

is probably different from the luminescent species in the TEOS- and TMOS-based silicates. The APTES-derived materials do not require heating over 100°C to be luminescent, and the FTIR spectra display strong absorption bands characteristic of amide (1663 cm⁻¹), ammonium (3277 cm⁻¹ and 2500 to 2000 cm⁻¹), and aliphatic (2950 to 2850 cm⁻¹) functionalities (Fig. 4, top curve). The Si-O asymmetric stretching bands (1126 and 1024 cm⁻¹) are characteristic of long-chain linear siloxanes (38). The PL quantum yield of the APTES-formic acid material (measured with 365-nm excitation) is 0.15 ± 0.03 in a dilute aqueous solution (39) and 0.35 ± 0.1 in the solid state.

The reaction of alkoxysilanes with organic acids is not new and has been used to prepare both SiO₂ glasses and molecular silicate complexes (40, 41). There are also reports of PL materials generated from the reaction of alkoxysilanes with photoluminescent organic acids (42, 43). Even more widely studied are the sol-gel reactions of organofunctional alkoxysilanes that give molecular solids with properties intermediate between organic polymers and inorganic ceramics (44–47). It is therefore surprising that the efficient PL of silicate sol-gels made from carboxylic acids has not previously been reported.

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under an atmosphere of nitrogen. The mixture was stirred for 15 min and the clear liquid was allowed to gel. After 3 days, the container was opened to the air and the excess liquid was decanted. The remaining clear glass was then air dried at 298 K for at least 1 day. The sol-gel was then placed into a programmable tube furnace with the following heating parameters: 1°C min⁻¹ from 25° to 150°C, followed by a 1-hour isothermal hold. The gel was then heated to 400°C at a 2°C min⁻¹ ramp, followed by a 4-hour isothermal hold. This procedure resulted in a transparent orange-colored glass with bright PL.

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The Late Neogene ⁸⁷Sr/⁸⁶Sr Record of Lowland Himalayan Rivers

Jay Quade, Lois Roe, Peter G. DeCelles, Tank P. Ojha

Fossil shells and paleosol carbonate from ancestral Himalayan river deposits provide a ⁸⁷Sr/⁸⁶Sr record of lowland Himalayan river water during the late Neogene. Reconstructed ⁸⁷Sr/⁸⁶Sr river values increased sharply in the late Miocene, probably marking the beginning of exhumation of high-⁸⁷Sr/⁸⁶Sr metalimestones, more in the central than in the western Himalayas. These results imply that the marine ⁸⁷Sr/⁸⁶Sr record may not be a proxy for silicate weathering or consumption of atmospheric CO₂ resulting from that weathering.

Large volumes of sediment were eroded and weathered as the Himalayas were uplifted starting ~60 to 50 million years ago (Ma). Weathering of these sediments—and specifically of silicate minerals—would have consumed significant quantities of atmospheric CO₂ (1), perhaps sufficient to cool global climate. Several records, including the ⁸⁷Sr/⁸⁶Sr ratio of the ocean, have been used as proxies for the extent of silicate weathering during this and other major uplift events. Starting ~40 Ma, there is a marked increase in the slope of the marine ⁸⁷Sr/⁸⁶Sr curve, which is thought to reflect the onset of significant weathering of high-⁸⁷Sr/⁸⁶Sr minerals in the Himalayas (2, 3). Himalayan rivers, mainly the Ganges and

Brahmaputra systems, are able to increase the marine ⁸⁷Sr/⁸⁶Sr ratio because of their high ⁸⁷Sr/⁸⁶Sr (>0.720) ratios and high Sr concentrations, which is the reverse of the usual relation in rivers (3). Edmond (3) suggested that this reversal is caused by Himalayan metamorphism, which redistributed Sr with a high ⁸⁷Sr/⁸⁶Sr ratio from Rb-rich silicate phases to more weatherable silicates such as Ca-feldspar. Others have argued that the weathering of carbonate rocks accounted for the major ion chemistry of many large Himalayan rivers (4) and that the source of high ⁸⁷Sr/⁸⁶Sr ratios may be metamorphically altered carbonate minerals (5).

Siwalik Group paleosols and fossils provide an archive for studying the impact of weathering reactions on lowland river composition during the late Neogene. The Si-

Department of Geosciences/Desert Laboratory, University of Arizona, Tucson, AZ 85721, USA.

walik Group was deposited by rivers that drained the Himalayas over the past ~14 million years (Fig. 1). Paleosols and accompanying soil carbonate are common in these deposits and formed in seasonally wetted floodplains adjacent to rivers. Oncolites and well-preserved mollusk shells, which once grew in rivers and river-fed floodplain swamps, are also locally present. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of soil carbonate represents a record of the weathering reactions in floodplain soils averaged over $\sim 10^3$ to 10^4 years. The carbonate is precipitated from soil so-

lutions infiltrating through the base of the soil en route to the water table and eventually into a river. Therefore, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of paleosol carbonates can be used to reconstruct the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of lowland Himalayan river water through time. This is supported by the similarity in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of modern ground water and local rivers (5). Moreover, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of soil carbonate (representing weathering reactions) is similar to that of well-preserved fossil mollusks, fish, and oncolites from the same stratigraphic levels (representing local

river water composition) (6) (Fig. 2). Finally, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of carbonate from the youngest Quaternary-age paleosols are close to the ratios of local modern rivers (Fig. 3).

Paleosol carbonates from five sections in Pakistan display a marked increase in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios starting ~7 Ma, but the magnitude of the shift varies (Fig. 3). On the Potwar Plateau, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary between 0.7086 to 0.7096 before 7 Ma and generally fall to between 0.710 and 0.716 after 5 Ma (Fig. 3C). Siwalik sediment in the Potwar Plateau was eroded from the western Himalayas and transported by large tributaries of the paleo-Indus (7) or possibly of the paleo-Ganges rivers (8). The shift in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios is much more subdued in Siwalik paleosols at Panir, where values never exceed 0.7087 (Fig. 3D). The lower two-thirds of this section probably represents deposits of the ancestral Indus River (9), perhaps fed by rivers flowing through the Potwar area.

Siwalik Group sediments in Nepal were deposited by large south-flowing tributaries of the Ganges, akin to the modern Karnali, Narayani, and Kosi rivers (10). Paleosol carbonates from three sections in Nepal display a marked increase in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios starting ~8 to 9 Ma, which is slightly earlier than in Pakistan, but then shows a major drop after 3 Ma, approaching the values found in local rivers today (Fig. 3A). The magnitude of the shift is similar to that in pedogenic clays from the Bengal Fan (11) (Fig. 3B) but appears to start earlier in the Nepal record, which is the larger data set. In general, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of paleosol carbonates from Nepal are markedly higher than those in Pakistan and range from 0.7147 to 0.7531.

The data show that the Ganges river system, past and present, is typified by high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, at all times well above the global average for rivers of ~0.7119. The rivers draining the western Himalayas (and

Fig. 1. Map of the Himalayan foreland, showing major river systems and Siwalik outcrops (outcrops in western Pakistan are not shown). We sampled nine measured sections extending from westernmost Pakistan to central Nepal. Detailed locations of the Potwar sections are given in (15). A magnetostratigraphic correlation (18) adjusted by us to the Cande and Kent (19) time scale provides the age control.

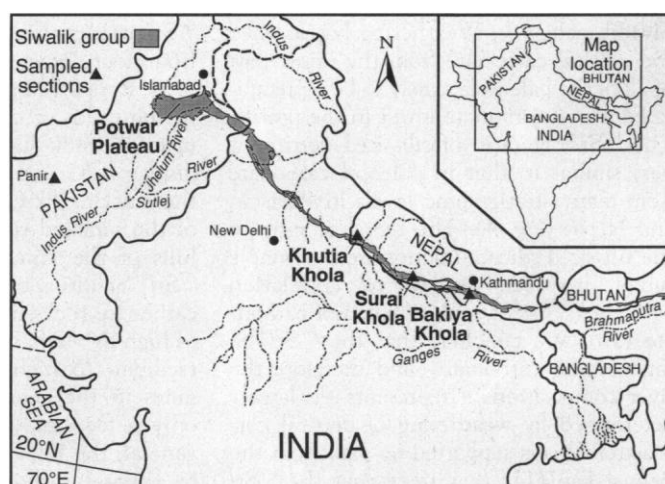


Fig. 2. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of soil carbonate versus $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of shell/oncolites/fish from adjacent stratigraphic levels. Soil carbonates and fossil shells (eight samples), oncolites (one sample), and fish (four samples) occurred in close (2 to 60 m) stratigraphic proximity. Soil carbonate is composed of dense micrite that has remained a closed system isotopically since burial (13). Shells are nearly all aquatic bivalves and are nacreous and aragonitic, which indicates good preservation. Oncolites are composed of solid micrite and are from channel lags.

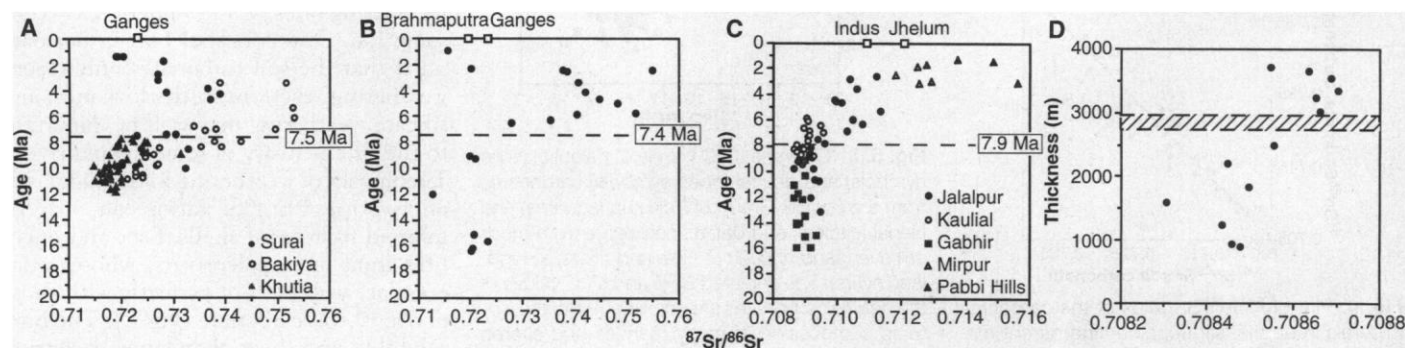
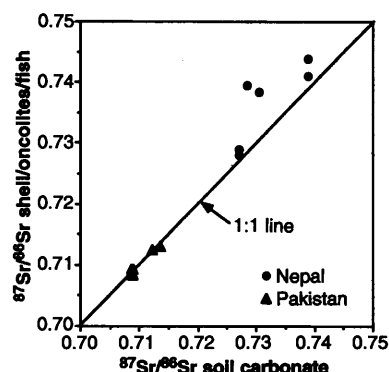


Fig. 3. Plots versus time or stratigraphic level of (A) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of soil carbonate in Nepal, with an inset of three sections sampled, (B) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of pedogenic clays in the Bengal Fan (11), (C) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of soil carbonate from the Potwar Plateau, with an inset of sampled sections [see

(15)], and (D) $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of soil carbonate from Panir (largely undated). River data [(4, 20) and our results] are indicated by open squares; dashed lines with dates or cross-hatched zone denote first appearances of definite C_4 plants in each section (13, 14).

represented by the Potwar Siwaliks), like the modern Indus, had low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, especially before 7 Ma. We have no data from the ancestral Brahmaputra system in the Siwaliks, but the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the modern Brahmaputra River suggest that it was most like the Ganges system.

A late Miocene-age shift in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Nepal and Bengal Fan records has been attributed to changes in source rocks undergoing weathering (12) or to changes in weathering intensity caused by climate change (11). Evidence for possible climate change comes from carbon isotopes in paleosols (13) and the Bengal Fan (14), which record a continent-wide expansion of C_4 grasses beginning 8 to 7.5 Ma (Fig. 3). The expansion may be related to an increase of wet summer (monsoonal) conditions in the region (15), which may have also enhanced chemical weathering of silicate minerals (11).

Our data show that the relation between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of ancestral Himalayan rivers and climate change—if it exists at all—is a complex one. First, the major shift of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the Potwar Siwalik system lagged behind the C_4 expansion by ~1 million years, whereas the same shift in Nepal (Ganges tributaries) preceded the local C_4 expansion there by ~1 to 2 million years. Moreover, the Ganges $^{87}\text{Sr}/^{86}\text{Sr}$ ratios drop after ~3 Ma, unlike the ratios in the Potwar. This drop in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios after 3 Ma in the Ganges record has been explained by the onset of glacial conditions in the Himalayas (11). Why then is it not apparent in the western Himalayan record (Potwar Siwaliks), where Quaternary-age glaciation has also been extensive? Finally, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the western Himalayan river system, past and present, are markedly lower than those in the Ganges River. Here climate differences could be invoked: Lowland Nepal is slightly warmer and re-

ceives over twice as much rain as the Potwar Plateau, a condition that might lead to increased chemical breakdown of silicates.

Alternatively, variation in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of sediment being shed off the Himalayas, not the effects of climate, could explain the regional differences and temporal shifts in the $^{87}\text{Sr}/^{86}\text{Sr}$ record from rivers. Detrital silt and sand in the Siwaliks and many modern Himalayan rivers are dominated by silicate minerals but also contain from 3 to 20% carbonate in the silt fraction. Unaltered floodplain silt containing this carbonate is exposed above and below most Siwalik paleosols. Weathering has leached the detrital carbonate from the upper part of all of the paleosols, partly to be reprecipitated as soil carbonate lower in the profile. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of silt-sized detritus is very similar to that in paleosol carbonate from many stratigraphic levels in Pakistan and Nepal (Fig. 4). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the silt-sized silicate fraction from a sample subset, however, displays no correlation with the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of paleosol carbonate (16). We conclude that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of soil carbonate—and therefore the river compositions it represents—is largely determined by weathering of detrital carbonate. This is supported by data from the Bengal Fan (11) that show that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of at least the whole-rock silicate fraction does not vary greatly and therefore cannot explain the large $^{87}\text{Sr}/^{86}\text{Sr}$ variations in pedogenic clays in that record with time. The $^{87}\text{Sr}/^{86}\text{Sr}$ values of the carbonate

fraction in the Bengal Fan have not been determined.

Low oxygen isotopic values [$\delta^{18}\text{O}$ [Pee Dee Belemnite (PDB)] = -15 to -9 per mil] set the detrital carbonate apart from most Siwalik soil carbonate. These values, combined with low carbon isotopic values (-6 to -2 per mil), imply that the source of detrital carbonate is metamorphosed carbonate rocks (Fig. 5).

Our petrographic observations of sands in modern Nepali rivers verify the presence of coarsely crystalline, metamorphosed carbonate grains, mixed with lesser amounts of micritic limestone grains (10). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of this carbonate in sand and silt from four large lowland rivers in Nepal range from 0.722 to 0.734, which are similar to the ratios of carbonate in silt from the upper Siwalik Group. The same samples display $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values that overlap those of Siwalik Group silt (Fig. 5). Several of the sampled rivers drain only the foothills of the Himalayas. In foothill areas, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of slightly metamorphosed carbonate rocks in the lesser Himalaya are as high as ~0.8, and 0.709 to 0.714 in the medium- to high-grade metamorphic terranes in the central Himalayas (11), but only a few analyses have been made. In general, the high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios displayed by detrital carbonate in rivers would be unusual for carbonate rocks on a regional scale, although locally marbles and limestones are known to acquire high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios through exchange of Sr with silicates during metamorphism (17).

The strong correlation between the $^{87}\text{Sr}/^{86}\text{Sr}$ value of soil carbonate and detrital carbonate, both in space and time, implies that widespread unroofing of metamorphosed carbonate rocks beginning in the late Miocene can explain the marked increase in Himalayan riverine $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. If our interpretations are correct, then the record of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Himalayan rivers (and late Neogene oceans) cannot be used to infer silicate weathering rates or atmospheric CO_2 consumption. One potential bias in our data set is that the soil carbonates only record weathering reactions in the lowlands, and silicate weathering may well be important to the Sr chemistry of some upland rivers.

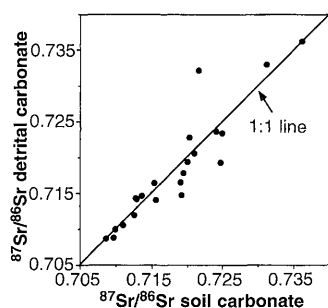


Fig. 4. Plot of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the carbonate minerals in detrital silt (representing parent material) and of soil carbonate (representing weathering products) from similar stratigraphic levels. The strong similarity implies that carbonate detritus in silt is the main source of radiogenic Sr from weathering.

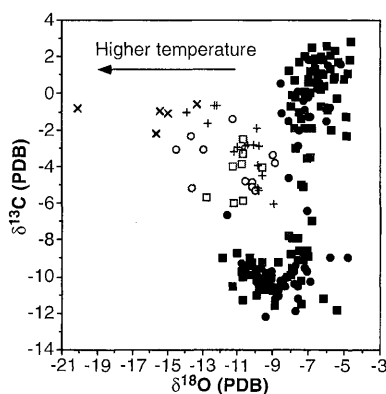


Fig. 5. $\delta^{13}\text{C}$ versus $\delta^{18}\text{O}$ values of paleosol (solid symbols) and detrital (open symbols) carbonates from the Siwalik Group of Pakistan (squares) and Nepal (circles), and detrital carbonate from modern river sand and silt (+, lowland rivers; x, highland rivers). The depleted $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the detrital carbonates are consistent with the isotopic composition of many marbles and altered limestones (21) outside the Himalayas. Carbonate detritus in the Siwalik Group appears to derive mainly from carbonate rocks drained by lowland rivers, not from higher temperature carbonate rocks eroded by highland rivers.

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6. Carbonates were selectively dissolved for Sr analysis with doubly distilled 1 M acetic acid, which has been shown to leach Sr from silicates negligibly [J. Quade, A. R. Chivas, M. T. McCulloch, *Paleogeogr. Paleoclimatol. Paleoecol.* **113**, 103 (1995); Y. Asahara *et al.*, *Earth Planet. Sci. Lett.* **133**, 105 (1995)]. $^{87}\text{Sr}/^{86}\text{Sr}$ analyses were performed on a VG 354 at the University of Arizona. Sixty-nine NBS-987 standards during this study yielded a mean of 0.710218 ± 11 (2 σ). All light stable isotope analyses on carbonates are reported relative to PDB with the use of standard notation, where $\delta^{13}\text{C}(\text{PDB})$ or $\delta^{18}\text{O}(\text{PDB}) = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$ and $R = {}^{13}\text{C}/{}^{12}\text{C}_{\text{sample}}/{}^{13}\text{C}/{}^{12}\text{C}_{\text{standard}}$ or ${}^{18}\text{O}/{}^{16}\text{O}_{\text{sample}}/{}^{18}\text{O}/{}^{16}\text{O}_{\text{standard}}$, respectively. We used the single-vessel fractionation factor between CO_2 and CaCO_3 of P. K. Swart, S. J. Burns, and J. J. Leder [*Chem. Geol.* **86**, 89 (1991)]; no correction was made for the presence of dolomite grains in some of the detrital samples.
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9. Petrographic evidence from the Panir section suggests that the provenance is distant Himalayan metamorphic rocks and more local Eocene Kirthar limestone. The low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios displayed by soil carbonate in this section may result from weathering input by Eocene limestone into the ancestral middle Indus River system. Evidence that the lower two-thirds of this section represents the ancestral Indus River are that paleocurrent directions are generally southward and that phyllite and metaquartzite grains with accessory garnet indicate a Himalayan source.
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Topographically Induced Mixing Around a Shallow Seamount

Rolf G. Lueck* and Todd D. Mudge

Measurements of the rate of dissipation of kinetic energy around a shallow seamount in the eastern North Pacific show that mixing there is 100 to 10,000 times as large as that far away from the seamount. If such values are typical of other seamounts, mixing across density surfaces in the ocean occurs mainly at their boundaries, and topographically induced mixing may help to explain the discrepancy between the observed intensity of mixing in the interior of the oceans and that required to satisfy models of ocean circulation.

Predictive models required for scientific and practical problems associated with the present and future climate, with biological activity, and with waste disposal require a firm understanding of mixing in the ocean. The distribution of heat, salt, and chemical substances depends on mixing along and across surfaces of equal density (1). Many indirect measurements (2–5) and the recent direct measurement of vertical diffusivity, obtained through the intentional release of an inert tracer (6), show that mixing across density surfaces is weak within the thermocline and that the eddy diffusivity (K_v) is only $\sim 10^{-5} \text{ m}^2 \text{ s}^{-1}$ (7), one-tenth the value predicted by most models of ocean circulation (8, 9). This discrepancy has motivated the search for intense localized mixing, which may increase the basin-wide average, and has renewed interest in the notion that mixing occurs primarily at the boundaries of the ocean (8, 10).

Temperature, salinity, and other characteristics acquired at the boundaries are readily transferred along isopycnals or, more correctly, along neutral surfaces (11) by mesoscale eddies. Therefore, mixing near boundaries generates an apparent cross-isopycnal diffusion in the interior of the ocean (10, 12, 13), but it must be larger by several orders of magnitude than mixing in the open ocean to increase the basin-average diffusivity.

The effectiveness of mixing near the bottom of oceans is uncertain. Various processes can propel mixed water at a sloping boundary into the ocean interior (12, 14), but with little effect if the strongest turbulence occurs within the diminished stratification of a mixed layer at the bottom (15) (which is only a few tens of meters thick). Topographically related processes that can generate mixing hundreds of meters above the bottom, where the water is stratified, include the reflection of internal waves (16–18) and the generation of internal tides (19, 20). Tidal energy may be an important source for mixing. The rate of tidal dissipation by friction is $(2.5 \pm 0.05) \times 10^{12} \text{ W}$ (21), and shallow seas can account for one-half to three-quarters of it (22). The missing dissipation has been puzzling, but tidal energy can also be converted into internal waves by interaction with topography (19), and the energy flux to internal waves may account for almost half of all tidal dissipation (23).

Here we describe large amounts of mixing around Cobb Seamount, located 500 km west of the United States at $46^\circ 45' \text{N}$ and $130^\circ 50' \text{W}$ (Fig. 1), and discuss the implications for basin-wide diffusivity. The proximity of this seamount to the coast and its shallow depth make it amenable to measurements of mixing that would otherwise be difficult and limited in scope. Cobb Seamount rises from the abyssal sea floor at a depth of 3000 m to a narrow pinnacle 27 m below the surface of the water. Slopes are small inward from the rim at 250-m depth. Microstructure

Centre for Earth and Ocean Research, University of Victoria, Post Office Box 1700, Victoria, British Columbia V8W 2Y2, Canada.

*To whom correspondence should be addressed.