

An improved single-step distillation of chromium-reducible sulfur

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The determination of elemental sulfur by chromium distillation is a controversial subject. Since elemental sulfur is an important intermediate in sulfur transformations in natural environments, a reliable method for quantitative recovery is required. Especially in the assessment of risks from acid sulfate soils a quantitative determination of all reduced inorganic sulfur compounds (RIS) is essential. In this field the chromium distillation has already been shown to be superior to other methods (e.g. Sullivan *et al.*, 1999).

In the analysis of elemental sulfur Canfield *et al.* (1986) found a recovery of 92 % but did not specify any further the form of elemental sulfur deployed. Wieder *et al.* (1985) observed 94,4 % recovery by using powdered elemental sulfur but only in minor amounts. Fossing and Jørgensen (1989) and Kallmeyer *et al.* (2004) proved that the recovery of elemental sulfur is clearly limited. In their experiments only in dissolved state a quantitative recovery could be obtained. Neither granular nor colloidal sulfur showed recoveries >50%. Our experiments carried out with the procedure according to Canfield *et al.* (1986) yielded recoveries of less than 50% in the analysis of powdered elemental sulfur.

Our modified method provides recoveries >90% (mean value: 94 %) for powdered, colloidal and dissolved elemental sulfur up to at least 16 mg S (approx. 3,2% of a 0,5 g sample). Nevertheless all other reduced inorganic sulfur species are quantitatively recovered. The modified method is selective towards RIS. It does not affect organosulfur compounds or sulfates. The selectivity was verified with methionine, cystine, cysteine, taurine, gypsum and barite.

The obvious advantage of this method is the ensured quantitative recovery of elemental sulfur. Furthermore no additional toxic solvents, e.g. dimethylformamide (DMF) (Kallmeyer *et al.*, 2004), are required. Besides that the selectivity of procedures involving DMF has not been tested with organosulfur compounds.

References

- Canfield D. E., Raiswell R., Westrich J.T., Reaves C.M., and Berner R.A. (1986), *Chemical Geology* **54** 149-155.
 Fossing H., and Jørgensen B.B. (1989), *Biogeochemistry* **8** 205-222
 Kallmeyer J., Ferdelman T.G., Weber A., Fossing H., and Jørgensen B.B. (2004), *Limnol. Oceanogr.: Methods* **2** 171-180
 Sullivan L.A., Bush R.T., McConchie D., Lancaster G., Haskins P.G., and Clark M.W. (1999), *Australian Journal of Soil Research* **37**, 255-265.
 Wieder R.K., Lang G.E., and Granus V.A. (1985), *Limnol. Oceanogr.* **30(5)**, 1109-1115

Determining mineral solubilities at high pressures: A new method combining weight-loss and *in situ* approaches

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Although a fairly extensive dataset is now available on the solubility of minerals in aqueous fluids at high pressure and temperature, almost all of the data above 0.5 GPa have been obtained by *ex situ* quench methods in piston-cylinder apparatus. A few comparative studies between such indirect weight-loss techniques and direct disappearance-of-phase, *in situ* methods are available, but only for trace elements (e.g. Ayers and Watson, 1993; Audetat and Keppler, 2006; Tropper and Manning, 2005). The results show huge differences, which are not yet satisfactorily explained. Here we introduce a new approach for determining solubilities of dissolved components using a hydrothermal diamond anvil cell (HDAC). We propose to exploit the tendency of crystals to approach an idiomorphic habit during HDAC runs, as observed by Wang *et al.* (2004), and also in our own HDAC studies. By defining the habit of a crystal before the run, its changing geometry can be modeled at various stages of the experiment. Knowing its original volume and mass, absolute solubilities can be determined. By comparing masses at various PT conditions, relative changes in solubility can be calculated. Our specially designed HDAC (Burchard *et al.*, 2003) allows fluid pressures up to 4.0 GPa to be reached. The results should allow a more fundamental and objective comparison between *in situ* and *ex situ* experiments. The initial focus is on quartz solubility in pure water, in order to assess the voluminous published data at hand, most of which has been obtained by *ex situ* methods. However, important rock-forming minerals such as feldspar and mica appear viable targets for this approach.

References

- Audetat A. and Keppler H. (2005), *Earth Plan. Sci. Lett.* **232**, 393-402.
 Ayers J.C. and Watson E.B. (1993), *Contrib. Mineral. Petrol.* **114**, 321-330.
 Burchard M., Zaitsev A.M. and Maresch W.V. (2003), *Rev. Sci. Instr.* **74**, 1263-1266.
 Tropper P. and Manning C.E. (2005), *Am. Mineral.* **90**, 502-505.
 Wang H.M., Henderson G.S. and Brenan J.M. (2004), *Geochim. Cosmochim. Acta* **68**, 5197-5204.