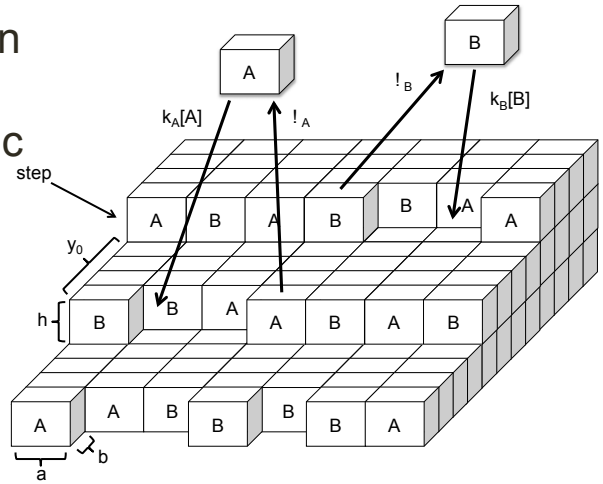
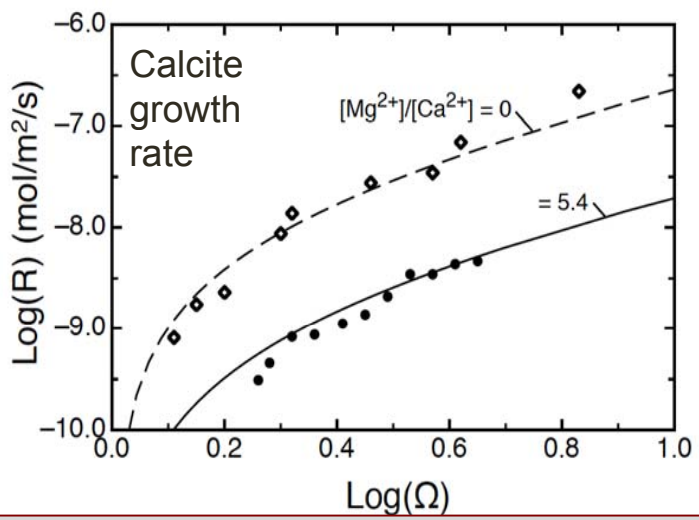
General model for calcite growth kinetics in the presence of impurity ions (Nielsen, DeYoreo, DePaolo; 2013)

Ion-by-ion growth schematic





Geochim. Cosmochim. Acta ***115****, 100–114*

Scientific Achievement

A single model employing ion-by-ion growth concepts can account for (1) calcite growth rate in presence of Sr and Mg, (2) Sr and Mg incorporation rates vs. growth rate, and (3) isotopic fractionation of Ca vs. growth rate

Significance and Impact

1. **First ever demonstration of a general model that accounts for growth kinetics under varying chemical conditions and oversaturation states**
2. **More realistic kinetics in reactive transport models**
3. **Guides interpretation of tracers for CO_2 injection**

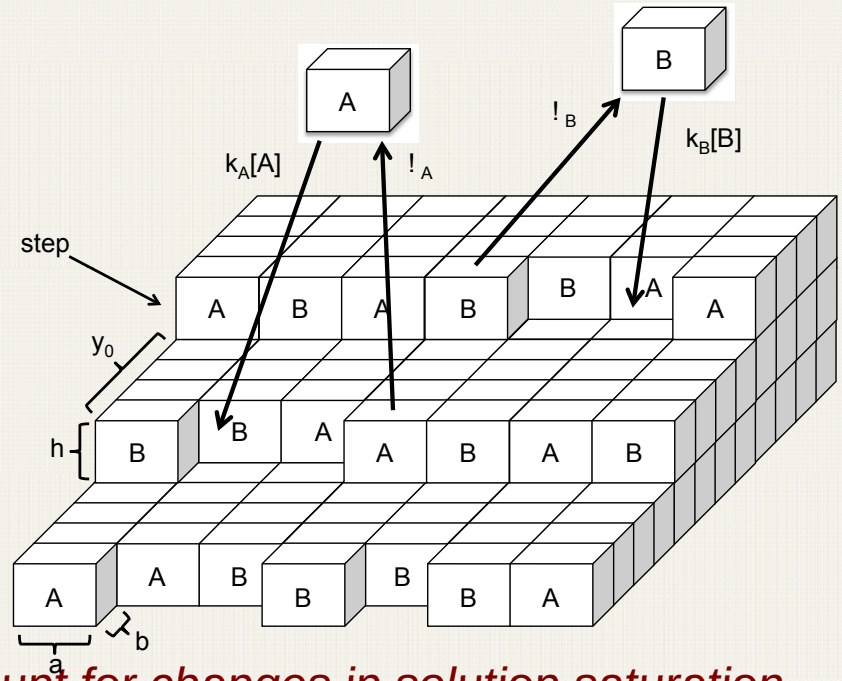
Research Details

1. **Equations for ion-by-ion growth are used in combination with experimental data to calibrate attachment/detachment rates and their dependence on composition**
2. **Derived parameters lead to expressions for elemental and isotopic ratios vs. growth rate**

Microscopic view of calcite growth at the solid-aqueous interface

(Nielsen, DePaolo, DeYoreo, 2012)

- Attachment and detachment of ions at kink sites controls precipitation rate andmineral composition
  - k_i = attachment rate coefficient (s^{-1})
  - v_i = detachment rate coefficient (s^{-1})
- Growth occurs if rate of attachment exceeds rate of detachment
- Attachment rate depends on concentration in solution eg. $k_{Ca}[Ca]$
- Detachment rate depends on kink density and <u>energetics (bonding)</u>

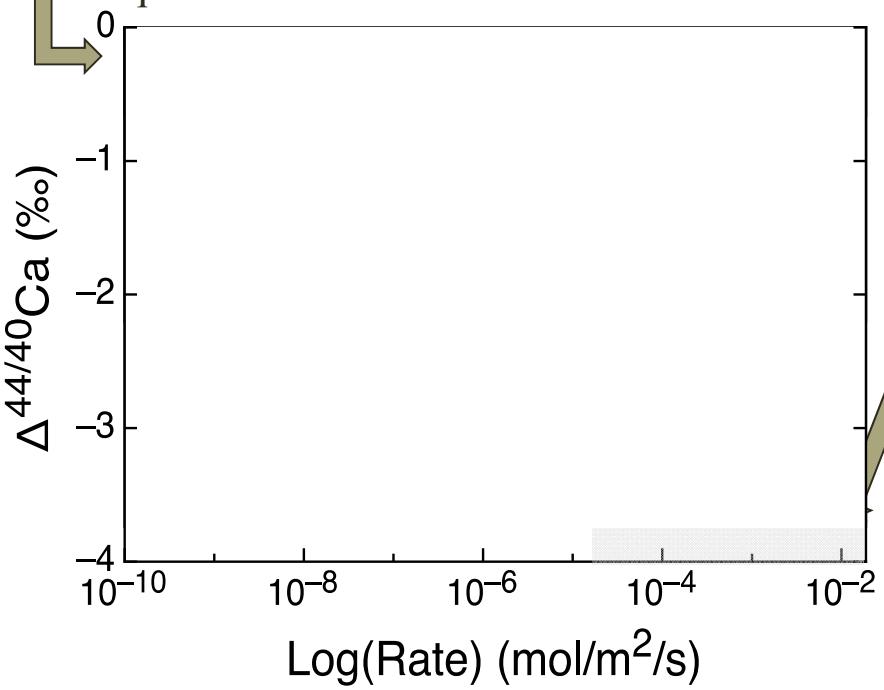


- *This model can simultaneously account for changes in solution saturation, solution stoichiometry, and presence of impurity ions in solution and in the solid*

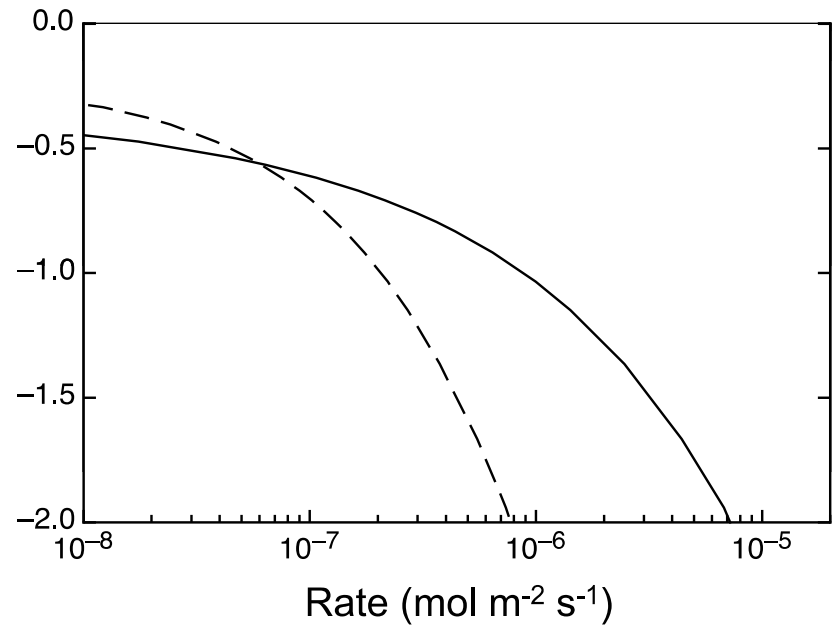
Zhang & Nancollas (1998) *J Colloid Interface Sci*, **200**

Model parameters are constrained by experimental data: AFM and $\Delta^{44}Ca$ vs Ω or precipitation rate

$\alpha_{eq} \approx 0.9998$



$\alpha_{kin} \approx 0.9963$

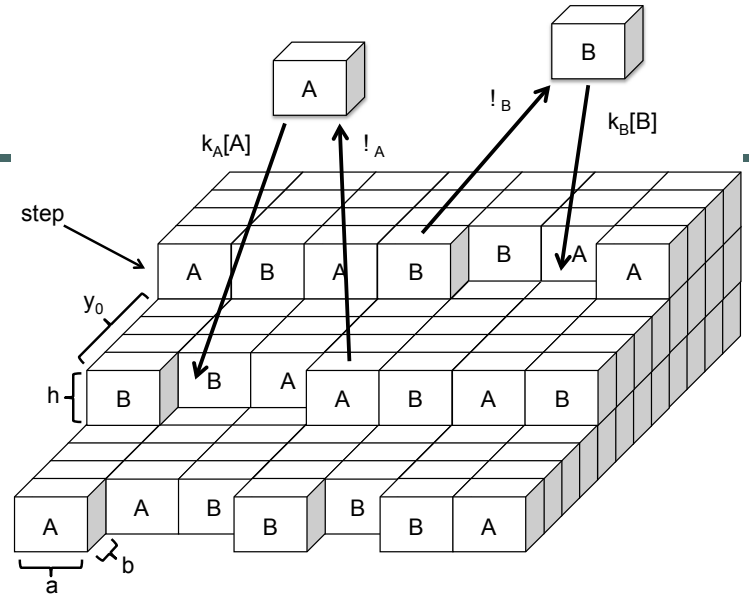


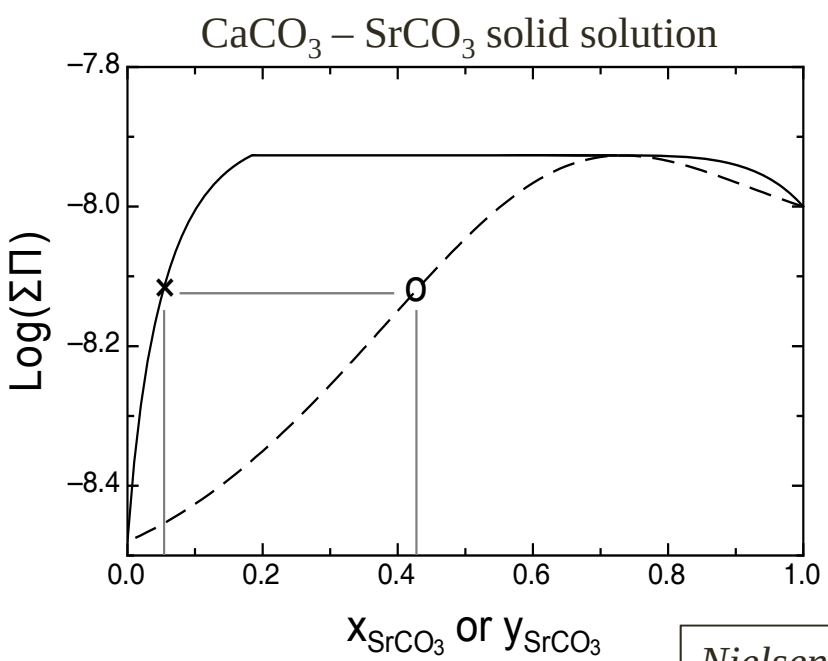
Still uncertainties in relating Ω to precipitation rate

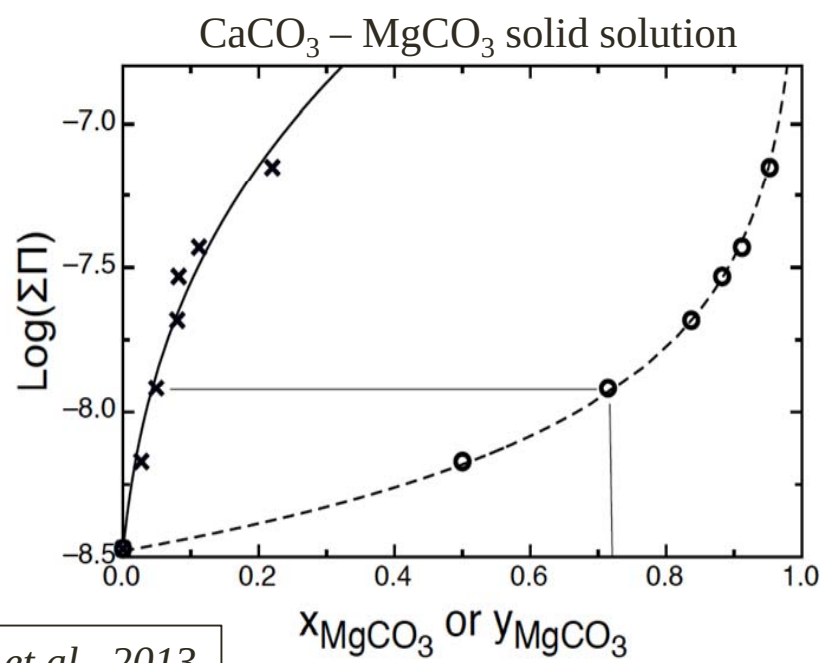
Adapted from Nielsen, DeYoreo and DePaolo, 2012

Incorporating thermodynamics into kinetic models

Challenge:
Microscopic exchange rates and energies are not directly measured; accessible only through solid solution *thermodynamics**
(*but depends on "equilibrium" experiments)

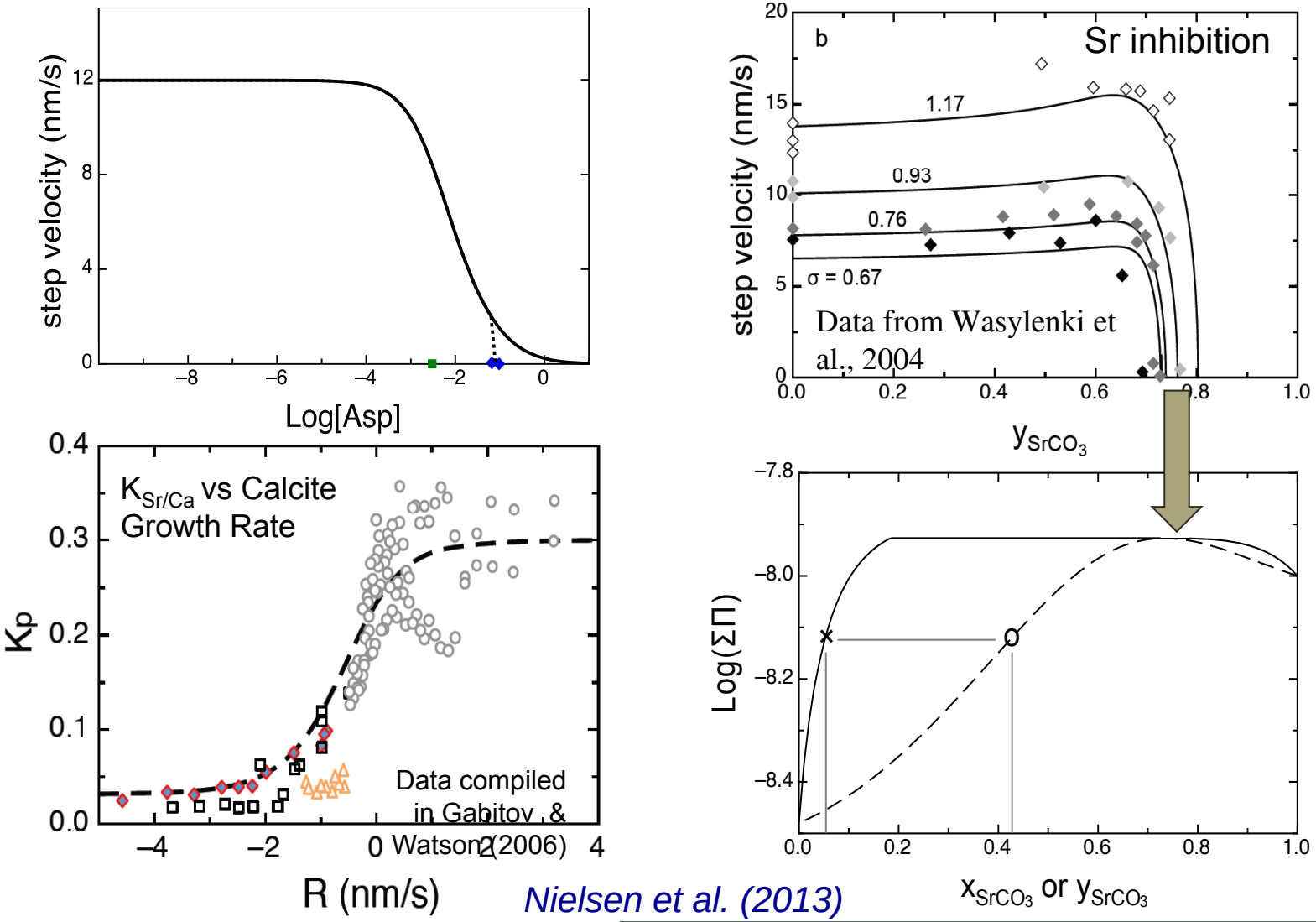






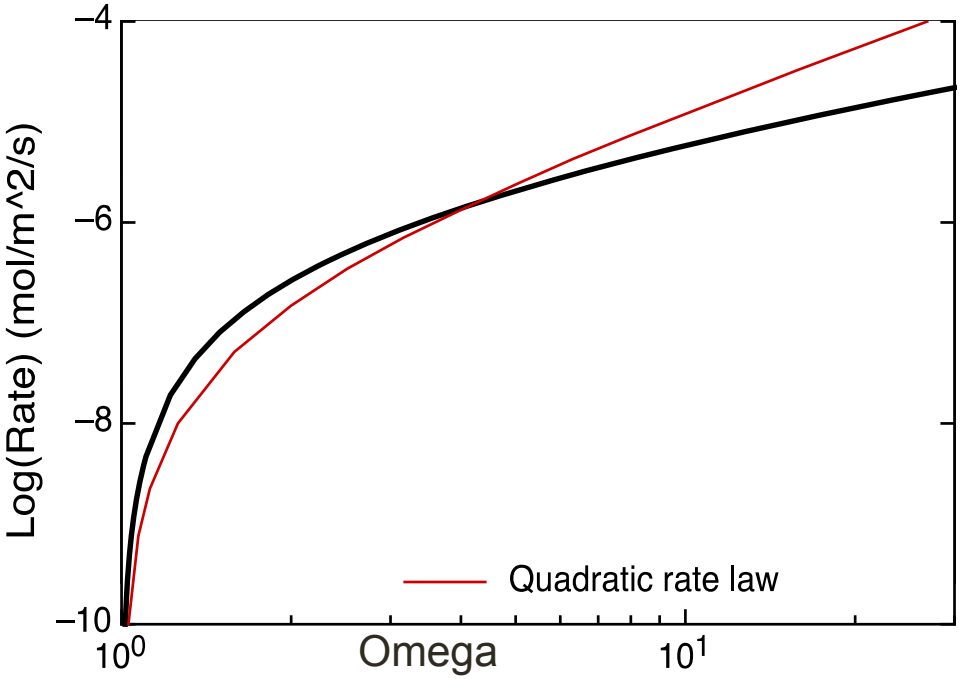
Nielsen et al., 2013

Ion-by-ion growth model concurrently treats partitioning and growth inhibition during calcite growth



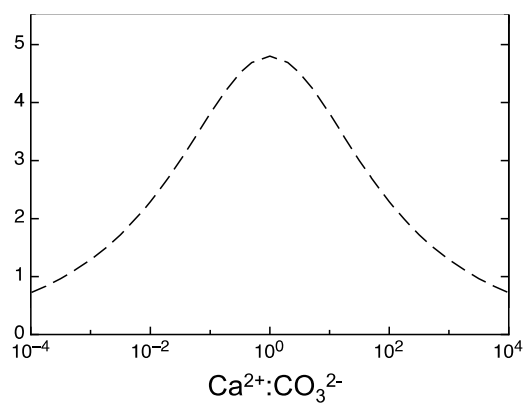
Nielsen et al. (2013)

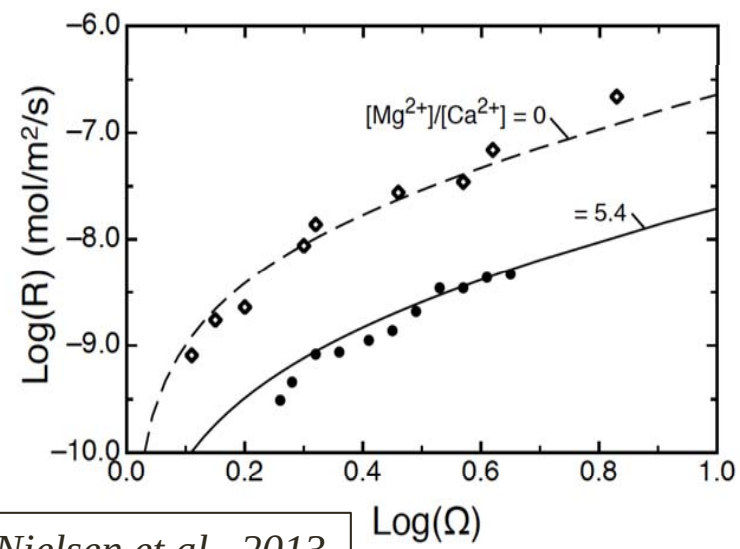
Ion-by-ion models provide comprehensive description of precipitation kinetics



- Ca isotopes augment microscopy by giving surface fluxes (rate constants)
- Trace elements lead to better description of impurity effects on growth kinetics

Single model describes calcite growth rates vs. saturation, Ca/CO_3 and Mg/Ca





Nielsen et al., 2013