Interfacial water:properties explored with an Atomic Force Microscope

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Structure and dynamics of ions and water at mineral-water interfaces: Insights from experimental and computational studies

The dynamic behaviour of water within nanometres of the solid interface and or under confinement has particularly interesting properties. One among many interests lies in the various geochemical applications [1]. Here**,** we present Atomic Force Microscope (AFM) force spectroscopy experiments which simultaneously capture the normal (structural) forces and lateral (viscous) forces as a function of tip-sample distance. To link the lateral force and interfacial viscosity, we modify the definition of Newtonian viscosity. When two plates are separated by d, the shear force required to slide one plate parallel to is proportional to the gradient of the fluid velocity, v_x, in the direction perpendicular to the plates.

$$F_L / A = \eta \, (dv_x/dz) \qquad (1)$$

The proportionality factor, η, is the viscosity of the liquid and A is the area of the shear. With substitution, we can relate the viscosity on a wetting surface Fig. 1(a), to that of a non-wetting surface, Fig. 1(b) to solve for the slip length, b [2]

$$\eta_{eff} = \eta^{b=0} \, v_{shear}/(d + b) \qquad (2)$$

Where $\eta^{b=0}$ is the interfacial viscosity of water, measured on a surface with zero slippage, and η_{eff} is the interfacial viscosity of water on a surface with slippage. This suggests the boundary viscosity of water strongly depends on the wetting properties of the surface.

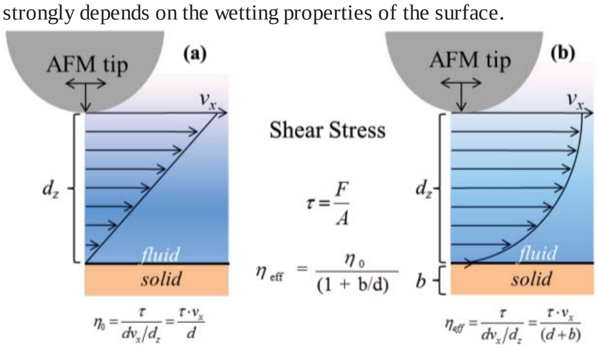

Figure 1. **Schematic of slip length from a shearing an AFM tip.** The wetting case is conveyed in (a) and non-wetting in (b).

We investigated the boundary viscosity and slip length as a function of gap size for mineral, crystalline and other carbon and carbon like surfaces. The slip length values will be discussed relative to surface properties, as well as surface wettability (contact angle), and viscosity.

[1] Stumm (1992) *Chemistry of the Solid-water Interface* **Wiley**.

The Pliocene closure of the Central American Seaway: reconstructing surface-, intermediate- and deep-water connections.

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Timing of Gateway Closure

The shoaling of the Isthmus of Panama and the associated reorganisation of deep-ocean circulation have been controversially reported as contributing to both a warming and a cooling of global climate. A resulting increase in moisture supply to the northern hemisphere, through the initiation or strengthening of the Gulf Stream, may have been an important precondition for Northern Hemisphere Glaciation. A robust timeframe for the closure of this major ocean gateway is essential for understanding its direct and indirect effects on global climate.

Method

We use radiogenic isotopes of Nd and Pb to reconstruct the history of shallow, intermediate and deep water connections between the Caribbean Sea and the eastern Equatorial Pacific Ocean from 5.0 to 2.0 million years ago. Surface water exchange is characterised using the Nd isotope composition of planktonic foraminiferal calcite. The Nd and Pb isotope compositions of early diagenetic ferromanganese coatings of the same sediment samples are employed to reconstruct intermediate and deep water exchange.

Results and Conclusion

Our results indicate that Caribbean Intermediate Water continued to diverge from a relatively constant Pacific deepwater Nd composition from 5.0 to 2.0 Ma. Comparison with published stable isotope and Mg/Ca records from the same ODP Sites 999, 1000 and 1241 suggest that Caribbean Intermediate Water composition continued to change even after a decrease in surface water exchange with the Pacific (4.5 Ma onwards [1]). A more rapid restriction of mixing between the Pacific and Caribbean at intermediate depths from 4 to 3.5 Ma clearly preceeded the major increase in ice-rafted-debris north of Iceland [2].

[1] Groeneveld *et al.* (2008) G^3 **9**, Q01P23. [2] Jansen *et al.* (2000) *Paleoceanography* **15**, 709-721.