

Impact of interfacial free energy on weathering rates

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The natural weathering rates of primary minerals can be orders of magnitude lower than the rates of mineral dissolution found in laboratory experiments. As primary dissolution rates are thought to be determined by the rate of secondary mineral precipitation, understanding the factors controlling precipitation rates could be the key to resolving this apparent discrepancy. Using model calculations we demonstrate that the effects of interfacial energy in systems close to equilibrium, and which possess a large number of micron and nanometer scale crystals, can have a critical impact on net mineral precipitation rates [1]. Net rates can be much lower than those predicted by standard kinetic formulations; moreover, when the proportion of small crystals is high enough, net dissolution can dominate even when the system is supersaturated with respect to large crystals. Importantly, secondary minerals that form from the incongruent dissolution of primary phases are often submicron in size, and field conditions are often far closer to equilibrium than those typically encountered in laboratory experiments. Thus, we propose that standard rate models - which do not account for interfacial energy effects in small crystals - may be unsuitable to describe reaction rates in weathering systems.

[1] Emmanuel and Ague (2011) *Chem. Geol.*, **282**, 11-18.

Metalliferous organic-rich black shales: Where do the metals come from?

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The amount of metal contained in a metalliferous black shale (MBS) can rival or surpass any ore deposit. Currently anomalous metal and carbon contents of these shales are thought to be controlled solely by ordinary oceanographic processes. Elevated metal and carbon contents of these shales are considered to reflect anoxic, high productivity conditions that optimize extraction of metals from normal seawater.

This explanation is challenged by the lack of modern analogs of ancient MBS. Despite intense study, modern euxinic environments of high productivity fail to form sediments with comparable metal enrichments. Moreover, mass balance constraints that consider the total mass and recharge of metal to the ocean, ocean circulation, and sedimentation rate suggest that typical seawater may not be an adequate source for the mass of metal in some MBS.

An alternative metal supply is apparent in the fluids that form, syndepositional exhalative (sedex) deposits. The metal supplied by the discharge of these hydrothermal fluids into ocean basins can be shown to surpass global riverine fluxes. The metal mass in a sedex deposit requires discharge of 1000's of km³ of warm saline fluid over a period of 10's ky. The large volume would have impacted ocean chemistry far beyond the extent of the deposit.

A genetic link between MBS and sedex deposits is reinforced by their common occurrence in age correlative strata. Although this temporal relationship has been previously ascribed to euxinic conditions necessary to form sedex deposits, the sedex fluids may, themselves, have enhanced or caused euxinic conditions.

An overlooked aspect of sedex systems is the flux of nutrients (i.e. NH₄, reduced C, trace metals, Ba, Si) added to the oceans by the ore fluids that may exceed the entire modern riverine flux. Such fertilization would undoubtedly promote massive increase in bioproductivity and spur basin-wide anoxic/euxinic conditions. Overall, the enormous flux of nutrients and metals delivered to the ocean by sedex systems may provide a plausible explanation for the enigmatic metal-rich end members of MBS.