

Peculiar arsenic, copper, nickel, uranium, and yttrium-rich stone coatings in a high mountain stream in the Austrian Alps

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Abstract

Peculiar coatings rich in arsenic, copper, nickel, uranium, and yttrium were found to cover stones in a high mountain stream downstream of the confluence of small acidic tributaries, which emerge at the front of the Krummgampen rock glacier (Ötztal Alps, Tyrol, Austria). The hard mineral coatings are characterized by a white color, a x-ray amorphous structure and showed properties of hydrous aluminium silicates like allophane ($\text{Al}_2\text{O}_3(\text{SiO}_2)_2 \cdot x \text{ n H}_2\text{O}$) and/or imogolite ($\text{Al}_2\text{SiO}_5(\text{OH})_4$). Main constituents of the coatings are aluminium, silica, and sulfur. Contrary to high concentrations of arsenic, copper, nickel, uranium, and yttrium in the stream stone coatings, corresponding element values are below the limit of detection both in the Krummgampen stream and - except for nickel and traces of copper - also in acidic outflows from the rock glacier. Stone coatings are neither present in rock glacier outflows nor in the Krummgampen stream upstream of the rock glacier, nor in other streams in the catchment. The coatings are interpreted as a precipitate on or an accretion to stone surfaces in the Krummgampen stream, which is characterized by moderate solute concentrations and a neutral pH. In acidic outflows of the rock glacier high concentrations of dissolved sulfate, calcium, magnesium, silica, aluminium, manganese, and nickel prevail. Some constituents of stream stone coatings like arsenic, copper, nickel, uranium, and yttrium have also been measured in paragneiss rocks in the catchment of the rock glacier which are characterized by heavily weathered accessory minerals monazite, xenotime, and pyrite. It is therefore very likely that minerals which occur in the bedrock of the catchment represent a major source for elements accumulated in stream stone coatings even though processes like element release from the ice-rock matrix in the rock glacier, transport to and accumulation on Krummgampen stream stone surfaces are not yet completely understood.

1. Introduction

Some high mountain freshwaters in the European Alps have recently shown a substantial change in their chemical composition, particularly due to increasing concentrations of major ions sulfate, calcium, and magnesium, which can be accompanied by high values of metals exceeding threshold values for drinking water, e.g. for aluminium and nickel (Thies et al., 2007, 2013; Nickus et al., 2015). The catchments of these freshwaters are characterized by the presence of active rock glaciers and melting of this widespread form of mountain permafrost is discussed as the most likely cause for observed pronounced changes in high mountain freshwater chemistry (e.g. Williams et al., 2006; Thies et al., 2007; Todd et al., 2012). Out of more than 3000 existing rock glaciers in the Tyrolean Alps (Austria), 517 have been classified as active rock glaciers by Krainer and Ribis (2012) and most of them are located in the Ötztal and Stubai Alps. With a mean ice content of 30 to 40%, the corresponding cumulative ice volume of active rock glaciers in Tyrol has been estimated by Krainer and Ribis (2012), to be within the range of 0.16 to 0.22 km³. A study of an ice core from the Lazaun rock glacier in the southern Ötztal Alps (Schnals valley, Italy) revealed a radiocarbon dated age of the

permafrost ice of up to 10000 years B.P. (Krainer et al., 2015), and its ice layers contain very high concentrations of calcium, magnesium and sulfate, accompanied by high values of metals like aluminium and nickel (Nickus et al., in prep). The high element concentrations in the Lazaun rock glacier ice core indicate that melt waters draining from an active rock glacier can impact the water quality of nearby high mountain freshwaters as has been observed at other sites in the European Alps (e.g. Thies et al., 2007; Thies et al., 2013; Nickus et al., 2015). Recently, another potential impact of a rock glacier on a high mountain stream has been discovered in the Krummgampen catchment (Tyrol, Austria). There, peculiar white coated stream stones with high values of arsenic, copper, nickel, uranium, and yttrium have been found. As the coated stones were only found downstream of the Krummgampen rock glacier, we argue that the formation of such coatings are very likely related to the presence of an active rock glacier which releases highly concentrated waters into a high mountain stream (Thies et al., 2013).

Here we report on the characteristics of peculiar stone coatings in a high mountain stream at Krummgampen (Tyrol,

Austria), which is impacted by an active rock glacier (Thies et al., 2013).

2. Study site and methods

The Krummgampen valley is situated in the Upper Kauner Valley (Ötztal Alps, Austria, 10°42' E, 46°53' N) at an altitude between 2400 and 3300 m. Its catchment area is 5.5 km² and the bedrock is composed of paragneiss, orthogneiss, amphibolite and mica schist of the Ötztal-Stubai metamorphic complex (Purtscheller, 1978; Krainer, 2010; Strauhel et al., 2016). An active rock glacier extends from 2400 to 2700 m altitude with a surface area of 0.1 km² (Fig. 1). The Krummgampen stream drains the Krummgampen valley and passes the terminal front of the rock glacier at an altitude of 2465 m where it is overridden by the terminal rock glacier tongue tip. At the front of the rock glacier a few small acidic streams (KG-1, KG-2, KG-3) emerge with an average discharge of one to two L/s, which feed into to the Krummgampen stream with a discharge of up to 2000 L/s (Fig.1; Thies et al., 2013). The white-coated stones are only present in the Krummgampen stream downstream of the confluence of the streams KG-1, KG-2, and KG-3 (Fig. 1). Coated stones in the Krummgampen stream were sampled in July 2008 and in September 2010 during a period of low discharge, and then transported to the laboratory in pre-cleaned polyethylene bags. Prior to analysis, the coating was carefully removed from the stones by a sharp stainless steel knife. Phase analyses of the coating was performed by x-ray powder diffraction (XRPD) using a Bruker-AXS D8 diffractometer, and a Micro-Raman spectrometer (Horiba Jobin Yvon HR 800). Elemental analyses of the powdered coating were performed with a Spectro Xepos Plus X-ray fluorescence spectrometer and verified for major components with a JEOL 8100 electron probe microanalyzer (EPMA). High-resolution scanning electron microscope images of the coatings were available by a field-emission scanning electron microscope (Auriga 40 – Zeiss). Back scattered electron images of corroded minerals from bedrock samples were obtained by a scanning electron microscope (JEOL JSM-6010 LV).

Paragneiss bedrock was sampled in September 2010 close

to the Krummgampen rock glacier tongue and accessory minerals (monazite CePO₄, and pyrite FeS₂) were analysed by electron probe microanalysis (JEOL-JXA 8100 Superprobe) using the wavelength-dispersive (WDS) mode. Xenotime (YPO₄) was analysed using the energy-dispersive (EDS) mode only. Operating conditions were 15 kV acceleration voltage and 10 nA beam current. The analyses file for monazite contained the elements Si, P, Ca, Y, Pr, La, Ce, La, Sm, Dy, Nd, Pb, U, Th and Gd and counting times ranged from 20 to 300 s. The analysis file for pyrite contained the elements S, Cu, Fe, Zn, Hg, Mn, Cd, Ni, Pb, Au, Ag, As, Sb, Se. The counting times were 20 s for the peak and 10 s for the background.

Krummgampen stream water grab samples were taken from 2008 to 2011 during summer and autumn in each year. Electrical conductivity and water temperature in Krummgampen streams were measured in the field with a WTW LF 92 conductivity meter. Water probes were sampled in pre-cleaned polyethylene bottles and kept cool and dark until chemical analysis. Ions were analysed with a Dionex DX-500/ICS-1000 ion chromatograph and metals with a Horiba Jobin Yvon ICP-OES. pH was measured in the laboratory with a WTW pH 91 device and a Hamilton pH flushrode. Further details on ana-

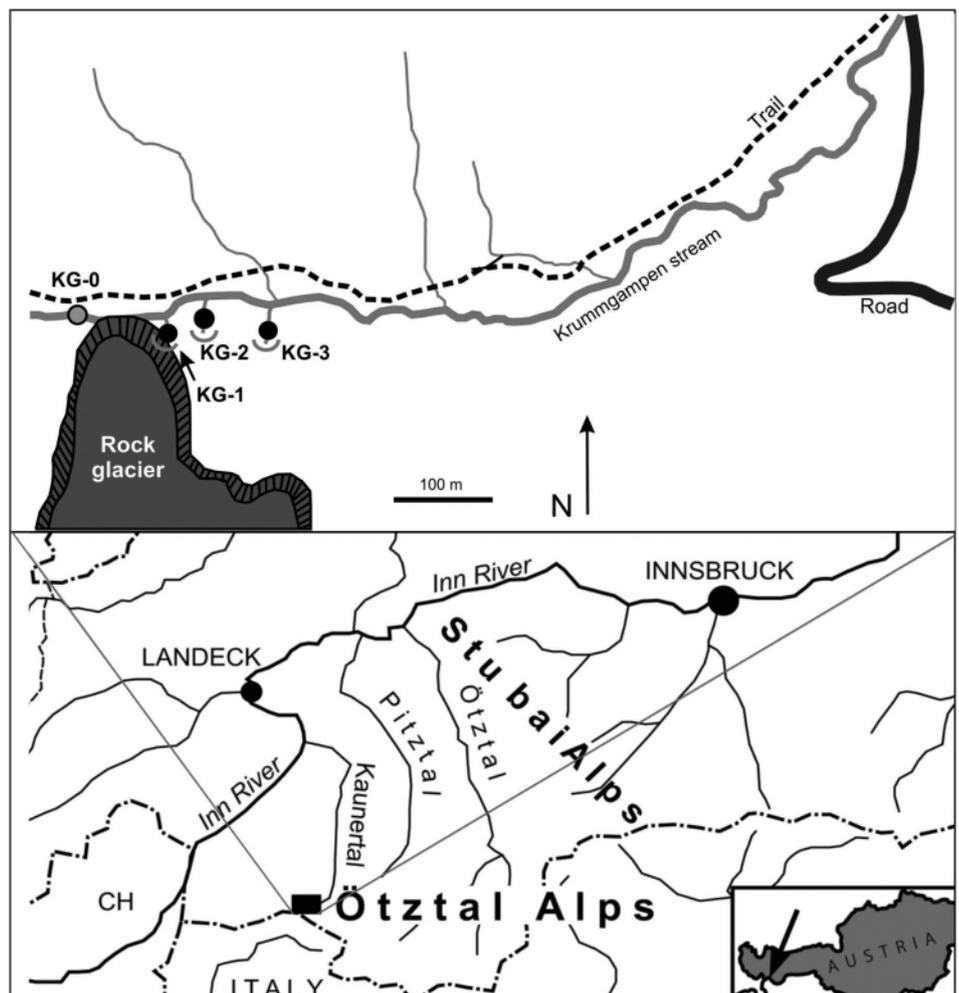


Figure 1: Location of the study area with the sampling sites at Krummgampen rock glacier (Krummgampen stream KG-0, rock glacier streams KG-1, KG-2, KG-3).

lytical procedures are reported elsewhere (Thies et al., 2007; Thies et al., 2013).

3. Results and Discussion

The white coated stones in the Krummgampen stream occur only downstream of the confluence of acidic outflows from the rock glacier to this stream and are further visible in this stream up to several hundred meters downstream from the rock glacier tongue (Figs. 1, 2). Coated stones which emerge from Krummgampen stream above the water surface are white (Fig. 2), while submerged coated stones in the stream



Figure 2: White coated stones exposed in Krummgampen stream.



Figure 3: White coated submerged stone, retrieved from the bed of Krummgampen stream.

are grey to green, which turn white when dried (Fig. 3). Stream stone coatings were neither found in the acidic outflows from the rock glacier, nor anywhere upstream of Krummgampen rock glacier, nor in other streams draining from slopes of the Krummgampen valley without any impact of the rock glacier. The stone coatings are about 0.5 mm x 10-3 m thick and exhibit a hardened texture. X-ray diffractograms of the stone coatings show amorphous patterns (i.e. by broad peaks from 3 to 3.5 Å, and 10 to 14 Å) indicating affinities to allophane ($\text{Al}_2\text{O}_3(\text{SiO}_2)_2 \cdot n \text{H}_2\text{O}$) and/or imogolite ($\text{Al}_2\text{SiO}_5(\text{OH})_4$), which is as well supported by Raman spectra. The electron probe microanalysis (EDS mode) indicates an elemental composition of Al-Si-O-S. The amorphous and botryoidal structure of the stream stone coatings is shown at the micro-scale by scanning electron microscope images (Fig. 4a, 4b). EDXRFA revealed 52 to 66% Al_2O_3 , 29 to 31% SiO_2 , 6 to 9% SO_3 , and a few percent of $\text{Na}_2\text{O-MgO-Fe}_2\text{O}_3\text{-K}_2\text{O}$. It is not yet resolved to which mineral compound the sulfur in the coatings can be attributed, but presumably the coatings form a mixture of allophane and/or imogolite together with an aluminium sulfate. In addition, very high values of arsenic (up to 5500 ppm), copper (up to 700 ppm),

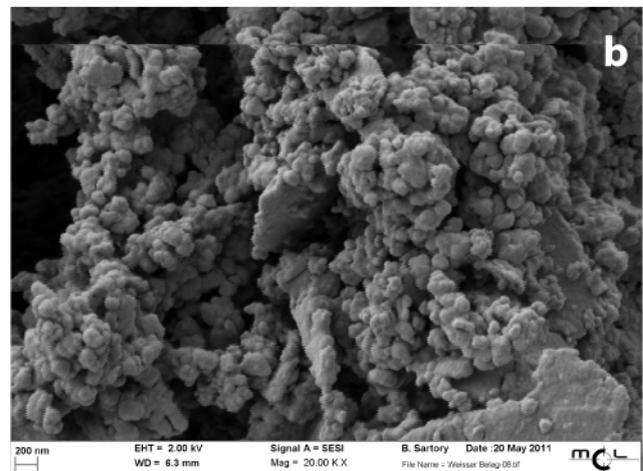
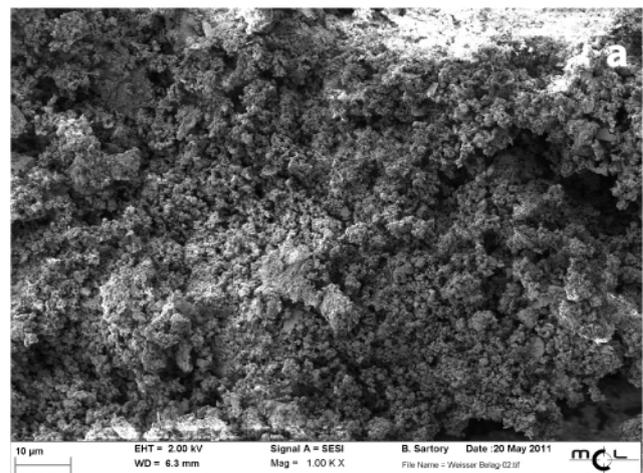


Figure 4: a: Scanning electron microscope image of stone coatings in Krummgampen stream. Note the amorphous structures at micro-meter range. b: Scanning electron microscope image of stone coatings in Krummgampen stream. Note the botryoidal structures at nanometer range.

uranium (up to 900 ppm), yttrium (up to 400 ppm) as well as nickel (100 ppm) were detected in the Krummgampen stream stone coatings (Table 1), which to our knowledge has not been reported so far for high mountain streams elsewhere.

Paragneiss samples from the debris layer of the Krummgampen rock glacier tongue contain the mineral assemblage garnet, biotite, muscovite, plagioclase, quartz, staurolite, and chlorite. Among the accessories are apatite, rutile, ilmenite, zircon, xenotime, pyrite, and monazite (Figs. 5 – 7), which are potential sources for arsenic, copper, nickel, sulfur, uranium, and the rare earth element yttrium detected in Krummgampen stream stone coatings (Table 1). Textures of monazite and xenotime grains in paragneiss samples display corroded grain boundaries of these minerals as shown in the backscattered electron (BSE) images in figures 5 and 6. This indicates partial dissolution due to an accompanying fluid, which may be related to acidic conditions in rock glacier outflows and the fact of an almost complete replacement of pyrite by iron hydroxides. As a consequence, most of the iron will remain in the rock and only minor elements such as nickel (Table 3) which are not incorporated into these hydroxides will be released into the water. A peculiar feature is the partial alteration of monazite, xenotime, and zircon. Rare earth element (REE) phosphates such as monazite and xenotime are generally highly resistant to weathering as shown by its widespread occurrence as detrital minerals in sands and sandstones (Roy, 1999). Although the solubilities of the REE-phosphates monazite and xenotime are extremely low in water at low temperatures (Wood, 1990), some highly aggressive fluids may partially or totally alter monazites even at low temperatures (Oelkers and Poitrasson, 2002). This has also been found by Cetiner et al. (2005) who showed that REE-phosphate solubility is strongly governed by pH. In their study, the solubility of the REE phosphates decreases strongly with increasing pH. Log-molalities of La, Nd, Sm and Y at 23 °C changed from -3 to -4.5 at pH 1 down to -4.5 to -5.5 at pH 2. Oelkers and Poitrasson (2002) showed a similar trend for monazite dissolution and hence the release of Ce, U and Th although at higher temperatures of 50-70 °C. Again, Ce concentrations in the coexisting fluid decreased by one order of magnitude from pH 2 to pH 6 and then increased again at pH 10.

Microprobe data revealed ~ 0.4 wt% Ni in pyrite, and 1.0-1.3 wt% UO₂ and 0.1-1.9 wt% Y₂O₃ in monazite. SEM-EDS of xenotime revealed 45.0 wt% Y₂O₃. Except for As the release of these elements from the accessory carrier phases is consistent with the analytical data in Table 3.

Krummgampen rock glacier outflows KG-1, KG-2, and KG-3 differ considerably in discharge and water quality with respect to the upstream site of Krummgampen stream at KG-0

	As ppm	Cu ppm	Ni ppm	U ppm	Y ppm
Paragneiss	< 1	80 – 160	20 – 30	5 – 8	40 - 80
Orthogneiss	1 - 200	5 - 1817	2 - 24	1 - 65	3 - 43
Stream stone coatings	1000 – 5500	300 - 700	90 - 135	300 - 900	100 - 400
KG-1, KG-2, KG-3	< DL	0.004-0.02	0.14	< DL	< DL
KG-0	< DL	0.003	< DL	< DL	< DL

Table 1: Arsenic, copper, nickel, uranium, and yttrium in bedrock, in Krummgampen stream stone coatings, in water samples of rock glacier streams (KG-1, KG-2, KG-3) and of Krummgampen stream (KG-0). Krummgampen paragneiss (Schönherr, 2009), Koefels orthogneiss (Purtscheller et al., 1995). DL: detection limit.

		KG-0	KG-1	KG-2	KG-3
N		15	30	27	25
T	°C	8.0	1.6	3.3	1.0
Cond.	µS/cm	89	295	381	293
pH		7.16	4.63	4.88	4.82
SO ₄	mg/l	25	111	157	112
Mg	mg/l	1.1	12	18	14
Ca	mg/l	12	24	33	23
Al	mg/l	<DL	1.48	0.87	0.68
Cu	mg/l	0.003	0.02	0.01	0.004
Mn	mg/l	<DL	0.23	0.04	0.09
Ni	mg/l	<DL	0.13	0.15	0.13
Si	mg/l	1.09	2.69	3.57	2.99
Sr	mg/l	0.02	0.04	0.05	0.03
Zn	mg/l	<DL	0.09	0.08	0.08

Table 2: Mean values of water temperature T, water chemistry of Krummgampen stream (KG-0) and three rock glacier streams (KG-1, KG-2, KG-3), 2008 to 2011. N= Number of samples, Cond.: Conductivity, DL: detection limit.

	Mon 1	Mon 2	Mon 3	Xnt 1		Py-1	Py-2
SiO ₂	n.d.	0.05	n.d.	n.d.	As	n.d.	0.06
P ₂ O ₅	28.00	28.05	25.83	45.94	S	38.65	38.40
Pr ₂ O ₃	3.70	3.28	3.45	n.d.	Ag	0.03	0.01
CaO	0.77	1.17	0.94	n.d.	Cu	n.d.	0.02
UO ₂	0.97	1.29	1.02	3.00	Zn	0.01	0.11
Nd ₂ O ₃	11.54	11.00	11.07	n.d.	Pb	0.02	n.d.
Ce ₂ O ₃	29.44	27.70	28.39	n.d.	Fe	60.82	59.79
Dy ₂ O ₃	0.60	0.81	0.66	5.84	Ni	0.37	0.43
La ₂ O ₃	13.99	13.09	13.55	n.d.	Se	<0.01	n.d.
PbO	0.11	0.15	0.09	n.d.	Cd	0.10	n.d.
Y ₂ O ₃	1.59	1.85	0.13	44.99	Hg	n.d.	0.04
Gd ₂ O ₃	1.59	1.81	1.65	n.d.	Mn	0.05	<0.01
Sm ₂ O ₃	2.22	2.11	2.09	n.d.	Au	n.d.	0.07
ThO ₂	3.07	5.39	4.72	0.24	Sb	0.06	0.05
Total	97.6	97.8	95.2	*100.0		100.2	99.0

Monazite (Mon) and xenotime (Xnt) analyses are given in wt% oxides, pyrite (Py) analyses in wt% elements. *EDS analysis normalized to 100.0 wt%.

Table 3: Representative EPMA analyses of monazite, xenotime (wt% oxides), and pyrite (wt% elements).

(Fig. 1, Table 2; Thies et al., 2013). Rock glacier outflows KG-1, KG-2, and KG-3 are characterized by high conductivity values, high concentrations of the major ions sulfate, calcium, and magnesium, an acidic pH, high metal concentrations (e.g. for aluminium and nickel), and high silica concentrations (Table 2). On the contrary, Krummgampen stream water at the upstream site KG-0 is characterized by neutral pH, lower conduc-

tivity ($< 100 \mu\text{S}/\text{cm}$) and lower silica values, and metal concentrations below the detection limit (Table 2). Surface streams in the Krummgampen valley draining from northern slopes opposite to the rock glacier show even lower conductivity values (10 to $30 \mu\text{S}/\text{cm}$), neutral pH and metal concentrations below detection limits (Thies et al., 2013), which corroborates the hypothesis that intense (bio)geochemical processes aside from carbon dioxide driven bedrock weathering are accountable for rock glacier derived stream solute composition (Thies et al., 2007). The particular water quality in rock glacier outflows indicates processes of intensified mineralisation to occur within the complex rock-ice matrix inside of a rock glacier (Krainer et al., 2015), triggered e.g. by heavily fractured rocks (Strauhal et al., 2016), freshly exposed mineral surfaces, fine-grained sediment material, downhill movement of the rock glacier, freeze-thaw cycles of ice layers, meltwater percolation through the rock-ice matrix, acid dissolution of silicates and accessory REE-bearing minerals (e.g. Oelkers and

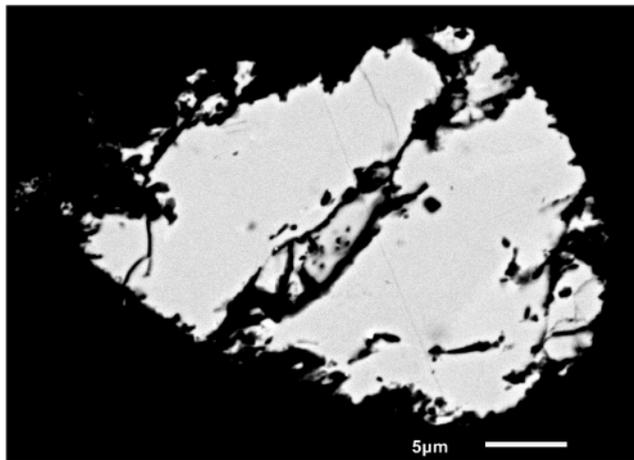


Figure 5: Back scattered electron image of a weathered monazite with fractures, corroded grain boundaries and pits from a paragneiss rock sample (Krummgampen).

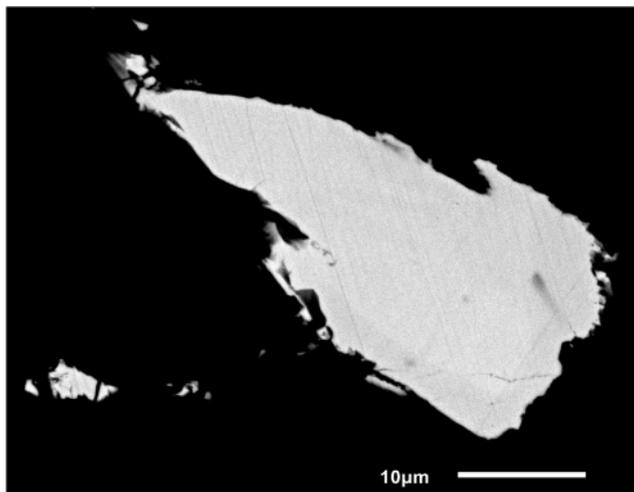


Figure 6: Back scattered electron image of a weathered xenotime with corroded grain boundaries and pits from a paragneiss rock sample (Krummgampen, sample PT 184 from Tropper 1993).

Poitrasson, 2002; Cetiner et al., 2005), and a related release of metals as induced by pyrite oxidation (Strauhal et al., 2016), which can be strongly enhanced by microbial activity (Sonnleitner et al., 2011). Aquifer geochemistry of some slopes in the Upper Kauner Valley (Tyrol, Austria) has been shown to be controlled by water-rock interactions in strongly fractured and heavily weathered metamorphic rocks of the Ötztal-Stubai Basement Complex, which release highly mineralised but mostly circumneutral groundwater dominated by calcium, magnesium, and sulfate (Strauhal et al., 2016). There, the oxidation of pyrite and other sulfides was found to represent the major source for sulfate.

The elements arsenic, uranium, and yttrium present at high concentrations in the Krummgampen stream stone coatings were below the limit of detection in waters of both rock glacier outflows and the Krummgampen stream (Tables 1 and 2). Only copper and nickel were detectable in acidic rock glacier outflows, which are present at high concentrations in the stream stone coatings. Heavily weathered minerals like monazite (CePO_4), xenotime (YPO_4), and pyrite (FeS_2) detected in rock samples from the Krummgampen catchment (Figs. 5 to 7) appear so far as the most likely source for elements found in Krummgampen stream stone coatings (Table 1) due to 45 wt% Y_2O_3 in xenotime, up to 3 wt% UO_2 in monazite and xenotime and < 0.1 wt% As in pyrite (Table 3). Xenotime has been described as a rare mineral, but it has been identified at several localities in the Alps (Demartin et al., 1991) and monazite was also found at the Köfels landslide in the nearby Ötz valley (Purtscheller et al., 1995). Strauhal et al. (2016) recently reported on the presence of ore deposits containing As and Cu in the Upper Kauner valley close to our study site at Krummgampen. Schönherr (2009) analyzed rock samples from the Krummgampen catchment and detected nickel [20 to 30 ppm], arsenic [< 1 ppm], copper [80 to 160 ppm], uranium [< 10 ppm], and yttrium [40 to 80 ppm] (Table 1). Purtscheller et al. (1995) found in orthogneiss at Köfels (Ötz valley, Tyrol) nickel [2 to 24 ppm], arsenic [1 to 200 ppm], copper [5 to

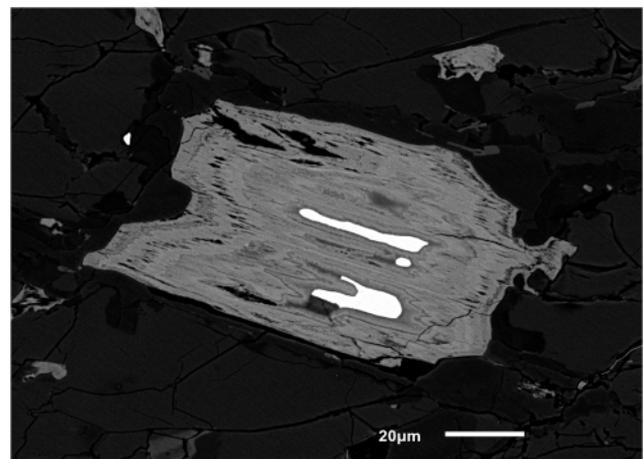


Figure 7: Back scattered electron image of weathered pyrites (white) surrounded by Fe-hydroxides from an amphibolite rock sample (Krummgampen, sample PT 238 from Tropper 1993).

1817 ppm], uranium [1 to 65 ppm], and yttrium [3 to 43 ppm]. According to Purtscheller et al. (1995), solution transport and precipitation of small ore concentrations can lead to elevated uranium concentrations in weathering residues of granitic gneiss. Purtscheller et al. (1995) and Schönherr (2009) revealed the presence of arsenic, copper, nickel, uranium, and yttrium in regional and local gneiss samples which supports our conclusion for a minerogenic source of these elements found in high concentrations in the stream stone coatings.

Manorcha and Dixon (2014) reported thin white microbially facilitated rock coatings in cold streams on mica schist in Swedish Lapland which were sulfate-dominated aluminium glazes identified as basaluminite, an amorphous aluminium oxyhydroxide sulfate $[Al_4(SO_4)(OH)_{10}\cdot H_2O]$. According to Darmody et al. (2007), these coatings consist of approximately 52% Al_2O_3 , 10% SiO_2 , 11% SO_3 , 1% K and Ca, and 0.1% Na, Mn, and Mg and their formation has been favored by chemical weathering under the presence of pyrite. Manorcha and Dixon (2014) report that microbial communities of such rock coatings are known for their abilities to scavenge, precipitate, concentrate and deposit ions and metals. These type of rock coating in Swedish Lapland streams shows several similarities to the stone coating in the Krummgampen stream with respect to the strong accretion to stream rock surfaces, the white colour, the amorphous structure, and the major components aluminium, silica, and sulfur. However, arsenic, copper, uranium, and yttrium were not reported by Manorcha and Dixon (2014) as constituents of Swedish stream rock coatings. Urrutia and Beveridge (1995) and Fortin and Beveridge (1997) showed that bacterial surfaces strongly enhance the formation of amorphous silicates like allophane and imogolite as well as the sorption of metals like Al and Zn. Urrutia and Beveridge (1993, 1994) report that silicate retention on bacterial cell walls was greatly favoured under the presence of heavy metals like Pb, Cd, Zn, Cr, Ni, and Cu, even at low temperatures of 4°C. These findings indicate that the formation of silicate coatings on Krummgampen stream rocks might have been favoured by the observed presence of As, Ni, Cu, U, and Y in the coatings. So far a potential contribution of microbial communities to the formation of stream stone coatings is not known for the Krummgampen study site.

4. Conclusions

We conclude that the formation of Krummgampen stream stone coatings rich in arsenic, copper, nickel, uranium, and yttrium downstream of the active Krummgampen rock glacier is most likely related to mineral corrosion in the bedrock of the rock glacier catchment. Coatings show an amorphous structure with the major elements Al-Si-O-S. Enhanced weathering by acidic meltwaters from the rock glacier could have triggered the release of silica, sulfur, metals, and a rare earth element, while a neutral pH in the Krummgampen stream could have favored the adsorption, accretion or precipitation of silica-rich melt waters on stream stone surfaces. So far we yet miss a proof for the element transfer from the rock glacier

to the stream stone coatings as some elements were at or below the limit of detection both in rock glacier melt waters and in Krummgampen stream water. However we consider it as most likely that water represents the medium for a transfer of aluminium, silica, sulfur, arsenic, copper, nickel, uranium, and yttrium from the rock glacier environment to the Krummgampen stream where they were found to accumulate in stream stone coatings.

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