# Solubility of Basaluminite from 0º to 25º C

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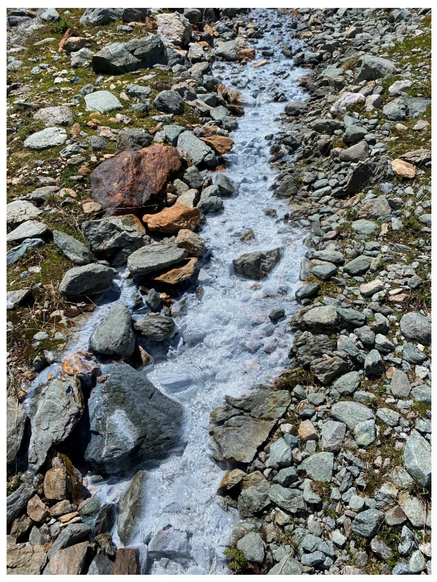
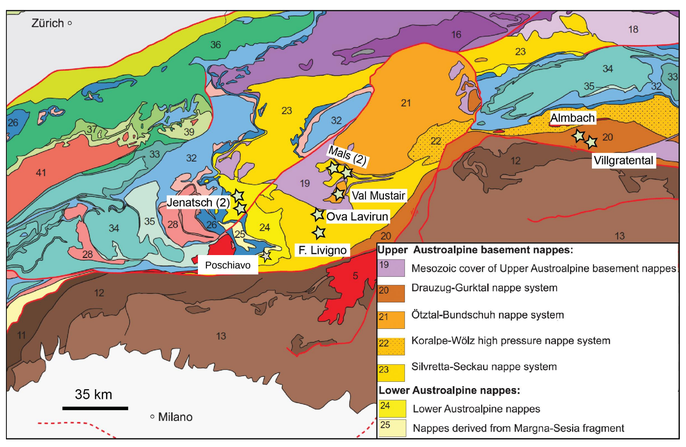
## Background

- The name **basaluminite ($Al_4(SO_4)(OH)_{10} \cdot 3\text{-}5H_2O$)** refers to nanocrystalline hydroxosulfates that form as white riverbed coating upon neutralization of acidic, Al-rich alpine streams in the Eastern Alps at temperatures from 0 to 8 ºC [1].

- Acidic conditions are inherited from the oxidation of pyrite occurring naturally in permafrost bodies at the origin of the streams. Basaluminite constitutes an excellent sink for toxic As and Al [2].

- Solubility data for basaluminite are only available at 25 ºC. To better assess the mobility of Al and As during the ongoing permafrost retreat, we have determined the solubility of basaluminite at the field temperatures (0-25 ºC).

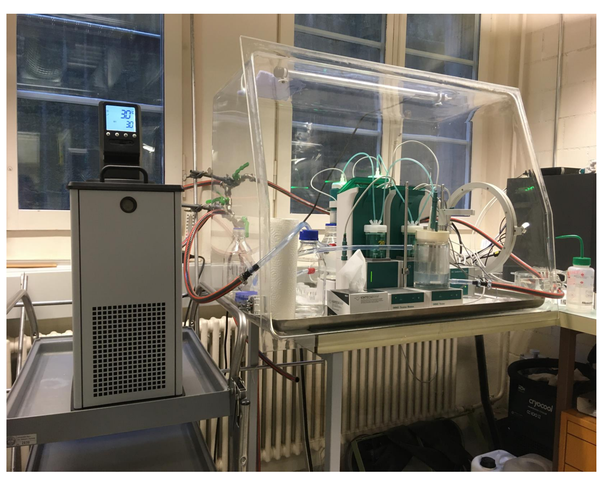





**Left: basaluminite precipitates in the river bed of a high-alpine stream in Val Poschiavo. Right: geological map illustrating the occurrences of basaluminite precipitates in the Eastern Alps.**

## Methodology

- Basaluminite was synthesized at 2, 5, 10, 15, 20 and 25 ºC by adding 214 mL of 0.015 M $Ca(OH)_2$ to 30 ml of 0.05 M $Al_2(SO_4)_3$ solution[2].



**Omnis titration system connected to a circulating bath (temperature control)**

- In situ precipitate, streamwater and rock samples from the Poschiavo area were collected for chemical analysis.

- Final experimental solutions were analysed for Al, $SO_4$ and Ca using ICP-OES

- The chemical solution compositions were processed using PHREEQC[3] to obtain the ion activity product (IAP):

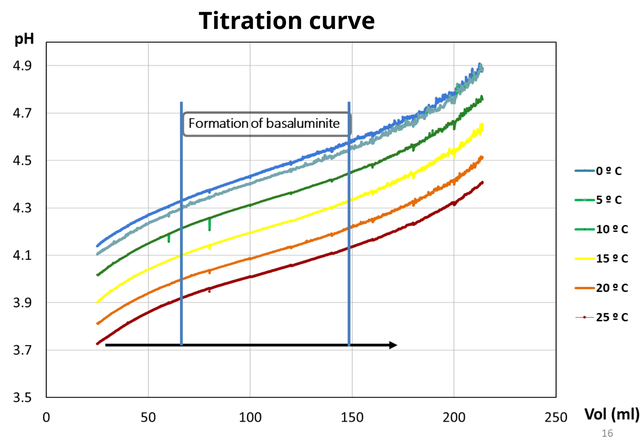
$$Log(IAP) = \frac{a(Al^{3+})^4 \cdot a(SO_4{}^{2-})}{a(H^+)^{10}}$$

## Results

- The recorded titration curves demonstrate that the formation of Basaluminite buffers the pH due to the consumption of $OH^-$.

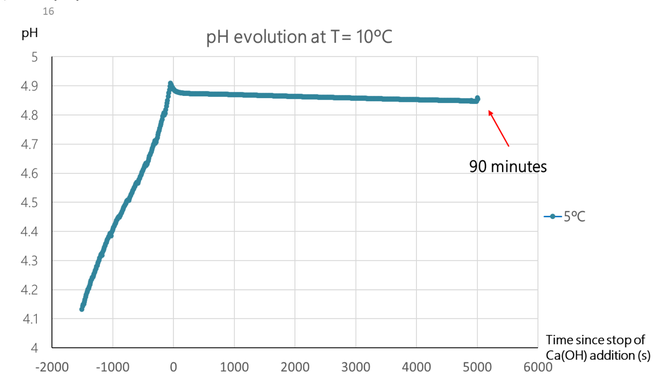
$$4Al^{3+} + 5H_2O + 1\,(SO_4)^{2-} + 10\,OH^- = Al_4(OH)_{10}(SO_4)\,(H_2O)_5$$

- The formation pH of basaluminite is inversely dependent on temperature: when the temperature increases, the formation pH is lower.

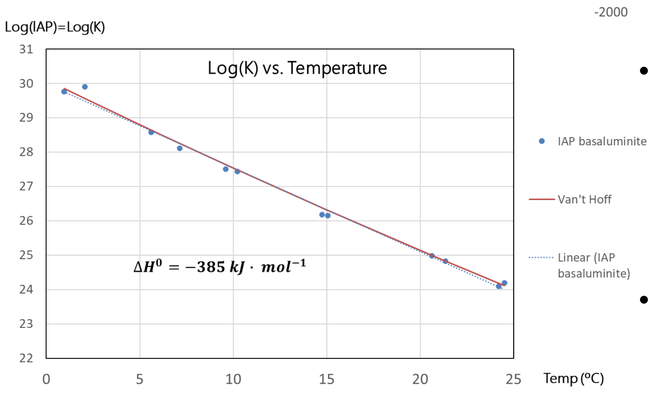



- The formation of basaluminite consumes Al and OH and **buffers** the pH. Then, as soon as the Aluminum in the solution is consumed, the pH starts to rise again.

- After the addition of $Ca(OH)_2$ is finished, little to no pH change is registered, implying that chemical equilibrium is quickly achieved.




Log(IAP)=Log(K)




- The temperature dependence of the ion activity product almost perfectly fits the Van't Hoff model, describing the variation of equilibrium constants with temperature [3].

- This allows calibrating the standard molar enthalpy of reaction, yielding a value of -385 kJ per mol.

## Conclusions

- Basaluminite forms almost instantaneous during addition of $Ca(OH)_2$ and buffers the pH of the solution, and chemical equilibrium is quickly achieved despite the low temperatures.

- The solubility of basaluminite shows a strong inverse dependence on the temperature.

- The calculated ion activity products refer to the log(K) of basaluminite. The determined log(K) and standard molar enthalpy values can be added to the PHREEQC databases

## Outlook

- Chemical and structural characterization of the precipitates synthesized in the lab and those collected in the field will be performed to confirm the presence of basaluminite (acid digestion, FTIR) .

- Chemical analyses of acid streamwater samples collected in the field will be used to determine the solubility of basaluminite under field-site, impure conditions

- The two data sets will be compared to determine if the obtained log(K) values can be used to model the mobility of Al and As under field-site conditions.

## References

[1] Wanner C., Pöthig R., Carrero S., Fernandez-Martinez A., Jäger C. and Furrer G. (2018) Natural occurrence of nanocrystalline Al-hydroxysulfates: Insights on formation, Al solubility control and As retention. Geochim. Cosmochim. Acta 238, 252-269.
[2] Carrero S., Fernandez-Martinez A., Pérez-López R., Poulain A., Salas-Colera E. and 865 Nieto J. M. (2017b) Arsenate and Selenate Scavenging by Basaluminite: Insights into the Reactivity of Aluminum Phases in Acid Mine Drainage. Environ. Sci. Technol. 51, 28-37.
[3] Parkhurst, David & Appelo, Tony. (1999). User's guide to PHREEQC version 3 - a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations.