Constraining rates of trace element supply and removal using long-lived thorium isotopes

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Radioactive disequlibria within naturally occurring U- and Th-decay series have been exploited to constrain the rates of a variety of processes in the ocean. Here we will illustrate the use of ^{230}Th and ^{232}Th to investigate certain processes that supply and remove trace elements, including:

1) Boundary Scavenging - the enhanced removal of trace elements by scavenging to particles in biologically productive ocean margin regions. Contrasting results from the North Pacific and North Atlantic Oceans reveal some expected findings and some surprises.

2) Bottom Scavenging - the enhanced scavenging of dissolved ^{230}Th by resuspended particles in benthic nepheloid layers. New evidence from the US GEOTRACES program will require reinterpretation of features in certain historical ^{230}Th profiles that were previously attributed to Atlantic overturning circulation. The rapid scavenging in benthic nepheloid layers that is evident in dissolved ^{230}Th profiles may apply to other particle-reactive trace elements as well.

3) Supply of trace elements by mineral aerosols (dust) - a new method employing ^{230}Th and ^{232}Th has gained a great deal of attention recently. We will examine evidence that raises questions about certain assumptions inherent in this approach including, most importantly, the assumption that ^{230}Th and ^{232}Th occur in the same chemical form and, therefore, have equivalent chemical residence times in the upper water column.

Adsorption of natural organic matter at the water/gibbsite interface

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Aluminum (Al) is one of the earth's most abundant elements and constitutes about 8% of the earth's crust. It exists mainly as silicates, oxides and hydroxides, combined with other elements or in complexes with natural organic matter (NOM). Speciation is a key factor for understanding the environmental impact of Al. It is therefore important to determine the chemical forms of Al that predominate in different natural media and under varying geochemical conditions. Adsorption of NOM to Al-based mineral surfaces is an important process that can alter the speciation of Al by influencing the rate and extent of dissolution of the mineral and thereby the overall solubility of Al. In this work, aquatic NOM from the Suwannee river (IHSS) has been studied in the presence and absence of an Al mineral surface (Gibbsite), using both *in situ* FT-IR spectroscopic measurements coupled with potentiometric titrations, and wet-chemical methods. These experiments were conducted as a function of time, pH, and concentration in order to follow the adsorption of NOM and the possible dissolution of the mineral surface.

Previous studies have indicated that fulvic and humic acids primarily adsorb to the surface of bohemite in an outer-sphere fashion with only minor formation of inner-sphere complexes **[1, 2]**. Our preliminary results indicate a significant shift in the asymmetric stretch of the carboxylate group in NOM at pH 3.5-5.5, possibly pointing towards a high amount of inner-sphere complexes at the gibbsite surface. Formation of inner-sphere complexes at the surface could promote a ligand-induced dissolution of the minerals. These indications are further suported by batch experiments where a dissolution of the gibbsite mineral are observed. Thus, complexation with NOM could potentially be one of the most important factors, other than pH, for controlling the solubility of Al in environmental systems.

[1] Yoon *et al*(2005) *Langmuir* **21**, 5002-5012. [2] Yoon *et al*(2004) *Langmuir* **20**, 5655-5658.

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