

TIME DEPENDENT PHASE ASSOCIATIONS OF IRON AND OTHER TRACE ELEMENTS ELUCIDATED BY $^{234}\text{Th}/^{238}\text{U}$ INVENTORIES IN TROPICAL COASTAL WATERS

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The in situ oxidation of iron plays an important role in the scavenging and subsequent particulate-phase transport and removal of other trace elements from coastal waters. Thermodynamically, the chemistry of iron in seawater is relatively well understood, conditions heavily favouring the formation of Fe(III) oxyhydroxides. However, a range of time dependent processes may induce significant departures from the anticipated equilibrium conditions, or severely retard the approach to equilibrium. Light has been shown to reduce and solubilise iron under acidic laboratory controlled conditions [1], suggesting that ferric oxyhydroxides can, in principle, be photo-reduced in seawater. However, the tendency is for photo-produced Fe(II) to remain at the particle surface forming a coating of relatively soluble amorphous iron oxides which limits major increases in solution phase iron [2]. Another complicating factor is the apparent ability of light to influence the size distribution of iron oxides, demonstrated in both laboratory and field experiments [2].

An understanding of time dependent particle formation and scavenging processes has been developed through observations of disequilibrium in the naturally occurring isotope pair ^{238}U and ^{234}Th . ^{234}Th with a half-life of 24.1 days and high affinity to bind with seawater particles, provides an excellent tracer to study processes with temporal ranges from days to months.

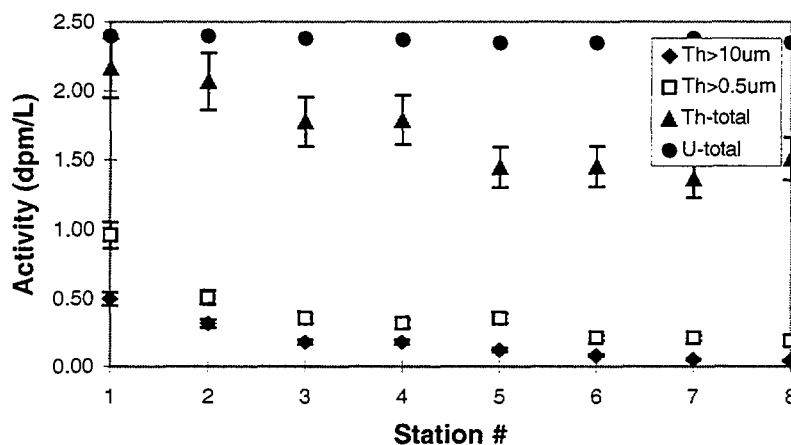


FIG 1. ^{238}U and ^{234}Th gamma activities in PNG coastal seawater.

In this study samples were collected in the Gulf of Papua region of PNG, on board the research vessel Franklin as part of a multidisciplinary study of factors influencing the fate of terrestrial material entering the tropical coastal ocean. Samples for ^{234}Th were collected using a in situ large volume pump device (Challenger Oceanic) passing seawater (1000-2000 litres) through a series of cartridge filters in polycarbonate housings. The cartridges and analytical techniques are detailed elsewhere [3]. Trace metals samples were collected from an inflatable dinghy using teflon-lined 5 litre Niskin GoFlo samplers (General Oceanics) suspended by a polypropylene rope and polyethylene encased lead weight. Duplicate samples were immediately returned to the research vessel for filtration and extraction in a Class 3.5 containerised Clean Laboratory using a C-18 Sep-Pak immobilised 8-hydroxyquinoline technique and ICP-MS detection [3]. Final iron determinations were performed by Zeeman GFAAS.

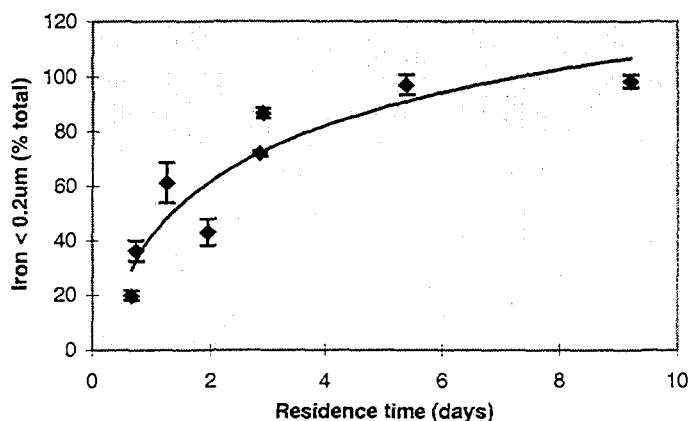


FIG 2. Proportion of total iron on particles less than $0.2\mu\text{m}$

In the Gulf of Papua residence times of particles, deduced by $^{234}\text{-thorium}/^{238}\text{-uranium}$ inventories (Fig. 1) varied from less than 1 to more than 20 days. The particle size distribution of iron (Fig. 2) was observed to vary according to residence time in surface waters, with increased illumination retarding particle formation, favouring the persistence of a more reactive fine fraction ($<0.2\mu\text{m}$). Concentrations of several dissolved trace elements were observed to increase with increasing residence times of particles (Fig. 3), allowing for greater illumination of incident particles, persistence of fine particles with high surface area for release/uptake of metals, saturation of available sorption sites and retardation of scavenging, resulting in higher incident metals concentrations as the rate of supply exceeds the rate of removal.

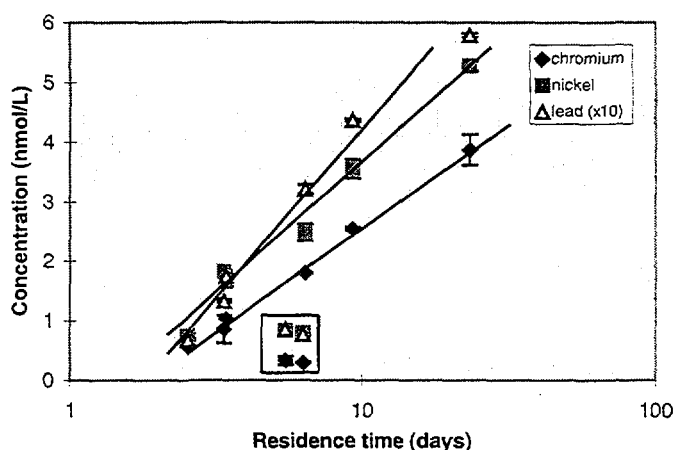


FIG 3. Dissolved trace metal concentrations versus residence times.

References

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