Uptake of As by nanocrystalline Al-hydroxysulfates naturally forming along a mountainous stream in the Engadin area

Christoph Wanner*, Rosemarie Pöthig**, Sergio Carrero***, Alejandro Fernandez-Martinez****, Christian Jäger***** & Gerhard Furrer******

*Rock-Water Interaction Group, Institute of Geological Sciences, University of Bern, Baltzerstrasse 3, CH-3012 Bern, Switzerland (wanner@geo.unibe.ch)
**Leibniz-Institute of Freshwater Ecology and Inland Fisheries, Berlin, Germany
***Department of Earth and Planetary Science, University of California Berkeley, USA
****Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, IRD, IFSTTAR, ISTerre, Grenoble, France
*****BAM-Federal Institute for Materials Research and Testing, Division I.3, Working Group NMR Spectroscopy, D-12489 Berlin, Germany
******Institute of Biogeochemistry and Pollutant Dynamics (IBP), Department of Environmental Systems Science, ETH Zurich, CH-8092 Zurich, Switzerland

Nanocrystalline basaluminite [$Al_4OH_{10}(SO_4)\cdot(H_2O)_{3\text{-}5}$] and aggregation of the ε-Keggin polyoxocation [$Al_{12}(AlO_4)(OH)_{24}(H_2O)_{12}]^{7+}$, referred to as Al_{13}, have both been described to form in acid mine drainage environments. Although the chemical composition is quite similar, their crystalline varieties significantly differ, demonstrating that various types of precipitates can form under very similar conditions and that their respective formation is not fully understood yet. Here we report the occurrence of large amounts of nanocrystalline Al-hydroxysulfates that form naturally in a small alpine catchment in the Engadin area where an acidic mountainous stream (pH~4) is neutralized successively after mixing with several neutral tributaries (Fig. 1). Synchrotron-based high-energy X-ray diffraction (HEXD) and subsequent pair distribution function (PDF) analyses demonstrate that these precipitates are structurally the same as basaluminite samples obtained from acid mine drainage sites (Wanner et al., 2018). In contrast, only minor amounts of tetrahedrally coordinated Al, as present in Al_{13}, were identified by nuclear magnetic resonance (NMR) spectroscopy. We hypothesize that in our field system, high sulfate and fluoride concentrations on the order of 1-2 and 100 mg/L, respectively, as well as low water temperatures (<8°C) favor the formation of basaluminite instead of Al_{13}-bearing sulfate precipitates. Interestingly, the basaluminite precipitates are characterized by elevated As concentrations up to 600 µg/g, whereas other heavy metals are at background concentrations only. Given the low As concentrations in the stream from which precipitation occurs (<0.03 mg/L), high As concentrations confirm that basaluminite serves as a highly efficient As sink. We conclude that the high affinity for As results from the high sorption capacity of basaluminite and hence from the uptake of arsenate anions under the prevailing oxidizing conditions.

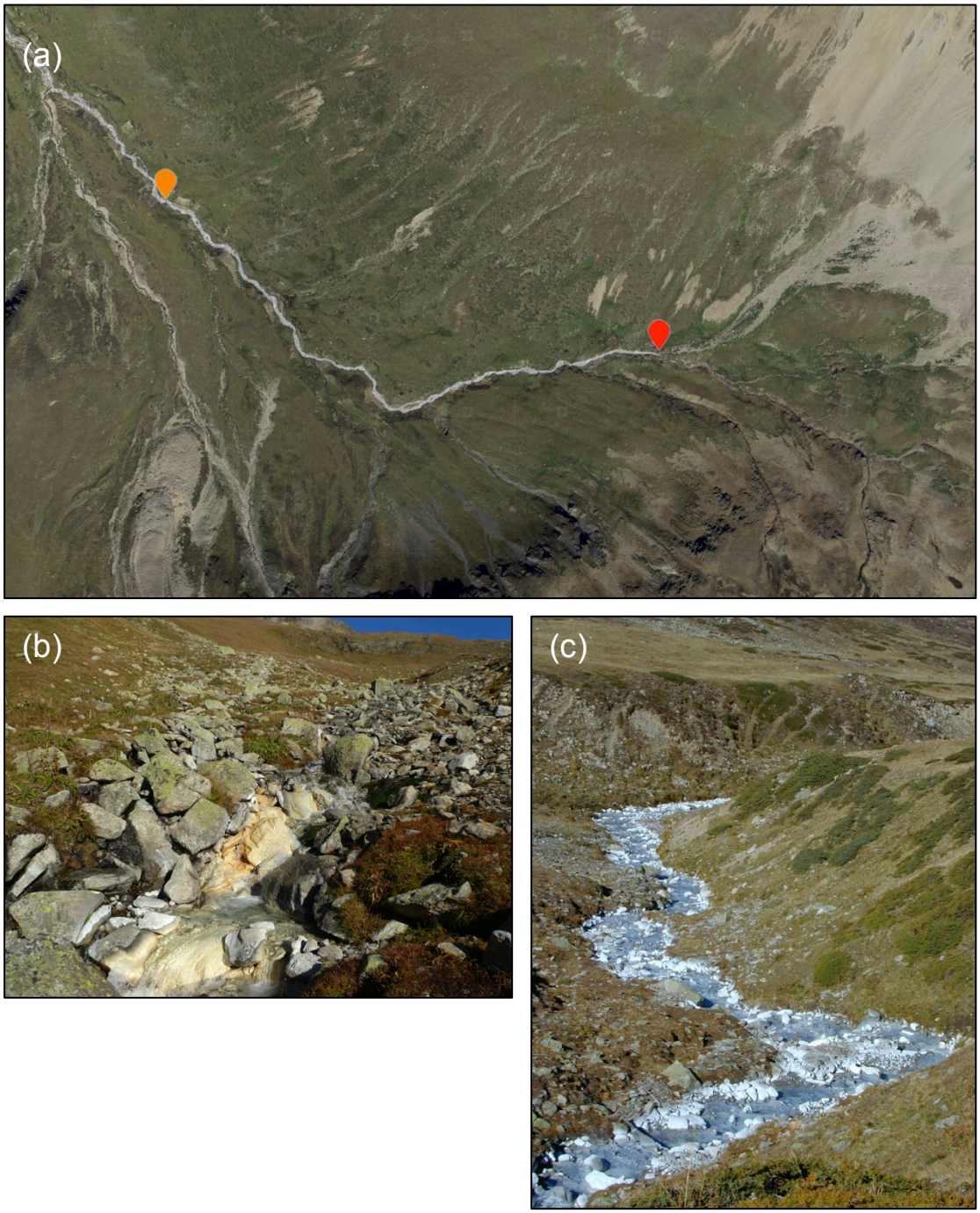

Figure 1. Photographs of basaluminite precipitation occurring along “Ova Lavirun”, a mountainous stream in the Engadin area. (a): Aerial photograph of the Ova Lavirun watershed, clearly illustrating the white bedload coating originating from basaluminite precipitation. (b) Photograph of the first basaluminite occurrence near the red marker shown in (a). (c) Photograph of the widespread basaluminite occurrence along a section near the yellow marker shown in (a).

REFERENCE

Wanner, C., Pöthig, R., Carrero, S., Fernandez-Martinez, A., Jäger, C. & Furrer, G. 2018: Natural occurrence of nanocrystalline Al-hydroxysulfates: Insights on formation, Al solubility control and As retention, Geochimica et Cosmochimica Acta, 238, 252-269.