



## Factors controlling the water quality of rock glacier springs in European and American mountain ranges



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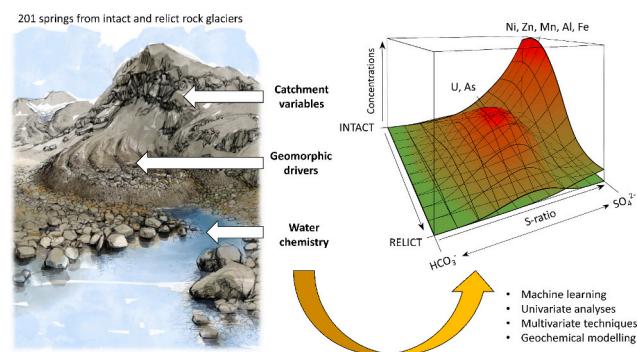
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## HIGHLIGHTS

- Rock glaciers (RGs) are increasingly important mountain water resources.
- We investigated the water chemistry of 201 intact (with ice) and relict (no ice) RGs.
- Under predisposing lithological settings, intact RGs were more enriched in solutes.
- One third of intact RG springs had water quality below drinking water standards.
- Solute export from intact RGs may adversely affect water quality in hotspot areas.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Rock glaciers (RGs) provide significant water resources in mountain areas under climate change. Recent research has highlighted high concentrations of solutes including trace elements in RG-fed waters, with negative implications on water quality. Yet, sparse studies from a few locations hinder conclusions about the main drivers of solute export from RGs. Here, in an unprecedented effort, we collected published and unpublished data on rock glacier hydrochemistry around the globe. We considered 201 RG springs from mountain ranges across Europe, North and South America, using a combination of machine learning, multivariate and univariate analyses, and geochemical modeling. We found that 35 % of springs issuing from intact RGs (containing internal ice) have water quality below drinking water standards, compared to 5 % of springs connected to relict RGs (without internal ice). The interaction of ice and bedrock lithology is responsible for solute concentrations in RG springs. Indeed, we found higher concentrations of sulfate and trace elements in springs sourcing from intact RGs compared to water originating from relict RGs, mostly in specific lithological settings. Enhanced sulfide oxidation in intact RGs is responsible for the elevated trace element concentrations. Challenges for water management may arise in mountain catchments rich in intact RGs, and where the predisposing geology would make these areas geochemical RG hotspots. Our work represents a first comprehensive attempt to identify the main drivers of solute concentrations in RG waters.

## 1. Introduction

Under ongoing global warming, the loss of glaciers (Hugonnet et al., 2021) and snow (Gottlieb and Mankin, 2024) is paralleled by permafrost warming and degradation (Biskaborn et al., 2019). These cryospheric changes have relevant effects on nature and society (Hock et al., 2019), including those related to modifications in hydrological systems (Drenkhan et al., 2023). Within this framework, rock glaciers (RGs), a visual indication of the current/past presence of ice-rich permafrost (Haeberli et al., 2006), have gained attention during the last decade because of their capability to host large quantities of frozen and liquid water (Jones et al., 2019; Wagner et al., 2021).

Due to the insulating properties of their rocky debris mantles, RGs lose ice at slower rates than glaciers (Wagner et al., 2021; Arenson et al., 2022). Concurrently, their capacity as aquifers increases as a consequence of internal ice loss (Hayashi, 2020), when RGs shift from intact (containing ice) to relict (without ice) under prolonged disequilibrium with climatic conditions (Rogger et al., 2017; Brighenti et al., 2021). Hence, RGs represent key elements for future water supply (Pandey et al., 2022), especially in arid and semi-arid mountain areas and during baseflow conditions (Reato et al., 2022; Munroe and Handwerger, 2023a). For this reason, increased attention is also being focused on the quality of the water discharging from them.

Long-term studies on surface waters fed by intact RGs have detected an increase of solute concentrations during the last decades (Thies et al., 2007; Steingruber et al., 2021). In addition, a number of studies established that RG waters are typically enriched in ions and trace elements when compared to close-by reference locations (i.e., not affected by RGs;

Thies et al., 2007, 2013; Ilyashuk et al., 2014; Brighenti et al., 2019b; Tolotti et al., 2020; Del Siro et al., 2023). Dissolved heavy metals/metalloids, not detectable or present at very low concentrations in these reference locations, often exceed the standards for drinking water quality in RG systems (Thies et al., 2013, 2018; Krainer et al., 2015; Colombo et al., 2018b, 2019; Ilyashuk et al., 2018; Engel et al., 2019; Liaudat et al., 2020; Sileo et al., 2020; Nickus et al., 2023; Wanner et al., 2023), with demonstrated influence on chemical conditions further downstream (Brighenti et al., 2019b; Bearzot et al., 2023; Brighenti et al., 2023; Munroe and Handwerger, 2023a). This situation raises concern about the potential for RGs to function as safe sources for drinking water supply.

A large mineral surface area in contact with water enhances chemical weathering within RGs (Williams et al., 2006; Ilyashuk et al., 2014). Solutes, including trace elements that are concentrated in spring waters, can also be sequestered in permafrost ice (Colombo et al., 2018a; Nickus et al., 2023), from which they are released with melt (Del Siro et al., 2023). Finally, the exposure of previously-frozen sulfide-bearing bedrock to oxygen and water due to permafrost thaw and ice melt can cause natural acid rock drainage (Wanner et al., 2023; O'Donnell et al., 2024).

Despite the increasing number of studies on RG hydrochemistry during the last years, the relevant scientific literature is composed of local-scale research on a limited number of springs. Therefore, an integrated understanding of the chemical properties of RG springs and of their similarities/differences across the various and often underexplored rock-glacierized settings is missing. Moreover, the hydrochemistry of relict RGs is poorly known. Geomorphological evidence suggests that

the same phenomena responsible for the solute enrichment in intact RGs are unlikely for relict ones. As a consequence, waters emerging from relict RGs are expected to be more depleted in solutes (Del Siro et al., 2023; Reato et al., 2023). Since most intact RGs are destined to become relict in the long term, understanding what controls the properties of waters from these two RG types is essential for future water management under climate change.

The aim of this work was to investigate how geographical and geological settings, together with cryospheric conditions, influence the water chemistry of intact and relict rock glaciers, and assess the potential implications for water quality. To do this, we assembled a unique dataset on 201 RG springs from mountain ranges across Europe, North and South America, and we applied a combination of machine learning, multivariate and univariate analyses, as well as geochemical modeling.

## 2. Material and methods

### 2.1. Data collection and homogenization

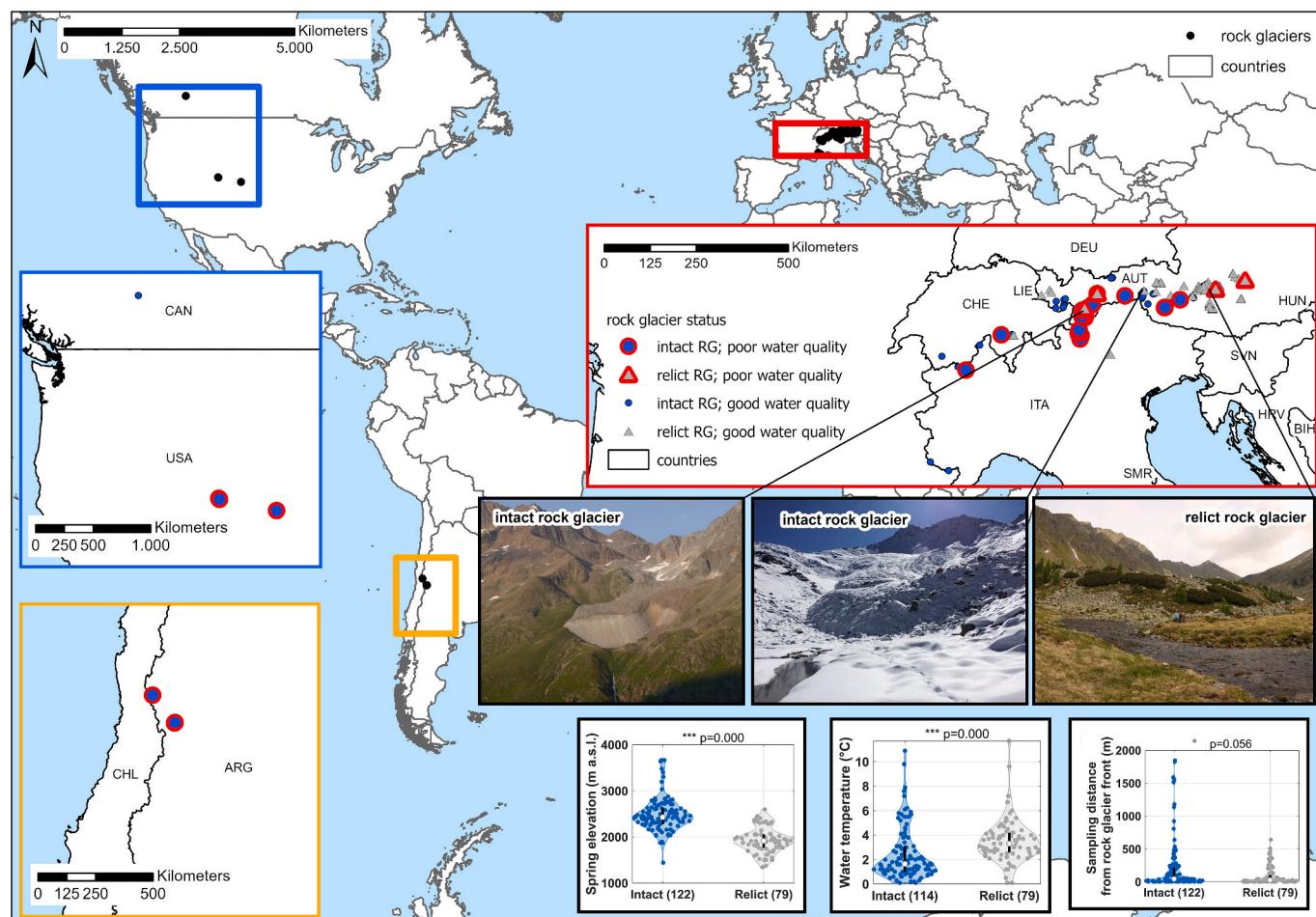
We collected the available published and unpublished data (years 2014–2021) describing water chemistry of 201 springs from RGs (intact  $n = 122$ , relict  $n = 79$ ) located in European, North and South American mountain ranges (Fig. 1, Table S1). Chemical data include pH, specific conductance (SpC at  $+25^\circ\text{C}$ ), and concentrations of major ions and trace elements (Table 1). Metadata include the cryospheric status of RGs (intact, relict), and additional geographical, geomorphological, geological, and topographic parameters (Table 1, Fig. S1, Tables S2 and

S3, Supplementary Dataset). The investigated springs were located in different geological settings represented by 29 units, mostly belonging to the Austroalpine domain of the European Alps (Supplementary Dataset). Felsic metamorphic rocks (mostly phyllites, micaschists, paragneisses, and orthogneisses) are the most represented type of lithology, when compared with mafic/ultramafic and carbonatic metamorphic, sedimentary, and volcanic rocks (Fig. S1).

We included in the dataset only one sample for each spring. Although most of the springs had only one observation (Fig. S2), for those sampled more than once, we selected the sample most representative of baseflow conditions (i.e. highest SpC value, according to Williams et al., 2006; Harrington et al., 2018; method described in Supplementary 1). Because samples were analyzed by different laboratories, limits of detection (LOD; see Supplementary Dataset) varied. To accommodate this, for each variable, we rescaled all values below the highest LOD among all samples to that LOD value. We used this updated, solute-specific LOD in the data analysis, assuming LOD/2 as the lowest concentration in the dataset. This value was in the range of  $0.25\text{--}1.5\text{ mg L}^{-1}$  for ions, and  $0.5\text{--}10\text{ }\mu\text{g L}^{-1}$  for trace elements (Table S4). All LOD values reported in the Supplementary Dataset are shown as half of the original LOD from each laboratory.

### 2.2. Water quality and random forest analysis

For each chemical parameter, we examined the guidelines provided by the World Health Organization (WHO), and the regulations of the countries where springs are located (Table S5), to define threshold



**Fig. 1.** Map of the investigated RG springs with good or poor water quality and related RG cryospheric status (intact or relict) and differences between intact and relict RG springs with respect to elevation, water temperature, and sampling distance from RG front (see also Fig. S3). Photographs present views of two intact and one relict RG with the respective spring runoff (left photo courtesy of G. Winkler, other two courtesy of T. Wagner).

**Table 1**

Chemical, geographic, cryospheric, topographic, geomorphological, and geological variables for each spring. See Table S1 for further details on the classification of the RG status and main lithology. \*Variable not considered in the analyses, because the investigated springs belong to contrasting climatic settings and geographic areas.

Category	Variables	Method
Chemical variables	pH, specific conductance (SpC at +25 °C), $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ , $\text{K}^+$ , $\text{Na}^+$ , $\text{SO}_4^{2-}$ , $\text{HCO}_3^-$ , $\text{Cl}^-$ , $\text{NO}_3^-$ , $\text{SiO}_2$ , Al, Mn, Fe, Ni, Cu, Zn, As, Cd, Pb, U	Various (see Table S1)
Geographic variables	Elevation (m a.s.l.)*, Sampling distance from the rock glacier front (m)	Remote sensing, GPS
Cryospheric status	Rock glacier status (intact, relict)	Most detailed literature (published papers/reports, maps from geological surveys of single countries) based on remote sensing, geophysical, and/or geomorphological surveys
Topographic variables	Area ( $\text{m}^2$ ) and mean slope (°) of the spring catchment	Remote sensing with Digital Elevation Models
Geomorphological variables	Glacier cover in the spring catchment (GCC, %), Rock glacier cover in the spring catchment (RGC, %)	Remote sensing with Digital Elevation Models
Geological variables	Geological unit, lithologies covering the catchment (%)	Most detailed literature (published papers/reports, maps from geological surveys)

values for drinking water quality. We used as a reference the regulation encompassing a higher number of parameters (European Union, EU), except for Uranium (not regulated in the EU) for which we used the WHO guidelines. We also considered parameters that have no direct effect on public health but are used by drinking water facilities to estimate the overall quality of water (Table S5). Based on these threshold values, we classified each spring according to its quality (Good - good water quality: all parameters below the thresholds. Poor - poor water quality: one or more parameters above the threshold).

We used random forest classification (RF; e.g., [Biau and Scornet, 2016](#)) in Scikit-learn (Python) to determine the relative importance of RG status, and the collected geographic, geomorphological, geological, and topographic parameters (predictor variables) in explaining the variation of water quality (response variable). A general description of RF as well as the hyperparameter tuning adopted in the study can be found in Supplementary 2 and Table S6. For each forest (ensemble of regression trees), we randomly split the dataset into learning ( $n = 100$ ) and testing ( $n = 101$ ) datasets. We applied a stratified splitting on the response variable and the RG status, so that each forest used a learning data set representative of both distributions. We calculated the permutation importance of each predictor variable, defined as the decrease in the minimization criterion when a single feature value is randomly shuffled ([Breiman, 2001](#)). We applied the permutation importance on the testing dataset, and repeated it 15 times with a new random shuffling for each variable. We used a random variable as predictor, and associated feature importance uncertainty, to monitor the risk of over-parameterization. Therefore, sorting of feature importance with a lower decrease in the minimization criterion than the random variable should not be considered.

Due to the relatively limited number of available observations, the learning and testing dataset random split could lead to under/over estimation of some feature importance depending on their representativity in the learning dataset, as the splitting cannot be stratified over each considered feature. To address this uncertainty, we repeated the random stratified splitting 100 times with a new random seed, and

selected the best 10 realizations, in terms of confusion matrix on the testing dataset. This allowed us to consider only those RF realizations having a good representativity of the pertinent features in the learning dataset, without any a priori assumption. Here we report the mean feature importance and associated standard deviation over the repeated shuffling and selected runs (e.g., [Guyennon et al., 2021](#)). We estimated the overall performance of the RF by using Cohen's Kappa statistic -  $k$ , obtained from the confusion matrices ([Landis and Koch, 1977](#)).

### 2.3. Drivers of solute concentrations

We used generalized linear mixed-effect models (GLMM) to investigate the relation between  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , trace element concentrations (response variables), and geological (lithology), topographic (slope, elevation) and cryospheric (glacier cover in the spring catchment, RG cover in the spring catchment, RG status) covariates (explanatory variables, [Table 1](#)), while accounting for spatial autocorrelation among springs. Before the analysis, we transformed the continuous lithological information (% catchment cover from different lithologies) into a categorical variable. This allowed us to define the covariate “main lithology”, for each spring based on the categories covering >40 % of the catchment (Supplementary 3). We discarded main lithologies (and related data) represented by less than three samples due to their poor representativity. Then, we renamed as “other lithologies” the main lithologies whose observations were all below the median value for each considered variable. This way, we could use this new category as a baseline against which to relate solute-specific concentrations, and identify the lithologies associated with higher concentrations than the average. We followed the procedure outlined by [Zuur et al. \(2009\)](#) to select the variables to use as fixed effects in the models, and to choose interactions among covariates. This was performed with Generalized Least Squares (GLS), imposing the heterogeneity of residuals for the interaction term “Rock glacier status” and “Main lithology” (VarIdent structure, *nlme* package in R; [Pinheiro, 2023](#)). In all models, the selected variables except Glacier cover in the spring catchment (GCC) were not significant and did not add further information on more simple models. We used this variable (log-transformed), and the interaction term between Rock glacier status and Main lithology as fixed effects. We set the “Geological Unit” as random effect, since springs in the same lithologies often belonged to different geological groups. We worked in a Bayesian framework, using the R-INLA package (version 23.05.30; [Rue et al., 2009](#); [www.r-inla.org](#)), and estimated the spatial correlation with the Stochastic Partial Differential Equation (SPDE) approach ([Lindgren et al., 2011](#)) following the procedure outlined by [Zuur et al. \(2017\)](#) to run and validate the models. We defined a mesh of triangles based on the distances among locations and imposing edges of triangles smaller than 0.5° (WGS84 system), resulting in 11,000–16,000 triangles in total depending on the solute (and related database available). In all analyses, the model with spatial correlation had lower Watanabe-Akaike Information Criterion (WAIC) and Deviance Information Criterion (DIC) values, and thus it was selected as the best model. The residuals of the models were inspected to ensure their normality, homoscedasticity, and the lack of any pattern with covariates in the models and those not in the models. We imposed a logarithmic transformation on response variables if homoscedasticity and normality of residuals were not met, while maintaining a Gaussian distribution. This simplified the analyses without losing any information on the importance of covariates (Supplementary 3 for further details).

### 2.4. Geochemical modeling and weathering proxies

We applied a hydrogeochemical model by using the PHREEQC computer code with the phreeqc.dat database ([Parkhurst and Appelo, 2013](#)) to investigate possible weathering processes associated with acid rock drainage ([Wanner et al., 2023](#)). We modeled the sulfide dissolution represented by the linear dissolution of pyrite ( $\text{FeS}_2$ ), considering the

thermodynamic equilibrium of relevant mineral phases that depict silicate rocks (Table S9). The model accounted for the formation of typical weathering products (i.e., secondary phases) of amorphous  $\text{Al}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{SiO}_2$ , and kaolinite, alongside the exchange of  $\text{O}_2$  and  $\text{CO}_2$ . We considered dolomite and calcite as representative phases for carbonate dissolution. The equilibrium reactions in our model incorporated average saturation indices derived from thermodynamic calculations using data from all samples. We calculated ideal sulfide dissolution trends of three different mineral assemblages: i) a silicate mineral assemblage representing paragneiss rock (quartz, K-mica, K-feldspar, and albite), ii) silicates with minor carbonate influence (calcite and dolomite), and iii) silicates with major carbonate influence (calcite and dolomite) (Supplementary 4). Finally, we used the S-ratio ( $\text{SO}_4^{2-}/(\text{SO}_4^{2-} + \text{HCO}_3^-)$ , in  $\mu\text{eq L}^{-1}$ ; Tranter et al., 1997) to distinguish between sulfate-dominated ( $\text{SO}_4^{2-}$ ; S-ratio = 1) and bicarbonate-dominated ( $\text{HCO}_3^-$ ; S-ratio = 0) RG springs, and assess the predominance of sulfuric acid vs. carbonic acid dominated weathering processes.

### 2.5. Multivariate chemical similarities among springs

We applied non-metric multidimensional scaling (NMDS) to group the sampling locations based on their similarities in trace element concentrations. We used the *vegan* package (Oksanen et al., 2022) in R (version 4.2.2), and calculated Euclidean distances on square-root transformed and 0–1 normalized data. Before the analyses, we discarded those sampling locations lacking data for at least one element ( $n = 31$ ), and Pb and Cd variables (concentrations above the maximum LOD among samples found on one and six springs only, respectively). Based on the two-dimensional space produced using the NMDS intrinsic variables (trace element concentrations), we estimated the correlations with different extrinsic variables: major ions, pH, SpC, S-ratio, and lithological composition of the spring catchment. A significance threshold of  $p = 0.05$  was set for all intrinsic and extrinsic variables.

## 3. Results

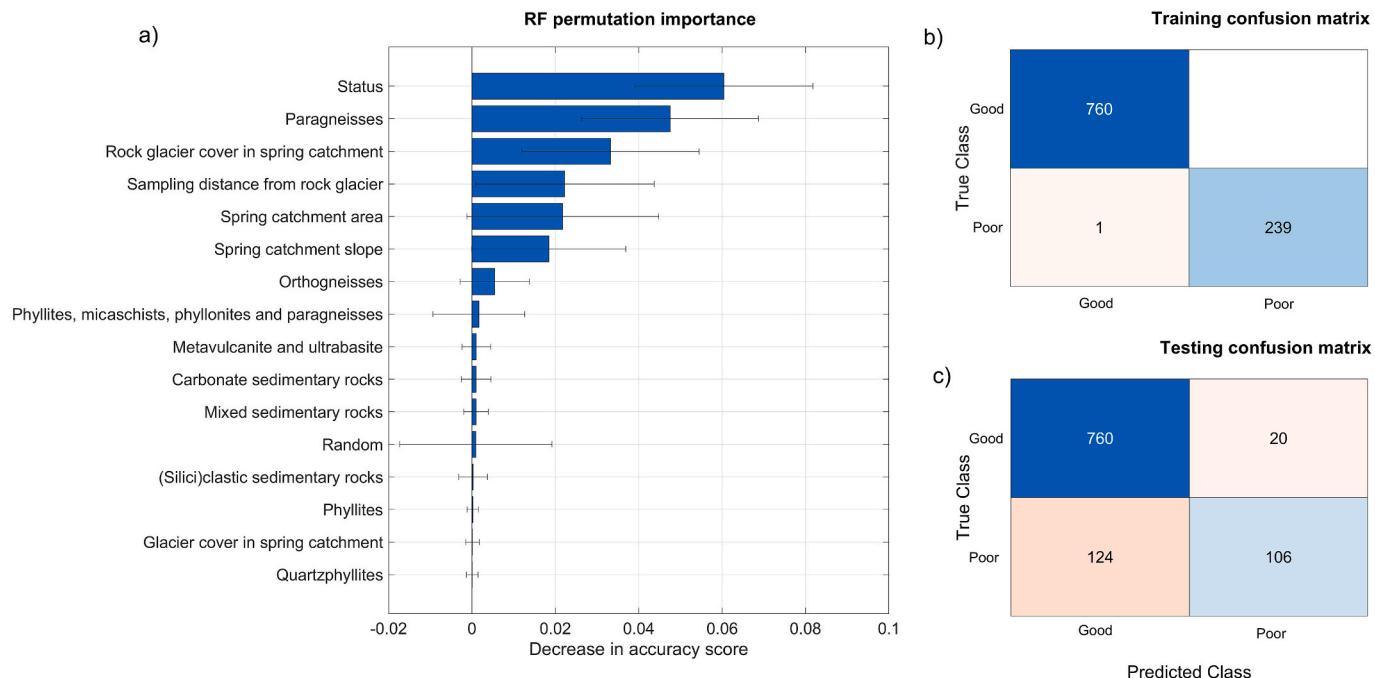
### 3.1. Poor water quality for intact rock glacier springs

More than one third (35 %,  $n = 43$ ) of intact RG springs had poor water quality with respect to drinking water quality standards, compared to only 5 % ( $n = 4$ ) of relict RG springs. For intact RGs, Ni was the parameter which most frequently exceeded the threshold ( $n = 23$ ; exceeding 1.1–46.4 times the standards), followed by Mn ( $n = 15$ ; 1.0–111.0 times), Al ( $n = 14$ ; 1.1–48.3 times), pH ( $n = 12$ ; measured values down to 4.9),  $\text{SO}_4^{2-}$  ( $n = 11$ ; 1.1–3.3 times), Fe ( $n = 6$ ; 1.8–5.2 times), U ( $n = 3$ ; 2–2.8 times), As ( $n = 2$ ; 1.1–2.9 times), and  $\text{Na}^+$  ( $n = 1$ , 1.6 times). For relict RGs, Ni (1.6–8.2 times) and As (1.5–2.0 times) exceeded their thresholds for two springs, followed by pH (5.5), Mn (8.1 times), and Al (7.1 times) for one spring. Approximately half ( $n = 21$ ) of the poor-water quality springs from intact RGs, and only one relict RG spring, had two or more parameters exceeding their thresholds.

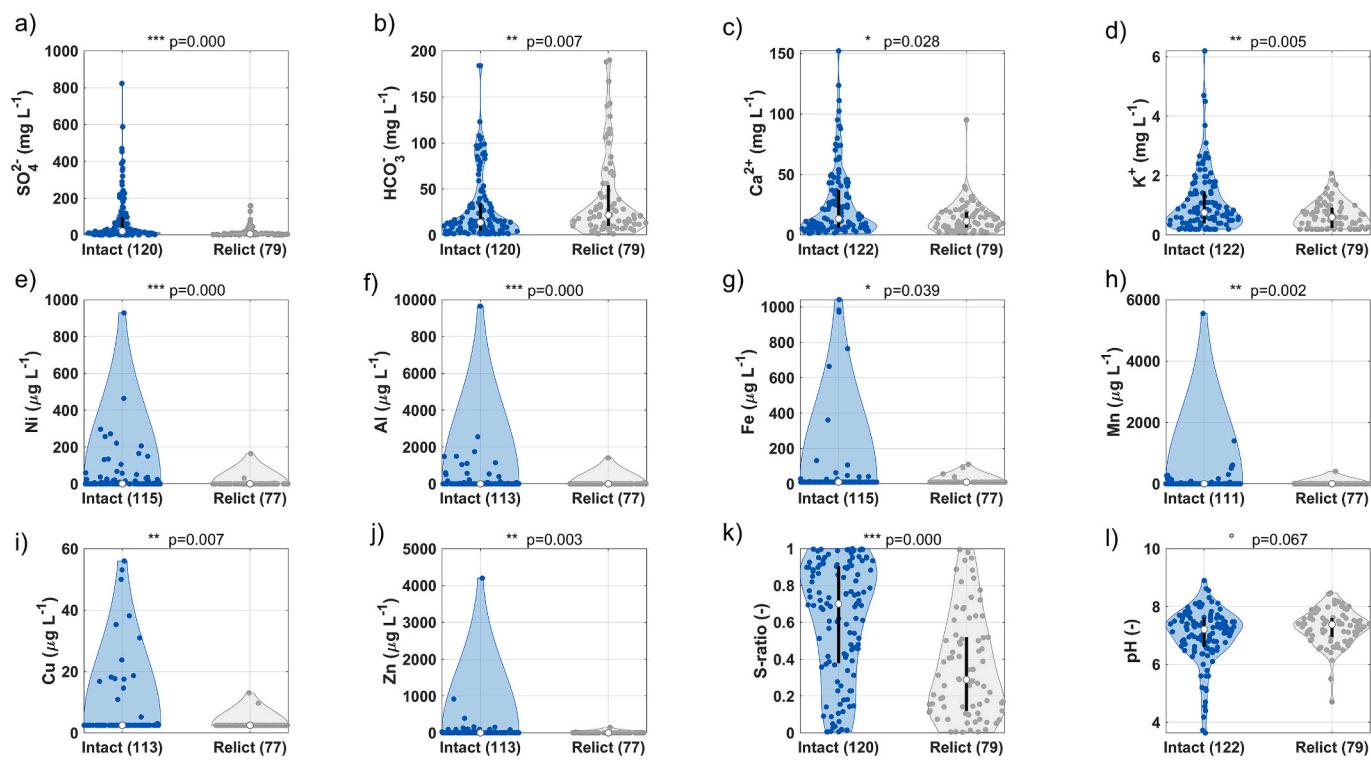
According to RF analysis, RG status was the most important predictor variable of spring water quality (Fig. 2a), followed by the “Paragneisses” lithological class, and the RG cover in spring catchment. Sampling distance from RG, spring catchment area and slope, and five lithology classes were more important than the random variable but with relatively large uncertainties. The confusion matrices (Fig. 2b,c) show that the model had an almost perfect performance in learning ( $k = 0.99$ ) and a moderate performance in testing ( $k = 0.52$ ), allowing us to reject the null hypothesis that the observed agreement was accidental ( $p < 0.001$ ).

### 3.2. Cryospheric status and lithology drive the export of solutes from rock glaciers

Concentrations of dissolved  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ , Ni, Al, Fe, Mn, Cu, Zn, and S-ratio were significantly higher ( $p < 0.05$ , Kruskal-Wallis test) in intact than in relict RG springs, and those of  $\text{HCO}_3^-$  were significantly higher in relict with respect to intact RG springs (Fig. 3). Differences between the two spring types were not significant for the other



**Fig. 2.** Results of the RF analysis. a) Predictor variable permutation importance in classifying water quality of RG springs. The importance of each predictor variable is indicated by the associated decrease in accuracy score. Error bars report the uncertainty of both permutation importance and random stratified splitting. A random predictor was inserted to further assess the relative importance uncertainty (see Methods). b) and c) Confusion matrices obtained over the ten selected runs for training and testing, respectively. We considered only lithologies with at least 6 observations and 2 springs for each RG status. Good - good water quality; Poor - poor water quality relative to drinking water standards.

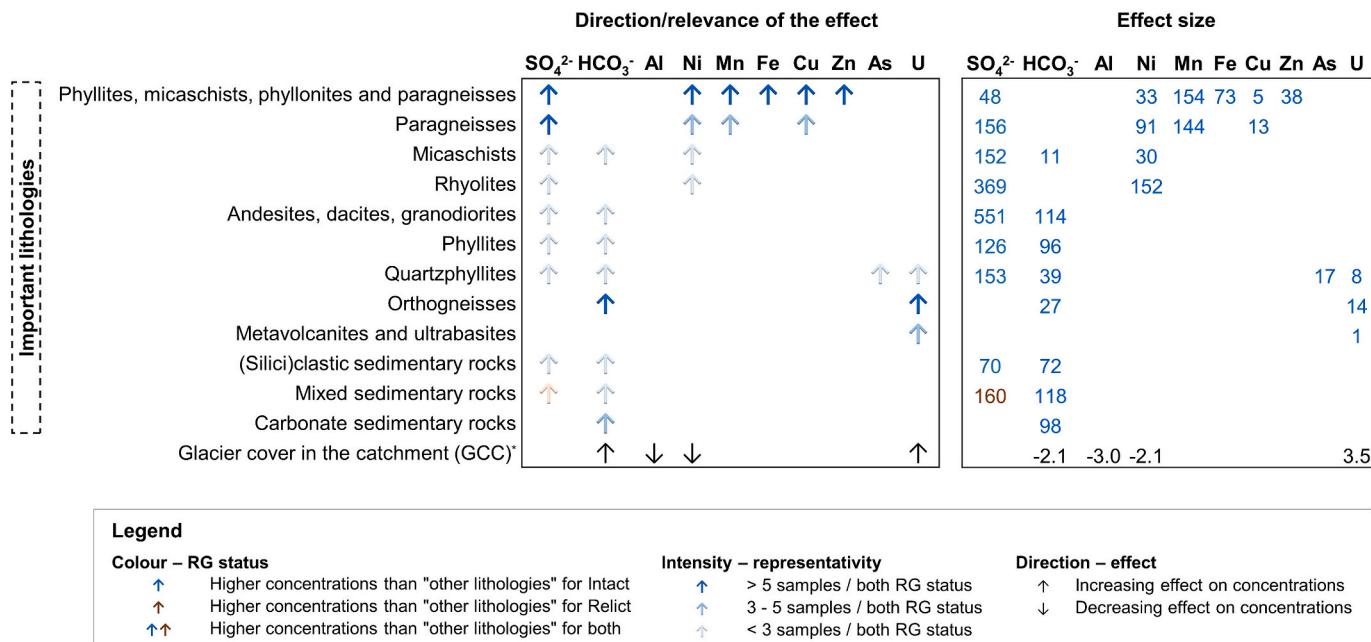


**Fig. 3.** Violin plots of chemical variables. Significance levels result from the non-parametric Kruskall-Wallis test (\*\*\* indicates significance at  $p < 0.001$ ; \*\*  $p < 0.01$ ; \*  $p < 0.05$ ; °  $p < 0.1$ ).

investigated parameters (Fig. S4).

According to GLMM, the interaction term between the covariates “cryospheric status” and “main lithology” was the most important explanatory variable for concentrations of  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ , Ni, Fe,

Mn, Cu, Zn, As, and U (Fig. 4, Supplementary 3). Accordingly, the status “Intact” had an increasing effect on solute concentrations only when interaction with particular main lithologies was considered. These lithologies include some felsic metamorphic and volcanic rocks for  $\text{SO}_4^{2-}$ ,



**Fig. 4.** Summary of GLMM analyses. For each solute (columns), the list of variables identified as important by Bayesian models (rows) is provided. Cells are filled based on the representativity (number of samples available for each RG status and main lithology) and direction (increase/decrease) of the effect. The left box represents the direction of the effect only (arrows, intensity of colors depending on the representativity of the effect). The right box represents the effect size, with numbers indicating the difference between the mean concentrations for the interaction term and the reference concentrations of the “other lithologies” category. \*The effect size for glacier cover was calculated assuming a relatively large glacier cover in the spring catchment (GCC = 50 %) to highlight the influence from glaciers, and using the mean value of the explanatory variable (GCC) resulting from the Bayesian outcomes.

Ni, Mn, Fe, Cu, Zn, As, U, and some sedimentary rocks for  $\text{HCO}_3^-$  (Fig. 4). However, these outcomes were supported by a sample size of at least three springs per cryospheric status only for five “Main lithology” classes. All other covariates that we included in GLMM analyses (Table 1) were not important explanatory variables for solute concentrations, except the glacier cover in spring catchment, which had a very weak effect (Supplementary 3, Tables S7 and S8) of enhancing concentrations of  $\text{HCO}_3^-$  and U, and reducing those of Al and Ni.

### 3.3. Higher sulfide weathering intensity in intact rock glaciers

The proposed end-members of weathering reactions (solely silicate weathering and weathering dominated by carbonate dissolution) enclosed almost all water samples. Most of the intact RG springs followed the trend of silicate rock dissolution with or without a minor carbonate influence, and showed higher S-ratio values ( $>0.5$ , Fig. 5a). Conversely, most of the relict RG springs followed the gradient of weak to strong carbonate dissolution, with lower S-ratios ( $<0.5$ ). We grouped the poor-water-quality springs into Ni-group (Ni, Al, Mn, Fe, and Zn) and U/As-Group (U and As), based on the elements exceeding the selected threshold concentrations. The Ni-Group was strongly associated with  $\text{SO}_4^{2-}$  dominated waters (S-ratio close to 1), whereas the U/As-Group depended more on the influence of carbonate dissolution (Fig. 5b).

### 3.4. Chemical similarities among springs are related to lithology and weathering intensity

According to the NMDS analysis based on trace element concentrations, all considered elements were significant intrinsic variables ( $p < 0.05$ ) driving the spread of samples according to the first two dimensions (Fig. 6). In the dual plot, most relict RG springs were close to the axis origin, because of similarly low trace element concentrations. In contrast, several intact RG springs spread far from the axis origin, with their location in the dual space driven by contrasting concentrations of different trace elements. A gradient of pH conditions follows the spread of points according to chemical similarities, with springs having higher

concentrations of Ni, Al, Zn, Cu, and Al at lower pH values (Fig. 6a).

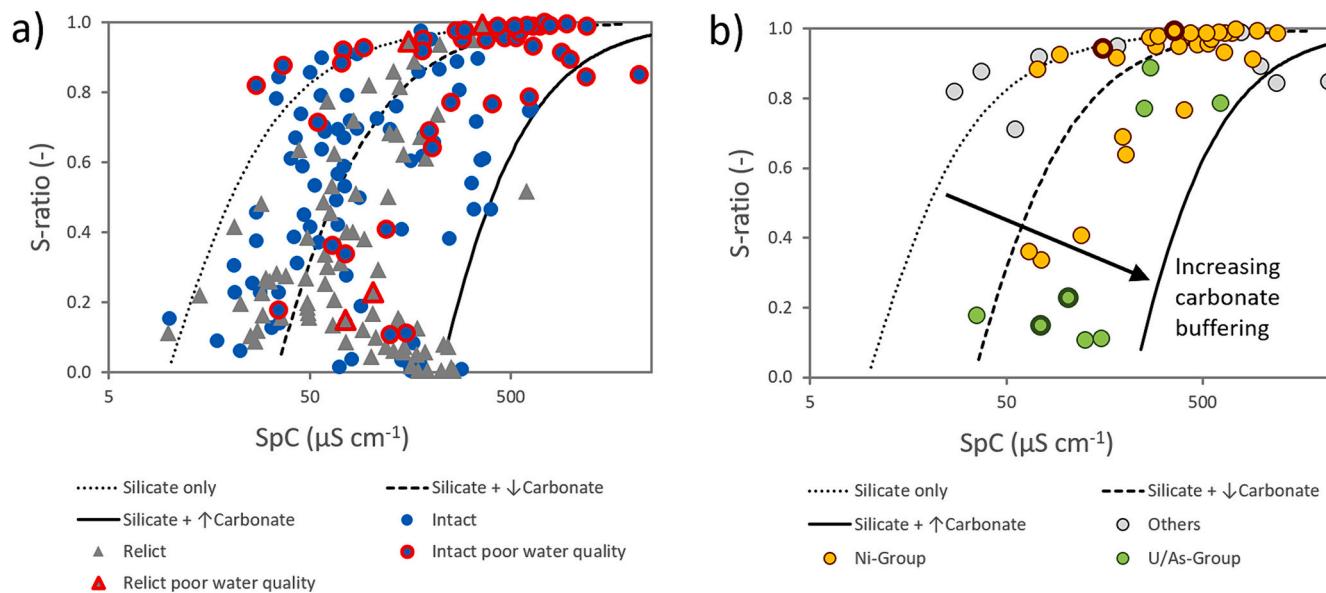
The concentrations of ions (significant extrinsic variables; Fig. 6b) plot in agreement with the dual space defined by trace element concentrations, and suggest that groups of springs with contrasting trace element concentrations also have different concentrations of ions. A gradient of increasing S-ratio clearly defined the separation of spring samples dominated by  $\text{HCO}_3^-$  from others increasingly dominated by  $\text{SO}_4^{2-}$  and other ions. This pattern is reflected by an overall good agreement of SpC with  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$  in the dual space. Furthermore, the extent (%) of some felsic metamorphic rocks in the spring catchment was a significant extrinsic variable in the NMDS (Fig. 6c). Abundance of paragneisses, along with lower pH and higher S-ratio, significantly agreed with Ni, Mn, Al, Cu, and Zn. Orthogneisses and  $\text{HCO}_3^-$  were significantly correlated with U and As. Phyllites, micaschists, phyllonites and paragneisses significantly correlated in agreement with Fe (Fig. 6).

## 4. Discussion

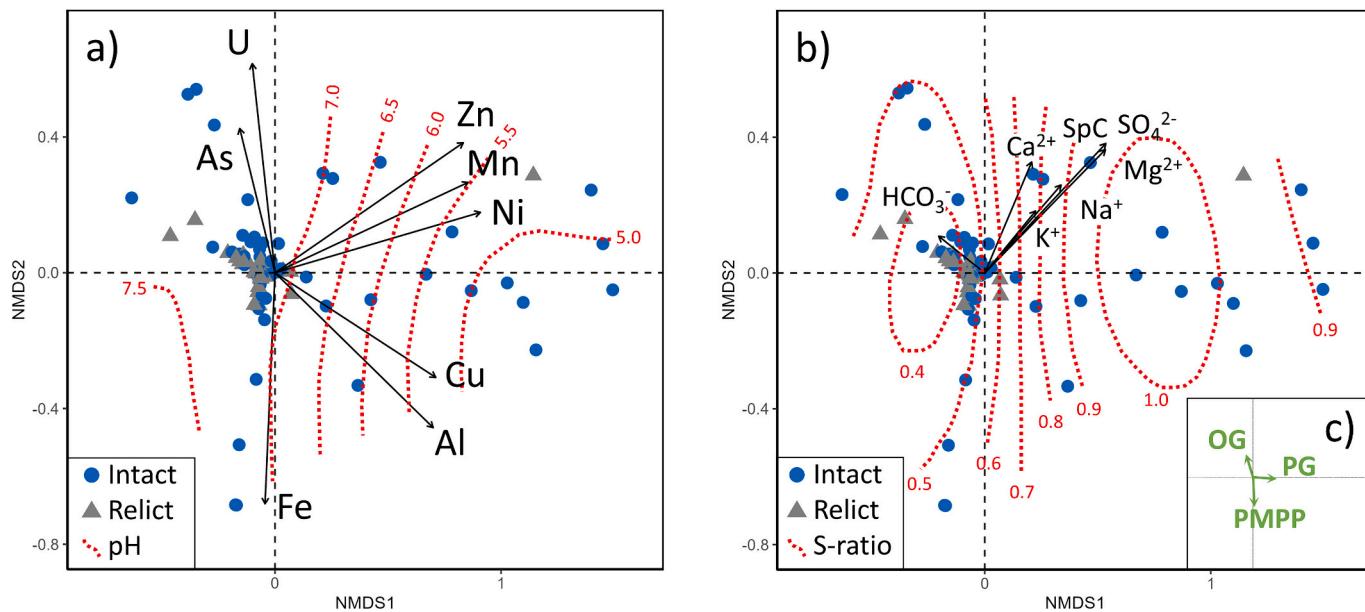
RGs are key hydrological resources in mountain areas (Jones et al., 2018, 2019). Our results demonstrate that the chemistry of water sourced from RGs is strongly influenced by RG geology and ice content. These variables drive the concentrations of different solutes and thus the overall quality of spring waters, under a strong influence from contrasting geochemical processes.

### 4.1. Enhanced sulfide weathering in intact rock glaciers and relation to water quality

In our analyses, presence or absence of ice within RGs was the main driver of solute concentrations in RG springs. Several works highlighted particularly high concentrations of solutes from intact RG waters, especially when compared with those not influenced by these ice-rich landforms (e.g., Brighenti et al., 2019a; Brighenti et al., 2023; Del Siro et al., 2023). When compared with intact RG springs, relict ones showed generally lower concentrations of major ions and trace elements, less



**Fig. 5.** Plot of S-ratio versus SpC of all samples, differentiated by a) RG state “intact” and “relict” and b) samples with poor water quality, differentiated by source of contamination (Ni-Group and U/As-Group) or other factors. Circles and triangles with bold red outline in a) show water samples with poor water quality. The bold outline in b) shows the four relict RG springs with poor water quality. Two samples (intact RGs in North America) were excluded due to unavailable  $\text{SO}_4^{2-}$  concentrations. The black lines indicate sulfide dissolution including silicate weathering reactions, with either no (dotted line), minor (dashed line) or major (continuous line) carbonate influence, calculated with PHREEQC. The outliers are from samples with either too low pH ( $<6.5$ ) and with very low SpC ( $<50 \mu\text{S cm}^{-1}$ ) or from samples with very high SpC values ( $>1000 \mu\text{S cm}^{-1}$ ) which were influenced by a NaCl component, which was not accounted for in the model (i.e., two springs in South America).



**Fig. 6.** Results from NMDS analyses. a) Similarities in trace element concentrations of intact and relict RG springs according to the first two dimensions (stress = 0.05,  $R^2 = 0.997$ ,  $n = 175$ ). Three outliers (STP\_SPR1, STP\_SPR2, 7RG2621\_BLGL70063) representing influential observations (Ni, Zn, Mn, and/or Al) were removed. Contour lines represent a pH gradient based on GAM fitting (*ordisurf* R function). b) Same NMDS plot, including the significant ( $p < 0.05$ ) extrinsic chemical variables, and a gradient of S-ratio. c) Inlet box: significant lithologies (cover in the catchment) plotted in the NMDS space as extrinsic variables. OG = Orthogneisses; PG = Paragneisses; PMPP = Paragneisses, micaschists, phyllonites and paragneisses.

intense geochemical processes, and water chemistry better aligned with drinking water quality standards. The poor water quality at a few (exceptional) relict RG springs may be related to the geological background and complex hydrological processes. For example, faults and deep seated gravitational slope deformations can have a strong control on the water chemistry of mountain springs (Binet et al., 2009; Brighenti et al., 2023), although we do not have this information for the catchments that we investigated. Also, the occurrence of permafrost and/or intact RGs in the catchment of relict landforms can influence the water chemistry of relict RG springs (Wagner et al., 2019). Furthermore, our distinction between intact and relict RGs suffers from some uncertainties. For instance, the ice content in RGs is difficult to estimate and validate (Colucci et al., 2019), and for most landforms considered in our study this categorical classification was based on available inventories (Supplementary 1). Furthermore, the cryospheric status of RGs encompasses a continuum where ice progressively and slowly melts away, with ice remnants persisting for centuries to millennia even in unfavorable climatic conditions (Haeblerli et al., 2017). Our study suggests that geochemical processes responsible for the solute export in RG waters follow this continuum, being more intense in ice-rich RGs and fading out in the final stages of permafrost degradation and ice loss in these landforms.

The oxidation of sulfides (if present within the host rock in minerals such as pyrite) produces sulfuric acid, lowering the pH. This, in turn, results in elevated concentration of major and trace elements leached from sulfides and the host rock (Wanner et al., 2023). This process is most frequently the cause of lower water quality in intact RG springs, as emphasized by the geochemical model results. The sulfide oxidation is likely enhanced by (i) rock glacier motion, which generates fresh fine-grained material with reactive mineral surfaces through grinding and crushing, and (ii) permafrost thawing and related ice melting, which gradually releases solutes from mineral surfaces previously stored in the ice under non-oxidizing conditions (Wanner et al., 2023). The combination of these processes supplies sulfides that can be oxidized, enhancing rock weathering through production of sulfuric acid. Enhanced sulfide oxidation, in intact RGs and in general in areas of thawing permafrost, would also promote acid rock drainage, which is

associated with orange-colored iron hydroxides (Ilyashuk et al., 2014; O'Donnell et al., 2024) or white-colored Al-hydroxysulfate precipitate coatings (Thies et al., 2018; Wanner et al., 2023) on lake bottoms and streambeds (Fig. S5). Conversely, in relict RGs, immobile landforms where ice no longer exists, sulfide oxidation is limited by the reduced abundance of freshly-ground minerals, and by prior oxidation and elution of sulfides (where present) as the RG lost ice. Therefore, the dominant chemical weathering process in RGs shifts from sulfuric acid in intact features, to the weaker carbonic acid in relict RGs in comparable lithological settings.

Our findings further emphasize the importance of geology in shaping the quality of RG waters. For example, RF analysis highlighted the cover of paragneisses as second in importance to explain water quality, immediately following the cryospheric status. Indeed, although 35 % of intact RG springs had a poor water quality, this percentage was 91 % where paragneisses were the main lithology. According to GLMM analyses, only the interaction between RG status and main lithology (i.e., not the two variables alone) could successfully explain the concentrations of single solutes. In addition, intact RG springs had higher concentrations than reference values depending on the solute that was considered, with lithologies belonging to felsic metamorphic and volcanic rocks driving the concentrations of  $\text{SO}_4^{2-}$ , and some lithologies (e.g., paragneisses) even controlling trace elements such as Ni, Mn, Fe, Cu, and Zn. This tendency was also highlighted by the NMDS and the geochemical model.

High weathering intensities are enhanced by high  $\text{SO}_4^{2-}$  concentrations and S-ratio, which decrease pH and promote dissolution of the rock material under conditions of low (or negligible) carbonate buffering. This process enhances concentrations of trace elements belonging to the Ni-Group. According to our analyses, other rock types were more related to  $\text{HCO}_3^-$  concentrations, and some with U (e.g., orthogneisses) and As (e.g., quartzphyllites). Under pure silicate weathering, As and U can be released by sulfide oxidation, but they are likely directly adsorbed on newly formed Fe-phases and other secondary minerals (Wanner et al., 2018) resulting from silicate weathering itself. Since the mobility of these elements is generally enhanced by neutral/slightly alkaline conditions and high  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations (Skierszkan et al.,

2020), As/U may be easily remobilized when the main geochemical processes are a combination of silicate and carbonate weathering.

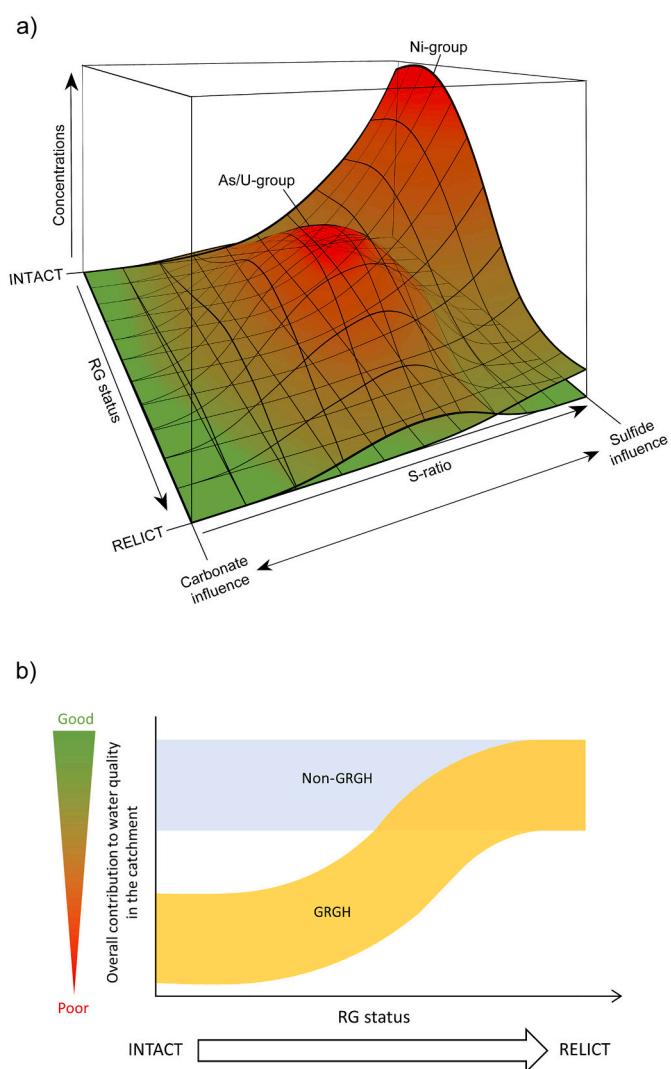
Although our results converge on the fact that RG status and bedrock weathering are the main drivers of solute export from RGs, RF modeling revealed that the water quality was also influenced by RG cover in the catchment and sampling distance from these landforms. The influence of RGs on water quality declines with increasing hydrological contributions from non-RG water sources in the catchment, possibly due to solute dilution and/or metal precipitation/adsorption (Brighenti et al., 2023; Wanner et al., 2023). Moreover, size and slope of the spring catchments exerted some influence on water quality according to RF analyses. While it is not clear how the spring catchment area influenced the water quality, it is possible that steeper slopes of the spring catchment correspond to higher erosion rates, that in turn could enhance mineral weathering, especially sulfide oxidation (Calmels et al., 2007; Torres et al., 2017). However, the same variables were not important for GLMM, likely because of the limited sample size and because of the greater importance of geology in driving absolute concentrations of solutes in our dataset.

#### 4.2. Environmental concerns for freshwater quality in mountain areas

With ongoing glacier and snow loss, RGs are becoming key hydrological resources in some mountain areas due to their solid and liquid water storage (Wagner et al., 2021; Pandey et al., 2022). However, the suitability of this water should not be taken for granted as previously assumed, at least for mountain catchments where geological setting and the abundance of intact RGs make these areas “geochemical rock glacier hotspots - GRGHs”. In GRGHs, freshwater ecosystems are affected by heavy metal contamination from RGs, with effects potentially propagating downstream along entire river networks (e.g., Brighenti et al., 2019b). In mountain areas affected by RG contamination, the related effects on freshwater ecosystems may be exacerbated by local-scale human pressures (e.g., water diversions, mining, agriculture) with stronger ecological consequences. Finally, since the geochemical processes involved in solute export from RGs are related to the ice abundance in these landforms, the slow pace at which they become (pseudo) relict and the progressive establishment of new RGs in deglaciating areas pose additional challenges for future water management (Fig. 7).

#### 4.3. Addressing future research on rock glacier chemistry

Given the strategic relevance of RGs as water resources, and the potential ecological implications of heavy metal concentrations in water, further research is needed to estimate the extent of possible water contamination from RGs, and identify GRGHs to inform water governance strategies. This need is particularly urgent in large, understudied mountain areas such as the Himalayas, that provide water for billions of people (Immerzeel et al., 2020), and in arid and semi-arid mountain areas, where alternative water sources are already scarce (Jones et al., 2019). We argue that careful temporal monitoring of RG spring water quality is necessary, in conjunction with consideration of eventual effects on downstream areas, to adequately plan water governance strategies in mountain areas for the forthcoming years. The export of trace elements in RG waters results from a complex interplay between the presence of these elements in the rock, and the occurrence of distinct weathering mechanisms. Understanding what types of lithologies promote the export of different trace elements in RG waters, and under which circumstances, remains little explored. Thus, efforts dedicated to a more comprehensive understanding of large-scale drivers for solute enrichment in RG waters should also be paralleled by standardized collection of metadata considering a wide range of geological and lithological settings. Further work on rock glacier hydrochemistry would greatly benefit from climatic and hydrological numerical models, allowing prediction of hydrochemical and runoff shifts in the context of a changing climate. Also, it is still unclear if/how microbial communities



**Fig. 7.** Conceptual model of RGs as weathering reactors in a changing climate. a) Ice presence and movement in RGs are predisposing factors for solute export from RGs. Depending on lithology, the dominance of sulfides and carbonates enhances or hinders (respectively) sulfide oxidation, which boosts the concentrations of dissolved trace elements such as Ni, Mn, Al, Fe, and Zn (Ni-group), when these are present in the rock. As the RGs progressively become relict (no perennial ice and no movement), weathering processes are less intense and concentrations of sulfates and trace elements decline. Elements such as U and As (U/As-group), if present in the bedrock and rock fragments, can be weathered where carbonate dissolution is coupled with sulfide oxidation, and as such can be mobilized in an intermediate stage of RG status. b) Since the geochemical processes involved in trace elements enrichment are a direct/indirect consequence of RG status and predisposing lithological settings, water quality of RG springs is generally poor in GRGH (geochemical rock glacier hotspots), but could progressively improve as RGs become relict (less internal ice). In non-GRGH, the overall quality of RG springs is generally good over the entire cryospheric continuum.

and biological processes influence water quality at rock glacier springs, and the role of biogeochemical processes in hydrochemical climatic feedback is still overlooked.

Moreover, our work did not consider the hydrochemical seasonality of RG springs, despite evidence of seasonal periods of rising/peaking solute concentrations (Brighenti et al., 2021; Munroe and Handwerger, 2023b). Under warmer and prolonged summers the overall solute export from RGs may increase. In this framework, the establishment of long-term monitoring programs for RG water quality may provide greater statistical power to detect interannual variations and potential changes

on long time scales. Globally, these long-term monitoring programs should be based on the collection of high-quality and intercomparable chemical data. We suggest that these efforts should be made under the framework of a global network such as the International Permafrost Association.

Furthermore, some metals (e.g., Ti, Rb, Hg, Sr), metalloids (e.g., Sb, B), and rare earth elements (e.g., Li, Y), that we did not investigate in our study, might also influence water quality. Some of them might also be potentially related to distinct geochemical processes.

Finally, although RGs are the most visible geomorphic expression of ice-rich permafrost, other landforms (e.g., talus and moraines), that are also abundant in mountain landscapes, could behave similarly as water sources (Hayashi, 2020) and may host comparable geochemical processes. Thus, water contamination by toxic elements exported from a variety of cold-climate landforms in mountain regions may be more pervasive than can be assumed from the present study.

## 5. Conclusions

Our study investigated the hydrochemistry and water quality of intact and relict RG springs at an unprecedented scale, spanning different mountain ranges around the globe. We demonstrated that solutes are generally more concentrated in intact RG springs than in relict ones, with lithology serving as a predisposing factor for the preferential weathering of different major ions and trace elements. Sulfide oxidation is the main driver of bedrock weathering, and is more intense in intact RGs where the water quality is lower relative to drinking water standards.

RGs are emerging as key mountain water resources as well as potential threats to water quality. Our study offers guidelines for identifying geochemical RG hotspots, where ecological integrity and the use of water might be potentially affected by the intense solute export from RGs under predisposing lithological conditions.

Further research and monitoring are needed to increase knowledge about water quality in areas influenced by RGs under different lithological settings, and to broaden the perspective to under-investigated mountain areas.

## CRediT authorship contribution statement

**Stefano Brighenti:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Nicola Colombo:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Thomas Wagner:** Writing – review & editing, Visualization, Validation, Investigation, Data curation, Conceptualization. **Michael Pettauer:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis. **Nicolas Guyennon:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis. **Karl Krainer:** Writing – review & editing, Validation, Data curation. **Monica Tolotti:** Writing – review & editing, Data curation. **Michela Rogora:** Writing – review & editing, Data curation. **Luca Paro:** Writing – review & editing, Data curation. **Sandra M. Steingruber:** Writing – review & editing, Data curation. **Chantal Del Siro:** Writing – review & editing, Data curation. **Cristian Scapozza:** Writing – review & editing, Data curation. **Noelia R. Sileo:** Writing – review & editing, Data curation. **Cristian D. Villarroel:** Writing – review & editing, Data curation. **Masaki Hayashi:** Writing – review & editing, Data curation. **Jeffrey Munroe:** Writing – review & editing, Data curation. **Dario Trombotto Liaudat:** Writing – review & editing, Data curation. **Leonardo Cerasino:** Writing – review & editing, Data curation. **Werner Tirler:** Writing – review & editing, Data curation. **Francesco Comiti:** Writing – review & editing, Data curation. **Michele Freppaz:** Writing – review & editing, Data curation. **Franco Salerno:** Writing – review & editing, Data

curation. **M. Iggy Litaor:** Writing – review & editing, Data curation. **Edoardo Cremonese:** Writing – review & editing, Data curation. **Umberto Morra di Celli:** Writing – review & editing, Data curation. **Gerfried Winkler:** Writing – review & editing, Visualization, Validation, Investigation, Data curation, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2024.175706>.

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