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Riverine particulates rich in clay minerals may complicate “authigenic” extractions from marine sediments

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Metals bound by marine sediments and water-born particulates are hosted in a wide range of solid phases (eg, oxyhydroxides, sulfides, organic matter, aluminosilicates). These phases may precipitate during authigenesis, drawing dissolved metals from the overlying water column and sediment porewaters, or be delivered as a detrital component, which does not interact with dissolved metals after transport into the ocean. The abundance of metals associated with these solid phases is often distinguished using acid extractions, intended to dissolve specific mineral/particulate species and leave others unaltered. For metals including V, Mo, and Tl, it is increasingly common to target the authigenic component using HNO_3 (1 – 3M, for 12 – 24 hrs, at 25 – 60 °C; eg, [1]).

Solid phase Al is often hosted by chemically inert phases but may be bound to aluminosilicate clays, which accumulate both authigenically and detritally. Single step HNO_3 extractions performed on sediments from the Skagerrak seaway and Gullmar Fjord extracted 12 – 51 % of total Al. This result was replicated in a later experiment, where HNO_3 extracted 17 – 50 % of total Al. These samples had previously been reacted with ammonium-acetate, hydroxylamine-hydrochloride, and dithionite solutions, which did not extract Al. Suspended particulates from five Norwegian rivers were exposed to the same procedure, and HNO_3 extracted 30 – 70 % of total Al. These high proportions of HNO_3-extractable Al imply that clay minerals are easily digested using HNO_3. Since Norwegian riverine particulates partially supply the sediments of the Skagerrak and Gullmar Fjord, HNO_3-based digestions may result in the mobilization of detrital clay minerals and, thus, impure authigenic components.

If Al concentrations are not monitored across the course of an extraction (eg, as performed in [1]) the presence of extractable clays may be missed. In such cases, nitric acid extractions may remove an unrecognized detrital fraction, and the authigenic component will be overestimated. The composition of nearby riverine particulates may help distinguish between authigenic and detrital clays when such cases arise.

[1] Wu et al. (2020), *Geochemica et Cosmochemica Acta 284*, 134- 155.