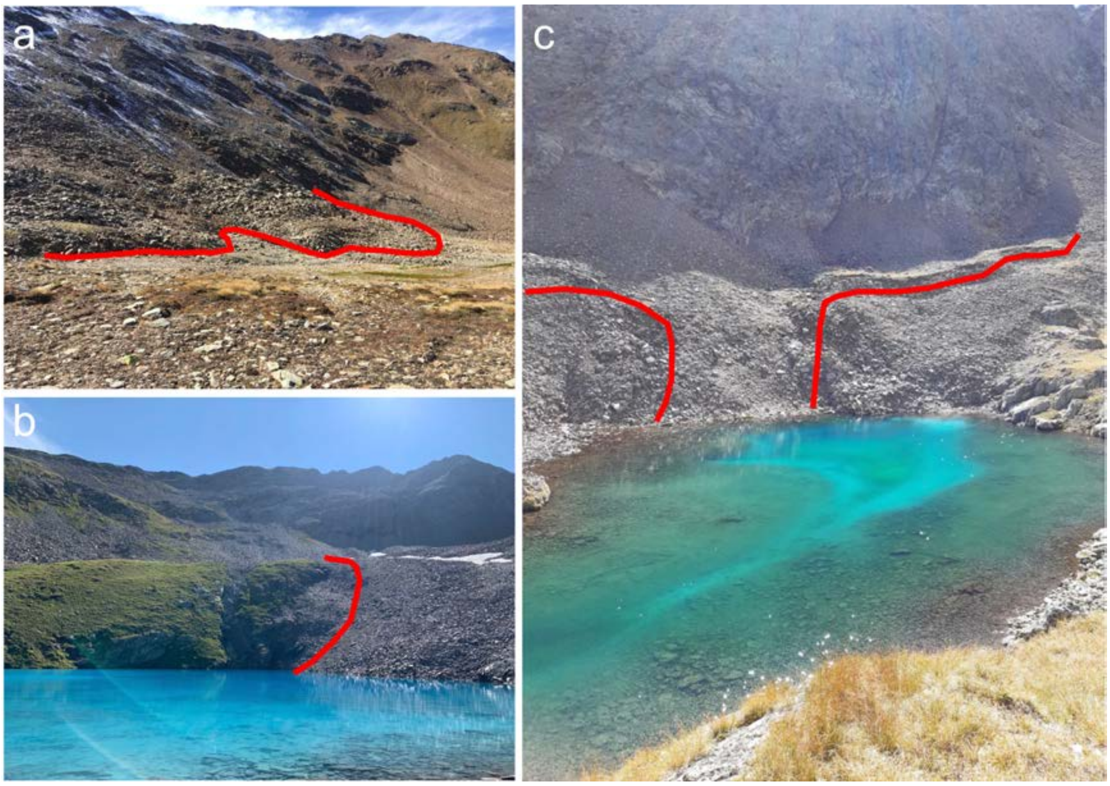

Figure S3: Photographs of selected stream origins where the occurrence of rock glaciers is clearly visible: a) Val Costainas. b) Lago Vago. c) Schlandraun. The red lines mark the approximate boundaries of the rock glaciers. Photograph c) was kindly provided by Andrea Kuntner.

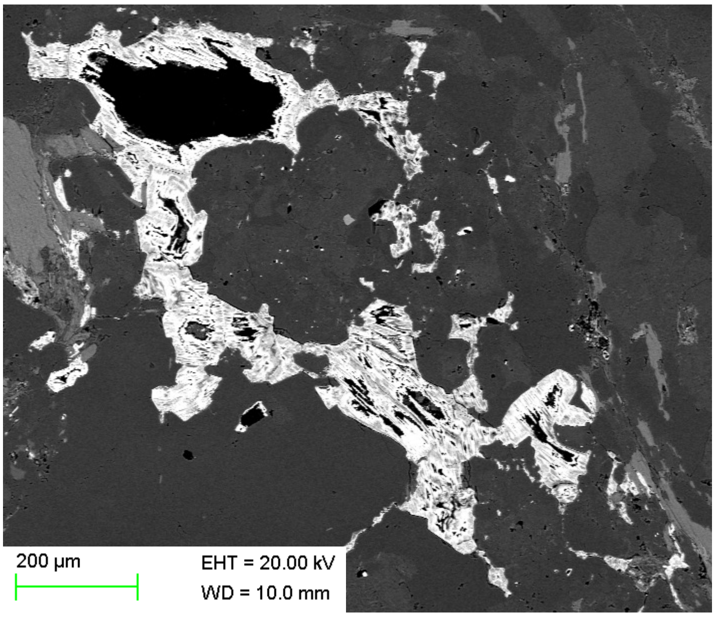

Figure S4: Back-scattered electron image of a pyrite crystal (bright color) identified in the thin section of the parageneiss specimen collected from the Ova Lavirun system (Fig. 1) and used to run Column 2 and 3.

Figure S5: Photographs taken along the Schlandraun system in 2003 and 2021 at the location of sample ST3 (Table 2, Figure S3), demonstrating the strong intensification of ARD as manifested by the increase in the white-coloring of the streambed caused by basaluminite precipitation. Pictures kindly provided by Raimund Rechenmacher and Klaus Bliem.

Table S1: Chemical composition of crushed material used to run the three column experiments. Concentrations are given in wt. %.

Experiment	*Al_2O_3 [%]*	*Ba [%]*	*CaO [%]*	*Cd [%]*	*Ce [%]*	*Cl [%]*	*Co [%]*	*Cr [%]*
Column 1	18.734	0.1050	1.807	0.0121	0.0590	0.0123	0.0194	0.0151
Column 2	25.783	0.1550	0.646	0.0127	0.0963	0.0070	0.0154	0.0231
Column 3	26.877	0.1820	0.477	0.0126	<0.003	0.0102	0.0167	0.0185

Experiment	*Cu [%]*	*Fe_2O_3 [%]*	*Ga [%]*	*I [%]*	*K_2O [%]*	*MgO [%]*	*MnO [%]*	*Na_2O [%]*
Column 1	0.0074	8.316	0.0039	0.0008	3.820	2.513	0.0967	2.449
Column 2	0.0073	9.941	0.0041	0.0005	5.774	2.616	0.0828	1.384
Column 3	0.0082	11.77	0.0056	0.0001	6.064	2.908	0.0900	1.247

Experiment	*Nb [%]*	*Ni [%]*	*P_2O_5 [%]*	*Pb [%]*	*Rb [%]*	*SO_3 [%]*	*Sc [%]*	*SiO_2 [%]*
Column 1	<0.003	0.0050	0.1870	0.0042	0.0167	1.066	<0.003	59.664
Column 2	<0.003	0.0064	0.1830	0.0048	0.0199	0.2190	<0.003	51.782
Column 3	<0.003	0.0049	0.2070	0.0037	0.0218	0.2450	0.0040	48.444

Experiment	*Sn [%]*	*Sr [%]*	*Th [%]*	*TiO_2 [%]*	*W [%]*	*Y [%]*	*Zn [%]*	*Zr [%]*
Column 1	<0.003	0.0494	<0.003	0.880	0.1040	0.0035	0.0136	0.0312
Column 2	<0.003	0.0335	0.0031	1.095	0.0526	0.0032	0.0122	0.0340
Column 3	<0.003	0.0299	<0.003	1.247	0.0498	0.0037	0.0142	0.0295

Experiment	*LOI = CO_2 + H_2O [%]*
Column 1	17.2
Column 2	19.8
Column 3	22.1

Table S2: Chemical analysis of streamwater samples collected between Jul 2019 and August 2021 along seven high-alpine streams in the Eastern Alps (Fig. 1, S3, Table 2). Also shown are the logarithmic values of the basaluminite ion activity product (log(IAP)) calculated by PHREEQC.

	Method	Unit	AP1	AP5	AP8	AP9	AP10	PC1	PC4	PC5	PC6
Site	n.a.	n.a.	Val Costainas	Val Costainas	Val Costainas	Val Costainas	Val Costainas	Val Poschiavo	Val Poschiavo	Val Poschiavo	Val Poschiavo
Sampling date			July 6, 2020	July 6, 2020	July 6, 2020	July 6, 2020	July 6, 2020	July 7, 2020	July 7, 2020	July 7, 2020	July 7, 2020
Coordinates	n.a.	Lat N/ Long E	46°32'50.47"/10°27'42.49"	46°33'5.75"/ 10°27'44.43"	46°33'46.79"/10°27'46.35"	46°34'9.24"/10°27'44.50"	46°34'47.58"/10°26'24.96"	46°19'32.5"/9°59'0.64"	46°19'40.05"/9°59'10.77"	46°19'41.89"/9°59'12.59"	46°19'43.15"/9°59'17.00"
Sample type	n.a.	n.a.	Stream origin	White-colored segment	White-colored segment	White-colored segment	White-colored segment	Stream origin	White-colored segment	White-colored segment	White-colored segment
Temperature	Electrode	°C	0.7	4.9	7.5	5	10.6	5.1	11.6	12.2	12.5
pH	Electrode	-	4.98	5.56	5.74	6.2	6.21	4.5	5.15	5.17	5.53
El. conductivity	Electrode	uS/cm	1316	852	639	513	464	440	n.m.	n.m.	n.m.
O_2 Saturation	Electrode	%	>90	>90	>90	>90	>90	>90	>90	>90	>90
Na^+	IC	mg/L	7.07	4.33	3.22	2.85	2.43	2.34	0.721	0.727	0.726
K^+	IC	mg/L	1.57	<1	<1	0.578	<1	<1	0.118	0.139	0.133
Ca^{2+}	IC	mg/L	157	88.6	62.3	54.9	43.3	57.2	13.6	13.1	12.8
Mg^{2+}	IC	mg/L	220	97.4	61.3	49.4	36.7	23.7	5.54	5.09	4.63
Al	ICP-OES	mg/L	14.8	3.64	2.13	1.37	0.215	9.63	1.50	1.14	0.731
Co	ICP-OES	mg/L	0.122	<0.05	<0.05	<0.05	<0.05	0.214	<0.05	<0.05	<0.05
Cu	ICP-OES	mg/L	0.099	0.034	0.020	0.014	<0.01	0.045	<0.01	<0.01	<0.01
Fe	ICP-OES	mg/L	<0.005	<0.005	<0.005	<0.005	<0.005	0.008	<0.005	<0.005	<0.005
Pb	ICP-OES	mg/L	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Mn	ICP-OES	mg/L	2.29	0.898	0.570	0.399	0.282	2.04	0.429	0.381	0.333
Ni	ICP-OES	mg/L	0.841	0.514	0.338	0.268	0.198	0.513	0.138	0.127	0.112
Sr	ICP-OES	mg/L	0.193	0.185	0.150	0.141	0.126	0.156	0.044	0.043	0.044
Zn	ICP-OES	mg/L	2.33	1.25	0.845	0.692	0.498	0.301	0.077	0.071	0.062
Si	ICP-OES		3.16	3.16	2.94	2.94	2.93	6.41	2.54	2.44	2.36
As	AAS	ug/L	4.37	<4	<4	<4	<4	<4	<4	<4	<4
F^-	IC	mg/L	14.96	4.92	3.03	2.29	1.59	1.64	0.364	0.332	0.295
Cl^-	IC	mg/L	1.04	0.500	0.310	0.266	0.211	0.450	0.083	0.093	0.089
Br^-	IC	mg/L	<0.16	<0.16	<0.16	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016
NO^{3-}	IC	mg/L	1.49	0.940	0.800	0.741	0.663	1.40	0.185	0.820	0.169
SO_4^{2-}	IC	mg/L	1248	592	402	327	254	288	60.9	55.8	51.2
TIC	C-analyzer	mg/L	2.77	0.576	0.58	0.71	1.18	0.85	<0.5	<0.5	<0.5
TOC	C-analyzer	mg/L	<0.5	0.802	<0.5	<0.5	0.623	<0.5	<0.5	0.61	<0.5
TDS		mg/L	1677	800	540	445	345	395	86	81	74
Water typ	n.a.	-	Mg-Ca-SO4	Mg-Ca-SO4	Mg-Ca-SO4	Mg-Ca-SO4	Mg-Ca-SO4	Ca-Mg-SO4	Ca-Mg-SO4	Ca-Mg-SO4	Ca-Mg-SO4
log(IAP) basaluminite	PHREEQC	-	25.3	26.2	26.8	29.1	21.3	24.6	28.2	27.7	28.4

Table S2 continued

	Method	Unit	TO1	TO2	TO3	TO4	VA4	VA5	VA6	LV7B	LV8	ST1	ST3
Site	n.a.	n.a.	Traunter Ovas	Traunter Ovas	Traunter Ovas	Traunter Ovas	Vadret Agnel	Vadret Agnel	Vadret Agnel	Lago Vago	Lago Vago	Schlandraun	Schlandraun
Sampling date			July 8, 2020	July 8, 2020	July 8, 2020	July 8, 2020	July 18, 2019	July 18, 2019	July 18, 2019	July 17, 2019	July 17, 2019	August 19, 2021	August 19, 2021
Coordinates	n.a.	Lat N/ Long E	46°30'52.26"/9°44'18.96"	46°30'50.72"/9°44'19.98"	46°30'53.33"/9°44'28.44"	46°30'54.12"/ 9°44'29.79"	46°31'4.49"/ 9°42'45.01"	46°31'2.80"/ 9°42'53.29"	46°31'9.91"/9°42'58.89"	46°26'27.70"/10°4'14.33"	46°26'28.00"/10°4'12.52"	46°43'10.00"/ 10°44'22.00"	46°42'56'.00"/ 10°44'21.00"
Sample type	n.a.	n.a.	Stream origin	White-colored segment	White-colored segment	White-colored segment	Stream origin	White-colored segment	White-colored segment	Stream origin	White-colored segment	Stream origin	White-colored segment
Temperature	Electrode	°C	3.5	7.5	8.8	9.8	1.4	5.3	8.5	1.9	9.1	1.9	7.7
pH	Electrode	-	4.7	5.15	5	5.08	4.46	5.18	6.6	4.89	5.3	5.1	5.23
El. conductivity	Electrode	uS/cm	562	573	421	413	133	137	128	308	215	610	476
O_2 Saturation	Electrode	%	>90	>90	>90	>90	>90	>90	>90	>90	>90	>90	>90
Na^+	IC	mg/L	5.12	4.42	3.05	2.75	1.43	1.45	1.59	1.56	1.28	2.77	2.33
K^+	IC	mg/L	<1	1.00	<1	0.679	0.76	0.87	0.88	0.72	0.62	1.710	1.68
Ca^{2+}	IC	mg/L	71.9	82.5	55.5	56.2	27.7	30.1	33.1	53.1	36.4	111	72.5
Mg^{2+}	IC	mg/L	33.5	27.9	17.8	16.6	1.63	1.50	0.96	30.6	18.9	77.1	44.2
Al	ICP-OES	mg/L	21.7	10.0	8.63	5.63	4.51	3.07	0.297	4.51	1.49	5.26	3.51
Co	ICP-OES	mg/L	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.064	<0.05
Cu	ICP-OES	mg/L	0.318	0.271	0.109	0.083	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Fe	ICP-OES	mg/L	0.038	<0.005	<0.005	<0.005	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Pb	ICP-OES	mg/L	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Mn	ICP-OES	mg/L	6.00	2.82	2.31	1.80	0.640	0.455	<0.05	0.959	0.493	1.14	0.607
Ni	ICP-OES	mg/L	0.078	0.046	0.039	0.031	<0.05	<0.05	<0.05	0.159	0.104	0.693	0.363
Sr	ICP-OES	mg/L	0.340	0.443	0.427	0.490	<0.05	<0.05	<0.05	0.091	0.082	0.303	0.228
Zn	ICP-OES	mg/L	1.81	1.66	0.965	0.769	0.306	0.209	0.096	0.214	0.122	0.270	0.153
Si	ICP-OES		4.40	4.70	3.31	3.11	4.13	3.50	2.73	3.08	2.78	8.88	6.06
As	AAS	ug/L	5.32	<4	<4	<4	<4.0	<4.0	<4.0	<4.0	<4.0	<4	
F^-	IC	mg/L	5.27	6.21	2.97	2.51	0.076	0.094	0.642	0.060	0.063	1.860	0.820
Cl^-	IC	mg/L	0.215	0.190	0.114	0.131	0.103	0.134	0.106	1.51	0.244	1.110	0.800
Br^-	IC	mg/L	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.16	<0.16
NO^{3-}	IC	mg/L	0.751	0.765	0.728	0.630	1.45	1.53	2.29	1.55	1.22	1.420	1.250
SO_4^{2-}	IC	mg/L	421	351	251	230	103	99.4	79.0	289	179	639	367
TIC	C-analyzer	mg/L	0.99	2.04	<0.5	<0.5	0.24	0.72	1.56	0.72	0.72	<0.5	<0.5
TOC	C-analyzer	mg/L	<0.5	<0.5	<0.5	<0.5	n.m.	n.m.	n.m	n.m.	n.m	<0.5	<0.5
TDS		mg/L	573	496	347	322	146	143	123	388	244	853	502
Water typ	n.a.	-	Ca-Mg-SO4	Ca-Mg-SO4	Ca-Mg-SO4	Ca-Mg-SO4	Ca-Mg-SO4	Ca-Mg-SO4	Ca-Mg-SO4	Ca-Mg-SO4	Ca-Mg-SO4	Mg-Ca-SO4	Mg-Ca-SO4
log(IAP) basaluminite	PHREEQC	-	27.5	29.2	28.8	28.5	24.1	30.2	29.6	27.6	29.4	28.3	29.5

Table S3: Chemical analysis of column effluent samples.

Column	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Sampling site	*Lago Vago*	*Ova Lavirun*	*Ova Lavirun*	*Lago Vago*	*Ova Lavirun*	*Ova Lavirun*	*Lago Vago*	*Ova Lavirun*	*Ova Lavirun*	*Lago Vago*	*Ova Lavirun*	*Ova Lavirun*	*Lago Vago*	*Ova Lavirun*	*Ova Lavirun*
Residence time (week)	1	1	1	2	2	2	4	4	4	8	8	8	16	16	16
pH	6.7	5.9	5.8	6.3	5.4	5.6	6	5.3	5.7	6.1	5.9	6.1	-	5.75	5.36
Na^+ (mg/L)	1.48	0.644	1.06	0.974	0.707	0.929	0.995	0.739	0.773	1.29	0.99	0.84	1.52	0.963	1.22
K^+ (mg/L)	9.79	1.82	5.11	5.31	1.81	4.52	5.05	1.56	3.83	5.54	1.59	3.24	5.29	6.32	1.26
Ca^{2+} (mg/L)	38.9	2.19	3.06	20.4	2.6	2.713	20.8	2.97	2.15	19	3.21	2.08	17.31	3.64	3.99
Mg^{2+} (mg/L)	9.4	0.602	1.83	5.18	0.747	1.66	5.03	0.874	1.37	4.78	0.953	1.17	4.29	2.21	1.13
Sr^{2+} (mg/L)	0.296	<0.1	<0.1	0.12	<0.1	<0.1	0.165	<0.1	<0.1	0.152	<0.1	<0.1	0.169	<0.1	<0.1
Al (mg/L)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.117	0.117	0.139	<0.1	<0.1	<0.1
Mn (mg/L)	0.051	0.129	0.251	0.067	0.118	0.15	0.08	0.104	0.19	0.089	0.096	0.227	0.237	0.108	0.16
Ni (mg/L)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.025	<0.02	<0.02
Zn (mg/L)	<0.01	0.022	<0.01	<0.01	0.021	<0.01	<0.01	0.031	<0.01	0.01	0.021	<0.01	0.018	0.037	0.032
F^- (mg/L)	0.057	0.028	0.041	0.044	0.024	0.04	0.038	0.031	0.037	0.064	0.074	0.056	0.073	0.055	0.051
Cl^- (mg/L)	5.73	3.9	4.02	6.26	8.99	8.72	0.194	0.211	0.215	11.9	4.94	4.91	8.8	21.3	7.54
Br^- (mg/L)	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	<0.016	0.017	<0.016
NO_3^{-} (mg/L)	0.203	0.294	0.233	0.195	0.061	0.233	0.121	<0.016	0.093	0.036	0.119	0.033	0.02	0.04	0.025
SO_4^{2-} (mg/L)	150	14	24.4	75.4	15.1	21.9	77.2	15.9	17.6	73.9	17.3	16.3	69.8	25.4	20.4
Si (mg/L)	10.1	16.8	11.6	11.7	15.3	9.11	12.6	13.5	9.69	13.4	14.8	13.5	14.507	14.091	13.992
TOC (mg/L)	2.86	2.51	12.07	1.92	2.19	4.51	3.02	3.65	4.9	3.32	2.27	5.19	4.96	7.12	4.49
TIC (mg/L)	2.18	0.72	0.95	2.48	0.8	1.35	1.3	0.65	0.93	0.86	0.84	1.24	0.528	0.702	0.607
HCO_3 (mg/L)	11.1	3.68	4.82	12.62	3.91	6.85	6.6	3.33	4.72	4.36	4.26	6.31	2.68	3.57	3.09
TDS (mg/L)	242	47	69	143	52	63	133	44	46	139	52	55	130	86	58
***Water type after* Jäckli (1970)**	*Ca-Mg-(K)-SO_4*	*Ca-K-(Na)-(Mg)-SO_4*	*K-Ca-Mg-(Na)-SO_4*	*Ca-Mg-(K)-SO_4*	*Ca-K-(Na)-(Mg)-SO_4*	*K-Mg-Ca-(Na)-SO_4*	*Ca-Mg-(K)-SO_4*	*Ca-K-(Mg)-(Na)-SO_4*	*K-Mg-Ca-(Na)-SO_4*	*Ca-Mg-(K)-SO_4*	*Ca-Na –(K)-(Mg)-SO_4*	*K-Ca-Mg-(Na)-SO_4*	*Ca-Mg-(K)-SO_4*	*Ca-Na –(K)-(Mg)-SO_4*	*K-Ca-Mg-(Na)-SO_4*

Table S4: SEM EDX analysis of pyrite grains identified in thin sections of rock specimen collected from Ova Lavirun and used to run Column 2 and 3.

Spot Nr.	S (wt. %)	Fe (wt. %)	Co (wt. %)	Ni (wt. %)	Zn (wt.%)
1	54.7	45.3	<0.1	<0.1	<0.1
2	55.0	45.0	<0.1	<0.1	<0.1
3	43.1	56.9	<0.1	<0.1	<0.1
4	39.2	60.8	<0.1	<0.1	<0.1
5	58.0	42.0	<0.1	<0.1	<0.1
6	55.3	44.7	<0.1	<0.1	<0.1
7	56.6	43.4	<0.1	<0.1	<0.1
8	55.3	44.7	<0.1	<0.1	<0.1
9	55.6	44.4	<0.1	<0.1	<0.1
10	57.3	42.7	<0.1	<0.1	<0.1
11	55.1	44.9	<0.1	<0.1	<0.1
12	56.6	43.4	<0.1	<0.1	<0.1
13	56.9	43.1	<0.1	<0.1	<0.1
14	53.6	46.4	<0.1	<0.1	<0.1
15	58.8	41.2	<0.1	<0.1	<0.1
16	58.3	41.7	<0.1	<0.1	<0.1
17	55.7	44.3	<0.1	<0.1	<0.1
18	54.9	45.1	<0.1	<0.1	<0.1
19	55.8	44.2	<0.1	<0.1	<0.1
20	55.4	44.6	<0.1	<0.1	<0.1
21	55.5	44.5	<0.1	<0.1	<0.1
22	51.4	48.6	<0.1	<0.1	<0.1
23	47.9	52.1	<0.1	<0.1	<0.1
24	59.5	40.5	<0.1	<0.1	<0.1
25	53.5	41.9	1.5	3.0	<0.1
26	52.6	40.7	2.4	4.3	<0.1
27	58.0	40.6	<0.1	0.6	<0.1
28	54.6	45.5	<0.1	0.8	<0.1
29	52.6	43.8	<0.1	0.6	<0.1
30	54.5	45.7	<0.1	0.8	<0.1
31	56.1	47.3	<0.1	0.8	<0.1
32	57.9	48.2	<0.1	1.2	<0.1
33	56.0	41.4	<0.1	<0.1	2.6
34	55.2	41.6	<0.1	<0.1	3.2
35	50.0	46.8	<0.1	<0.1	3.2
36	54.7	40.0	<0.1	<0.1	5.3

REFERENCE

Boeckli L., Brenning A., Gruber S. and Noetzli J. (2012) Permafrost distribution in the European Alps: calculation and evaluation of an index map and summary statistics. *The Cryosphere* **6**, 807-820.