

# Nanogeochemical methods to investigate critical metal occurrence in stream and groundwater environments

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Critical metals (CMs) are essential for transitioning to low carbon energy sources, but are often subject to global supply chain disruptions. Demand for CMs is expected to rise significantly in the coming decades, necessitating increases in supply. Future CM resources are expected to come from geologically-hosted ore deposits as well as unconventional resources including aqueous environments. Investigation of both resource types can be advanced through nanogeochemistry. Here we present two case studies of nanogeochemical insights into critical metal mobility and speciation in aqueous systems. First, we apply single particle ICP-MS (spICP-MS), an emerging technique for analysis of individual metal nanoparticles, to investigate nanoscale metal occurrence in stream sediments. By measuring individual Au and Ag particles in aqueous sediment suspensions, detection limits were lowered significantly (50-fold) compared to conventional bulk methods. Occurrence, number, and size of Au and Ag NPs were related to upstream mineralization, with no NPs detected at a background site (Figure 1). This proof-of-concept study demonstrates spICP-MS as a new method to measure ultra-trace metals in stream sediments and to supplement mineral exploration surveys.

Unconventional resources of CMs include acidic aqueous environments such as acid mine drainage (AMD), where high metal solubility may simplify recovery. Waters proximal to dredge material placement facilities (DMPFs) constitute a similar acidic environment and are now being considered as a potential resource. Elevated CMs including Rare Earth Elements (REEs), Co, and Ni were measured in groundwaters surrounding two DMPFs in Maryland, USA. Asymmetric flow field flow fractionation (AF4) hyphenated to ICP-MS (AF4-ICP-MS) was used to characterize the nanogeochemistry of these groundwaters. REE containing NP species were identified, showing variable association with Al indicating REE adsorption onto clay minerals or (oxy)hydroxides. All REEs occur together in NP species, regardless of their bulk shale-normalized REE patterns. One groundwater contained two REE-bearing NP species that lacked any additional metals (Figure 2). By considering nanoparticulate phases we gain unique insights into REE speciation, which may benefit CM recovery efforts.

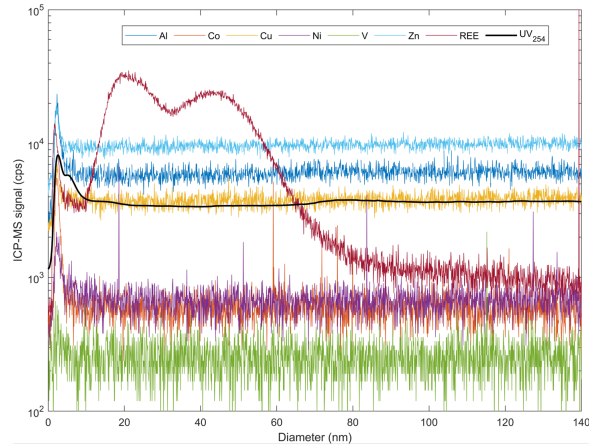


Figure 2: AF4-ICP-MS fractogram showing REE-bearing NP species that lack major and trace element associations.

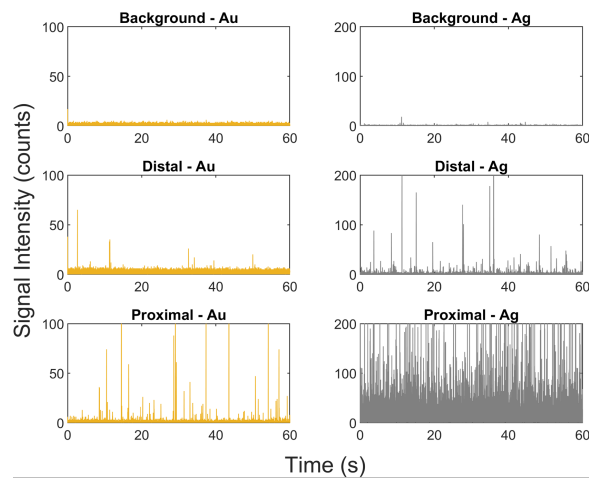


Figure 1: Time resolved spICP-MS data for three stream sediment samples. Each spike corresponds to an individual Au or Ag NP.