

Errors in sequential extractions of sediments: the freeze-drying effect

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Introduction

It is well known that any kind of drying of sediment prior to sequential extractions will result in a shifted trace metal partitioning pattern compared to extracting wet sediments in N₂ atmosphere. In this study, wet sediments from four geochemically different lakes were subjected to the BCR sequential extraction method, followed by an extraction of freeze-dried subsamples. Precautions were made to minimise contact with oxygen while all sediments showed reduced conditions. Here, emphasis has been made on the difference in the partitioning pattern obtained from the two runs, for the major elements in trace metal scavenging fractions (Al, Ca, Fe, Mn and S). Results for K, Mg, Na, Si are also presented.

Discussion of results

Analysis shows that all elements considered are more or less affected by freeze-drying, at least for anoxic sediments. Carbonate associated elements (Ca and Mn) seems to be least affected. Fe and S are clearly shifted toward the fraction defined as oxides after freeze-drying. Generally, Al, Si, Mg, K and Na also show a shift from the sulphide / organic matter fraction towards the fraction defined as oxides or carbonates.

Element	Carbonates	Oxides	Sulfide / OM
Al	SI	I	D
Ca	SI	-	SD
Fe	D	I	-
K	SI	-	SD
Mg	SI	-	SD
Mn	SI	-	SD
Na	SI	SI	SD
S	I	SI	D
Si	-	I	D

Table showing the relative change in partitioning pattern in freeze-dried sediment compared to wet sediment (I=Increase; SI=small increase; SD=small decrease; D=decrease).

Conclusions

Freeze-drying of anoxic sediments will affect the partitioning pattern for major elements to varying degree. In some cases the iron shift only (carbonate to oxide fraction), corresponds to 3-4 % (w/w) of the total sediment. Clearly, this will also change the trace metal partitioning pattern.

References

- Rapin F., Tessier A., Campbell P.G.C and Carignan R., (1986), *Env. Sci. and Techn.* **20**, 836-840.
 Kersten M., Förstner U., (1987), *Mar. Chem.* **22**, 299-312.
 Quevauviller P., Rauret G., López-Sánchez J-F, Rubio R, Ure A., Muntau H. (1997) *EUR Report*, EN 17554, European Commission, Brussels.

The influence of amorphous Fe-rich surface coatings on the dissolution of anorthite at pH 2.6

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Introduction

63 – 53 µm anorthite powders were dissolved in continuous flow reactors in either pH 2.6 HCl or pH 2.6 FeCl₃ solution. Calculations using PHREEQ indicated that the FeCl₃ solution was saturated with respect to goethite. FeCl₃ solution was chosen in order to maintain feldspars in a far from equilibrium environment, as in the HCl experiment, in which a reaction product (goethite) would precipitate. It was hoped that the goethite would precipitate on the feldspar surfaces so that the effects of surface precipitates on dissolving minerals in soils could be determined.

Results and discussion

The feldspar samples which had been in the FeCl₃ solution developed a strong brown orange colour (7.5YR 5/8) typical of Fe oxyhydroxides (Schwertmann and Taylor, 1989). Coatings were observed on these particles using a field emission SEM. The precipitates covered all observed surfaces. Analytical electron microscopy of polished grain sections revealed discontinuous Fe-rich rims up to 6 µm thick on the feldspar grains.

The surface area of the HCl and FeCl₃ dissolved samples increased from an initial $0.16 \pm 0.00 \text{ m}^2 \text{ g}^{-1}$ to 1.44 ± 0.16 and $3.89 \pm 0.29 \text{ m}^2 \text{ g}^{-1}$ respectively. After removal of the Fe-rich coating the surface areas of the reacted samples were identical. The gas adsorption isotherm data of the samples indicates that prior to extraction the FeCl₃ sample was microporous whilst the others were not.

Dissolution rates of the samples, calculated from changes in Si concentration in solution were $3.0 \pm 0.3 \times 10^{-10}$ moles feldspar $\text{m}^2 \text{ s}^{-1}$ for the Fe-coated feldspar and $2.7 \pm 0.3 \times 10^{-10}$ moles feldspar $\text{m}^2 \text{ s}^{-1}$ for the HCl dissolved feldspar. The Fe-rich precipitate had no significant effect on the dissolution rate of the feldspar, most likely due to the porous nature of the precipitate which would therefore not constitute a barrier to the diffusion of reactive species to the feldspar surface and diffusion of released ions from the feldspar surface into the main solution. The precipitate would appear not to inhibit dissolution by nucleating on or blocking reactive sites on the feldspar. These results would appear to confirm the suggestion of Velbel (1993) that Fe oxyhydroxide precipitates would not inhibit feldspar dissolution. In addition they imply that the lack of surface precipitates on grains in laboratory dissolution experiments does not diminish their relevance to dissolution in the field.

References

- Schwertmann, U. and Taylor, R.M. (1989) In: J.B. Dixon and S.B.Weed (eds.) *Minerals in Soil Environments*. Soil Science Society of America. Pp. 379 – 438.
 Velbel, M.A. (1993) *Am. Min.* **78** 405 – 414.