

Tracers in deep-sea sediments cores

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It has previously been noted that there is a trend of increasing Ca and decreasing Mg and $\delta^{18}\text{O}$ with depth in pore fluid from deep-sea sediment cores (Fig. 1). This pattern has been interpreted as a signature of high-temperature alteration of basalt, where the Ca, Mg, and $\delta^{18}\text{O}$ profiles reflect diffusion upward through the pore fluid in the sediment column. It has recently been noted that δD also decreases in sediment pore fluid with depth (total decreases from top to bottom of a few ‰, examples shown in Figure 2) in virtually all sediment cores, regardless of other variables such as organic content, sedimentation rate, and chemistry of sediment.

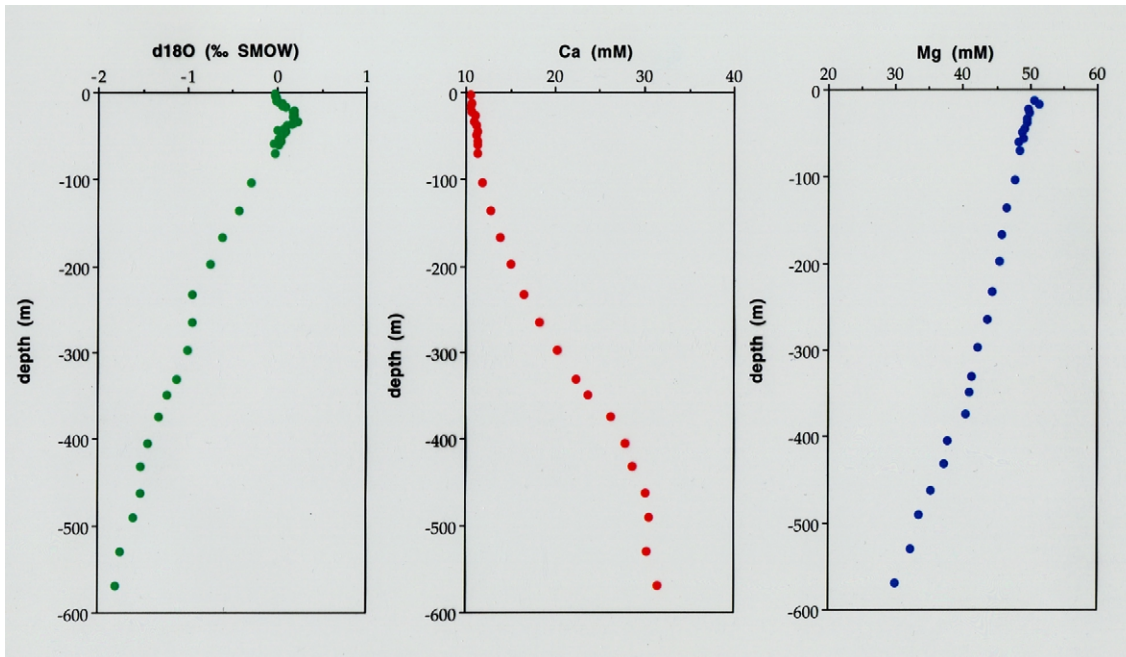


Figure 1. Examples of Mg, Ca, and $\delta^{18}\text{O}$ profiles measured in sediment cores.

The main question to be addressed is what process can account for these patterns in chemical tracers, and, ultimately, what does this imply for the flux of deuterium into the mantle from the subducted slab? Several explanations for the data have been proposed, which are summarized below (together an evaluation of each explanation by Dan Schrag during his talk).

1. *Deuterium content decreases because of alteration of oceanic crust and diffusive exchange with water involved in this reaction (similar to the explanation of patterns in Ca, Mg, $\delta^{18}\text{O}$).*

This model is unsatisfactory because alteration of plagioclase and pyroxene results in clay minerals with lower δD than seawater. This alteration would result in a correspondingly higher δD in the residual water, and thus the effects of diffusive mixing of residual water with pore fluid would produce the opposite of the observed trend.

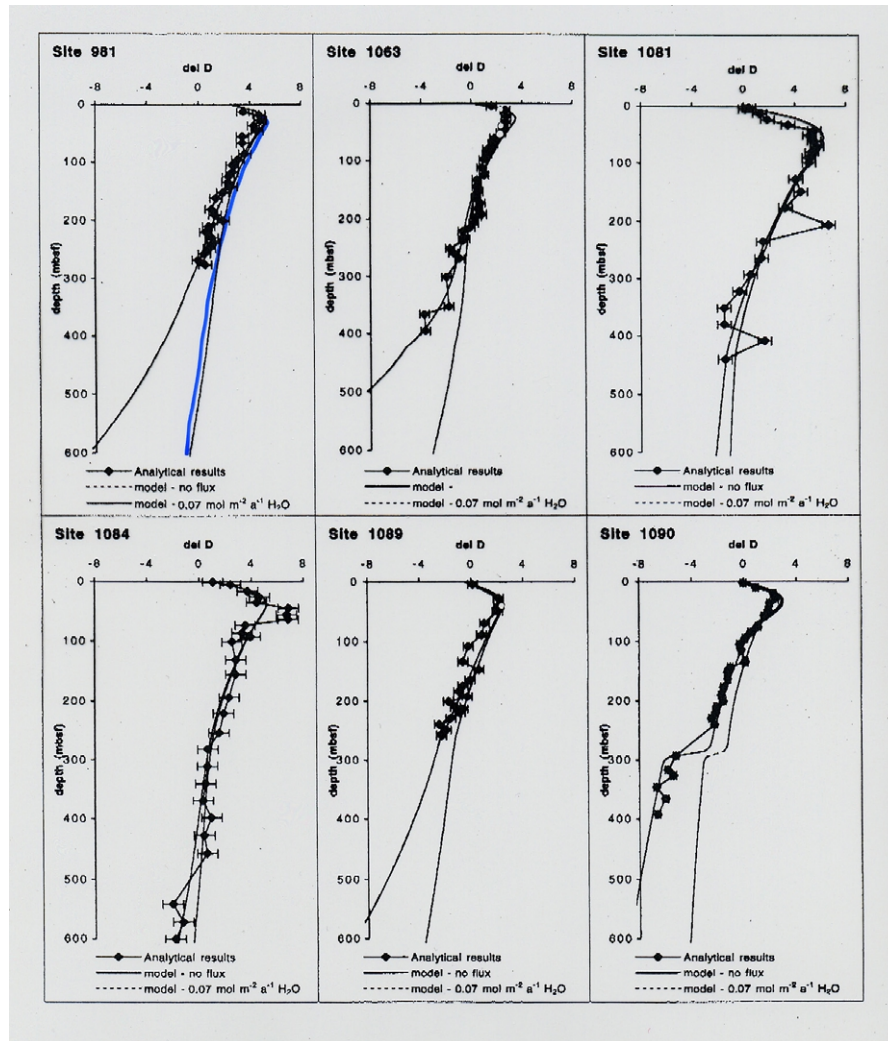


Figure 2. Examples of δD profiles and model calculations (Schrag et al., in press, EPSL). In most cases, models considering only low- δD paleo-ocean water without a flux of water from the crust (e.g., blue line in upper left panel, site 981) do not fit the data, whereas models incorporating a small flux of mantle water produce satisfactory fits.

2. Deuterium decreases because of adsorption of interlayer water in clays

Although adsorption could fractionate hydrogen isotopes, the volume of interlayer water is too small (in terms of mass balance of the pore fluid system) to explain the total decrease

observed down-hole. Furthermore, there is no systematic variation of δD with clay content of the sediment, as would be expected if this process were the major control on pore-fluid δD .

3. *Paleo-seawater had lower δD (at ~ 50 Ma, the δD of ocean water was about 10‰ lower than present-day, due to the lack of ice sheets), and the observed profile could simply be a record of this lower value.*

In diffusion/advection model calculations (Fig. 2), Schrag found that it cannot explain the general trend that persists across all profiles, although paleo-ocean water could explain the variations observed in some of the profiles.. Furthermore, paleo-ocean water could not explain the fact that the same decrease with depth is observed in profiles in young (<40 Ma) cores where the paleo-ocean water δD was more similar to present-day.

4. *Mantle water flux from underlying crust (δD of mantle water of about -70‰ has been estimated from analyses of hydrated mantle minerals in xenoliths and massifs)*

The residual water from alteration should have positive δD , because we know that alteration of oceanic crust is occurring, and that clays produced in this process are light (negative δD). In order for diffusion of mantle water to explain the pore fluid pattern two fluxes need to be considered. The flux of water out of the underlying crust must be greater than the flux of water into the crust that is required by alteration. This contradicts the general assumption that, because basalt is effectively anhydrous, there should be a net flux of water into the crust during alteration.

5. *H₂ and/or CH₄ from the mantle*

Serpentinization of the crust produces methane and H₂, which have δD of approximately -200 and -400, respectively. These might be end-members for mixing, which could explain the decrease in δD with depth. The complication is that in order to explain the signal measured in the pore water, the methane and H₂ would have to be oxidized again. This would destroy the negative δD signal that they originally carried – unless somehow they were oxidized again within the oceanic crust, in some unidentified sink for deuterium.

Discussion/implications

Thus the data appear to be best explained by a flux of low- δD water from the oceanic crust or upper mantle into the base of the sediment pile. Some other possible explanations that were raised in discussion include:

1. If $\delta D = -70$ is not actually representative of the true mantle value, and if the true value is substantially lower than -70, a small flux of mantle water could overwhelm the slight positive δD of residual water after alteration of oceanic crust to produce the observed trends.
2. Some as-yet-unidentified sink for deuterium exists in the oceanic crust (which would have to reside below the base of the sediment, otherwise it should have been identified in the cores, which for the most part go to basement).
3. Hubert Staudigel suggested that if there were massive alteration of oceanic crust at the ridge, and if the water formed during that alteration were lost, then subsequent dehydration of the altered oceanic crust off-axis could release water that is depleted in

deuterium relative to ocean water. Schrag's response was to say that such a process could explain the deuterium data, but not the corresponding patterns in Mg, Ca and $\delta^{18}\text{O}$, which would require continuing alteration to maintain the gradients after long-term diffusion. He also suggested that if heating of the (previously-altered) upper crust as it moves off-axis produces dehydration of alteration minerals, then there could be a net flux of water out of the oceanic crust which would overwhelm the ongoing alteration signal.

4. Jason Morgan suggested that if there were no net flux of water to the crust during low-T alteration of the crust off-axis, then diffusive exchange of pore fluid with deuterium-depleted water bound in serpentine could potentially explain the net decrease.

The importance in terms of fluxes between GERM reservoirs is that if the deuterium depletion in pore fluid is due to flux of mantle water from the crust, then this process could represent an important exchange between ocean water and mantle water.