Sampling Devices for Monitoring Dissolution and Precipitation Reactions in Acidic Mine Lakes: Sediment Traps vs. Precipitation Traps

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INTRODUCTION AND SCOPE.

Geochemical studies on acidic mining lakes (AML) have been usually focussed on field measurement of water characteristics in depth profiles with multiparametric probes (e.g., pH, Eh, DO, SpC, turbidity; Sánchez-España et al., 2009), and subsequent water sampling at selected depths for chemical analysis. Later, geochemical modelling and in-situ mineral precipitation is speculated on the basis of calculated saturation indices by means of codes like PHREEQ-C or Geochemical Workbench. Sometimes they offer confusing results because of its dependence on the used databases. Nevertheless, the actual mineral precipitation in lake environments is not as easy to monitor as acidic mine drainage (AMD) surficial settings, hence the need for sampling the solid phase in the lake water.

In the course of our investigations in meromictic AMLs of Iberian Pyrite belt (IPB), commercial sediment traps and our new designed prototypes of mineral precipitation traps (hereafter "precipitation traps") were installed at different depths on the water column of different lakes to sample the solid phases which are actually formed in these environments over time.

The solids commonly found in standard sediment traps include sedimented mineral, rock-fragments and biotic remains transported chiefly by wind and run-off waters and gently settled on the surfaces of the lake banks at different depths. Moreover, crystalline and very low crystallinity, chemical precipitates are actually forming at some depths of the lake depending on the water characteristics. Finally, evidence of deposited particle dissolution and/or alteration is often found (Sánchez-España et al., 2010). Therefore, recovered sediments (e.g. using gravity corers) contain solids of different sources, thoroughly mixed, and generally dominated by the detrital component.

In the sediments of the IPB pit lakes, XRD spectra are invariably dominated by quartz, phyllosilicates (muscovite, chlorite) and jarosite. Chemical analyses also represent the mean content of detrital and precipitated fractions. SEM morphological and chemical analyses of the deposits recovered in cores and/or sediment traps are hampered by detrital components and sometimes give confusing data which are difficult to interpret. EDS determinations of newly precipitated phases are obscured by the signals from other minerals located in the interaction volume, such as occurs in extremely fine (μm- to nm-scale) Fe precipitates. For that reason we designed a new precipitation sampler which prevents sediment deposition inside samplers but allows mineral precipitation to take place in mother waters.

PRECIPITATION TRAP DESIGN AND METHODS.

The developed prototype consists of (Fig. 1a to c):

- Conventional polyethylene flasks of 7.7 cm high x 5 cm diameter.
- Six perforations (ϕ=8mm) in the plastic walls to permit water renewal.
- A plastic net to prevent mineral seeds looses or disturbances of mineral precipitation surfaces.
- Selected microsamples (máx. ϕ= 4mm) that act as mineral seeds.

For this work we selected well-characterized samples of minerals and rocks, similar to those found in the surroundings of the lakes, and some

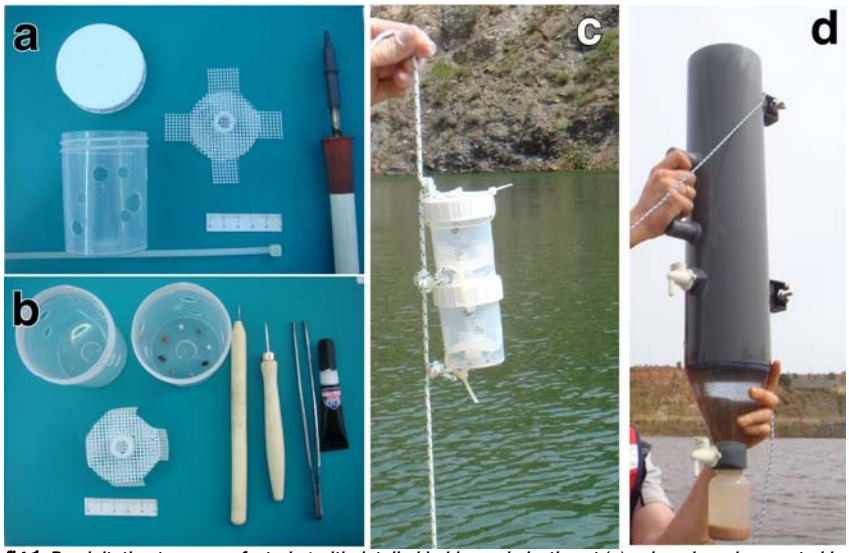

fig 1. *Precipitation trap manufacturing with detailed holder and plastic net (a), mineral seeds mounted in the holder (b), aspect in field prior to submersion (c). Sample recovering from a sediment trap (d).*

palabras clave: Meromixis, Minería metálica, Precipitados minerales, SEM-EDS, Trampas de precipitados.

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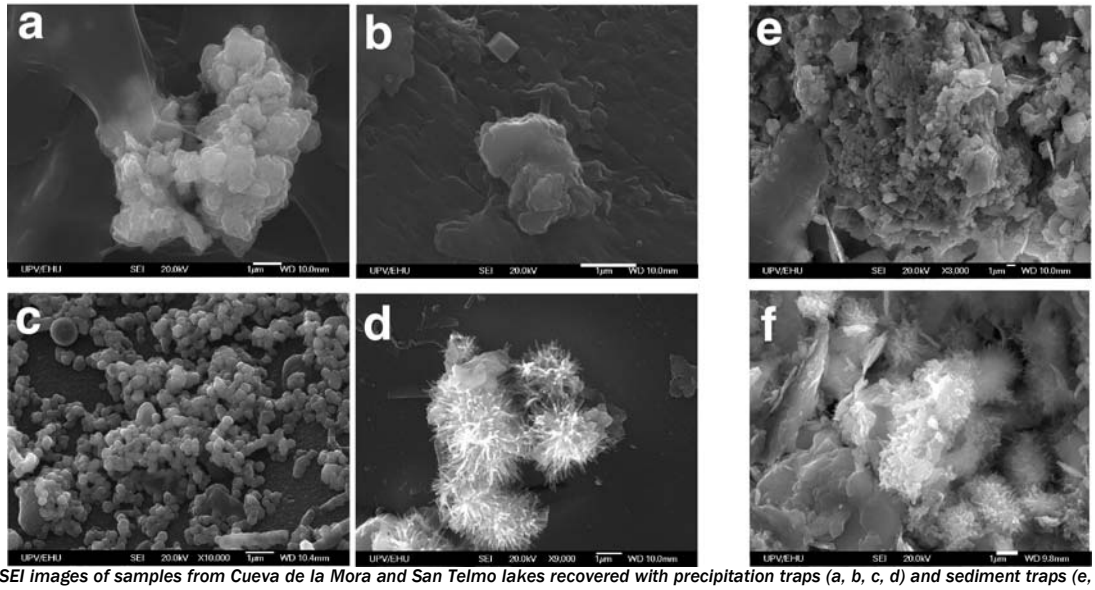

fig 2. *SEM-SEI images of samples from Cueva de la Mora and San Telmo lakes recovered with precipitation traps (a, b, c, d) and sediment traps (e, f). Globular aggregates of schwertmannite (sch) over charcoal at 7m (a), sch and pseudo-cubic jarosite (jar) precipitated over altered feldspar at 7m (b); sch over quartz at 19m (c), pin-cushion morphology of sch over pyrite at 35m (d); sch and jar from sediment traps at 7m (e) and 35m (f). Note the more complex nature of samples from the sediment traps.*

other which make easier the interpretation of SEM-EDS data. The following materials were selected: coarse-grained hydrothermal quartz, K-feldspar, muscovite schist and pyrite; fine-grained pyrite and hematitic gossan from San Telmo mine; charcoal and also metallic Cu.

Microsamples were carefully studied and described by binocular microscope and later glued in the inner base of the sampler (Fig. 1b) and protected with a plastic net. Two days before being installed in the lake, all the sampling devices were submerged in a solution of formaldehide and ethanol to prevent microbial contamination. Samplers were installed with devices composed of buoys and ropes and fixed with simple knots and sterile plastic ties. In order to monitor precipitation during residence times of 4 and 8 months, double mineral traps (Fig. 1c) were installed in Cueva de la Mora (at 7 and 19m) and San Telmo (25 and 35m) lakes in July 2010 and were recovered in November 2010 and March 2011. Samplers were kept in their respective mother solutions, refrigerated and washed with deionized water to prevent efflorescence formation. The samples were then air-dried and studied by binocular microscope and SEM-EDS (JEOL JSM-7000F).

Simultaneously, in 2009 commercial sediment traps (Fig. 1d) were installed at similar depths to determine solid composition and sedimentation rates. These devices consist of a 50 cm-long, 15 cm-diameter PVC tube with a plastic flask in the lower end of the funnel.

RESULTS FOR CUEVA DE LA MORA AND SAN TELMO LAKES.

At a first glance, microsamples from oxic mixolimnetic water of 7 and 25m were clean and did not show precipitation evidences apart from an alteration *cortex* in feldspar and dissolution morphologies characteristic of acidic attack. Samples from the anoxic monimolimnion (19 and 35m depth), in turn, showed a completely different aspect: dull surfaces covered with white, yellowish or orange deposits, even dendritic black, with evident signs of mineral precipitation in seeds. Precipitates were both related with the composition of the substrate (e.g. Cu sulphides over Cu chips), but can also grow with independence of the mineral surface (e.g. schwertmannite over pyrite, muscovite, quartz or even charcoal; Fig. 2a to d). These delicate precipitates coexist with biotic material (which role is currently under study), and highly contrast with the appearance of similar deposits found in the sediment traps (Fig. 2e and f). Apart from biotic remains and a very minor proportion of clay-sized phyllosilicates and quartz, the studied material is clean enough to characterize their morphology and chemical composition by SEM-EDS. Precipitates over charcoal offer a signal free of interferences, giving more confident results (Fig. 2a).

Material from the sediment traps also provided good examples of schwermannite, jarosite crystals, and some Cu and Fe sulphides in anoxic settings, but as noted earlier, samples are more difficult to study and interpret.

In conclusion, the described "precipitation traps" consist of easy-to-manufacture sampling devices which allow dissolution or precipitation processes in known minerals to be studied. We use them in conjunction to sediment traps as a method to ascertain the "in-situ" precipitation of minerals that were previously found in the sediment traps. Later on, we are sistematically installling them at even greater depths (e.g., 100m in San Telmo lake) or in operationally difficult settings (e.g., with very high dissolved gas content in water).

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