

# 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

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

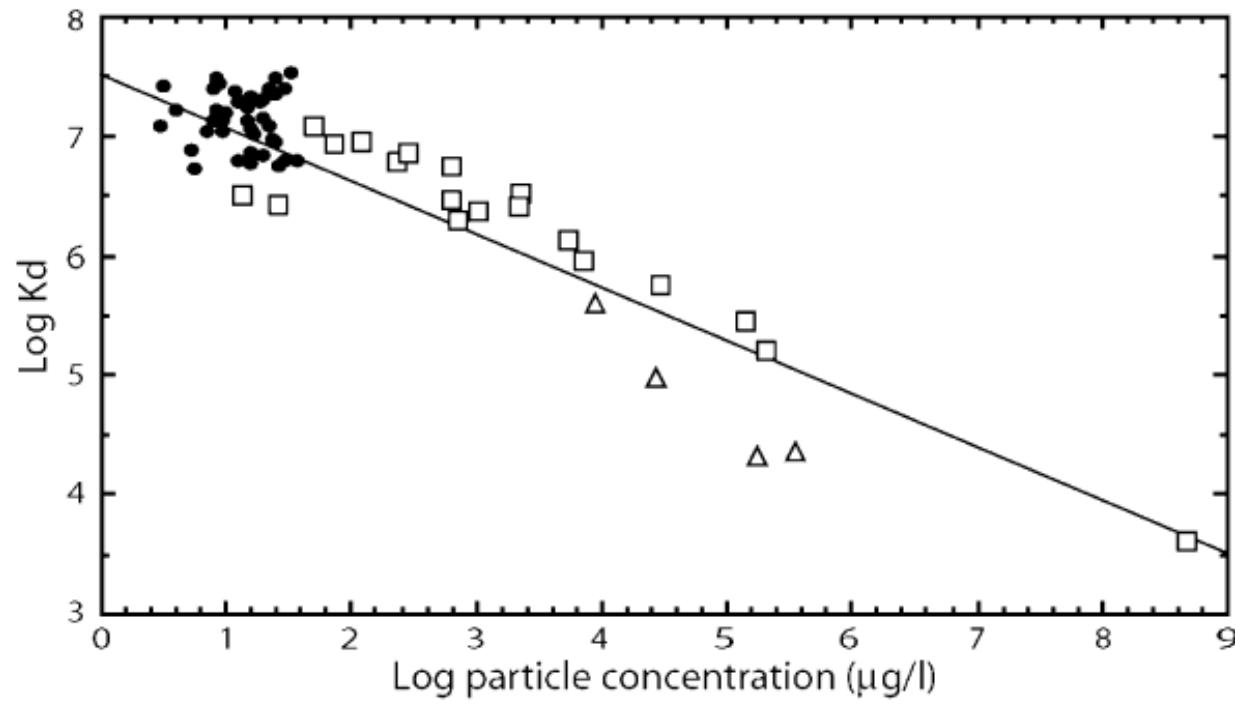
depends of the particle composition

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

depends of the particle composition  
the particle concentration

$$K = K_d \times C_p$$

## Particle concentration effect on $K_d$ due to colloids

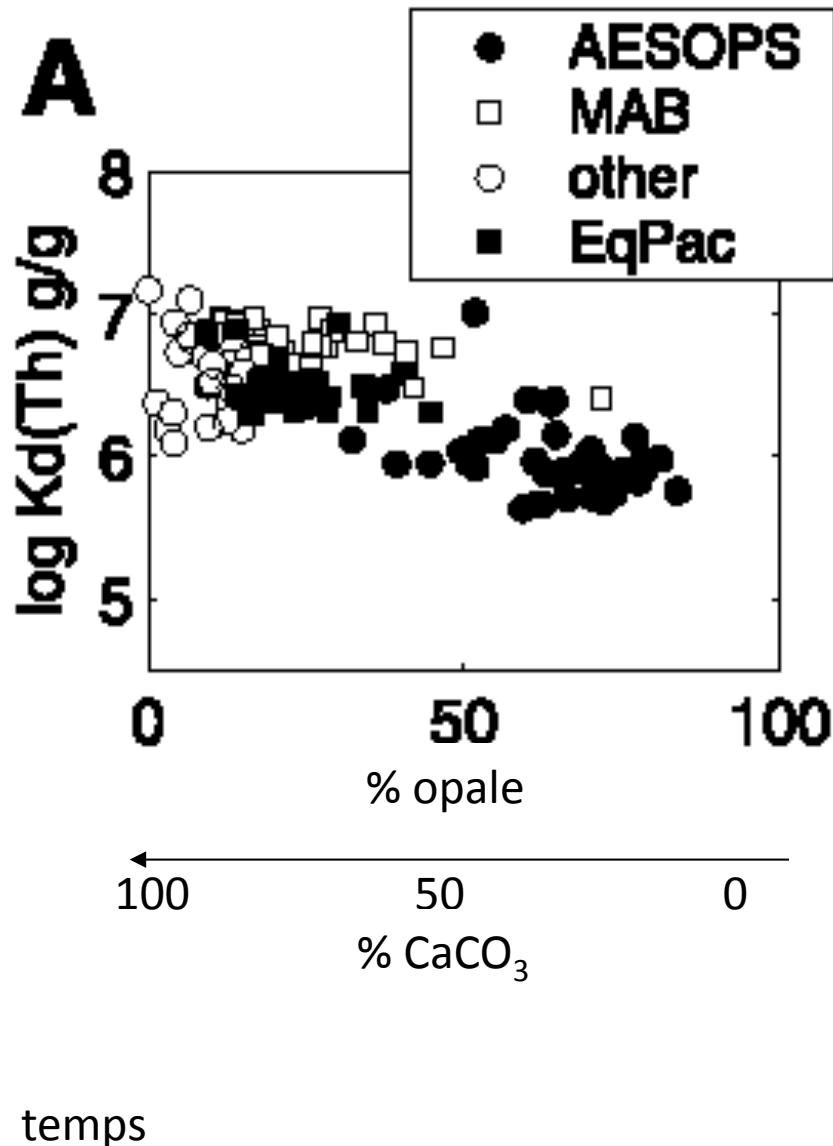


Honeyman et al., 1988

**$^{230}\text{Th}$ ,  $^{234}\text{Th}$**

The influence of particle composition and particle flux on scavenging of Th, Pa and Be in the ocean

Zanna Chase<sup>a,b,\*</sup>, Robert F. Anderson<sup>a,b</sup>, Martin Q. Fleisher<sup>a</sup>,  
Peter W. Kubik<sup>c</sup>



$\text{CaCO}_3 + \text{Litho}$   
2002

## Sediment trap data

Litho →

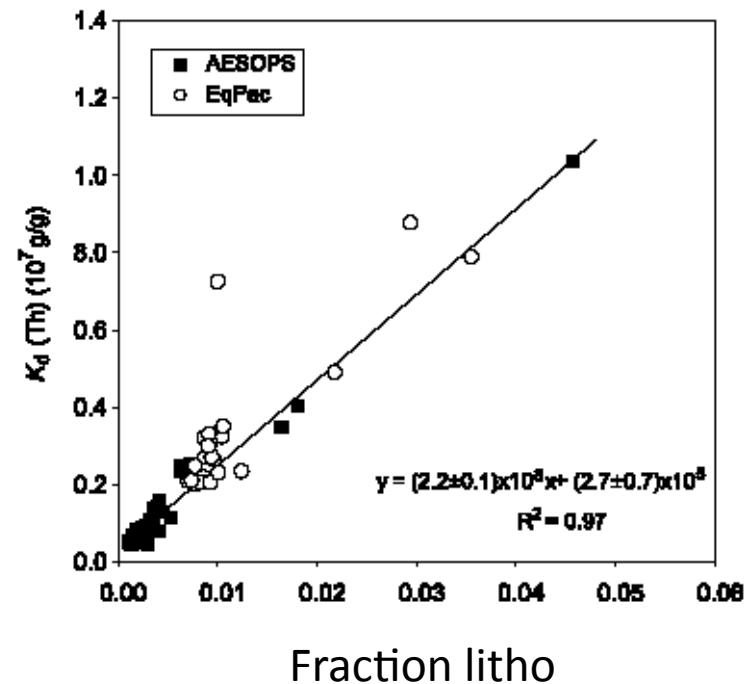
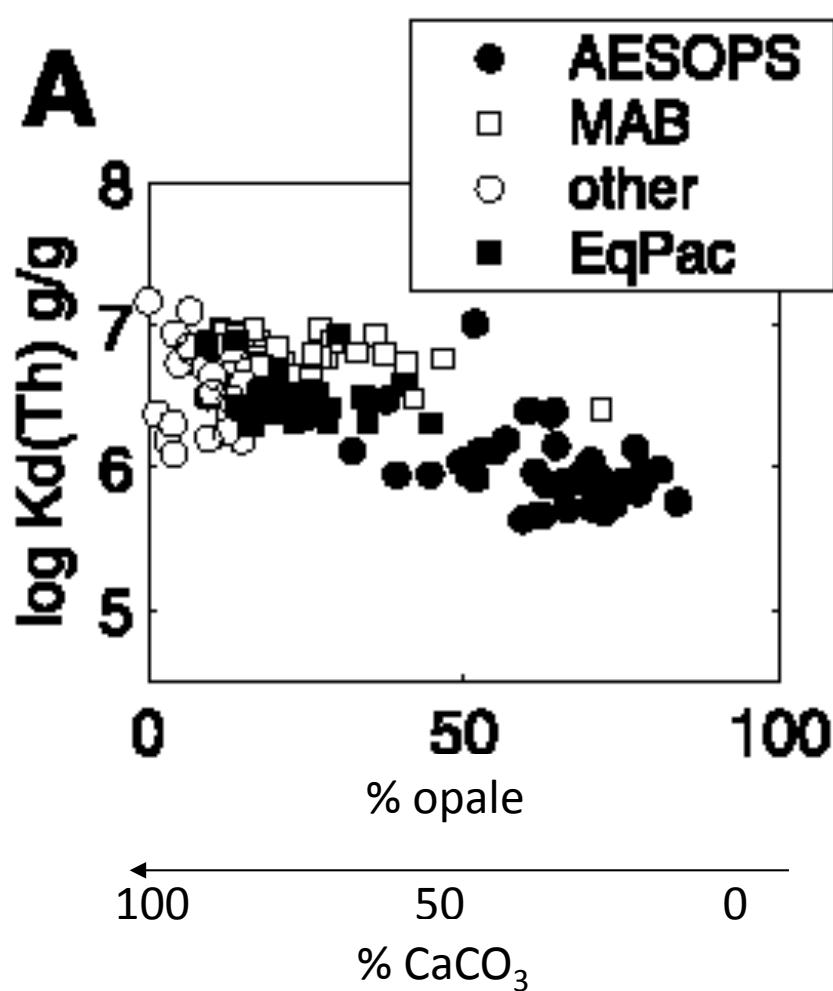
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Yuan-Hui Li\*

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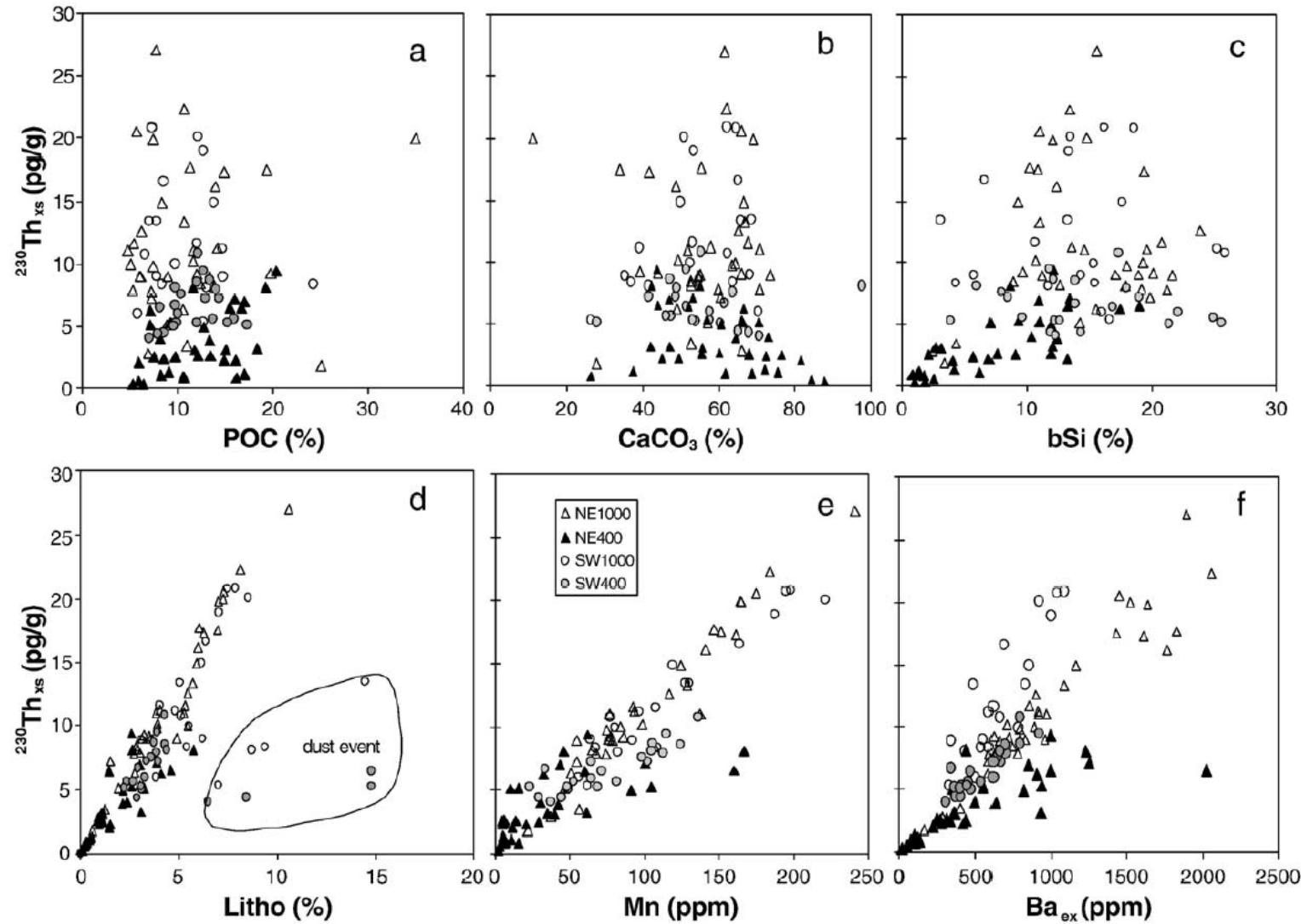
Radionuclide fluxes in the Arabian Sea: the role of particle composition

J.C. Scholten<sup>a,\*</sup>, J. Fietzke<sup>a,1</sup>, A. Mangini<sup>b</sup>, P. Stoffers<sup>a</sup>, T. Rixen<sup>c</sup>, B. Gaye-Haake<sup>d</sup>,  
T. Blanz<sup>e</sup>, V. Ramaswamy<sup>f</sup>, F. Sirocko<sup>g</sup>, H. Schulz<sup>h</sup>, V. Ittekkot<sup>c</sup>

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

M. Roy-Barman<sup>a,\*</sup>, C. Jeandel<sup>b</sup>, M. Souhaut<sup>b</sup>, M. Rutgers van der Loeff<sup>c</sup>,  
I. Voegel<sup>c</sup>, N. Leblond<sup>d</sup>, R. Freydier<sup>e</sup>

# Sediment trap data



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

Roy-Barman et al, 2005

# Kd (Th)<sub>MnO<sub>2</sub></sub> variability

Partition coefficient of Th between lithogenic particles, MnO<sub>2</sub> and seawater.

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

K<sub>d</sub> varies by a factor

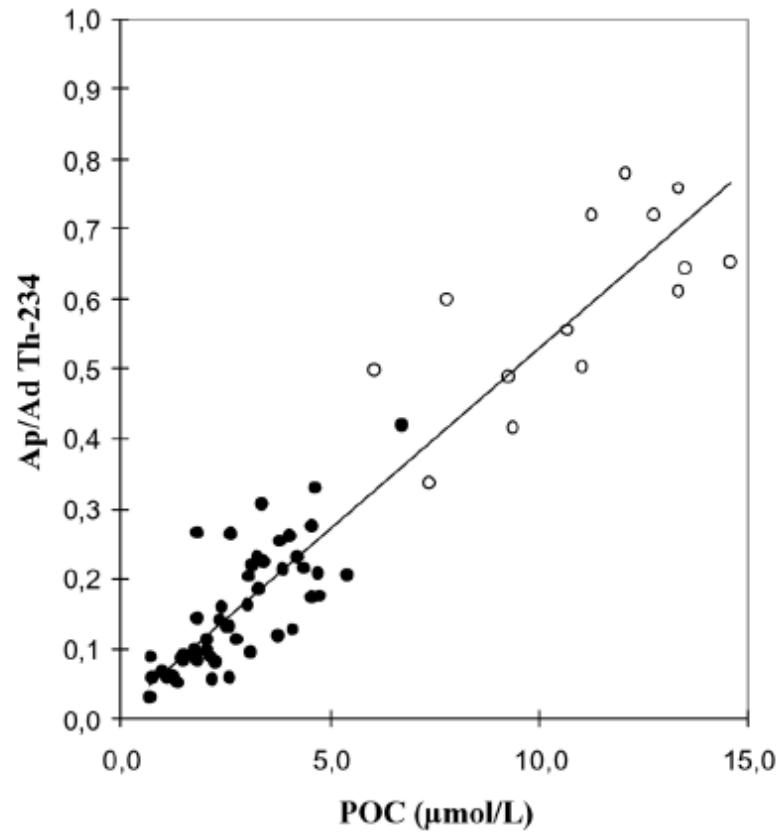
60

⑥

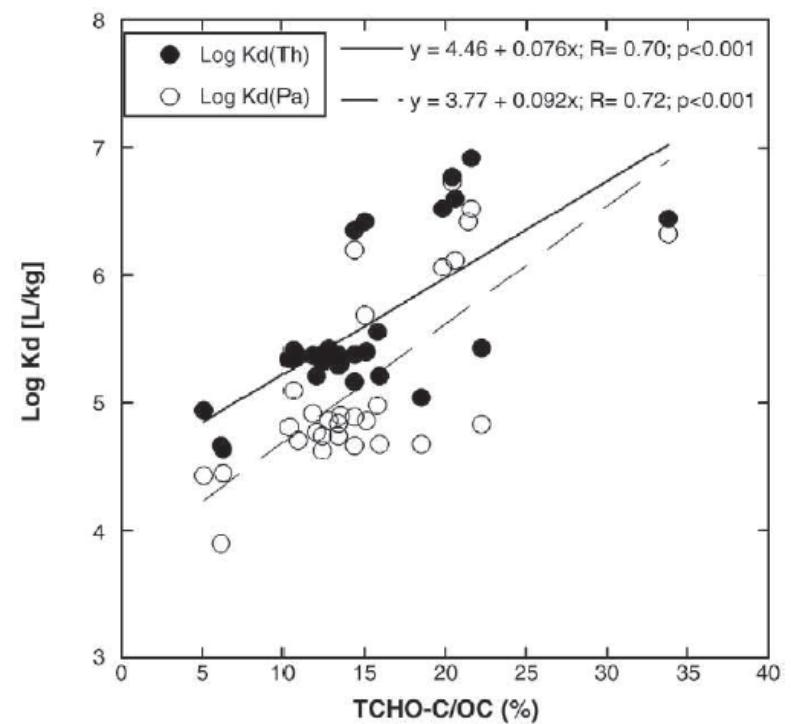
could be used  
for modelling

Roy-Barman et al., 2009

# What about organic matter?

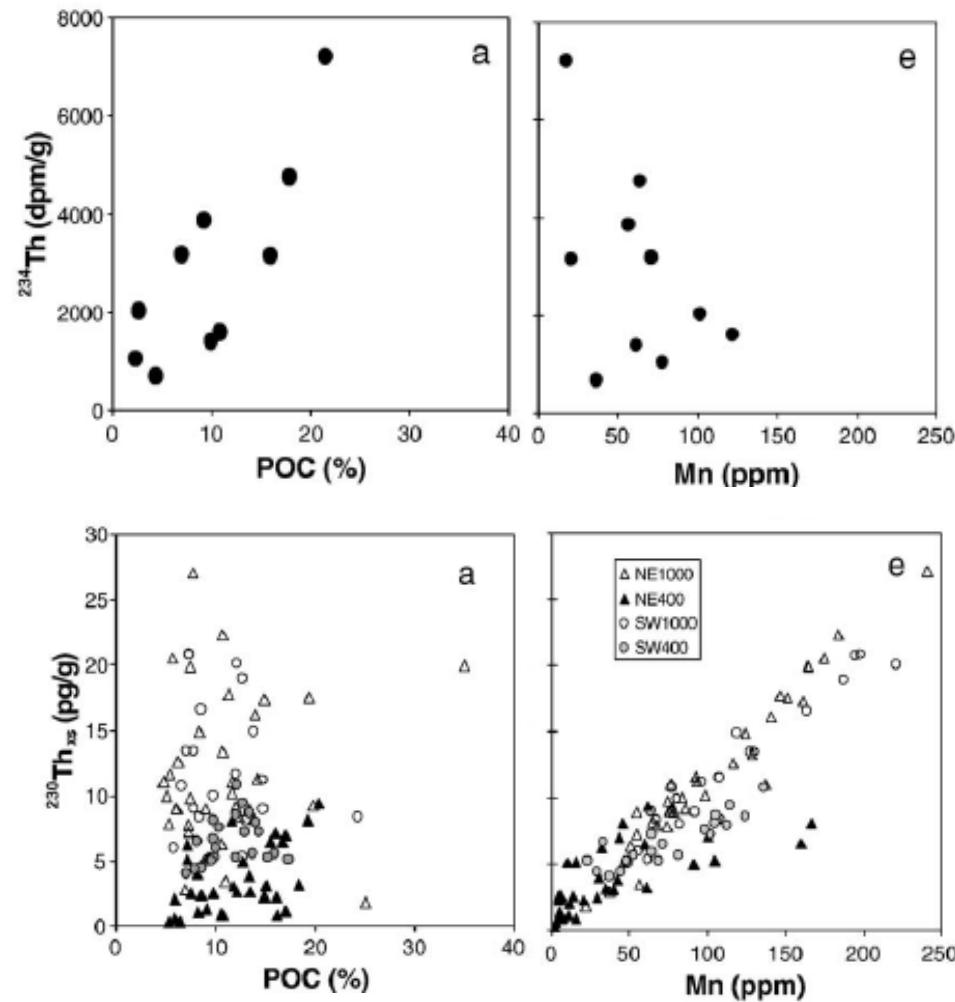


Rutgers van der Loeff et al., 2002



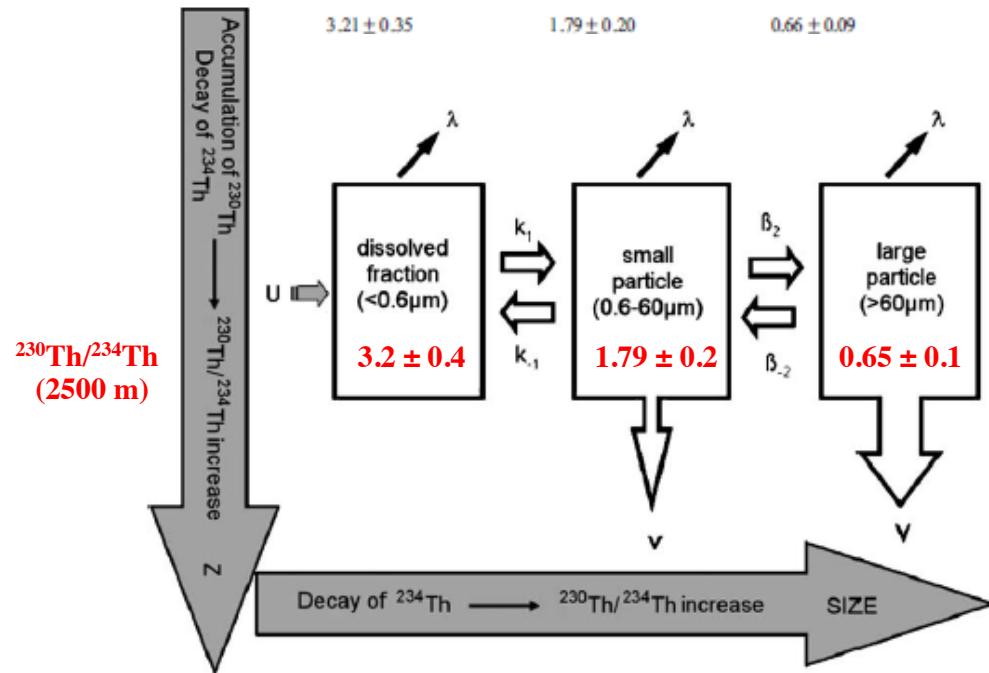
Roberts et al., 2009

# Timescale problem?



Roy-Barman et al., 2005

# Timescale problem? equilibrium versus disequilibrium

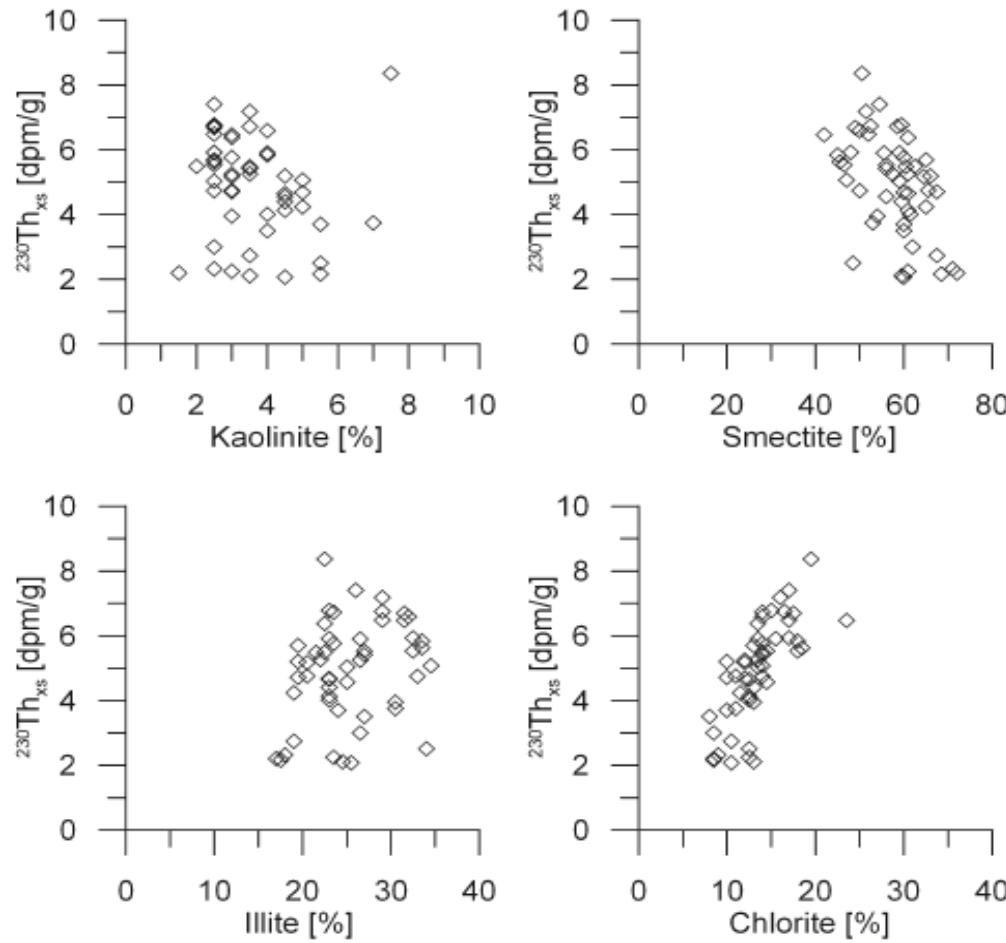


Coppola et al., 2006

But

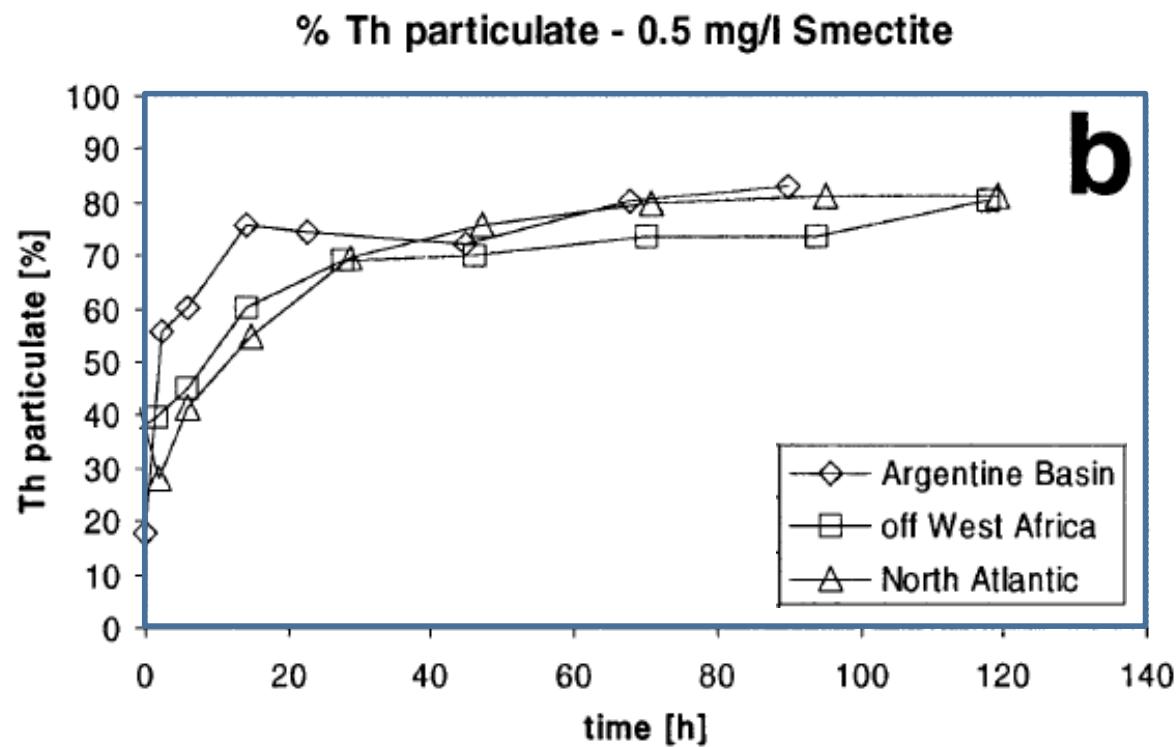
not confirmed by Venchiarutti et al., 2011

# Do all phases have the same affinity for $^{230}\text{Th}$ ?



Kreshtmer et al., submitted to paleoceanography

# Sorption experiment



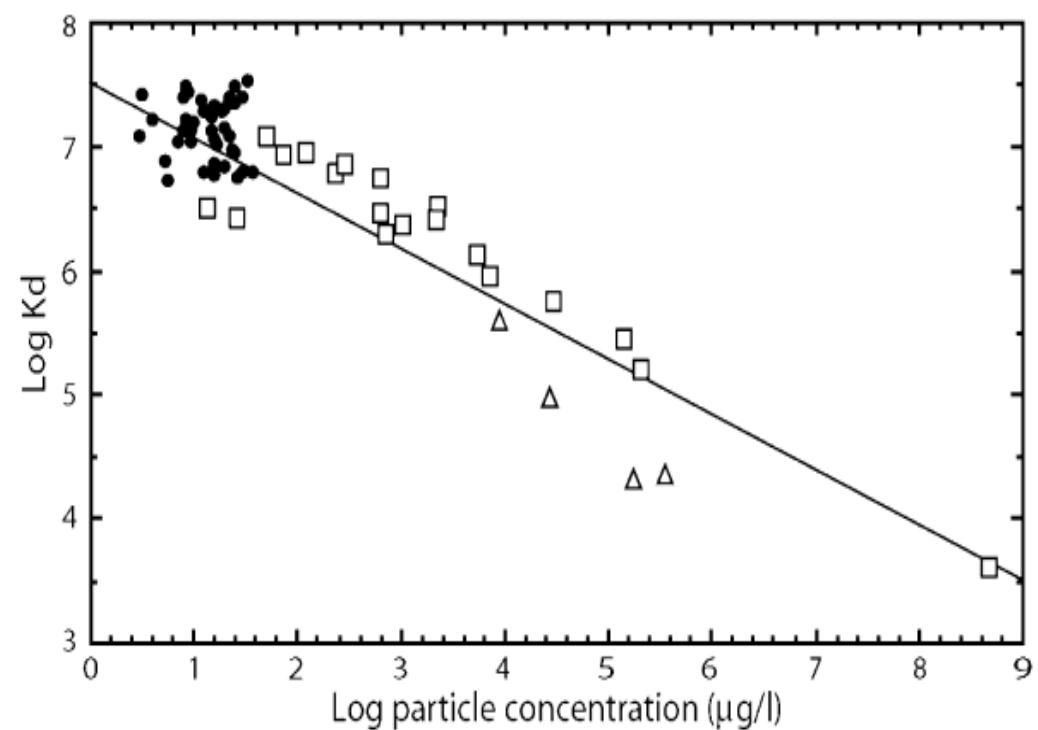
Geibert et al., 2002

# Sorption experiment

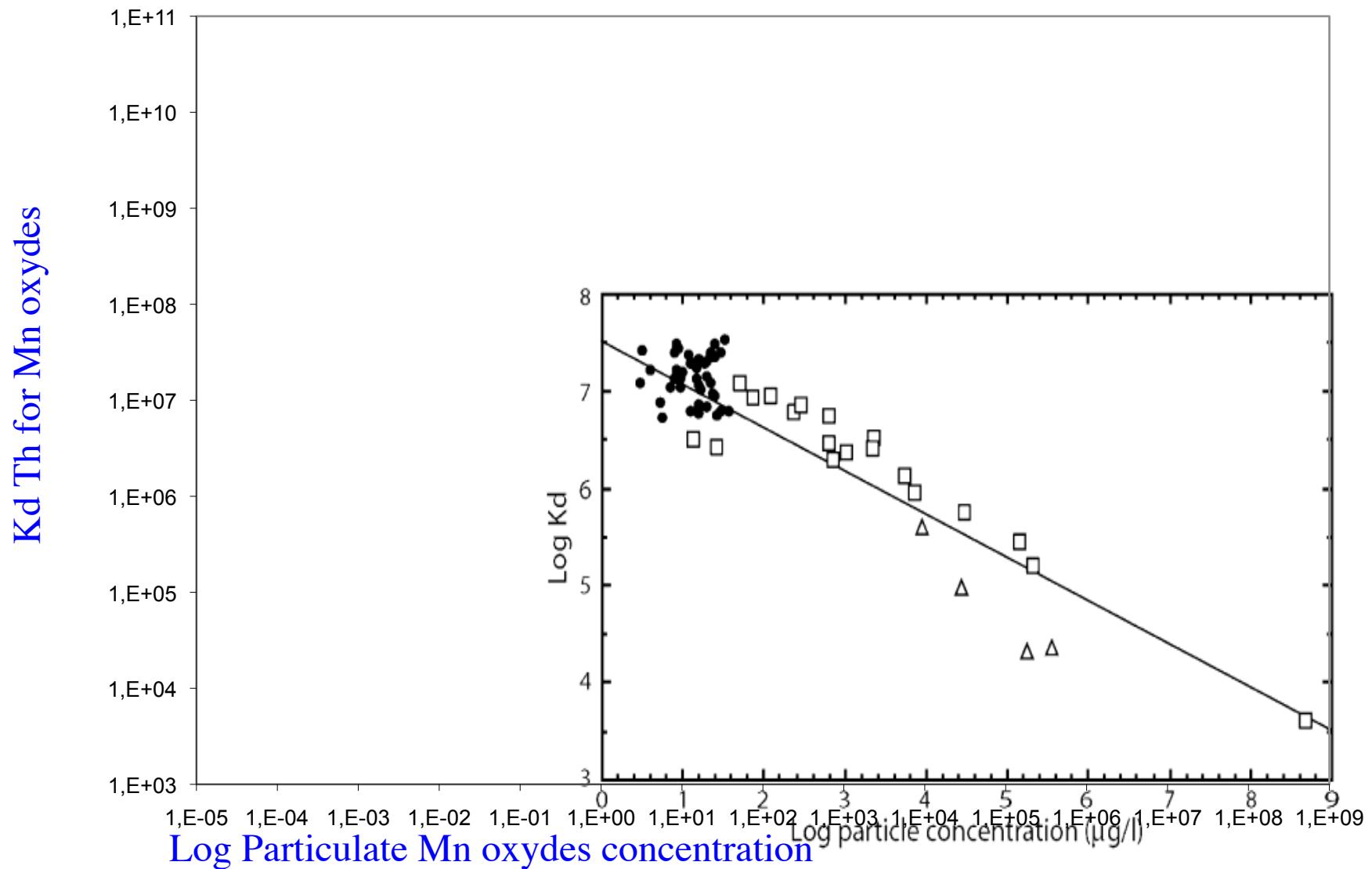
Mineral or organic phase	$\log K_d$	References <sup>a</sup>	$-\log C_p$	$f_p$ (predicted)
$\text{SiO}_2$	3–5	1	8	$<10^{-3}$
$\text{CaCO}_3$	4–5	2, 3	8	$<10^{-3}$
$\text{Al}_2\text{O}_3/\text{clays}$	5.6–6.8	4, 8	9	$<10^{-2}$
$\text{FeOOH}$	5.1–5.8	3, 5	9	$<10^{-3}$
$\text{MnO}_2$	4.4–7.6	3, 6, 8	10	$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

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

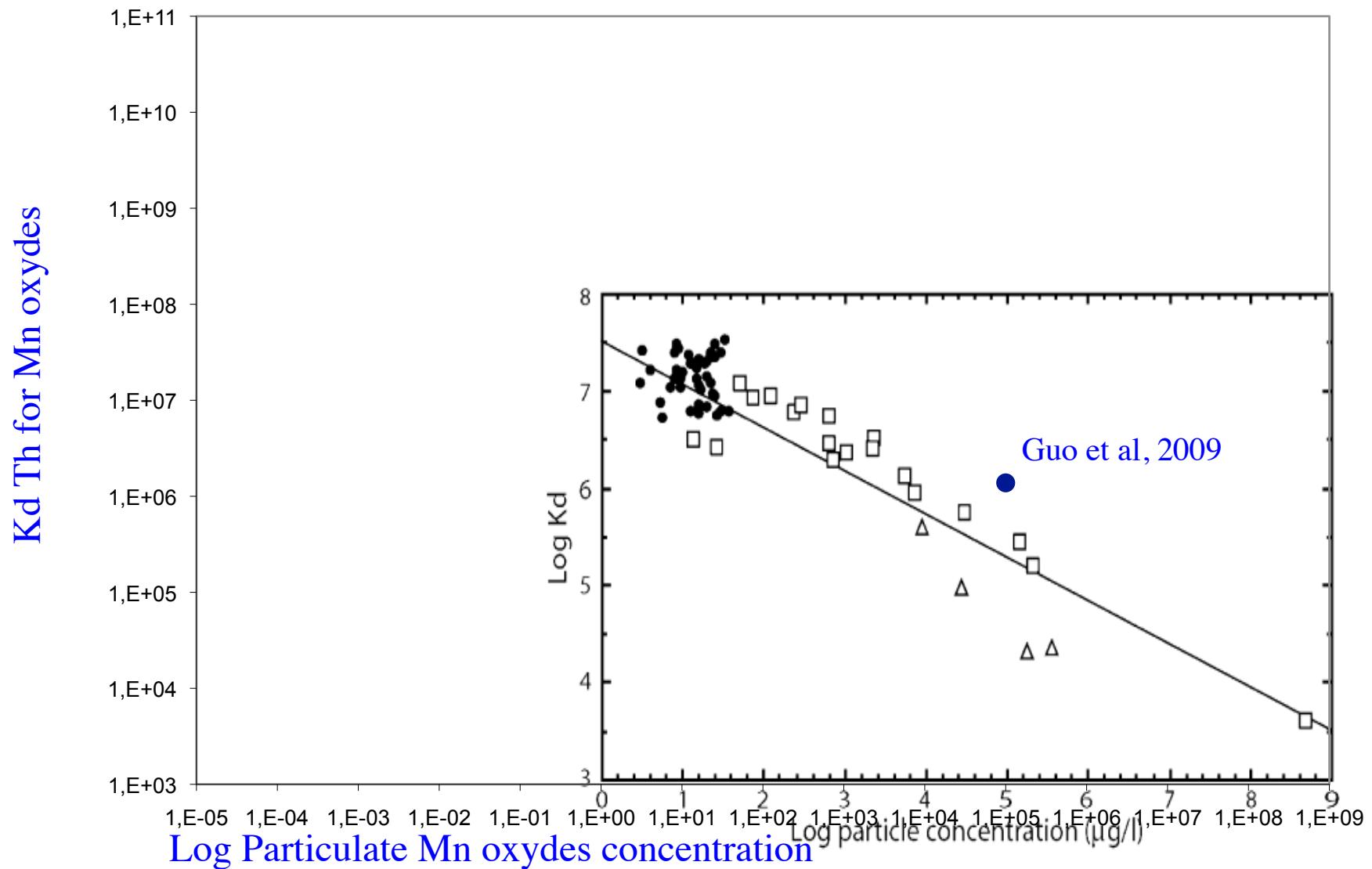
# Particle concentration effect for sorption experiments of $^{234}\text{Th}$ on Mn oxydes



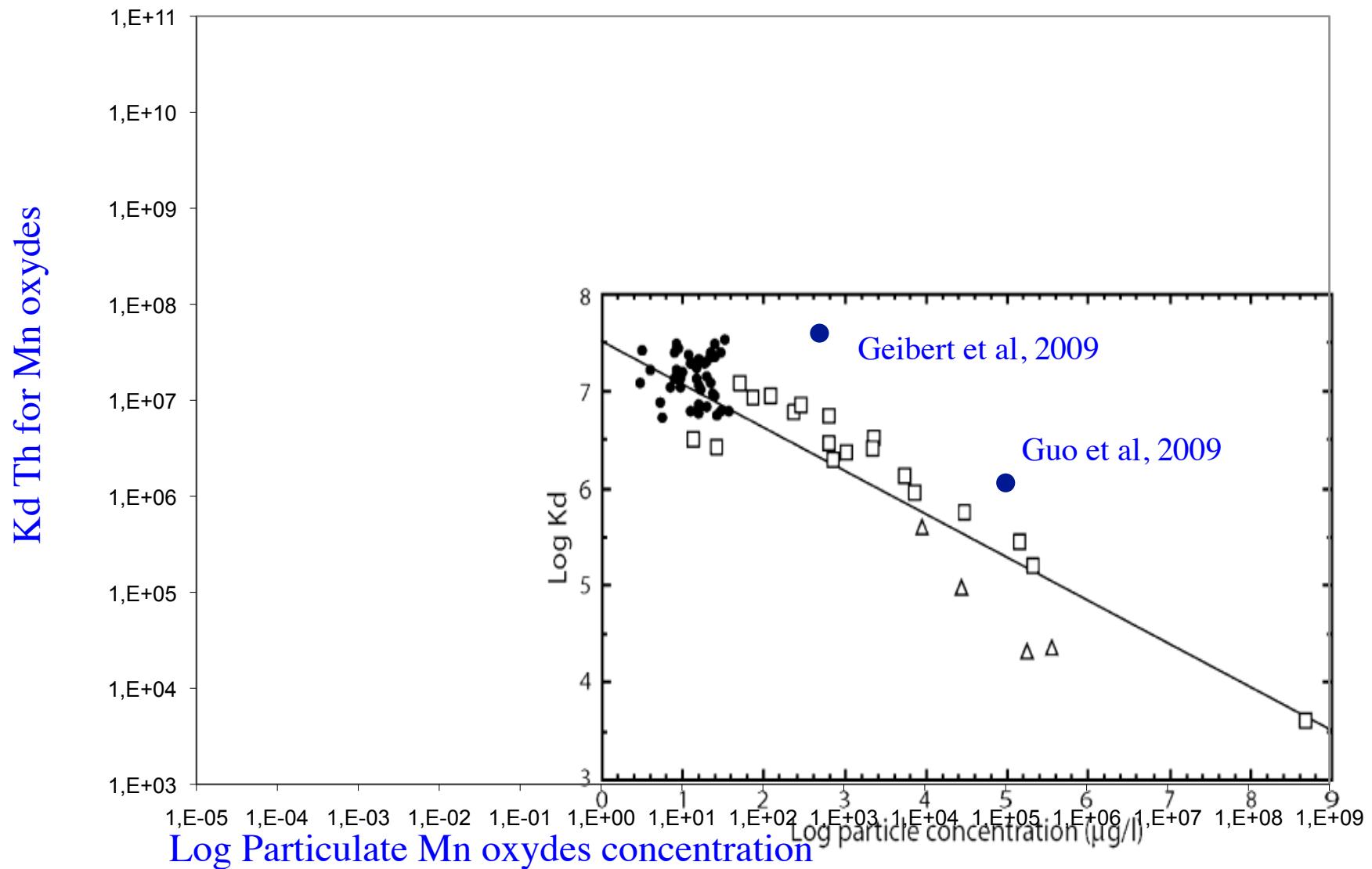
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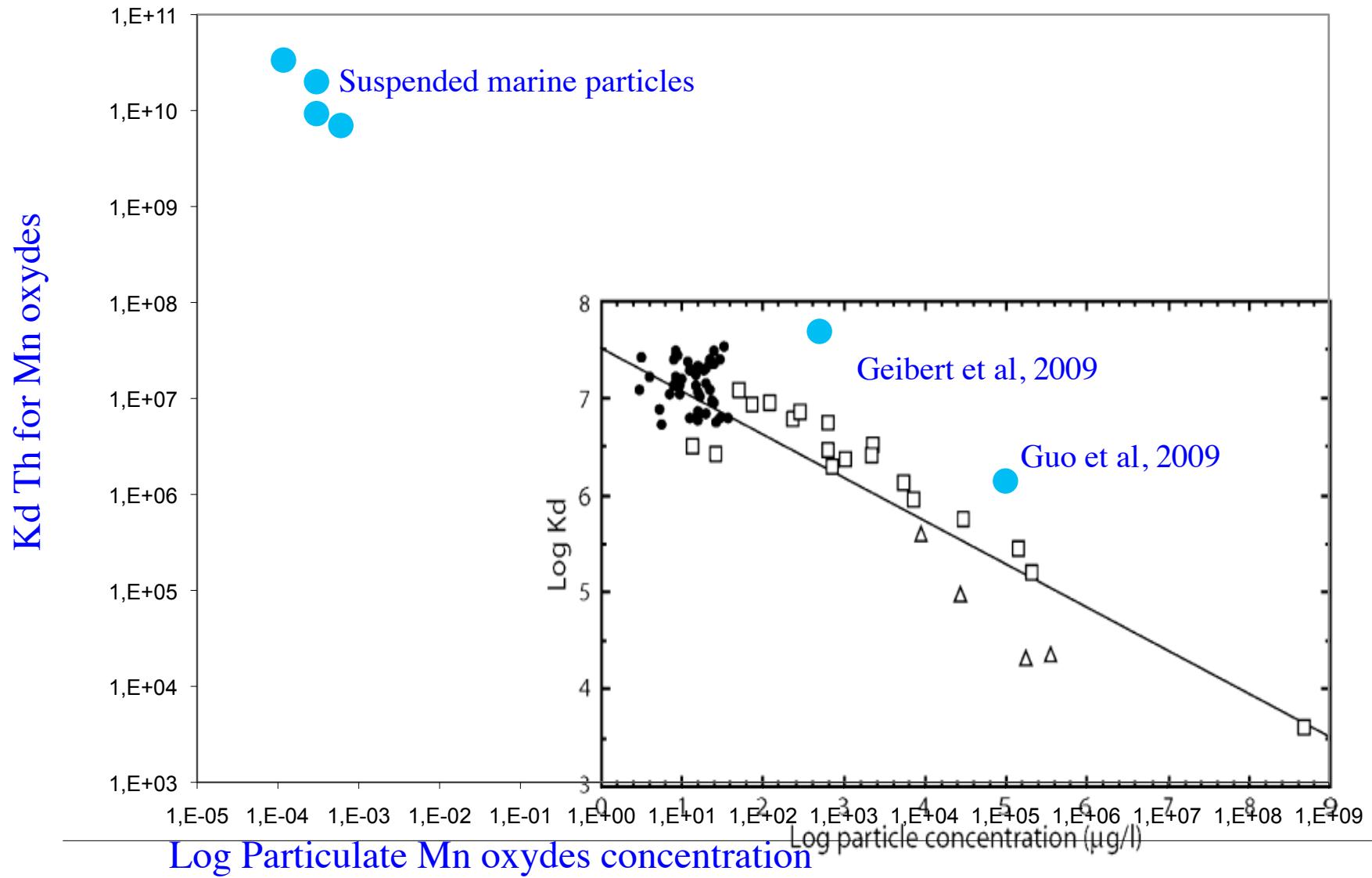
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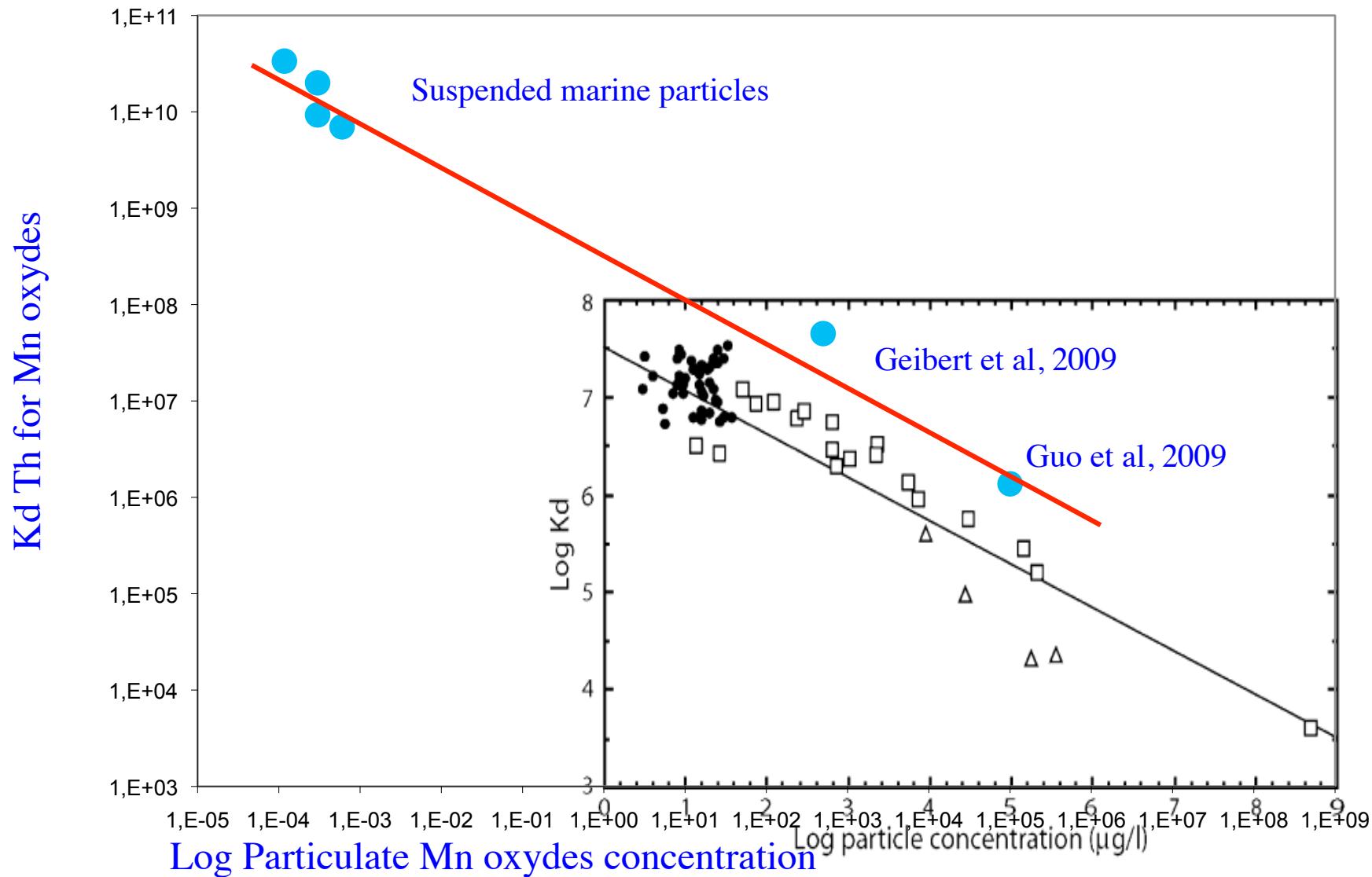
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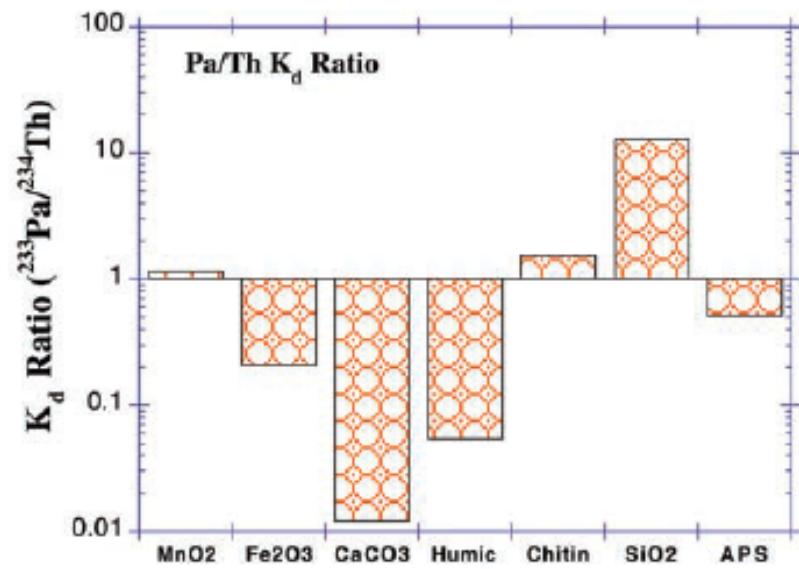
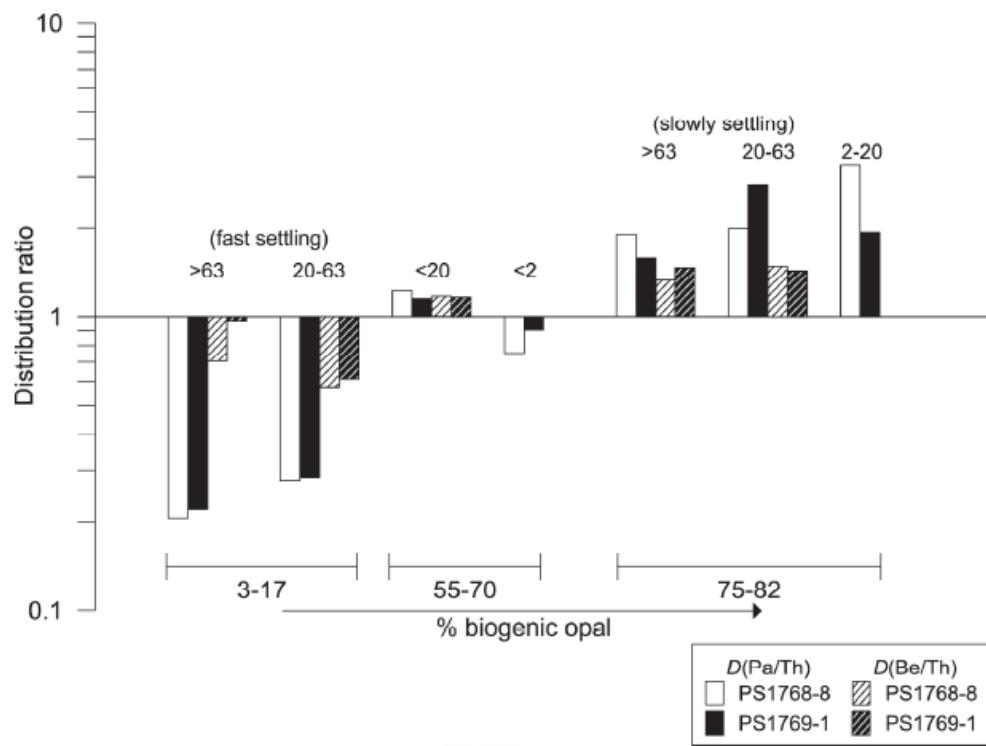


# Particle concentration effect for sorption experiments on Mn oxydes



# Fractionation coefficient

$$F_{\text{Pa/Th}} = K_{d\text{-Pa}} / K_{d\text{-Th}}$$
$$= K_{\text{Pa}} / K_{\text{Th}}$$



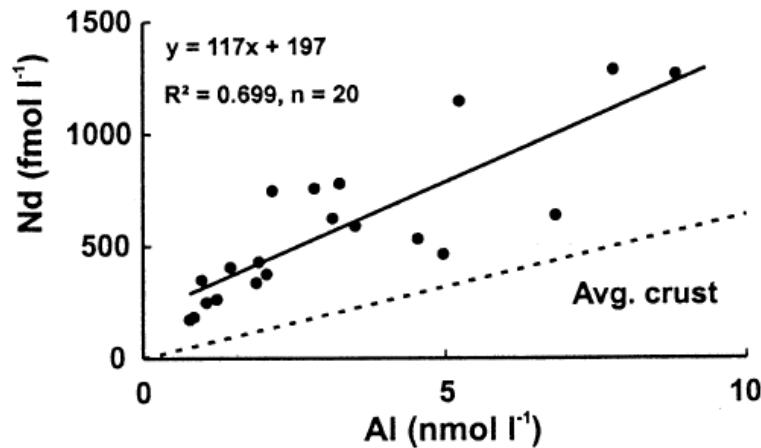
Kretshmer et al., 2011

Guo et al., 2002

# **Neodymium**

# Determination K<sub>d</sub> for Nd: 2 methods

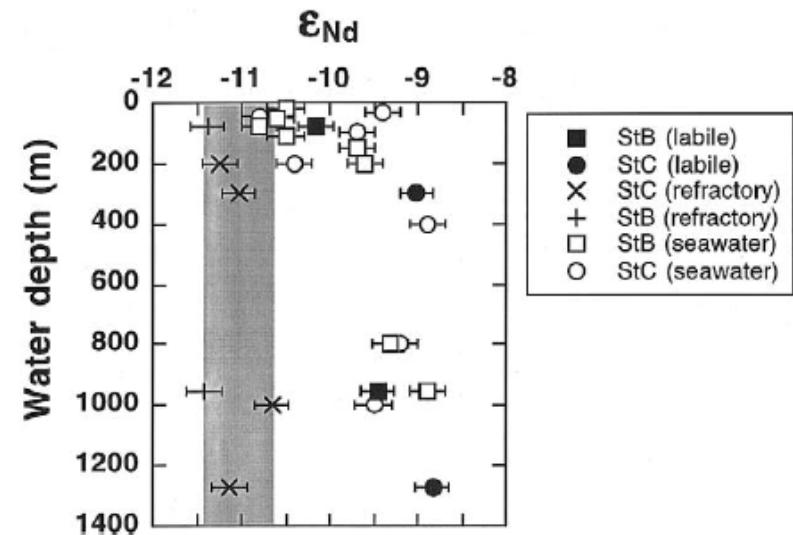
## Substracting the lithogenic fraction



$$X_{\text{auth}} = 1 - \left( \frac{\text{Al}}{\text{REE}} \right)_{\text{bulk}} \cdot \left( \frac{\text{REE}}{\text{Al}} \right)_{\text{lith 2}}$$

Kuss et al, 2001

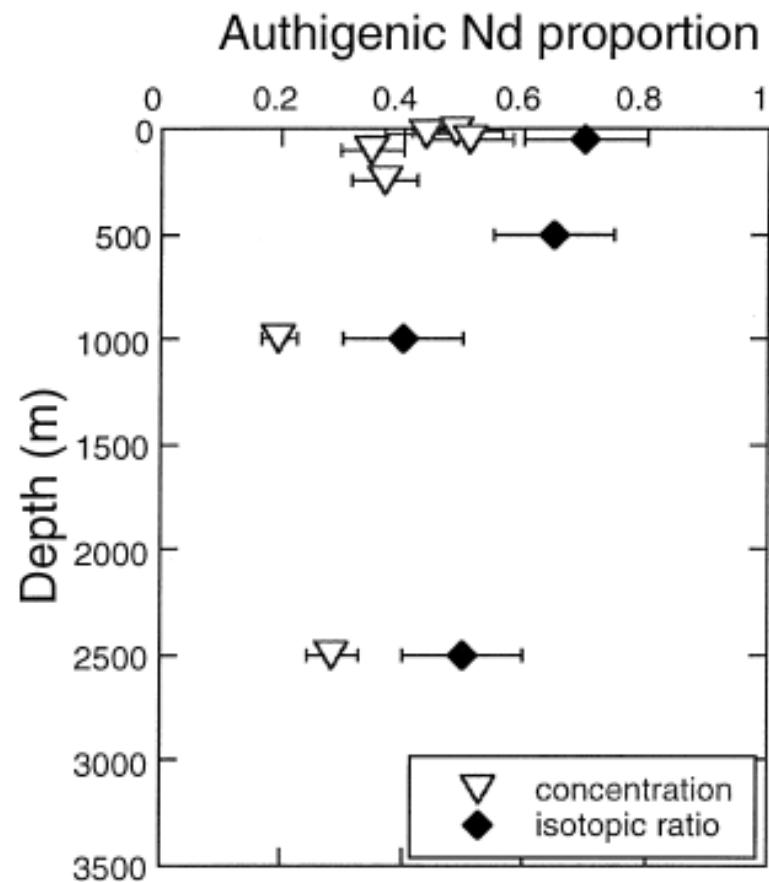
## leaching



$$X_{\text{auth}} = \frac{(\varepsilon_{\text{Nd}})_{\text{bulk}} - (\varepsilon_{\text{Nd}})_{\text{lith 2}}}{(\varepsilon_{\text{Nd}})_{\text{auth}} - (\varepsilon_{\text{Nd}})_{\text{lith 2}}}$$

Tachikawa et al., 2004

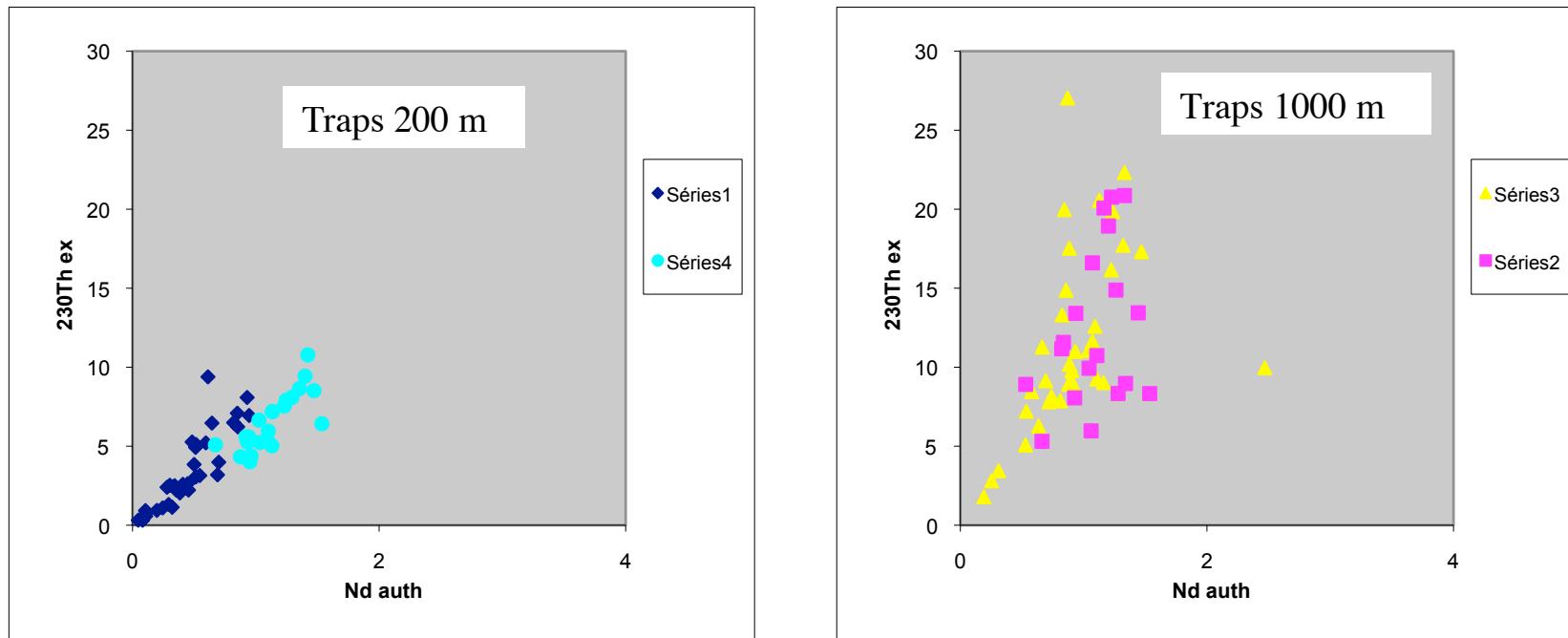
# Determination $K_d$ for Nd: Comparison of the 2 methods



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  $^{230}\text{Th}$

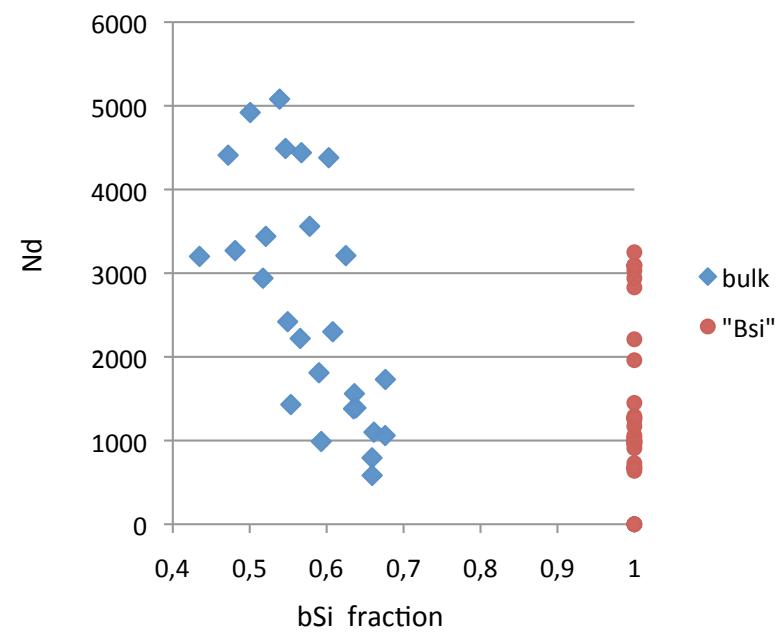
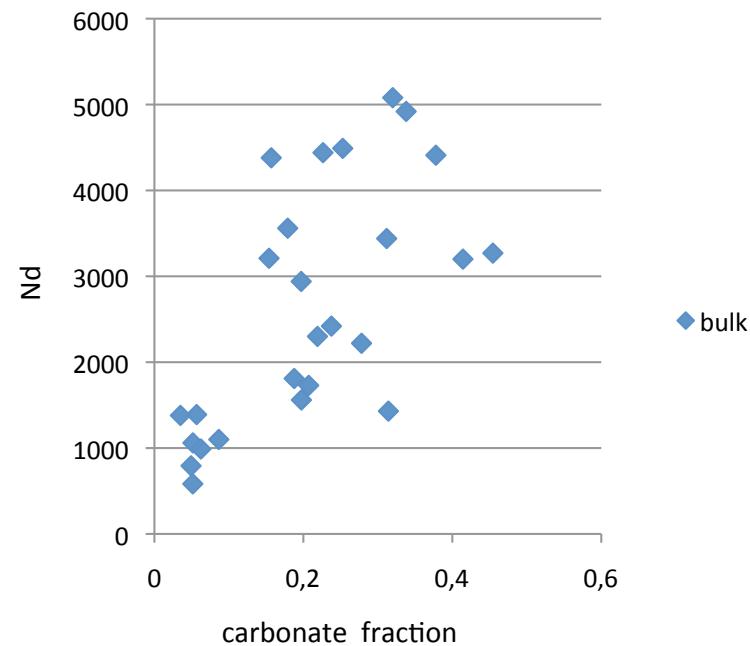


Adapted from Roy-Barman et al., 2005 and Guieu et al., 2004

# Determination K<sub>d</sub> for Nd:

## Do all phases have the same affinity for Nd?

## Carbonate versus bSi



Akagi et al., 2011

# Which phases carry $^{232}\text{Th}$ 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.

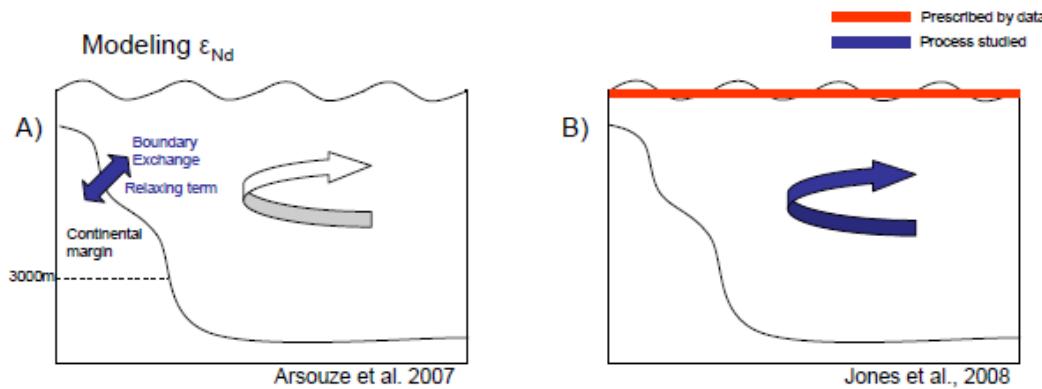
## **K<sub>d</sub> in models**

what appears in models  
(~30-50 m/y)

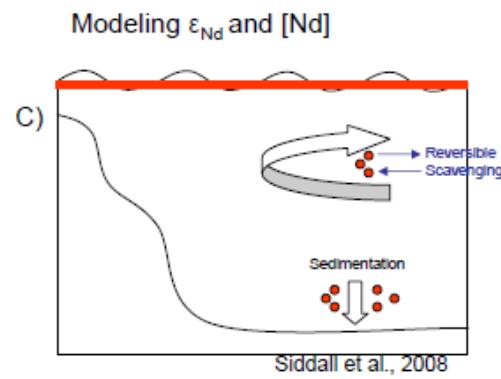
$$\frac{d[\text{tracer}]_{\text{total}}}{dt} = \text{Source} - \frac{d(S \times K_d \times C_p [\text{tracer}]_d)}{dt}$$

# Nd modeling: the role of particles

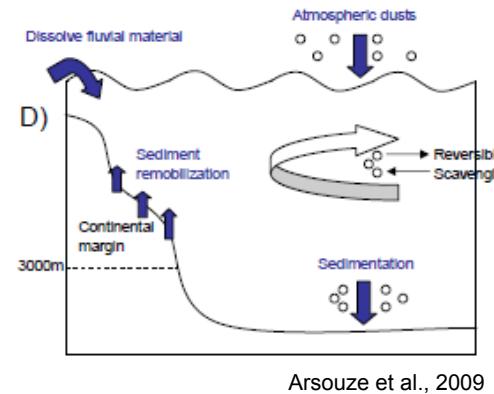
No particles



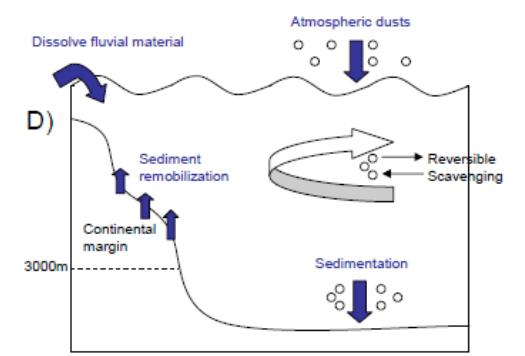
Particles composition  
Boundary input



bSi/CaCO<sub>3</sub>/litho  
No



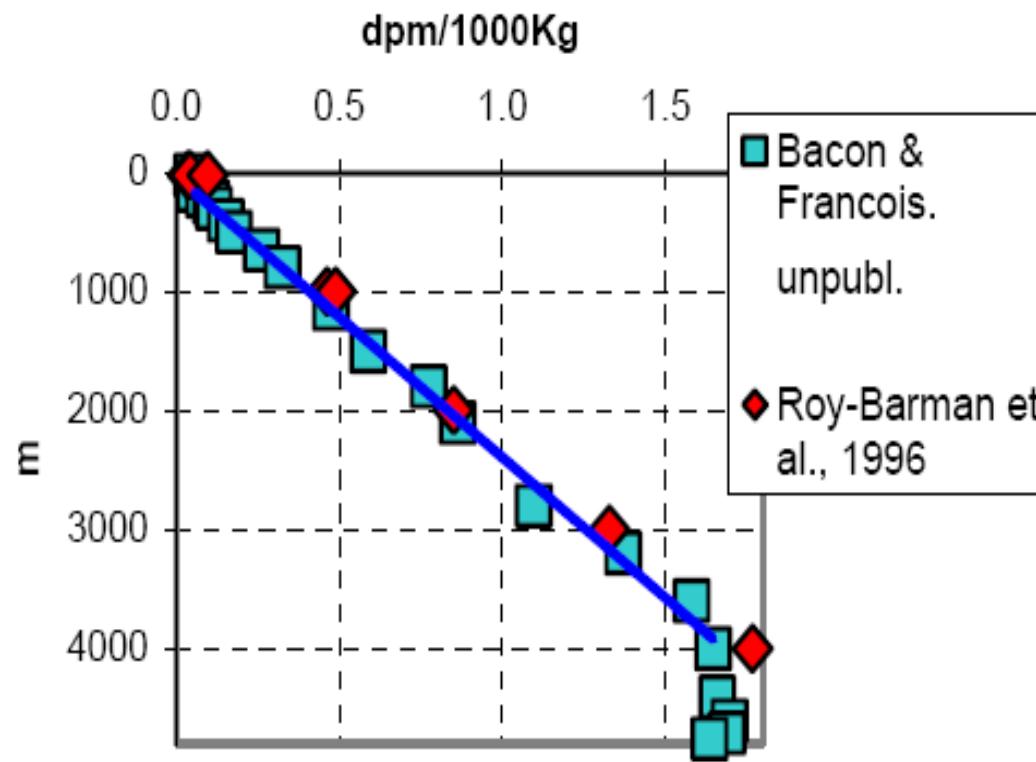
OM/litho  
yes



no  
yes  
Oka et al., 2009

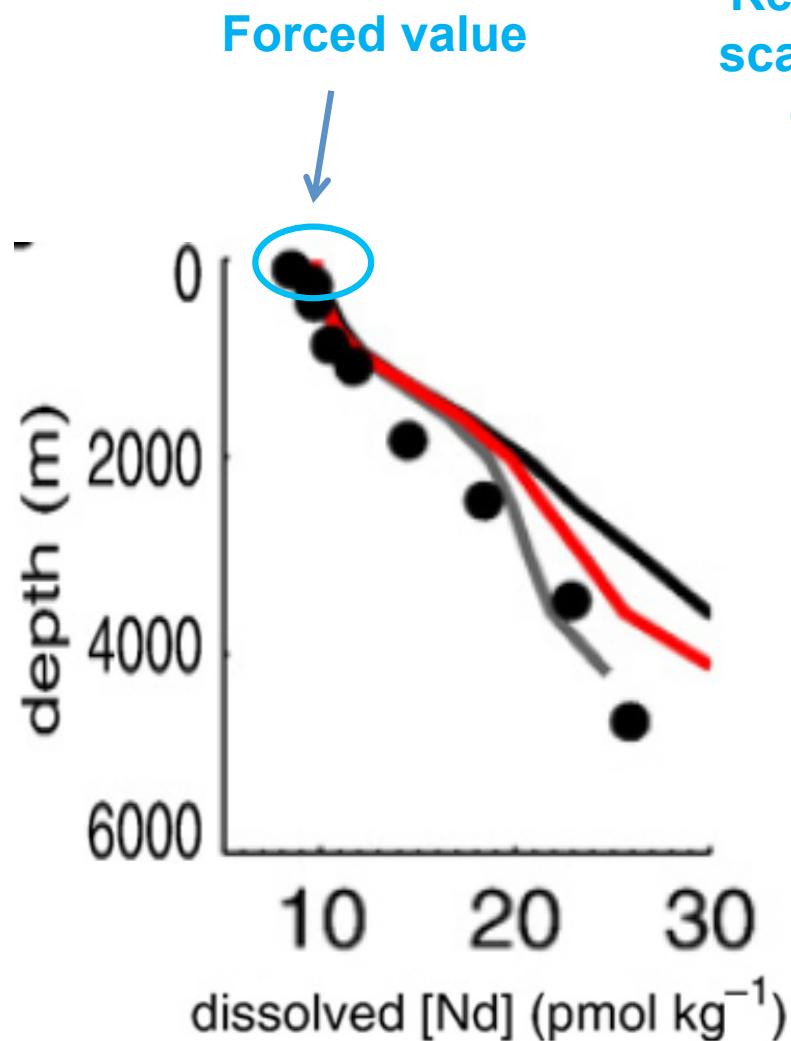
Adapted from Arsouze et al., 2009

# $^{230}\text{Th}$ argues against strong change of the Th bearing phase flux

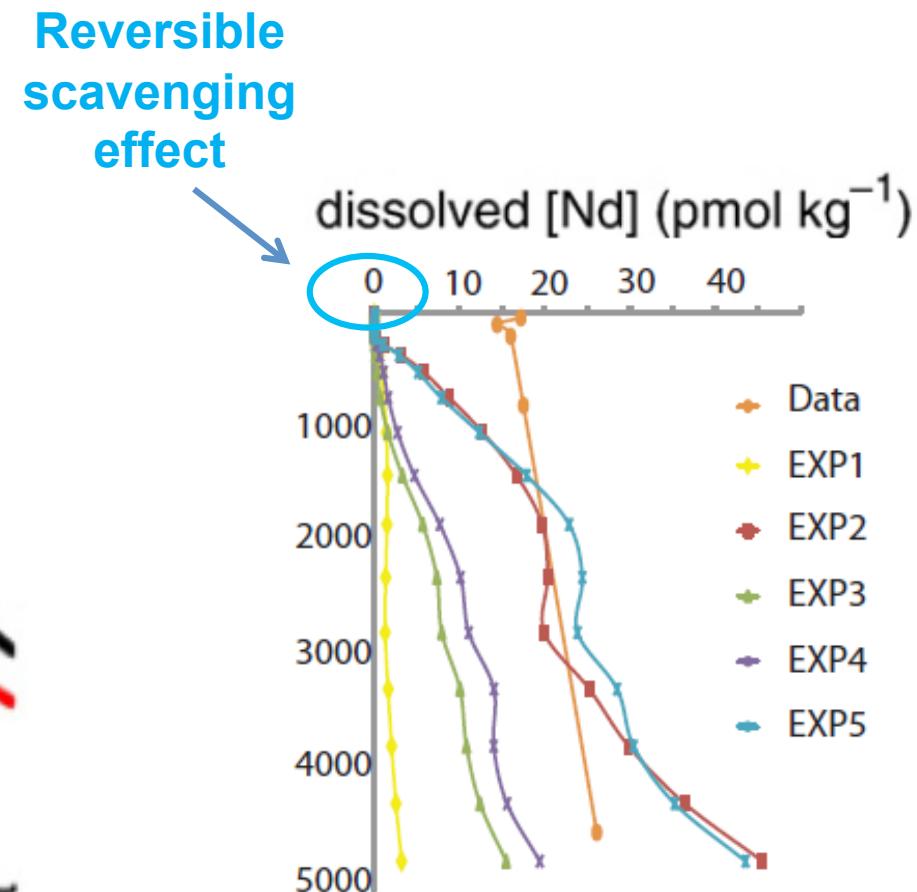


$^{230}\text{Th}$  and Nd are correlated so Nd bearing phases cannot be strongly dissolved.

## Nd modeling: the role of particles



Sidall et al., 2008



Arsouze et al., 2009

## Conclusions and recommandations

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