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14 February 1995; accepted 3 May 1995

Primitive Boron Isotope Composition of the Mantle

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Boron isotope ratios are homogeneous in volcanic glasses of oceanic island basalts [-9.9 ± 1.3 per mil, relative to standard NBS 951 (defined by the National Bureau of Standards)], whereas mid-oceanic ridge basalts (MORBs) and back-arc basin basalts (BABBs) show generally higher and more variable ratios. Melts that have assimilated even small amounts of altered basaltic crust show significant variations in the boron isotope ratios. Assimilation may thus account for the higher boron ratios of MORBs and BABBs. A budget of boron between mantle and crust implies that the primitive mantle had a boron isotope ratio of -10 ± 2 per mil and that this ratio was not fractionated significantly during the differentiation of the mantle.

Convection in the mantle governs the heat transfer through the mantle and the exchange of matter in the lower mantle, the upper mantle, and the crust. Isotopic tracers are powerful indicators of these fluxes and provide information on the uncertain patterns of convection. The presence of variable but generally high $^3\text{He}/^4\text{He}$ ratios in oceanic island basalts (OIBs) tapping hot-spot material and of intermediate and homogeneous $^3\text{He}/^4\text{He}$ ratios in MORBs is strong evidence for a two-layered mantle structure, with more efficient convection in the upper mantle than in the lower mantle (1). In addition, He isotopes are unequivocal tracers of primitive mantle [He is not thought to be recycled back into the mantle (2)]. Largely because of analytical difficulties, B isotopes have not been used as a tracer (3). However, (i) B is incompatible and should provide evidence for depletion events in the mantle (4); (ii) B isotopes do not fractionate significantly at magmatic temperatures and should therefore reflect

source compositions (5); (iii) B is not volatile under mantle conditions and is unaffected by degassing (6); and (iv) B isotopes are strongly fractionated during their transfer in seawater or crust (7, 8), so that they are potentially good tracers of subduction processes (9) and of shallow interaction between melts and crust. In this report, we present B isotope measurements of OIBs and in particular evaluate relations between $^3\text{He}/^4\text{He}$ and $^{11}\text{B}/^{10}\text{B}$ ratios. We examine the processes that control the B isotopic variations and the constraints they can pose for the origin and evolution of the different mantle reservoirs.

We measured B contents and $^{11}\text{B}/^{10}\text{B}$ isotopic ratios (Table 1) by ion probe in samples from five hot spots: Galápagos Islands, Loihi seamount (Hawaii), St. Helena Island, McDonald seamount (austral hot-spot track), and Afar hot-spot region (Gulf of Tadjoura). In addition, we studied samples from two back-arcs (Manus and Marianas basins). In all cases, only fresh submarine glassy lavas with a few phenocrysts were analyzed, and ion probe spots were carefully placed on glassy zones free of any bubbles or secondary products. For the OIB samples, we selected only samples that had already been analyzed for He (10–12) and that have variable $^3\text{He}/^4\text{He}$ ratios between $5R_a$ and $30R_a$.

The hot-spot lavas have very variable

$\delta^{11}\text{B}$ values (13), between -14.6 ± 1.5 and -4.3 ± 1.5 per mil, that are generally lower than BABB $\delta^{11}\text{B}$ values, from -8.0 ± 1.5 to $+7.5 \pm 1.5$ per mil (Table 1). The $\delta^{11}\text{B}$ values of OIBs partly overlap MORB values [from -6.5 ± 1.5 to -1.2 ± 1.5 per mil (3)], but this is probably largely due to secondary processes. In fact, the $\delta^{11}\text{B}$ of mantle melts, which have low B contents [generally ≤ 1 part per million (ppm)], may readily be modified at a magmatic stage as they interact with hydrothermally altered oceanic crust or seawater. This is due to the high $\delta^{11}\text{B}$ values and to the high B contents of seawater ($\delta^{11}\text{B} = +40$ per mil and 4.5 ppm) and of seawater-altered oceanic rocks (7). These effects are clear for the Loihi and Afar hot-spot basalts.

Shallow-level assimilation of small amounts of oceanic crust that interacted with seawater at low temperatures is suggested at Hawaii from the positive correlations between B contents, H_2O contents, δD and $\delta^{11}\text{B}$ values (3), and from the $\delta^{18}\text{O}$ values, which range between $+5.1$ and $+5.7$ per mil (14). The two samples from the Loihi seamount analyzed in this study may represent a primary composition for the Hawaiian hot-spot melts because (i) they have the lowest $\delta^{11}\text{B}$ values (-9.3 and -10.6 per mil) and the lowest B contents (0.94 and 0.98 ppm) of the suite (15) and (ii) they have very high $^3\text{He}/^4\text{He}$ ratios of 27.2 ± 0.9 and 28.4 ± 0.5 (12). In fact, all the Hawaiian samples plot along a mixing curve (Fig. 1A) between this low $\delta^{11}\text{B}$ pole ($\delta^{11}\text{B} = -11$ per mil and a B content of 0.9 ppm) and a pole enriched in B and in ^{11}B ($\delta^{11}\text{B} = +5.5$ per mil and a B content of 8.5 ppm), which could be seawater-rich, altered oceanic crust (3, 7, 16).

The samples from the Afar plume also show a large range of $\delta^{11}\text{B}$ values (Table 1), between -4.3 ± 1.5 and -14.6 ± 1.5 per mil, but the lowest $\delta^{11}\text{B}$ values are associated, at variance with the Hawaiian samples, with low $\delta^{18}\text{O}$ values of $+4.6$ to $+5.0$ per mil (Fig. 1B). These low $\delta^{18}\text{O}$ values have been interpreted as resulting from the interaction of the ascending mantle melts with a basaltic crust hydrothermally altered

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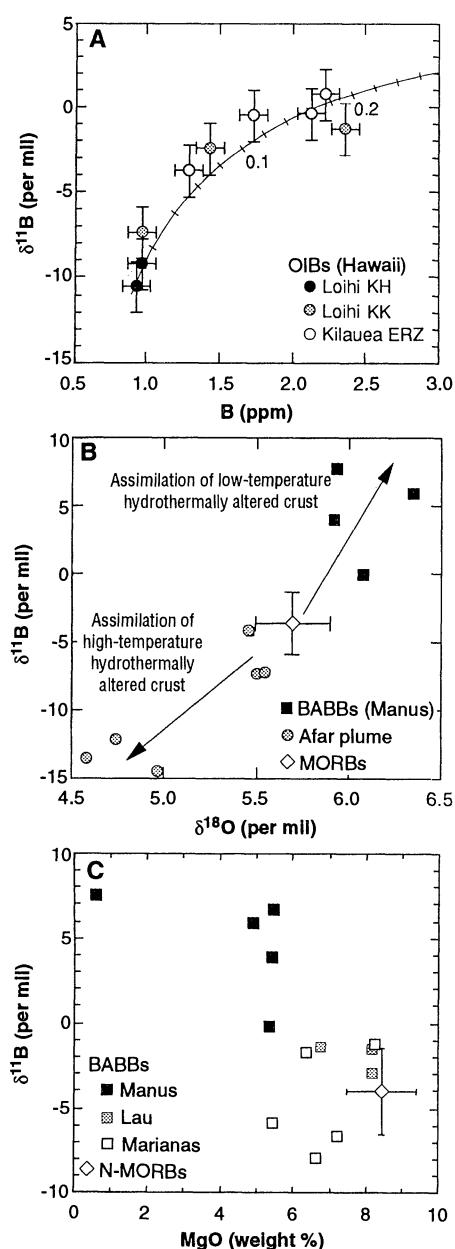


Fig. 1. Correlations demonstrating the effect of assimilation: (A) $\delta^{11}\text{B}$ versus B contents for the OIBs from Hawaii; (B) $\delta^{11}\text{B}$ versus $\delta^{18}\text{O}$ values for BABBs, the Afar hot spot, and MORBs; and (C) $\delta^{11}\text{B}$ versus MgO contents for the BABB and N-MORB samples. Assimilation processes can either increase or decrease the $\delta^{11}\text{B}$ values depending on the type of assimilated crust. Data for samples from the east rift zone (ERZ) of Kilauea and from Loihi seamount dredge KK in (A) are from (3) and data for Loihi dredge KH are from this study. Samples from Loihi KH appears to have the most primary $\delta^{11}\text{B}$ values for Hawaii at ≈ -10 per mil; data for other samples can be explained in terms of the assimilation of up to $\approx 20\%$ in mass of altered oceanic crust. Assimilation processes invoked to explain the $\delta^{18}\text{O}$ values of the Afar plume samples and of the Manus BABBs in (B) result in a huge range of variation of $\delta^{11}\text{B}$ values between ≈ -15 and $\approx +10$ per mil. Back-arc samples [data from (3) and this study] in (C) with MgO $> 6\%$ by weight show minimum fractionation-assimilation (see text); their $\delta^{11}\text{B}$ values are, however, very variable, between -2 and -8 per mil (see Fig. 2).

at high temperature (17). This process is also likely to decrease the $\delta^{11}\text{B}$ values because high-temperature fluid-rock interactions can preferentially leach ^{11}B from the solid phases (18). Thus, assimilation can either decrease or increase the $\delta^{11}\text{B}$ values of mantle melts, depending on the nature of the assimilated crust, the altered oceanic crust being highly variable in $\delta^{11}\text{B}$ values (7, 16).

Similar fractionation-assimilation processes could explain most of the spread of $\delta^{11}\text{B}$ values in BABBs, for which strong correlations are observed between $\delta^{11}\text{B}$ and $\delta^{18}\text{O}$ values, MgO contents, B contents, and $^3\text{He}/^4\text{He}$ ratios (Fig. 1, B and C; Fig. 2). Because the large variation observed for the MgO contents is due to fractionation of the melts and cannot be linked to source composition effects, most of the isotopic variations observed for B and He in BABBs are likely due to assimilation-fractionation pro-

cesses (19). Contamination of the BABB mantle source by fluids and melts derived from the subducted plate could also produce elevated $\delta^{11}\text{B}$ values and low $^3\text{He}/^4\text{He}$ ratios, but this process cannot explain the variation of the isotopic ratios with MgO and K_2O contents. Most of these secondary effects can be avoided if samples are selected with both high MgO contents ($> 6\%$ by weight) and high $^3\text{He}/^4\text{He}$ ratios similar to MORBs (Table 1, Fig. 2). Eliminating these samples defines a more restricted range of $\delta^{11}\text{B}$ variations for BABBs, between -8.0 ± 1.5 and -1.3 ± 1.5 per mil, with a mean at -3.7 ± 2.7 per mil (six samples) indistinguishable from that of MORBs. Contrary to what is observed for arc magmas (9, 20), our data do not point to the presence in back-arc magmas of a large amount of B derived from the subducted plate, suggesting that B is efficiently lost from the subducted plate during arc magmatism (21).

Table 1. Boron contents and isotopic compositions of OIBs, rift basalts, and BABBs. The B contents are given at $\pm 10\%$ and $\delta^{11}\text{B}$ values at ± 1.5 per mil (1σ) relative. The oxide concentrations are in percentages by weight. They were determined with an ims3f ion microprobe at the Centre de Recherches Pétrographiques et Géochimiques (Nancy) according to procedures described in (13).

Sample	B (ppm)	$\delta^{11}\text{B}$ (per mil)	SiO_2	MgO	K_2O
<i>OIBs</i>					
Galápagos Islands					
PL2-RC-01	1.13	-10.6	48.86	5.77	0.50
PL2-24-14	0.93	-9.8	48.85	5.85	0.44
PL2-24-32	0.95	-10.0	49.32	5.62	0.50
PL2-25-03	1.89	-8.2	45.95	4.79	0.55
PL2-29-03	0.44	-10.1	49.55	7.13	0.13
PL2-9-29	0.37	-6.6	47.59	9.54	1/M
PL2-14-8	0.42	-11.4	48.10	8.88	1/M
PL2-26-7	0.63	-10.6	48.49	7.26	0.23
Loihi seamount					
KH85-DE-36069	0.98	-9.3	49.61	6.76	0.39
KH85-DE-36061	0.94	-10.6	48.89	6.27	0.48
St. Helena Island					
SO84-63DS-1	1.45	-11.1	48.00	4.32	1.19
SO84-63DS-2	1.47	-9.4	48.38	4.15	1.26
SO84-63DS-3	1.39	-11.6	47.99	4.37	1.19
SO84-63DS-4	1.38	-9.8	48.02	4.40	1.22
MacDonald seamount					
SO47-64DS-2	2.08	-9.0	43.31	4.80	1.72
<i>Hot-spot basalts on a rift</i>					
Gulf of Tadjoura (Afar)					
DR1-3	0.74	-4.3	50.33	7.17	0.16
DR1-5	0.38	-6.2	50.46	7.39	0.15
106-1	0.21	-7.4	46.01	7.04	0.25
103-1	0.77	-7.4	50.45	7.06	0.16
124-2	0.32	-13.6	45.28	6.91	0.36
124-1	0.54	-12.2	46.57	6.80	0.39
102-2	0.81	-14.6	46.34	6.86	0.22
<i>BABBs and lavas</i>					
Manus Basin					
AQ48B-301	6.86	-0.3	55.18	5.37	0.79
AQ48B-31	2.69	5.8	54.67	4.96	0.84
AQ39C-108	7.62	3.8	55.44	5.45	0.81
AQ42-86	17.75	7.5	69.38	0.62	2.24
AQ43-12	6.36	6.6	55.22	5.54	0.79
Mariana					
KH84-1-24-1	0.55	-8.0	50.06	6.65	0.16
KH84-1-24X	0.57	-1.3	50.25	8.26	0.20
KH84-1-23-204b	1.88	-5.9	55.00	5.49	0.83

When the hot-spot samples that show obvious effects of assimilation (Afar, Hawaii, and Loihi KK) are excluded, OIBs have fairly constant $\delta^{11}\text{B}$ values (-9.9 ± 1.3 per mil). This value is significantly lower than the MORB mean (-4.0 ± 1.6 per mil). Several lines of evidence indicate that $\delta^{11}\text{B}$ values of $\approx -10 \pm 2$ per mil reflect the primary value of the mantle, whereas higher values, like those found in MORBs, are probably a result of interactions between mantle melts and the oceanic crust. Indeed, there seems to be no mantle process able to create a difference of 6 per mil in $\delta^{11}\text{B}$ values between the source of MORBs and the source of OIBs. (i) The B isotopes do not fractionate significantly during melting-crystallization processes in the mantle (5). (ii) The mean $\delta^{11}\text{B}$ estimated for the continental crust [between -13 and -8 per mil (22)] is indistinguishable from the present OIB mean (-10 ± 2 per mil), which implies that the depleted mantle from which the continental crust was extracted should have the same $\delta^{11}\text{B}$ value as the OIB source (5). (iii) The addition to the OIB source of a subducted component that could decrease the bulk $\delta^{11}\text{B}$ from ≈ -4 per mil (if it is assumed that the MORB value is primary and representative of the mantle) to ≈ -10 per mil seems impossible. It is not suggested by the data because the $\delta^{11}\text{B}$ values are constant even though the samples have different geochemical characteristics: the St. Helena and McDonald samples have typical HIMU (high source U/Pb ratio μ) signatures (23, 24) supposed to reflect the presence in the source of recycled hydrothermally altered MORBs (25), whereas the Hawaii and Galápagos samples have typical plume signatures with very high $^3\text{He}/^4\text{He}$ ratios sup-

posed to reflect the presence of deep mantle component (10). Furthermore, this hypothesis would require, from mass balance considerations, unrealistic $\delta^{11}\text{B}$ values for the subducted material: the subducted component must have a $\delta^{11}\text{B}$ value as low as -15 per mil in order to produce an OIB source with a $\delta^{11}\text{B}$ value of -10 ± 2 per mil from a homogeneous mantle with a $\delta^{11}\text{B}$ value of -4 per mil. Such low $\delta^{11}\text{B}$ values could only be produced in the subducted slab through large B isotopic fractionations, which should involve the entire subducted plate (sediments and basaltic layers) and which have not yet been demonstrated.

Mass balance of B between mantle and continental crust also indicates that the B contents of MORB glasses are too high to reflect a primary signature of the depleted mantle. Boron contents of 0.05 ± 0.01 ppm and of 0.11 ± 0.02 ppm can be estimated from glass compositions for the N-MORB ("normal" MORB) and the OIB sources, respectively (Table 2). This estimate is unrealistic for the N-MORB source for two main reasons. First, B is not as strongly depleted in MORBs relative to OIBs as is K, although both elements have similar melt-crystal partition coefficients (26) and the B/K₂O ratios are not strongly different between E-MORBs (enriched MORBs) and N-MORBs (3). In fact, with the present estimates, B is enriched by a factor of ≈ 2 in OIBs relative to MORBs whereas a factor of ≈ 6 exists for K enrichment (Table 2). Second, if we assume a B content for the primitive mantle identical to that of the OIB source, a maximum of $\approx 10 \times 10^{19}$ g of B could have been extracted from the upper mantle to create the MORB source, whereas $\approx 23 \times 10^{19}$ g of B reside within seawater and the continental crust (27).

To fulfill these mass balance arguments, the source of MORBs should be much poorer in B than inferred from MORB glasses, and, by scaling relative to K, it should have a B content of ≈ 0.010 to 0.015 ppm. The

overenrichment of B found in MORBs is likely due to assimilation processes occurring in the oceanic crust and not to a contamination of the MORB source itself. This would be in general agreement with constraints imposed by other isotopic tracers, which show that source effects are much stronger for OIBs than for MORBs (23). It is also consistent with the behavior of other elements, such as Cl, which, like B, is strongly enriched in seawater and for which assimilation by MORB melts has been shown (28). If we assume that the uncontaminated MORB source has a B content of 0.010 to 0.015 ppm and the same $\delta^{11}\text{B}$ as the OIB source (-10 ± 2 per mil), uncontaminated MORB melts should have a B content of 0.10 to 0.15 ppm and should have assimilated more than 50% of B to reach a B content of 0.5 ± 0.1 ppm. A $\delta^{11}\text{B}$ value of $\approx -1.5 \pm 1.0$ per mil is calculated by mass balance for the assimilated contaminant. This value is lower than that calculated for the assimilated component at Hawaii, $+5.5$ per mil corresponding to oceanic crust hydrothermally altered at low temperature, but is consistent with oceanic crust having undergone high-temperature hydrothermal interaction with seawater (16). However, the assimilation process is probably not a simple binary mixing between MORB melt and altered oceanic crust. It may take place through selective assimilation of B-rich fluids or secondary phases, thus leading to a variable isotope shift for B.

The B isotopes are powerful tracers to constrain the amount of assimilation that affected mantle melts, this process being one serious limitation to the interpretation of trace-element contents and isotopic compositions of oceanic basalts. The assimilation signature found for MORBs (up to 50% assimilation) relative to OIBs could reflect the different geodynamic settings of both types of basalts, MORB melts being, contrary to OIB melts, generated in large magma chambers at shallow depths under ridges

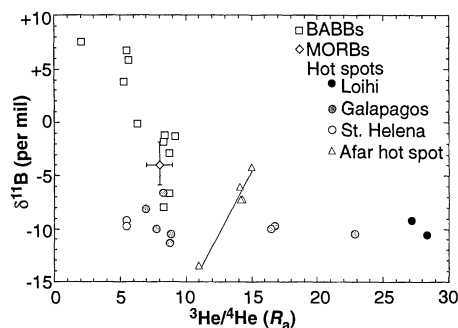


Fig. 2. Plot of $\delta^{11}\text{B}$ values versus $^3\text{He}/^4\text{He}$ ratios for BABBs, MORBs, and hot-spot lavas (OIBs). The $^3\text{He}/^4\text{He}$ ratios are from (10, 11, 31). Two trends are observed, one for BABBs and the other for the Afar hot spot, both due to assimilation-fractionation processes at low and high temperatures, respectively. The OIBs show very constant $\delta^{11}\text{B}$ values, significantly lower than the MORB values, that are likely to correspond to primitive mantle values.

Table 2. Inferred B contents and isotopic compositions for the mantle sources of MORB, OIB, and BABB melts. These values are obtained from the compositions of the glasses (3, this study), on the assumption that the OIB samples representative of uncontaminated mantle melts are those with low $\delta^{11}\text{B}$ values. The estimate of the B content for the MORB source is probably too high by approximately three times because of assimilation processes (see text).

Source	Melts			Mantle sources		
	[B (ppm)/K (ppm)]	B (ppm)	$\delta^{11}\text{B}$ (per mil)	K* (ppm)	B† (ppm)	B‡ (ppm)
N-MORB	$1.0 \pm 0.3 \times 10^{-3}$	0.5 ± 0.1	-4.0 ± 1.6	60	0.05	0.06
E-MORB	$6.6 \pm 3.6 \times 10^{-4}$	1.0 ± 0.4	-3.6 ± 1.9		0.10	
BABB	$7.3 \pm 4.7 \times 10^{-4}$	0.9 ± 0.5	-3.7 ± 2.7		0.09	
OIB	$2.4 \pm 1.0 \times 10^{-4}$	1.1 ± 0.5	-9.9 ± 1.3	370	0.11	0.09

*The K contents for the N-MORB and OIB sources are taken from (30). †The B content of the source is taken to be 0.1 of that of MORB, OIB, or BABB liquids. ‡The B content of the source is calculated from the B/K ratio of the melt [equivalent to that of the source; because B and K have similar partition coefficients (26), their ratio is not modified significantly during partial melting] and the K contents of the sources.

in a hydrothermally active oceanic crust.

The constancy of the $\delta^{11}\text{B}$ value of uncontaminated OIBs (-9.9 ± 1.3 per mil) and its striking similarity with that of the bulk continental crust (21) suggests, in agreement with some current geochemical models, that crustal extraction took place from an initially homogeneous mantle source. It would imply that the primitive mantle had a rather constant $\delta^{11}\text{B}$ value of $\approx -10 \pm 2$ per mil. This should pose strong constraints on the type of chondrites from which Earth was formed and on the processes able to produce this homogenization during its accretion and differentiation, because of the variable $\delta^{11}\text{B}$ values (29) found for chondritic materials.

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- The near-constant $^3\text{He}/^4\text{He}$ ratio of MORBs worldwide ($8 \pm 1 R_a$, where R_a is the atmospheric value of 1.386×10^{-6}) demonstrates that the source of MORBs, presumably the upper mantle, has been able to homogenize thoroughly ^3He , which was trapped from the solar nebula during Earth's formation together with U and Th, which are the radioactive parents of ^4He . In contrast, $^3\text{He}/^4\text{He}$ ratios registered in OIBs vary widely from about $5R_a$ up to $30R_a$, indicating mixing between a primitive He component enriched in ^3He and various amounts of ^4He generated from U-rich and Th-rich components such as subducted crust or sediments [J. E. Lupton, *Annu. Rev. Earth Planet. Sci.* **11**, 371 (1983)].
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- We thank K. Harpp, D. W. Graham, Y. Sano, and C. W. Devey for providing samples and making unpublished data available. We are indebted to C. France-Lanord for oxygen isotope measurements of Manus samples. This is Centre de Recherches Pétrographiques et Géochimiques-Centre National de la Recherche Scientifique contribution 1121.

14 February 1995; accepted 16 May 1995

Late Miocene Tidal Deposits in the Amazonian Foreland Basin

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Late Miocene tidal sediments of Acre, Brazilian Amazonia, were deposited in an embayment or interior seaway located in the sub-Andean zone. This late Tertiary embayment system may once have connected the Caribbean with the South Atlantic. The tidal coasts of the embayment-seaway have provided an avenue for the earliest waif (over water) dispersal phases of the great American biotic interchange in the late Miocene. The subsequent change from semimarine to terrestrial environments is of value in assessing the importance of earlier hypotheses on the evolution of the western Amazonian landscape and gives insight into the formation of several observed biogeographic patterns, especially of aquatic biota.

The southwestern Amazonian lowland is currently 100 to 200 m above sea level. The late Tertiary history of the area has been uncertain; a key area is the state of Acre, Brazil (Fig. 1). Several origins have been suggested for the fine-grained sedimentary deposits cropping out at Acre. One hypoth-

esis is that these deposits formed in a catastrophic Pleistocene flood resulting from sudden draining of glacial Lake Titicaca (1). Another is that they represent deltaic deposition in an enormous Pleisto-Holocene lake (Lago Amazonas) (2). A third is that they represent Mio-Pliocene fluvial deposition in an alluvial fan draining the Andes (3). Generally, they have been considered as fluvial in origin (4, 5) and part of the Plio-Pleistocene Solimões Formation (6). It has not been clear how these deposits relate to late Tertiary deposits farther south.

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