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**Riverine export of aged terrestrial organic matter to the North Atlantic Ocean**

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Global riverine discharge of organic matter represents a substantial source of terrestrial dissolved and particulate organic carbon to the oceans<sup>1,2</sup>. This input from rivers is, by itself, more than large enough to account for the apparent steady-state replacement times of 4,00–6,000 yr for oceanic dissolved organic carbon<sup>3–5</sup>. But paradoxically, terrestrial organic matter, derived from land plants, is not detected in seawater and sediments in quantities that correspond to its inputs<sup>6–8</sup>. Here we present natural <sup>14</sup>C and <sup>13</sup>C data from four rivers that discharge to the western North Atlantic Ocean and find that these rivers are sources of old (<sup>14</sup>C-depleted) and young (<sup>14</sup>C-enriched) terrestrial dissolved organic carbon, and of predominantly old terrestrial particulate organic carbon. These findings contrast with limited earlier data<sup>9</sup> that suggested terrestrial organic matter transported by rivers might be generally enriched in <sup>14</sup>C from nuclear testing, and hence newly produced. We also find that much of the young dissolved organic carbon can be selectively degraded over the residence times of river and coastal waters, leaving an even older and more refractory component for oceanic export. Thus, pre-ageing and degradation may alter significantly the structure, distributions and quantities of terrestrial organic matter before its delivery to the oceans.

We sampled four rivers that discharge to the western North Atlantic Ocean: the Amazon (Brazil), Hudson (New York, USA), York (Virginia, USA) and Parker (Massachusetts, USA). The Amazon was sampled during base flow in 1991, and the three US rivers were sampled during moderate to high flow regimes from 1996 to 1998. The four sampled rivers range over four orders of magnitude in freshwater discharge (160,000, 375, 70 and 11 m<sup>3</sup> s<sup>-1</sup>, respectively) and watershed size (7,050,000, 21,000, 4,350 and 609 km<sup>2</sup>, respectively). All water samples were taken from tidal freshwater sites except the Parker River sample, which was taken from above a dam feeding the Parker estuary. We report radiocarbon (<sup>14</sup>C) signatures for two operationally defined size fractions of organic matter: dissolved organic carbon (DOC; the fraction passing through a 0.7-μm glass-fibre filter) and particulate organic carbon (POC; the fraction collected on a 0.7-μm glass-fibre filter). Together these two size classes comprise the total organic carbon in these river waters. We also present for comparison data from four other western North Atlantic rivers<sup>10</sup> collected previously.

Mean DOC and POC concentrations for all rivers were 357 ± 280 μM and 95 ± 33 μM, respectively (Tables 1 and 2). The Δ<sup>14</sup>C of DOC exported from these rivers was highly variable, ranging over 415‰ (Δ<sup>14</sup>C is defined in Table 1.) The Hudson River DOC had the most depleted Δ<sup>14</sup>C value at -158‰ (equivalent radiocarbon age of 1,384 years before present, yr BP), while the DOC from the Susquehanna and Rappahannock rivers was also low in Δ<sup>14</sup>C-DOC, with corresponding ages of 680 and 766 yr BP (Table 1). In contrast, the Δ<sup>14</sup>C of DOC in the York, Parker, Potomac and Amazon rivers all contained 'bomb' <sup>14</sup>C (that is, Δ<sup>14</sup>C > -50‰), introduced by nuclear weapons testing in the 1950s and 1960s.

The corresponding Δ<sup>14</sup>C values for POC (Table 2) were all significantly depleted compared to DOC (Table 1). The average Δ<sup>14</sup>C-POC values for the Amazon, Hudson, York and Parker rivers were -145, -437, -68 and -138‰ and had corresponding average radiocarbon ages of 1,258, 4,609, 690 and 1,210 yr BP, respectively; the greatest ages for POC from these four rivers were 1,258, 4,763, 1,690 and 1,696 yr BP, respectively (Table 2). This suggests that on average, the bulk POC discharged from these rivers was photo-synthetically fixed several millennia ago, and a significant fraction of this POC aged on land and in river basins for hundreds to thousands of years. Very old riverine POC (>10,000 yr BP) has also been found in a subtropical mountainous river in Taiwan<sup>11</sup>. The average radiocarbon ages of POC in the present study were 1,260, 3,225, 690 and 1,210 years older than DOC in the Amazon, Hudson, York and Parker rivers, respectively (Tables 1 and 2). The Δ<sup>14</sup>C values of Amazon DOC and POC were ~200‰ lower than values found further upriver in 1984 for dissolved humic substances and POC<sup>9</sup>, and reflects a decrease in atmospheric Δ<sup>14</sup>C-CO<sub>2</sub> of 140‰ over the same period<sup>12</sup>, spatial variation in POC sources<sup>13</sup>, as well as our

**Table 1 Concentrations and isotope data for riverine DOC**

River	Date	DOC (μM)	Δ <sup>14</sup> C (‰)	Radiocarbon age (yr BP)	δ <sup>13</sup> C (‰)
Amazon	11/91	235	28±6	Modern	-28.0
Hudson	06/98	196	-158±7	1,384	-25.5
York	09/96	701	216±5	Modern	-28.8
	11/96	443	208±5	Modern	-27.9
	03/97	390	257±7	Modern	-28.0
	06/97	435	159±5	Modern	-28.0
Parker	06/98	986	109±6	Modern	-28.3
	1972	364	+161	Modern	-30.9
Potomac*	1972	292	-81	680	ND
Susquehanna*	1973	125	-91	766	-31.9
Rappahannock*	1973	167	+42	Modern	-28.0

Values of Δ<sup>14</sup>C are expressed as the deviation in parts per thousand (‰) from the <sup>14</sup>C activity of nineteenth century wood. δ<sup>13</sup>C values are expressed as ((R<sub>sample</sub>/R<sub>standard</sub>) - 1) × 10<sup>3</sup> in ‰, where R = <sup>13</sup>C/<sup>12</sup>C, and the standard is the Pee Dee Belemnite. DOC samples (100 ml of 0.7-μm-filtered river water) were oxidized to CO<sub>2</sub> by high-energy (2,400 V) ultraviolet (UV) irradiation for 2 h (refs 3, 5). The CO<sub>2</sub> samples were then converted to graphite and analysed for Δ<sup>14</sup>C by accelerator mass spectrometry (AMS)<sup>20</sup>. All Δ<sup>14</sup>C values were corrected for sample δ<sup>13</sup>C (ref. 31). Errors (± 1σ) associated with Δ<sup>14</sup>C AMS analyses averaged ±6‰ (±60 years for radiocarbon age), while those for δ<sup>13</sup>C analyses averaged ±0.1‰. Concentrations of DOC were determined as part of the UV oxidation and CO<sub>2</sub> purification procedure, with quantification by a positive pressure (Baratron) gauge. The average error (± 1σ) for DOC concentrations determined by this method was ±1 μM. ND, not determined.

\* Values from ref. 10, standard deviations not available.

**Table 2 Concentrations and isotope data for riverine POC**

River	Date	POC ( $\mu\text{M}$ )	$\Delta^{14}\text{C}$ (‰)	Radiocarbon age (yr BP)	$\delta^{13}\text{C}$ (‰)
Amazon	11/91	52	$-145 \pm 6$	1,258	-25.6
Hudson	06/98	118	$-447 \pm 21$	4,763	ND
	10/98	43	$-426 \pm 27$	4,456	ND
York	09/96	70	$24 \pm 13$	Modern	ND
	11/96	30	$-38 \pm 18$	316	-28.2
	06/98	218	$-190 \pm 6$	1,690	-30.0
Parker	06/98	208	$-85 \pm 20$	715	-30.0
	10/98	75	$-190 \pm 25$	1,696	-33.7

Suspended POC samples were collected by filtering river water through a baked (>550 °C) 0.7- $\mu\text{m}$  glass-fibre filter. Filters were exposed to fuming HCl to remove carbonates before analysis, thoroughly dried, and processed by sealed quartz-tube combustion (900 °C using a CuO/Ag metal catalyst) to produce  $\text{CO}_2$  (ref. 32). Procedures and errors associated with POC,  $\Delta^{14}\text{C}$  and  $\delta^{13}\text{C}$  analyses averaged  $\pm 17\%$  ( $\pm 160$ yr for radiocarbon age), while those for  $^{13}\text{C}$  analyses averaged  $\pm 0.1\%$ . ND, not determined.

analysis of the total DOC pool (as opposed to just the humic fraction).

The origins of natural riverine organic matter include terrestrial soils, continental and marine sedimentary rocks, and autochthonous production<sup>2</sup>, although the dominant source of DOC and POC to most rivers is of terrestrial origin<sup>2,14</sup>. For this study, the  $\Delta^{14}\text{C}$  of dissolved inorganic carbon available for photosynthesis indicates that it was enriched by at least 100‰ compared to DOC and POC (P.A.R. and J.E.B., unpublished data). This enrichment and the low concentrations of chlorophyll *a* (< 5.0  $\mu\text{g l}^{-1}$ ) in most samples both argue against significant contributions from autochthonous phytoplankton production. Soil profiles of temperate forests indicate the presence of distinct organic carbon components that range from modern in the litterfall and upper-soil horizons to > 9,000 years in age in deeper horizons<sup>15–18</sup>. In soils, the DOC of pore water is often enriched in  $^{14}\text{C}$  with respect to the atmosphere<sup>18</sup>, and solubilized DOC is younger by hundreds to thousands of years than the residual organic matter (that is, POC)<sup>16,17</sup>. Therefore, because soils are the main source of riverine organic matter<sup>2,14</sup>, our data suggest that when there is low algal input, riverine POC contains a significant quantity of old, non-hydrolysable, recalcitrant soil organic matter originating from deeper soil horizons transported to rivers via erosion events. Conversely, riverine DOC consists of a somewhat younger, hydrolysable fraction that is transported to rivers following its continuous leaching from soils and  $^{14}\text{C}$ -enriched litter fall. For all rivers, the  $\delta^{13}\text{C}$  values for DOC and POC were depleted ( $-33.7\%$  to  $-25.5\%$ ; Tables 1 and 2), which is consistent with inputs of terrestrially derived plant matter and/or old (Mesozoic or older) sedimentary sources<sup>19</sup>.

In addition to the inherent differences in the ages of soluble versus insoluble (that is, particulate) organic matter in parent rocks and soils, the processes governing DOC and POC ages and variability in rivers include the weathering and denudation regimes of the watersheds, the absolute ages of parent rocks and soil organic matter, and the residence times of DOC and POC in feeder streams and rivers themselves. Some of the oldest POC was found in the Amazon and Hudson rivers (Table 2), which have relatively high-relief headwater regions<sup>20,21</sup> where there are thin soils continuously eroded by mechanical weathering. The contribution of significant amounts of  $^{14}\text{C}$ -depleted sedimentary carbon<sup>2,11</sup>, present in both these watersheds<sup>20,21</sup>, could explain the old ages of POC in such rivers. Alternatively, rivers draining areas of low relief with thicker, younger soils (for example, the York and Parker rivers) are dominated by chemical weathering (that is, solubilization of organic matter), and may have smaller relative contributions from deeper/older soil profiles and sedimentary rocks. We note that while rivers such as the Amazon have a significant contribution of suspended solids<sup>22</sup> and POC (ref. 13) from the Andean highlands, they would also contain modern DOC and POC from lowland floodplains<sup>13</sup>.

Our finding of much older POC than DOC in all of these rivers is

also consistent with a reservoir or storage effect associated with POC 'spiralling' (that is, suspension/re-deposition) in streams and rivers<sup>23</sup>. Because POC is believed to consist of soluble organic matter adsorbed on mineral surfaces<sup>24,25</sup>, the storage effects for POC and mineral particles may be similar. Thus, geomorphic and hydrologic variations between watersheds will have an important effect on the absolute ages of riverine DOC and POC, and will contribute to the pattern of older POC in rivers. Another factor potentially contributing to the old ages of POC is human disturbance. In the Hudson, for instance, the chief source of POC is from agricultural fields<sup>26</sup>, where older soil horizons have been tilled to the surface and are susceptible to erosion.

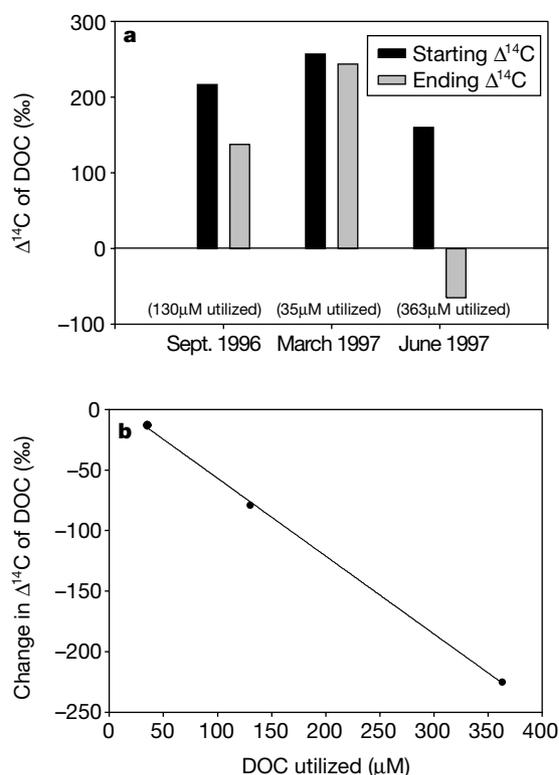
An important fate of DOC in rivers and estuaries is bacterial degradation<sup>27,28</sup>. We conducted long-term, dark incubations (2–12 months) with York River water to investigate how bacterial utilization of DOC in rivers alters the  $\Delta^{14}\text{C}$  signatures of riverine DOC prior to its discharge to the coastal ocean. The  $\Delta^{14}\text{C}$  values of DOC decreased in all incubations (Fig. 1a), indicating that there is preferential removal of  $^{14}\text{C}$ -enriched (that is, young) labile DOC by heterotrophic bacteria. In the one-year incubation, 63% of the initial bulk DOC pool ( $\Delta^{14}\text{C} = 160\%$ ) was degraded, and the residual fraction had a  $\Delta^{14}\text{C}$  of  $-65\%$  (or  $\sim 540$  yr in age). These findings indicate that riverine DOC consists of a larger pool of biologically labile,  $^{14}\text{C}$ -enriched (that is, young) DOC, and a smaller pool of biologically refractory,  $^{14}\text{C}$ -depleted (that is, old) DOC. The  $\Delta^{14}\text{C}$  of the refractory fraction of riverine DOC is also directly related to the amount of DOC utilized by bacteria (Fig. 1b). Thus we predict that, as younger DOC is degraded, the remaining DOC (which is available for export to the coastal ocean and beyond) will be much older than the original material. When measuring total  $\Delta^{14}\text{C}$ -DOC, this old pool may be further concealed because of the intrusion of bomb  $^{14}\text{C}$ .

The radiocarbon signatures of DOC and POC, and the shift towards older residual DOC following bacterial degradation, suggest that organic matter exported from rivers to the oceans is older, and much more variably aged, than previously thought. The limited previous data on ages of riverine organic matter<sup>9</sup> have led to the presumption that rivers in general transport—and export to the oceans—young DOC and POC originating from terrestrial sources. Approximately 40% of the organic matter transported to the North Atlantic is POC (ref. 14), and the present data suggest that this material is very old (on the order of  $10^3$  years or greater). The remaining 60%, transported as DOC (ref. 14), may be old or recently produced, depending on the region being drained. In addition, even initially young DOC may attain a considerably older mean age following modest preferential degradation of younger components by river and coastal bacteria (Fig. 1). Finally, the exchange of old organic matter adsorbed on mineral particles during mixing of river and marine waters<sup>24,25</sup> will probably be an additional source of old DOC within these waters—which are then exported to the coastal and open ocean. Thus we conclude that rivers are important sources of old POC, and net sources of old

DOC, and therefore supply organic matter to the ocean margins in a pre-aged form.

The rivers sampled as part of this study are a subset of the two dominant regions of freshwater discharge to the North Atlantic: the Amazon basin (~42%) and North America (~23%)<sup>29</sup>. The mean  $\Delta^{14}\text{C}$  values for the Amazon and North American rivers are respectively 28‰ and 27‰ for DOC, and -145‰ and -214‰ for POC. When these are normalized for freshwater discharge, the mean values are 28‰ for DOC and -175‰ for POC. Assuming that the  $\Delta^{14}\text{C}$  for DOC decreases by approximately 50‰ as a result of preferential removal of young components by bacteria during transport (Fig. 1), and using the proportions of organic carbon exported by rivers to the North Atlantic as 60% for DOC and 40% for POC (ref. 14), we calculate a net weighted mean  $\Delta^{14}\text{C}$  of organic carbon exported to the North Atlantic of -84‰, or about 670 years in age.

If we assume a greater degree of bacterial utilization of young DOC components (that is, a decrease of about 200‰ in  $\Delta^{14}\text{C}$ -DOC; Fig. 1b) over residence times approximating those of shelf waters (~1 yr), then the weighted mean  $\Delta^{14}\text{C}$  of organic carbon (DOC plus POC) exported from rivers to the North Atlantic becomes -173‰ or 1,500 years in age. Bacteria may also preferentially utilize young components of the POC pool, making our estimates conservative.



**Figure 1** Results from three  $\Delta^{14}\text{C}$ -DOC utilization experiments performed on water from the York River. Fresh water was filtered (0.7  $\mu\text{m}$ ), then incubated in the dark at *in situ* temperatures (23 °C, 10 °C and 20 °C for the September, March and June experiments, respectively). **a**, Changes in the  $\Delta^{14}\text{C}$  and concentrations of DOC during incubation. The concentrations of DOC and  $\Delta^{14}\text{C}$ -DOC values were measured at the beginning and end of each incubation by the methods outlined in Table 1. Values in parentheses indicate the amounts of DOC utilized by bacteria during each long-term incubation. September 1996 and March 1997 incubations both lasted for 60 d, while the June 1997 incubation lasted 365 d. The smaller DOC and  $\Delta^{14}\text{C}$  changes in the March 1997 incubation were probably due to low (10 °C) incubation temperatures. **b**, The change in  $\Delta^{14}\text{C}$  versus the amount of DOC utilized by bacteria for incubations in **a**. The strong relationship ( $r^2 = 0.99$ ,  $P < 0.05$ ) indicates that as bacteria utilize greater amounts of DOC, the  $\Delta^{14}\text{C}$  of the remaining fraction becomes progressively lower.

Industrial and agricultural activities in North America and Europe would be expected to result in petroleum-derived (that is, devoid of  $^{14}\text{C}$ ) older soil organic matter being introduced to watersheds, further biasing these estimates of DOC and POC to old mean ages. In order to extend such estimates of the ages of riverine and terrestrial organic matter to a global scale, it will be necessary to sample additional rivers world-wide. This area of research would further benefit from a more rigorous attempt to characterize the mechanisms behind ageing within the POC component. Even so, the present data show that the ages of DOC and POC exported to the North Atlantic are on average much older and more variable than previously assumed; the same may well be true for river water exported to other ocean waters. □

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## Geochemical evidence for the melting of subducting oceanic lithosphere at plate edges

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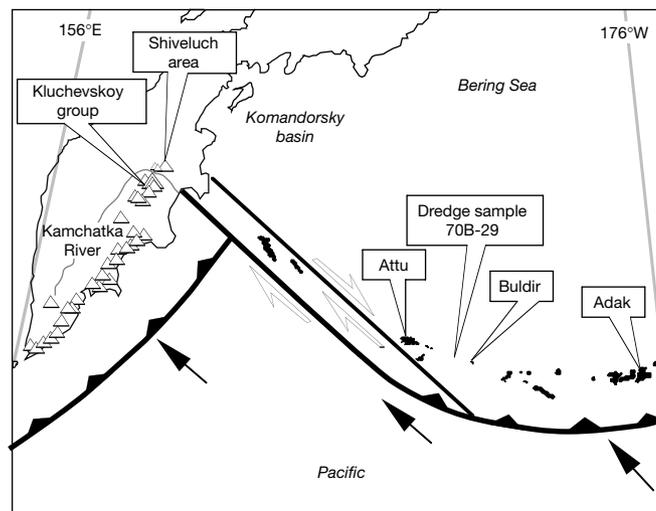
Most island-arc magmatism appears to result from the lowering of the melting point of peridotite within the wedge of mantle above subducting slabs owing to the introduction of fluids from the dehydration of subducting oceanic crust<sup>1</sup>. Volcanic rocks interpreted to contain a component of melt (not just a fluid) from the subducting slab itself are uncommon, but possible examples have been recognized in the Aleutian islands, Baja California, Patagonia and elsewhere<sup>2–4</sup>. The geochemically distinctive rocks from these areas, termed 'adakites', are often associated with subducting plates that are young and warm, and therefore thought to be more prone to melting<sup>5</sup>. But the subducting lithosphere in some adakite locations (such as the Aleutian islands) appears to be too old and hence too cold to melt<sup>6,7</sup>. This implies either that our interpretation of adakite geochemistry is incorrect, or that our understanding of the tectonic context of adakites is incomplete. Here we present geochemical data from the Kamchatka peninsula and the Aleutian islands that reaffirms the slab-melt interpretation of adakites<sup>2</sup>, but in the tectonic context of the exposure to mantle flow around the edge of a torn subducting plate. We conclude that adakites are likely to form whenever the edge of a subducting plate is warmed or ablated by mantle flow. The use of adakites as tracers for such plate geometry may improve our understanding of magma genesis and thermal structure in a variety of subduction-zone environments.

In the northwesternmost Pacific, there is a dramatic shift in subduction dynamics where the Aleutian and Kamchatka arcs meet at an angle of nearly 90° (Fig. 1). Well defined, deep seismic zones indicate that the subducting Pacific plate dips to the west beneath Kamchatka, and to the north beneath the central Aleutians, but the nature of subduction beneath the junction of these arcs is not well understood. One recent study suggests that the subducting Pacific

plate is not present beneath the western Aleutians, and therefore does not bend sharply beneath the corner formed by the Aleutian–Kamchatka junction<sup>8</sup>. This interpretation, which is a significant departure from some previous views<sup>9</sup>, implies that the western Aleutians are a simple transform boundary, and that there is a window through the subducting Pacific plate beneath the western Aleutians and the Aleutian–Kamchatka junction. In turn, this implies that as the Pacific plate passes beneath the Aleutian–Kamchatka junction, it is exposed to shearing and mantle flow around its northern edge—a situation that is likely to cause this edge to be anomalously hot and/or physically ablated<sup>8</sup>. Northward shoaling of seismicity beneath Kamchatka supports this view of slab geometry (Fig. 2). The implications for magma genesis in the Aleutian–Kamchatka junction are clear: if the edge of the slab is heated sufficiently, it may contribute a melt (not just a fluid) to the source of magmas erupted in the vicinity of Sheveluch volcano, the northernmost active strato-volcano in Kamchatka (Fig. 1).

The effects of slab melting on arc magma geochemistry are incompletely understood, but many workers believe that a distinctive class of magnesian and calc-alkaline andesites and dacites termed 'adakites'<sup>5</sup> (see Fig. 3 regarding our use of this term) may be examples of arc volcanic rocks that are produced in part by melting of subducting oceanic crust. Studies of adakites indicate that the geochemical consequences of slab melting may be anomalously steep rare-earth-element patterns, high Sr contents and high Sr/Y ratios in andesitic-to-dacitic rocks that may also be relatively rich in compatible elements such as Mg, Cr and Ni. These features, which are most commonly seen in arcs where the subducting oceanic lithosphere is relatively young<sup>5</sup>, are thought to be produced when subducting oceanic crust melts at high pressures to produce silicic magmas that rise through—and react with—the overlying wedge of mantle peridotite<sup>2</sup>.

Figure 3 shows that volcanic rocks of the Sheveluch area are significantly more Mg-rich (lower  $\text{FeO}^*/\text{MgO}$ ) at a given  $\text{SiO}_2$  content than are rocks from the adjacent volcanoes of the Klyuchevskoy group. ( $\text{FeO}^*$  is total iron content calculated as  $\text{FeO}$ .) Figure 4 shows that with regard to Sr/Y, the Sheveluch rocks fall



**Figure 1** Map view of the study area. The figure shows the oblique subduction zone of the central Aleutians (near Adak), the transform-type boundary in the westernmost Aleutians, and the sharp bend into the subduction system of the Kurile–Kamchatka arc. The Klyuchevskoy volcanic group and the Sheveluch area mark the location of the Kamchatka central depression. Exceptionally voluminous arc volcanism in the central depression, and the slight offset of the magmatic front in this area (apparently due to a slight flattening of the slab dip<sup>27</sup>) are believed to be evidence of mantle flow around the northern edge of the subducting Pacific plate as it passes beneath the Aleutian–Kamchatka junction<sup>8</sup>.