Partition coefficients of trace elements: from the ocean to the models

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Outline:

- what is a $K_d$?
- Thorium
- Neodymium
- $K_d$ in models
- recommendations
$K_d = \frac{\text{mass of particulate tracer per mass of particles}}{\text{mass of dissolved tracer per volume of seawater}}$

depends on the particle composition

$K = \frac{\text{mass of particulate tracer per volume of seawater}}{\text{mass of dissolved tracer per volume of seawater}}$

depends on the particle composition
the particle concentration

$K = K_d \times C_p$
Particle concentration effect on $K_d$ due to colloids

Honeyman et al., 1988
$^{230}\text{Th}$, $^{234}\text{Th}$
The influence of particle composition and particle flux on scavenging of Th, Pa and Be in the ocean

Zanna Chase a,b,c, Robert F. Anderson a,b, Martin Q. Fleisher a,
Deter W. Kuik b,c,

\[
\text{CaCO}_3 + \text{Litho}  \\
2002
\]

Sediment trap data

![Graph showing the relationship between % opale and % CaCO_3, with data points for AESOPS, MAB, other, and EqPac.]
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Controversy over the relationship between major components of sediment-trap materials and the bulk distribution coefficients of \(^{230}\text{Th},^{231}\text{Pa}\), and \(^{10}\text{Be}\)

Yuan-Hui Li\textsuperscript{*}

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Yuan-Hui Li\textsuperscript{a}

Radionuclide fluxes in the Arabian Sea: the role of particle composition

J.C. Scholten\textsuperscript{a,\dagger}, J. Fietzke\textsuperscript{a,1}, A. Mangini\textsuperscript{b}, P. Stoffers\textsuperscript{a}, T. Rixen\textsuperscript{c}, B. Gaye-Haake\textsuperscript{d}, T. Blanz\textsuperscript{e}, V. Ramaswamy\textsuperscript{f}, F. Sirocko\textsuperscript{a}, H. Schulz\textsuperscript{g}, V. Ittekkot\textsuperscript{h}

The influence of particle composition on thorium scavenging in the NE Atlantic ocean (POMME experiment)

M. Roy-Barman\textsuperscript{a,\dagger}, C. Jeandel\textsuperscript{b}, M. Souhaut\textsuperscript{b}, M. Rutgers van der Loeff\textsuperscript{c}, I. Voge\textsuperscript{g}, N. Leblond\textsuperscript{d}, R. Freydiere\textsuperscript{c}
Sediment trap data

intercorrelation problem: mixture of large and small particles
How to choose the right phase?

Roy-Barman et al, 2005
Kd (Th)$_{\text{MnO}_2}$ variability

Partition coefficient of Th between lithogenic particles, MnO$_2$ and seawater.

<table>
<thead>
<tr>
<th></th>
<th>$K_{\text{d-litho}}^{\text{Th}}$ (10$^7$ ml/g)</th>
<th>$K_{\text{d-MnO}_2}^{\text{Th}}$ (10$^{10}$ ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DYFAMED 1000 m, main correlation (this work)</td>
<td>0.8 ± 0.2</td>
<td>1.1 ± 0.4</td>
</tr>
<tr>
<td>DYFAMED 1000 m, winter samples (this work)</td>
<td>0.42 ± 0.04</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>Eastern North Atlantic$^a$</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Eastern North Atlantic$^b$</td>
<td>0.5–10</td>
<td>0.7–4.2</td>
</tr>
<tr>
<td>North Atlantic$^c$</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Equatorial Pacific and Southern Ocean$^d$</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Equatorial Pacific and Southern Ocean$^e$</td>
<td>20</td>
<td>3.5</td>
</tr>
<tr>
<td>Panama Basin$^f$</td>
<td>2–4</td>
<td>0.6–3.7</td>
</tr>
</tbody>
</table>

K$_d$ varies by a factor 60 could be used for modelling

Roy-Barman et al., 2009
What about organic matter?

Rutgers van der Loeff et al., 2002

Roberts et al., 2009
Timescale problem?

Roy-Barman et al., 2005
Timescale problem? 
equilibrium versus disequilibrium

Coppola et al., 2006

But

not confirmed by Venchiarutti et al., 2011
Do all phases have the same affinity for $^{230}$Th?
Sorption experiment

Geibert et al., 2002
Sorption experiment

<table>
<thead>
<tr>
<th>Mineral or organic phase</th>
<th>log $K_d$</th>
<th>References$^a$</th>
<th>$-\log C_p$</th>
<th>$f_p$ (predicted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>3–5</td>
<td>1</td>
<td>8</td>
<td>$&lt;10^{-3}$</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>4–5</td>
<td>2, 3</td>
<td>8</td>
<td>$&lt;10^{-3}$</td>
</tr>
<tr>
<td>Al$_2$O$_3$/clays</td>
<td>5.6–6.8</td>
<td>4, 8</td>
<td>9</td>
<td>$&lt;10^{-2}$</td>
</tr>
<tr>
<td>FeOOH</td>
<td>5.1–5.8</td>
<td>3, 5</td>
<td>9</td>
<td>$&lt;10^{-3}$</td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>4.4–7.6</td>
<td>3, 6, 8</td>
<td>10</td>
<td>$&lt;10^{-2}$</td>
</tr>
<tr>
<td>APS-EPS at 100% PS</td>
<td>8</td>
<td>7</td>
<td>8</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Relatively low affinity of inorganic phases
High affinity for organic matter.

Santchi et al., 2006
Particle concentration effect for sorption experiments of $^{234}$Th on Mn oxydes
Particle concentration effect for sorption experiments on Mn oxydes
Particle concentration effect for sorption experiments on Mn oxydes

Guo et al, 2009
Particle concentration effect for sorption experiments on Mn oxydes

Geibert et al, 2009
Guo et al, 2009

Log Kd Th for Mn oxydes vs Log Particulate Mn oxydes concentration

Log particle concentration (μg/l)
Particle concentration effect for sorption experiments on Mn oxydes

Kd Th for Mn oxydes

Log Particulate Mn oxydes concentration

Geibert et al, 2009

Guo et al, 2009

Suspended marine particles
Particle concentration effect for sorption experiments on Mn oxides

Geibert et al, 2009

Guo et al, 2009
Fractionation coefficient

\[ F_{\text{Pa/Th}} = \frac{K_{d_{\text{Pa}}}}{K_{d_{\text{Th}}}} = \frac{K_{\text{Pa}}}{K_{\text{Th}}} \]

Kretshmer et al., 2011

Guo et al., 2002
Neodymium
Determination $K_d$ for Nd: 2 methods

Subtracting the lithogenic fraction

$$X_{\text{auth}} = 1 - \left( \frac{\text{Al}}{\text{REE}} \right)_{\text{bulk}} \cdot \left( \frac{\text{REE}}{\text{Al}} \right)_{\text{lith}}$$
Kuss et al, 2001

leaching

$$X_{\text{auth}} = \frac{\left( \varepsilon_{\text{Nd}} \right)_{\text{bulk}} - \left( \varepsilon_{\text{Nd}} \right)_{\text{lith}2}}{\left( \varepsilon_{\text{Nd}} \right)_{\text{auth}} - \left( \varepsilon_{\text{Nd}} \right)_{\text{lith}2}}$$
Tachikawa et al., 2004
Determination $K_d$ for Nd: Comparison of the 2 methods

Tachikawa et al., 1999
Do all phases have the same affinity for Nd?

- Low affinity for organic matter (Elderfield, 1981, Fu et al., 2000)
- Similarities with $^{230}$Th

Adapted from Roy-Barman et al., 2005 and Guieu et al., 2004
Determination $K_d$ for Nd:
Do all phases have the same affinity for Nd?

Carbonate versus bSi

Akagi et al., 2011
Which phases carry $^{232}$Th and Nd?

< 30% lithogenic Th and Nd is carried by accessory phases. The remaining is dispersed in major phases (clays)?

Marchandise et al., in prep.
$K_d$ in models

what appears in models
($\sim 30$-$50$ m/y)

$$\frac{d[\text{tracer}]_{\text{total}}}{dt} = \text{Source} - \frac{d(S \times K_d \times C_p [\text{tracer}]_d)}{dt}$$
Nd modeling: the role of particles

Adapted from Arsouze et al., 2009

<table>
<thead>
<tr>
<th>Particles composition</th>
<th>Boundary input</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>biSi/CaCO$_3$/litho</td>
<td>No</td>
<td>Arsouze et al., 2007</td>
</tr>
<tr>
<td>OM/litho</td>
<td>yes</td>
<td>Jones et al., 2008</td>
</tr>
<tr>
<td>OM/litho</td>
<td>yes</td>
<td>Oka et al., 2009</td>
</tr>
<tr>
<td>no</td>
<td>yes</td>
<td>Rempfer et al., 2011</td>
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</tbody>
</table>
\(^{230}\)Th argues against strong change of the Th bearing phase flux

\[^{230}\)Th and Nd are correlated so Nd bearing phases cannot be strongly dissolved.
Nd modeling: the role of particles

Sidall et al., 2008

Arsouze et al., 2009
Conclusions and recommendations

- **Obtaining $K_d$ from suspended particles**
  - Complete analysis of the suspended particles (including major phases!!)
  - Difficulties to measure small $^{230}$Th quantities (intercalibration)

- **Better characterization of the particles**
  - Complete analysis of the particles
  - Phases constituting the particles
  - Profils/sections of carbonate, bSi, POC…

- **Equilibrium versus adsorption/desorption model**
  - Th based estimation of $k_1$ and $k_{-1}$
  - Ambiguity with mixed layer depth