

Supplemental Material for

Spatial variation of subduction zone fluids during progressive subduction: Insights from Mariana Serpentinite Mud Volcanoes (IODP Expedition 366)

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Overview

This document contains additional information pertaining to the thermodynamic and diffusion modelling and the two additional figures ([Supplemental Figures S1-S2](#)).

Thermodynamic modelling

Thermodynamic calculations were performed using the PhreeqC software (Parkhurst & Appelo, 1999), coupled with the EQ3/6 LLNL mineralogical database, in order to model various fluid compositions at equilibrium with the rock and sediments assemblages, at various temperatures. The initial aqueous composition chosen was that of bottom seawater (see [Table 1](#)).

Considered reactions were of the type: $wA + xB \leftrightarrow yC + zD$, with A and B as the reactants, C and D as the products of the reaction, and w, x, y and z as the stoichiometric coefficients.

Equilibrium between the aqueous solution (here starting with bottom seawater, outlined in [Table 1](#)) and the multi-phase mineral assemblages were calculated using laws of mass action: $K = [(a_C)^y (a_D)^z] / [(a_A)^w (a_B)^x]$, with K as the equilibrium constant.

The rock and sediments model composition (in wt.%) of basaltic rock and sediments entering the Mariana convergent margin are used as entry parameters ([Table S1](#)) were estimated from core analysis of Leg 185, which ran over the neighbouring Izu-Bonin arc, and which recovered non-altered sediments (site 1149) and altered volcanic rocks (site 801). A total of five mineral assemblages were considered, from 100% rock to 100% sediment, with a 20:80, 50:50 and 80:20 ratio ([Table S2](#)). The water-rock ratio remained fixed at 1:1 for every model.

Calculations to determine the composition of the fluid at equilibrium with those various assemblages were simulated in a closed “batch” system. The geochemical code CHESS (Van der Lee and De Windt, 2002) was used to calculate the molar concentrations (in mol/kg H₂O) of each mineral in the five mineral assemblages. This step was performed by dividing their massic percentage by their molar mass recorded in the LLNL EQ3/6 database. Those concentrations were then used as entry input parameters in the PhreeqC software as “Equilibrium phases”, coupled with the same LLNL EQ3/6 database, to calculate the final fluid composition at equilibrium, evolved from the initial fluid composition (bottom seawater).

The modeled fluid compositions were calculated over 12 discrete steps of 25°C, from 25°C to 300°C. Pressure was fixed at 1 bar between 273.15 and 373.15 K, then are obtained from the water liquid–vapour curve for $T > 373.15$ K. The values of log K were used as found in the databases. The extended Debye Huckel equation was used as the activity model. A Newton-Raphson method was used to solve the simultaneous mass-action equations. Depending on the mineral assemblages and the temperature conditions, it took between 100 and 200 iterations for the calculations to converge towards a stable set of aqueous concentrations.

Results of modelling are outlined in [Tables S2A-E](#)

Diffusion Modelling

We used the basic diffusion equation for sediment pore waters that are conservative and not affected by advection (Berner, 1980):

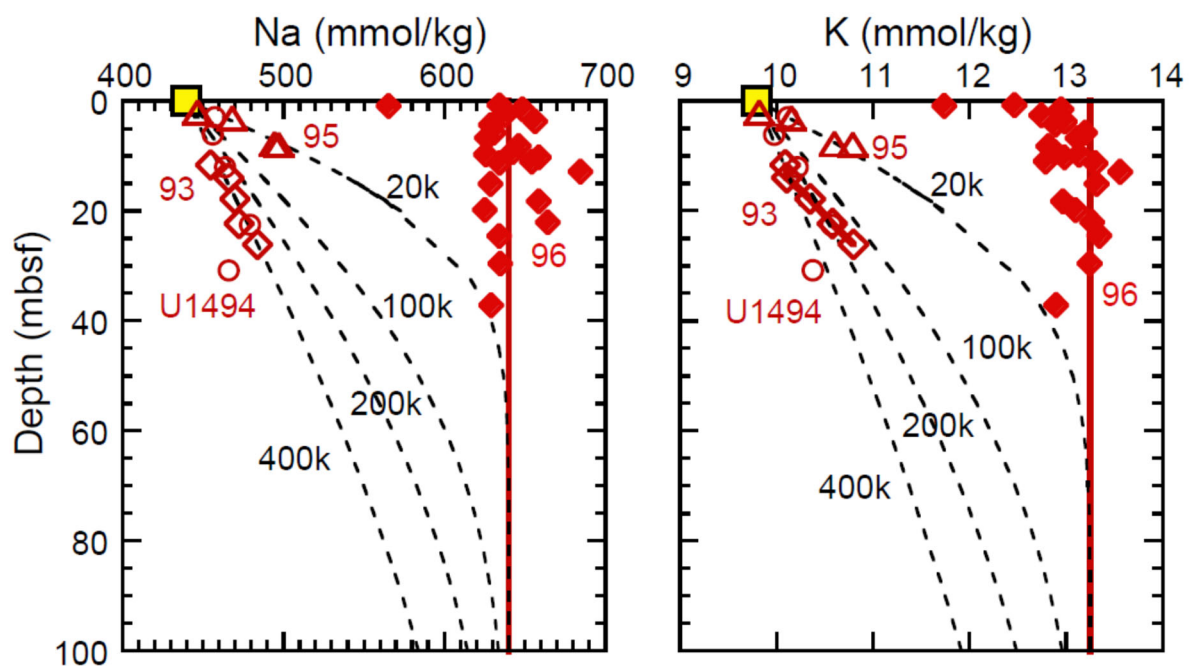
$$\delta C / \delta t = D_s (\delta^2 C / \delta x^2) \quad \text{equation 1}$$

where C is concentration, t is time, D_s is the sediment diffusion coefficient, and x is depth in a one dimensional system. We simply D_s assuming a constant temperature (2°C), values from Li and Gregory (1974), a constant porosity ($\phi = 0.5$), and a formation factor that is equal to ϕ^{-2} . Given the initial conditions of:

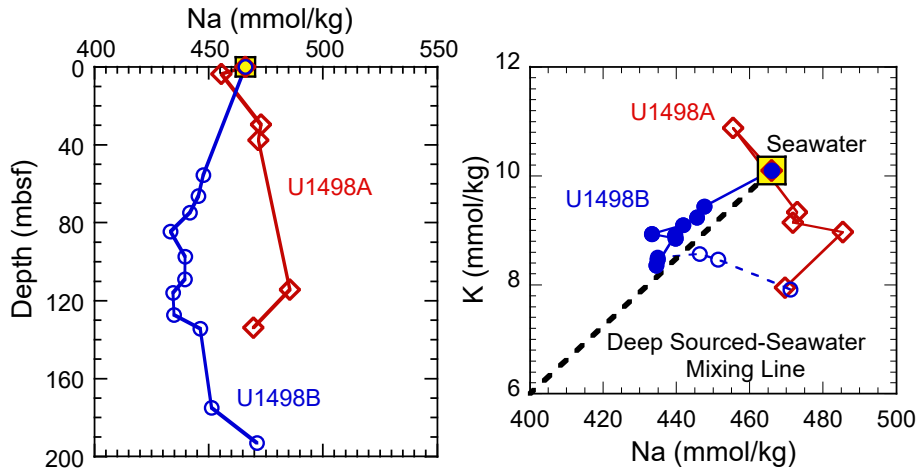
$C(x=0 \text{ m}) = C_o$ and $C(x) = 0$. In our simulation seawater at the sediment water interface is an infinite supply, thus $C(x=0 \text{ m}, t) = C_o$ holds. This situation has the following solution,

$$C(x,t) = C_o (1 - \text{erf}(x / (2 (D_s t)^{0.5}))) \quad \text{equation 2}$$

where erf is the error function (Crank, 1975). Thus, for a given depth and time we can calculate the concentration accounting for the offset between bottom seawater and the concentration of the deep-sourced fluid.



Supplemental Figure S1. Pore water concentrations of Na and K from Asut Tesoru Seamount plotted with depth. Bottom seawater is indicated by a yellow square. The solid vertical line represents the composition of the deep-sourced fluid. Dashed lines indicate simulations of the concentration based on the diffusion equation with boundary conditions that assume that the mass wasting event did not entrain seawater prior to deposition (equation 2). Several calculated profiles are provided to illustrate the maximum time since a mass wasting event deposited cored sediment.



Supplemental Figure S2. Plots of Na versus depth and K versus Na in pore waters from IODP Site U1498 on the flanks of Fantangisna Seamount. The C-shaped Na-depth profile of U1498B is indicative of diffusive exchange with bottom seawater and pore waters in the pelagic sediment below the serpentinite matrix. The K-Na trend from U1498B highlights the influence of the underlying pelagic sediment and seawater in diluting the deep-sourced serpentinite concentration (~ 400 mmol Na/kg and < 6 mmol K/kg, Table 1). Seawater is marked with a yellow square.

References

- Berner, R. A. 1980 Early Diagenesis. Princeton Univ. Press (21st August, 1980), 241 pp
- Parkhurst, D. L., & Appelo, C. (1999). User's guide to PHREEQC (Version 2) (Equations on which the program is based). *Water-Resources Investigations Report*, 99, 4259.
- van der Lee, J.; De Windt, L. CHESSTutorial and Cookbook, Updated for Version 3.0; Manual no. LHM/RD/02/13; Ecole des Mines de Paris: Fontainebleau, France, 2002; p 116.