

## Weathering of black shales and Re-Os isotope systematics

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Late Permian organic-rich shales from the Ravnefjeld Fm in East Greenland yield a precise isochron from drill core samples, but scattered data from outcrop samples. Using Re-Os isochroneity as a gauge to distinguish fresh undisturbed shale from macroscopically fresh but chemically altered shale, we explore additional geochemical parameters that evidence subtle weathering and oxidation of shale.

Systematic differences between weathered and fresh samples are used to characterize and quantify the effect of weathering on shale chemistry. Weathering oxidizes organic matter (OM) and sulfides (mainly pyrite framboids <6  $\mu\text{m}$  on average), sometimes imperceptibly. The kerogen oxygen content (approximated by the S3 parameter of Rock-Eval pyrolysis) is a more consistent proxy for weathering than major or trace element compositions. Comparison with time equivalent fresh shale from the mid-Norwegian shelf reveals that shale weathering is best detected and characterized by the combined use of Rock-Eval indices for oxidation of OM and sulfur content data that document oxidation of pyrite. Based on this example, we present a sampling strategy to optimize the potential for accurate and precise Re-Os geochronology.

Correlations among trace metals, total organic carbon and total sulfur show that both Re and Os are concentrated in OM rather than sulfides. While both Re and Os are mobile during weathering, isotopic disturbance may occur through several contrasting mechanisms depending on local factors from the outcrop to the mm-scale. Depending on the type of isotopic disturbance, weathered shales may yield erroneously younger or erroneously older model ages.

Late Permian shales in this study have exceptionally high Re/Os ratios that lead to rapidly increasing  $^{187}\text{Os}/^{188}\text{Os}$  with time. Mass balance shows that recent (or Cenozoic) weathering of such shales may influence the Os isotopic composition of seawater much more strongly than weathering of typical Phanerozoic shales; the effect will be comparable to weathering of Precambrian shales.

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## Modeling the effects of fertilization and pH on dissolved inorganic phosphorus in soils

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We used a set of mechanistic (macro-scale) adsorption models within the framework of the component additive approach in an attempt to determine the effect of repeated massive application of inorganic P fertilizer on the processes controlling the concentration of dissolved inorganic phosphorus (DIP) in soils. We studied a Luvisol with markedly different total concentrations of inorganic P as the result of different P fertilizer history (i.e. massive or no application for 40 years). Soil pH was made to vary from acid to alkaline.

Satisfactory results were obtained using generic values for model parameters and soil-specific ones, which were either determined directly by measurements or estimated from the literature. We showed that adsorption largely controlled the variations of DIP concentration and that, because of kinetic constraints, minor precipitation of Ca-phosphates may have occurred under alkaline conditions, particularly in the P-fertilized treatment. The adsorption of  $\text{Ca}^{2+}$  onto soil minerals promoted adsorption of phosphates through electrostatic interactions. The intensity of this mechanism was high under neutral to alkaline conditions. The variation in DIP concentration with pH can be related to changes in the contribution of the various soil minerals to P adsorption.