12. P. Jutzi, D. Kanne, C. Krüger, *Angew. Chem.* **98**, 163 (1986). [For a review, see (*11*).]
13. P. Jutzi, G. Reumann, *J. Chem. Soc., Dalton Trans.* **14**, 2237 (2000).
14. P. H. M. Budzelaar, J. J. Engelberts, J. H. van Lenthe, *Organometallics* **22**, 1562 (2003).
15. The gas-phase species $(Me_5C_5)Si^+$ has been observed in the mass spectrum of $(Me_5C_5)_2Si$ (*11*).
16. P. Jutzi, U. Holtmann, H. Bögge, A. Müller, *J. Chem. Soc., Chem. Commun.* **1988**, 305, 1988.
17. P. Jutzi, C. Müller, A. Stammler, H. G. Stammler, *Organometallics* **19**, 1442 (2000).
18. P. Jutzi *et al.*, in *Organosilicon Chemistry: From Molecules to Materials*, Vol. VI, N. Auner, J. Weis, Eds., Wiley-VCH, Weinhein, in press.
19. M. Otto *et al.*, *Angew. Chem.* **114**, 2379 (2002).
20. Prepared by reaction of Me_5C_5H with $H(OEt_2)_2{}^+$ $B(C_6F_5)_4{}^-$ in CH_2Cl_2. ^1H NMR data of the $Me_5C_5H_2{}^+$ cation correspond to those given in (*19*).
21. NMR data of **2** in CD_2Cl_2, δ (ppm): ^1H NMR (600.13 MHz) 2.23 (singlet, 15 H, methyl protons); ^{13}C NMR (150.92 MHz) 9.0 (methyl carbons) 122.7 (C_5-ring carbons), 124.0 (broad), 136.6 [doublet, ^1J(C,F) = 245 Hz], 138.5 [doublet, ^1J(C,F) = 244 Hz], 148.4 [doublet, ^1J(C,F) = 239 Hz (aromatic carbons)]; ^{29}Si NMR (99.34 MHz) −400.3; ^{11}B NMR (160.43 MHz) −16.7; ^{19}F NMR (470.46 MHz) −167.37 (8 F), −163.51 (4 F), −132.99 (8 F).
22. A colorless crystal (approximate dimensions 0.30 by 0.21 by 0.20 mm) of **2** · 0.75 CH_2Cl_2 used for x-ray diffraction on a Nonius KappaCCD (charge-coupled device) instrument equipped with monochromatized Mo K_α radiation (λ = 0.71073 Å). Crystal system triclinic; space group P$\bar{1}$ with a = 10.6900 ± 9 Å, b = 17.4170 ± 14 Å, c = 19.940 ± 3 Å, α = 101.416 ± 10°, β = 102.745 ± 9°, γ = 94.579 ± 7°, V = 3519.7 ± 7 Å^3, four molecules per unit cell, formular weight 906.05, calculated density 1.710 Mg/m^3. Data were collected at 100 K, Θ range from 3.0° to 27.5°. A total of 116,423 reflections were collected (16,140 unique, R_{int} = 0.04); R_F = 0.0399 for 12,334 reflections, with $I > 2\sigma$ (1), weighted R_{F^2} = 0.0984 for all reflections. More crystallographic data are available at the Cambridge Crystallographic Data Centre, CCDC number 242266.
23. The closest Si-Cl (CH_2Cl_2) distance was determined to a resolution of 5.34 Å.
24. R. Okazaki, R. West, *Adv. Organomet. Chem.* **39**, 231 (1996).
25. A yellow crystal (approximate dimensions: 0.30 by 0.30 by 0.16 mm) of **3** used for for x-ray diffraction on a Nonius KappaCCD instrument equipped with monochromatized Mo K_α radiation (λ = 0.71073 Å). Crystal system monoclinic; space group P21/n with a = 17.6670 ± 2 Å, b = 10.18800 ± 10 Å, c = 23.4380 ± 2 Å, β = 110.6080 ± 6°, V = 3,948.69 ± 7 Å^3, four molecules per unit cell, formular weight 647.41, calculated density 1.089 Mg/m^3. Data were collected at 100 K (range from 3.0° to 27.5). A total of 69,748 reflections were collected (9,000 unique, R_{int} = 0.04); R_F = 0.0313 for 7,739 reflections with $I > 2\sigma$ (1), weighted R_{F^2} = 0.0874 for all reflections. More crystallographic data are available at the Cambridge Crystallographic Data Centre, CCDC number 242267.
26. P. Jutzi, N. Burford, *Chem. Rev.* **99**, 969 (1999).
27. A. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **88**, 899 (1988).

28. We thank the Deutsche Forschungsgemeinschaft and the University of Bielefeld for financial support.

3 May 2004; accepted 23 June 2004
Published online 1 July 2004;
10.1126/science.1099879
Include this information when citing this paper.

Climatic Control of Riverine and Seawater Uranium-Isotope Ratios

Laura F. Robinson,*† Gideon M. Henderson, Lisa Hall,‡ Iain Matthews

The large variation in the ratio of uranium-234 to uranium-238 ($^{234}U/^{238}U$) in rivers is not well understood, but may provide information about past weathering and rainfall and is important because it controls seawater ($^{234}U/^{238}U$). Here, we demonstrate the importance of physical weathering and rainfall for ($^{234}U/^{238}U$), using rivers from South Island, New Zealand. These data allow interpretation of an existing speleothem ($^{234}U/^{238}U$) record and suggest that New Zealand glacier advance 13,000 years ago was influenced by increased rainfall rather than by Younger Dryas–like cooling. A model of seawater ($^{234}U/^{238}U$) during glacial cycles indicates that rejection of corals based on modern ($^{234}U/^{238}U$) ± <0.01 is not merited and may reject the highest quality ages.

The energetic alpha decay of ^{238}U makes its great-granddaughter, ^{234}U, relatively mobile and causes variability in the ratio of activities of ^{234}U and ^{238}U ($^{234}U/^{238}U$) in the surface-Earth environment (*1*). Rivers, for instance, have ($^{234}U/^{238}U$) varying from <1 to >3 (*2*). These surface-water ratios are recorded in precipitates such as riverine tufas or cave carbonates and are routinely measured during U/Th dating (*3*–*5*). Resulting ($^{234}U/^{238}U$) records may contain information about past rainfall and continental weathering that could be deciphered if the controls on the ratio were fully understood.

Department of Earth Sciences, University of Oxford, Parks Road, Oxford, OX1 3PR, UK.

*To whom correspondence should be addressed. E-mail: laurar@gps.caltech.edu
†Present address: California Institute of Technology, MS 100-23, 1200 East California Boulevard, Pasadena, CA 91125, USA.
‡Present address: RMS Inc., 7015 Gateway Boulevard, Newark, CA 94560, USA.

One example of such a record is Nettlebed Cave in New Zealand (Fig. 1). A speleothem from this location contains a sharp change of initial ($^{234}U/^{238}U$) 13 thousand years ago (ka) (*3*). This change is synchronous with the advance of some glaciers in New Zealand and, particularly, with the formation of the Waiho Loop moraine (*6*). The Waiho Loop advance is controversial because it suggests cooling of the Southern Hemisphere climate at the same time as Younger Dryas cooling in the Northern Hemisphere. Such Southern Hemisphere cooling differs from that seen in Antarctic ice cores and would complicate the idea of a bipolar seesaw as the cause for millennial climate changes (*7*).

Carbonate ($^{234}U/^{238}U$) ratios are used routinely to assess the quality of coral U/Th ages (*8*) and, more recently, to correct for alpha-recoil processes (*9*, *10*). Such an approach relies on a known history of ($^{234}U/^{238}U$) in seawater. Understanding the controls on surface-water ($^{234}U/^{238}U$) allows an assessment of the magnitude of possible changes in this seawater ($^{234}U/^{238}U$) history.

The South Island of New Zealand provides an ideal region to quantify the controls on surface water ($^{234}U/^{238}U$) because it features considerable and independent variation in rainfall and physical weathering, with a reasonably constant rock chemistry (*11*). Rainfall is very asymmetric, with extremely high levels (up to 12,000 mm/year) on the western flanks of the Southern Alps and levels as low as 400 mm/year to the east (Fig. 1). Physical weathering also varies substantially because tectonic uplift rates range from zero to as high as 17 mm/year (Fig. 1) (*12*, *13*). Higher uplift causes more rapid physical erosion and higher river sediment loading, commonly dominated by landslide-derived material (*14*). In general, catchments on the South Island are small, so rivers flow through a narrow range of rainfall and uplift environments. The rocks of the South Island have a rather uniform bulk chemistry and comprise predominantly Mesozoic silicates (*15*). Groundwater solute contributions also tend to be low (*16*, *17*), so that complications due to high or variable groundwater input are avoided (*18*, *19*).

We collected a suite of 27 river-water samples from the South Island (Fig. 1) in March 2001 and analyzed them for U concentration and isotope ratios (*20*, *21*). The size and shape of the catchment for each of these samples were calculated from a hydrologically accurate digital elevation model (DEM) (*22*) (Fig. 1). This DEM also allows an estimate of the average rainfall and average uplift rate for each catchment by using digitized versions of available rainfall (*23*) and uplift maps (*12*, *24*). A single groundwater sample was also analyzed to assess the possibility of an important contribution to riverine U from this source. A seawater sample was analyzed to confirm analytical accuracy and allow data comparison with other laboratories.

New Zealand rivers exhibit a very wide range of (^{234}U/^{238}U), from 1.09 to 4.61 (Fig. 2 and table S1) (*25*). This range spans that previously measured in rivers from elsewhere and includes values further from secular equilibrium than have previously been reported. The wide range of values cannot be explained by changes in rock chemistry because the chemistry and grain size of the source rock for all rivers is similar (*15*). The high values also cannot be caused by groundwater input as has been suggested in other regions (*18*, *19*), because the measured groundwater has, as expected (*16*, *17*), a low U concentration (2.7 parts per thousand) and also a reasonably low (^{234}U/^{238}U) of 1.42. The high and variable (^{234}U/^{238}U) must therefore be controlled by variations in the rate of mechanical erosion and rainfall.

Riverine (^{234}U/^{238}U) on the dry eastern side of the South Island correlates strongly with uplift rate (Fig. 2). This correlation is not dependent on samples from a single river or region and indicates a first-order control on the (^{234}U/^{238}U) ratio of surface waters by the rate of uplift-induced physical weathering. The rivers with the highest (^{234}U/^{238}U) are those draining uplifting fault scarps from the zone of high uplift in the north of the South Island. In this zone, bare rock is being eroded as the Kaikoura Range is being created (*24*). For example, the Kowhai River has a value of 4.60 and its catchment is uplifting at an average rate of ~7 mm/year. By contrast, in the southern region where there is virtually no tectonic motion (<1 mm/year), the Clutha River exhibits values of <1.10. At intermediate uplift rates, such as those of the Clarence River catchment (~3 mm/year), (^{234}U/^{238}U) is intermediate, at ~2.60. The short recoil distance of ^{234}U (~500 to 1000

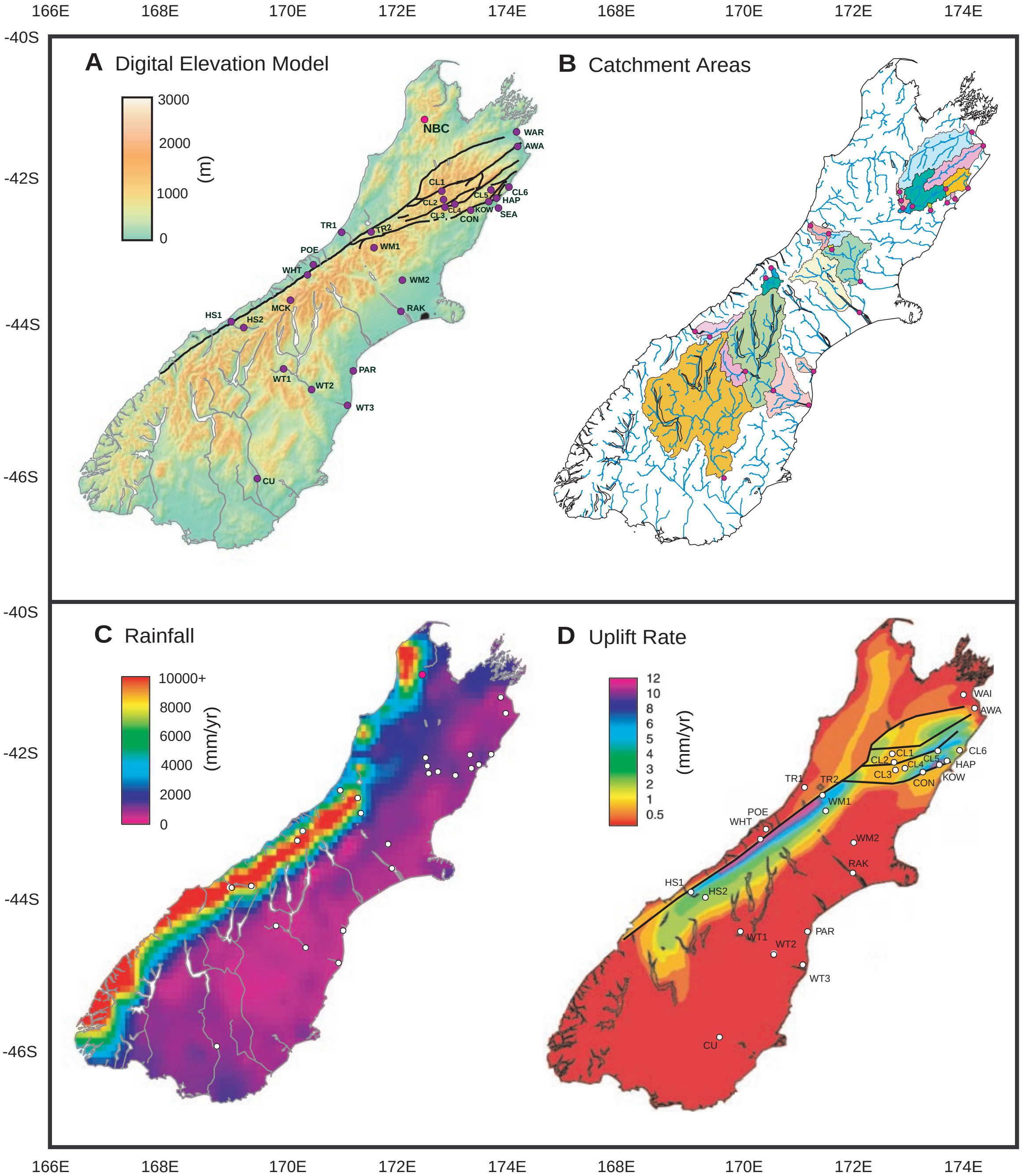

Fig. 1. (**A**) Digital elevation model of South Island, New Zealand, with sample locations marked in purple and major faults shown in black. The location of Nettlebed Cave is labeled NBC. All other three-letter location names are tabulated in table S1. (**B**) Drainage network and catchments areas for each sample. (**C**) Contour map of the average yearly rainfall (*23*). (**D**) Uplift rates, based on the models of (*12*) and (*24*) and adapted to account for more recent studies (*41*). Although the precision of this model is limited, the relative variation in uplift rates correlates well with the observed spatial variation of denudation rates from fission-track data (*42*). Despite being a simple representation of the complex tectonic deformation of the South Island, the model acts as a good guide to the relative uplift of the region. The map shows many similar features to the DEM, but the latter cannot be used as a proxy for uplift because topographic height is related to the total uplift integrated over time, not to uplift rate. Furthermore, the relation between topographic height and uplift is nonlinear as a result of the increasing influence of erosional processes on the landscape at higher uplift rates (*14*).

Å) (*26*) means that only a small fraction of ^{234}U is recoiled. This fraction increases linearly as grain radius decreases, so that reduction of grain size during physical weathering increases the ^{234}U release. Such physical weathering will also liberate ^{234}U from decay-damaged lattice sites within the mineral grains (*27*) to further increase (^{234}U/^{238}U). The New Zealand river data represent the first convincing evidence for the strong control that physical weathering exerts on surface water (^{234}U/^{238}U).

Rivers draining the wet western side of the South Island also show a correlation with uplift rate (Fig. 2). The most striking feature of these rivers, however, is that they all have considerably lower (^{234}U/^{238}U) than those draining to the east (Fig. 2). This is true even when comparing catchments with similar average uplift rates. The relation with rainfall reflects the constant rate of ^{234}U recoil from mineral grains (*26*). In regions of high rainfall, recoil ^{234}U will be washed away rapidly, whereas in regions of lower rainfall, it will have time to accumulate, resulting in higher ^{234}U concentrations in the water. This leads to the expectation that excess ^{234}U levels in rivers should have a reciprocal relation to rainfall (i.e., a doubling of rainfall should lead to a halving of the ^{234}U excess). Such a relation is consistent with the New Zealand river data, although the relation is somewhat masked because rainfall is only a secondary control on (^{234}U/^{238}U).

These modern river data indicate that a temporal change of (^{234}U/^{238}U) in catchment waters will result from a change either in the rate of physical weathering or in rainfall. Substrates that capture past drainage chemistry, such as tufas or near-surface cave carbonates, therefore provide a record of past weathering and/or rainfall. The abrupt change in (^{234}U/^{238}U) observed at 13 ka in the Nettlebed Cave Speleothem (*3*) can be interpreted in this context. This record shows a reasonably consistent value of 1.43 during the last glacial and a sudden change at 13 ka to values of ~1.37 (*3*). This abrupt shift is unlikely to represent a change in uplift rate and, because the location of Nettlebed Cave was not glaciated during the last glacial, changes in physical weathering due to ice grinding cannot be invoked. The shift is therefore very likely to be caused by an increase in rainfall. The continuous (^{234}U/^{238}U) values observed in the Nettlebed record on either side of this shift indicate a single change in rainfall at 13 ka rather than a millennial-style oscillation. This shift, therefore, probably represents a response of the climate to global deglaciation, perhaps due to the poleward movement of wind systems as the planet warms.

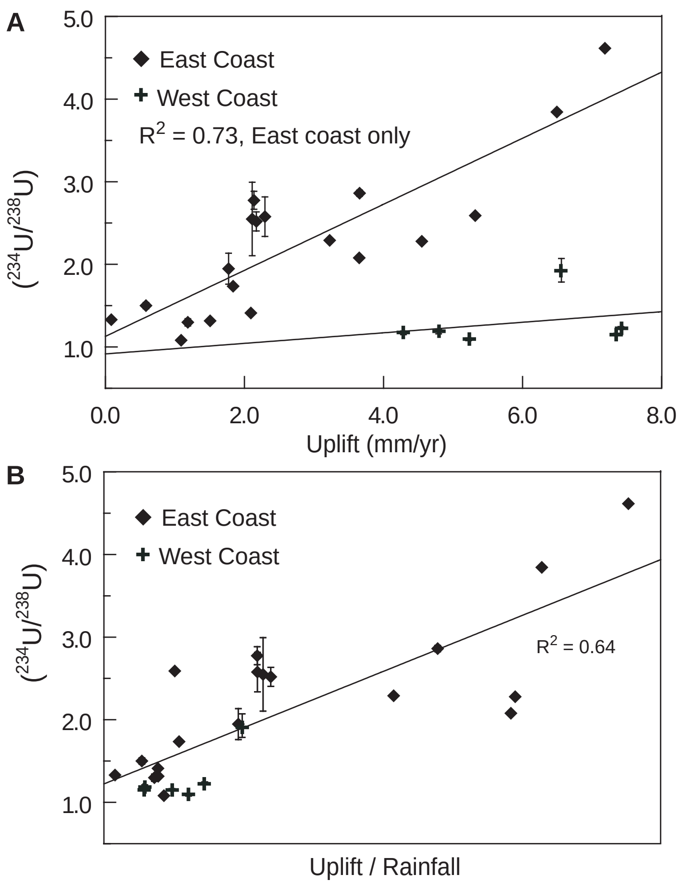

Fig. 2. Filled diamonds show samples from the east coast, with crosses from the west coast. Error bars are all 2σ. (**A**) Plot of (^{234}U/^{238}U) against uplift rate. Solid and dashed best-fit lines are for the east (R^2 = 73) and west coast data, respectively. (**B**) Plot of the same data, but with uplift rate normalized to rainfall and a best-fit line through all the data (R^2 = 64).

The timing of advance of some New Zealand glaciers dated at 13 ka (*6*) is not consistent with other Southern Hemisphere records, particularly those in the Antarctic ice cores, which show earlier cooling (~13.8 ka) followed by warming during the Younger Dryas (at ~13 ka) (*28*). Glacier growth is controlled by both temperature and moisture supply, so that an increase in rainfall at constant temperature can explain the advance at 13 ka. Such an interpretation is consistent with other data from the Nettlebed speleothem, particularly the δ^{18}O record (*29*) which, although complicated, can be interpreted as showing cooling at 13.8 ka rather than at 13.0 ka. Pollen records provide somewhat conflicting evidence for change at this time, with some showing little evidence for change (*30*) and others showing early cooling at ~13.7 ka (*31–33*). Three pollen records in the vicinity of the Waiho Loop location suggest an increase in precipitation, but the chronology is not as precise as the U/Th ages of the Nettlebed speleothem (*34*). A strong rainfall control of glacial advance at 13 ka suggests that cooling during a Younger Dryas–like event is not likely to have been as important in the mid-latitudes of the South Pacific as in areas of the Northern Hemisphere.

Understanding the controls on surface water (^{234}U/^{238}U) helps to interpret speleothem and tufa records from other regions and confirms the interpretation of a change in fluid regime suggested for the Soreq Cave, Israel (*4*). Care will be needed, however, in areas where major groundwater contributions to surface water are found because of the high and variable (^{234}U/^{238}U) in groundwaters.

The observation of a strong climatic control on riverine (^{234}U/^{238}U) also has implications for the value of seawater (^{234}U/^{238}U) during glacial cycles. Such changes in seawater (^{234}U/^{238}U) were first proposed by Esat and Yokoyama (*35*) on the basis of coral data but have remained controversial because of scatter of the coral data and the lack of a viable forcing mechanism. Existing coral data (Fig. 3) from the period 0 to 10 ka have an average initial (^{234}U/^{238}U) of 1.146 (n = 67), compared with a value of 1.139 for the period 10 to 70 ka (n = 29). The scatter of values within both intervals cannot be explained by changes in seawater and indicates that diagenesis must have affected at least some of the corals. The difference between the average values, however, suggests an ~0.007 change in seawater (^{234}U/^{238}U) between the glacial and interglacial. The possibility that such a difference can result from changes in rainfall and weathering during a glacial cycle can be investigated with the New Zealand river data as a guide. Two simple models were constructed based on a model used

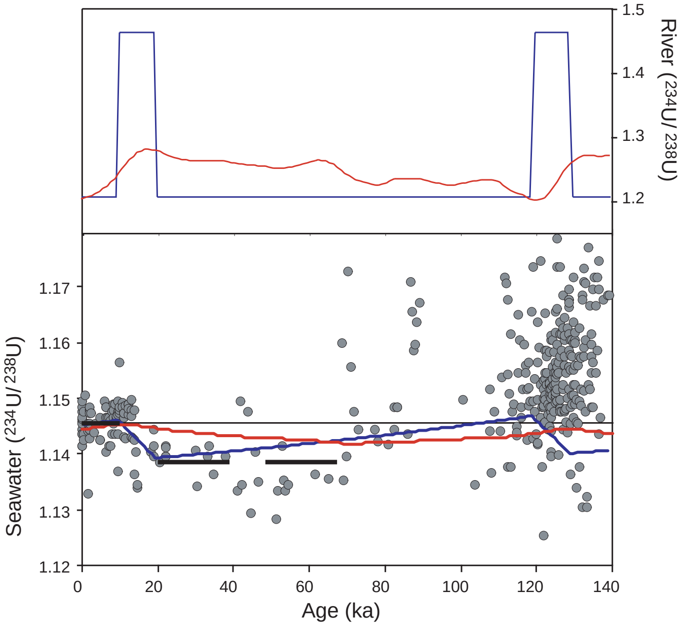

Fig. 3. A compilation of existing mass spectrometric initial (^{234}U/^{238}U) for corals of the past 140,000 years, compared with two models of possible changes in ocean (^{234}U/^{238}U) based on New Zealand river data. Thick dashed lines show the average coral values for the Holocene (1.146; $n = 67$) and for 70 to 20 ka (1.139; $n = 29$). The blue lines show a possible average riverine input (upper panel) and ocean response (lower panel) to a periodic release of high (^{234}U/^{238}U) during deglaciation. The red lines show the expected riverine forcing and ocean response for a change in rainfall expected during different global climate states.

previously to understand the longer-term history of seawater (^{234}U/^{238}U) (*36*).

The first model tests the effect of changes in physical weathering. The most important change in such weathering during a glacial cycle is that induced by subglacial grinding during glacials. We model this effect by assuming that 10,000-year deglaciations release pulses of high (^{234}U/^{238}U) from freshly ground rock. We assume that a percentage of global rivers equivalent to the fraction of continent uncovered at the end of the glacial (~15%) had increased (^{234}U/^{238}U) as a result of such subglacial grinding. The maximum possible value for these rivers based on the New Zealand data is 4.6, which predicts a seawater cycle in (^{234}U/^{238}U) of amplitude 0.013, about twice that suggested by the average coral data. To generate the average glacial-interglacial difference observed in corals requires that rivers draining deglaciated crust had an average (^{234}U/^{238}U) of ~3.0, well within the range observed for New Zealand rivers. Such a change would suggest a global average river (^{234}U/^{238}U) during deglaciation ~0.27 higher than at other times. This analysis implies that the amplitude of seawater (^{234}U/^{238}U) change suggested by coral data can be generated by changes in physical weathering.

The second model tests the expected seawater response to rainfall variability. The hydrological cycle during the glacial is thought to be ~70% of its Holocene strength. Assuming the expected reciprocal relationship between ^{234}U excess and rainfall suggests a glacial riverine ^{234}U excess 42% higher than during the Holocene. Scaling this change to climate using the SPECMAP curve (*37*) suggests a seawater (^{234}U/^{238}U) change of amplitude of ~4‰, with a low at ~70 ka and a high in the early Holocene (Fig. 3) (*38*). It is probable that both effects—weathering and rainfall—played a role in controlling seawater (^{234}U/^{238}U) during glacial cycles.

The two models indicate that seawater (^{234}U/^{238}U) was likely to have been lower than today by as much as 0.01 at times during the past 80,000 years. With measurement precision on (^{234}U/^{238}U) now routinely in the per mil range, there is a growing tendency to reject all corals with initial (^{234}U/^{238}U) more than a few per mil different from the modern value. The new river data and modeling presented here suggest that this criterion is in error and may, in fact, lead to the rejection of those corals that have remained a closed system.

References and Notes

1. V. V. Cherdyntsev, *Uranium-234* (Israel Program for Scientific Translations, Jerusalem, 1971).
2. F. Chabaux, J. Riotte, O. Dequincey, *Rev. Mineral. Geochem.* **52**, 533 (2003).
3. J. C. Hellstrom, M. T. McCulloch, *Earth Planet. Sci. Lett.* **179**, 287 (2000).
4. A. Kaufman *et al.*, *Earth Planet. Sci. Lett.* **156**, 141 (1998).
5. K. R. Ludwig *et al.*, *Science* **258**, 284 (1992).
6. G. H. Denton, C. H. Hendy, *Science* **264**, 1434 (1994).
7. W. S. Broecker, *Paleoceanography* **13**, 119 (1998).
8. C. H. Stirling, T. M. Esat, K. Lambeck, M. T. McCulloch, *Earth Planet. Sci. Lett.* **160**, 745 (1998).
9. G. M. Henderson, N. C. Slowey, *Nature* **404**, 61 (2000).
10. W. G. Thompson, M. W. Spiegelman, S. L. Goldstein, R. C. Speed, *Earth Planet. Sci. Lett.* **210**, 365 (2003).
11. A. D. Jacobson, J. D. Blum, C. P. Chamberlain, D. Craw, P. O. Koons, *Geochim. Cosmochim. Acta* **67**, 29 (2003).
12. H. W. Wellman, in *The Origin of the Southern Alps*, R. I. Walcott, M. M. Cresswell, Eds. (Roy. Soc. of N. Z., Wellington, 1979), vol. 18, pp. 13–20.
13. J. Adams, *Geol. Soc. Am. Bull.*, Part 1, **91**, 2 (1980).
14. N. Hovius, C. P. Stark, P. A. Allen, *Geology* **25**, 231 (1997).
15. R. P. Suggate, *The Geology of New Zealand* (E. C. Keating, Wellington, 1978).
16. M. A. Mongillo, L. L. Clelland, "DSIR Geothermal Report" (Department of Scientific and Industrial Research, Wellington, vol. 9, 1984).
17. R. G. Allis, Y. Shi, *N. Z. J. Geol. Geophys.* **38**, 585 (1995).
18. F. Chabaux, J. Riotte, N. Clauer, C. France-Lanord, *Geochim. Cosmochim. Acta* **65**, 3201 (2001).
19. D. Porcelli, P. S. Andersson, G. J. Wasserburg, J. Ingri, M. Baskaran, *Geochim. Cosmochim. Acta* **61**, 4095 (1997).
20. L. F. Robinson, G. M. Henderson, N. C. Slowey, *Earth Planet. Sci. Lett.* **196**, 175 (2002).
21. Water samples of between 100 and 300 g were acidified and spiked with ^{236}U. Iron co-precipitation was succeeded by chemical separation of U (*39*). Simultaneous measurements of ^{238}U, ^{236}U, ^{235}U (Faraday collectors), and ^{234}U (ion counting) were made on a Nu Instruments multi-collector inductively coupled plasma–mass spectrometer with two bracketing CRM 145 standards to correct for mass biases and ion counter–Faraday collector gain and to assess repeatability (*20*).
22. The DEM has a 200-m horizontal resolution and was created from digitized contour and drainage data, derived from 1:25,000 topographic maps. The contour interpolation process was conducted using the software ArcInfo, following the method of (*40*) to ensure hydrological accuracy.
23. National Institute of Water and Atmospheric Research Climate Database, South Island daily rainfall, 1980–2000. www.niwa.co.nz/services/clidb
24. S. H. Lamb, H. M. Bibby, *J. Struct. Geol.* **11**, 473 (1989).
25. Uranium concentrations in the rivers show no systematic relation with uplift, rainfall, or (^{234}U/^{238}U). This lack of correlation presumably reflects the active chemistry of uranium. Changes of redox, organic complexing, or carbonate concentration all influence the U concentration without directly changing (^{234}U/^{238}U).
26. K. Kigoshi, *Science* **173**, 3991 (1971).
27. J. Kronfeld, J. C. Vogel, *Earth Planet. Sci. Lett.* **105**, 191 (1991).
28. T. Sowers, M. Bender, *Science* **269**, 210 (1995).
29. J. Hellstrom, M. McCulloch, J. Stone, *Quat. Res.* **50**, 167 (1998).
30. C. Singer, J. Shulmeister, B. McLea, *Science* **281**, 812 (1998).
31. C. S. M. Turney, M. S. McGlone, J. M. Wilmhurst, *Geology* **31**, 223 (2003).
32. A. Sandiford, R. Newnham, B. Alloway, J. Ogden, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **201**, 235 (2003).
33. R. M. Newnham, D. J. Lowe, *Geology* **28**, 759 (2000).
34. M. J. Vandergoes, S. J. Fitzsimons, *Quat. Sci. Rev.* **22**, 1461 (2003).
35. T. M. Esat, Y. Yokoyama, *Eos* **80**, 581 (1999).
36. G. M. Henderson, *Earth Planet. Sci. Lett.* **199**, 97 (2002).
37. D. G. Martinson *et al.*, *Quat. Res.* **27**, 1 (1987).
38. Because the ^{234}U recoil rate is constant, a global increase in riverine (^{234}U/^{238}U) must be caused either by intermittent storage of recoil ^{234}U on the continents or by a decrease in the global ^{238}U flux to the oceans. Running the model with a simple (^{234}U/^{238}U) change (to mimic storage) or with a coupled (^{234}U/^{238}U) and U-flux change made no significant difference to the amplitude of the seawater (^{234}U/^{238}U) predicted. In the latter case, only a very small (3%) amplitude cycle in seawater U concentration is observed.
39. R. L. Edwards, J. H. Chen, G. J. Wasserburg, *Earth Planet. Sci. Lett.* **81**, 175 (1986).
40. M. F. Hutchinson, *J. Hydrol.* **106**, 211 (1989).
41. Y. Ota *et al.*, *N. Z. J. Geol. Geophys* **39**, 51 (1996).
42. J. M. Tippet, P. J. J. Kamp, *J. Geophys. Res.* **16**, 16119 (1993).

43. We thank the Gary Comer Fellowship program for financial support and N. Belshaw for help in the laboratory.

Supporting Online Material
www.sciencemag.org/cgi/content/full/305/5685/851/DC1
Table S1

27 April 2004; accepted 7 July 2004

Climatic Control of Riverine and Seawater Uranium-Isotope Ratios
Laura F. Robinson *et al.*
Science **305**, 851 (2004);
DOI: 10.1126/science.1099673