



Lead isotope provinciality of central North Pacific Deep Water over the Cenozoic

Tian-Yu Chen

State Key Laboratory for Mineral Deposits Research, Department of Earth Sciences, Nanjing University, Nanjing, China

GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany

Hong-Fei Ling and Shao-Yong Jiang

State Key Laboratory for Mineral Deposits Research, Department of Earth Sciences, Nanjing University, Nanjing, China (hfling@nju.edu.cn)

Rong Hu

State Key Laboratory for Mineral Deposits Research, Department of Earth Sciences, Nanjing University, Nanjing, China

Department of Earth Sciences, University of Cambridge, Cambridge, UK

Martin Frank

GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany

[1] Understanding the pre-anthropogenic Pb cycle of central North Pacific deep water has attracted a lot of attention in recent years, partly because of its unique geographical location in that it is a remote gyre system characterized by high dust fluxes and sluggish overturning circulation. However, the factors controlling Pb isotope evolution in this area over the Cenozoic are still controversial and various mechanisms have been proposed in previous studies. Here we report new Pb and Nd isotope time series of four ferromanganese crusts (two from the western Pacific near the Mariana arc and the other two from the central Pacific). Together with previously published records, we discuss for the first time the significance of a persistent and systematic Pb isotopic provinciality recorded by central North Pacific crusts over the Cenozoic. We propose that globally well mixed stratosphere volcanic aerosols could contribute Pb but have not been the major factors controlling the Pb isotope distribution in the central North Pacific over time. Island arc input (and probably enhanced hydrothermal input between about 45 and 20 Ma) likely controlled the Pb isotope provinciality and evolution prior to ~20 Ma, when coeval Pb isotope records in different crusts showed large differences and atmospheric silicate dust flux was extremely low. After the Eocene, in particular after 20 Ma, Asian dust input has become an isotopically resolvable source, while island arc-derived Pb has remained important to balance the dust input and to produce the observed Pb isotope distribution in the central North Pacific during this period.

Components: 9,200 words, 7 figures.

Keywords: Central North Pacific; Pb isotopes; Chinese loess; ferromanganese crusts.

Index Terms: 0330 Atmospheric Composition and Structure: Geochemical cycles (1030); 0473 Biogeosciences: Paleoclimatology and paleoceanography (3344, 4900); 1030 Geochemistry: Geochemical cycles (0330); 3344 Atmospheric Processes: Paleoclimatology (0473, 4900); 4900 Paleoceanography: PALEOCEANOGRAPHY.

Received 24 November 2012; **Revised** 5 March 2013; **Accepted** 11 March 2013; **Published** 17 May 2013.

Chen T.-Y., H.-F. Ling, R. Hu, M. Frank, and S.-Y. Jiang (2013), Lead isotope provinciality of central North Pacific Deep Water over the Cenozoic, *Geochem. Geophys. Geosyst.*, 14, 1523–1537, doi:10.1002/ggge.20114.

1. Introduction

[2] Lead isotopes are an important geochemical tool in studies of past and present climate change. The modern natural cycle of Pb in the ocean has been largely perturbed by human activities [e.g., *Schaule and Patterson*, 1981] which results in the dominantly anthropogenic origin of Pb in central North Pacific deep water [*Wu et al.*, 2010]. Therefore, it is not possible to directly study the natural cycle of marine Pb based on present-day seawater. Rather, such studies must be based on pre-anthropogenic authigenic precipitates from seawater. Though with low temporal resolution, ferromanganese crusts have been demonstrated to be reliable recorders of the temporal evolution of ambient seawater radiogenic isotope signatures of elements such as Nd and Pb [e.g., *Henderson and Burton*, 1999; *Frank*, 2002]. Recent studies have also implied that past bottom water Pb isotope signatures can be reliably extracted from deep sea sediments, not only for the late Quaternary [e.g., *Gutjahr et al.*, 2007] but also for the early Cenozoic [*Basak et al.*, 2011]. The seawater isotopic compositions of those elements with oceanic residence times shorter than the global ocean mixing time are affected by additions from local sources, as well as water mass mixing. Based on studies of ferromanganese crusts and nodules, the distribution of natural Pb isotopes in the oceans was found to be more sensitive to local inputs than Nd isotopes, consistent with its shorter oceanic residence time on the order of 100 years [*Schaule and Patterson*, 1981; *Henderson and Maier-Reimer*, 2002]. Interestingly, the Pb isotope evolution recorded in ferromanganese crusts from central north Pacific deep water nevertheless shows overall similar trends since the late Cretaceous [*Ling et al.*, 2005]. The signatures became less radiogenic (considering $^{208,207,206}\text{Pb}/^{204}\text{Pb}$) from the late Cretaceous to about 45 Ma and since then have progressively shifted to more radiogenic values at present. However, the major factors controlling Pb isotopic composition of central north Pacific deep water are still under debate.

[3] The distinct late Quaternary Pb isotope signature of North Pacific deep water [*von Blanckenburg et al.*,

1996] compared to other ocean basins requires more juvenile source rocks, such as volcanic arcs. Later, long-term Pb isotope time series data from the central North Pacific were obtained by *Ling et al.* [1997], *Abouchami et al.* [1997], and *Christensen et al.* [1997]. However, the sources and transport pathways of Pb were still largely unclear. *Ling et al.* [1997] suggested that a relatively constant supply of Pb to the North Pacific existed after about 30 Ma and that local island arc erosion was the most likely source. In contrast, *Christensen et al.* [1997] suggested that large-scale variations of continental weathering intensity and ocean circulation may have driven the oceanic Pb isotopic evolution, while differing records between their studied samples were attributed to different water masses as well as different subsidence histories of the sample locations. *Abouchami et al.* [1997] proposed that the Antarctic Circumpolar Current has contributed a significant amount of Pb to the North Pacific.

[4] Interestingly, records of ferromanganese crusts from the Northernmost, Northwest, and Southwest Pacific (Figure 1) showed completely different trends in their Pb isotope evolution and isotopic compositions compared with those of the central North Pacific over the last 20 Myr [*van de Flierdt et al.*, 2003, 2004a; *Chu et al.*, 2006]. Because the central North Pacific deep water receives inputs from the above regions via lateral water mass mixing and via external inputs, a relatively invariant Pb isotope signature of central North Pacific deep water seems not to be expected due to the short oceanic residence time of Pb.

[5] Subsequent studies revealed that eolian dust may have been an important source of Pb for North Pacific deep water [*Jones et al.*, 2000; *Godfrey*, 2002; *Ling et al.*, 2005]. *Jones et al.* [2000] showed that the Pb isotopic compositions of the leachable fraction of Chinese loess were close to those of the Quaternary central north Pacific ferromanganese crusts, though considerably less radiogenic than lattice-bound silicate Pb. On the other hand, the dominance of eolian supply of Chinese loess to central north Pacific sediments at least for the Quaternary is not debated [e.g., *Nakai et al.*, 1993; *Weber et al.*, 1996]. Therefore, *Jones et al.* [2000] proposed

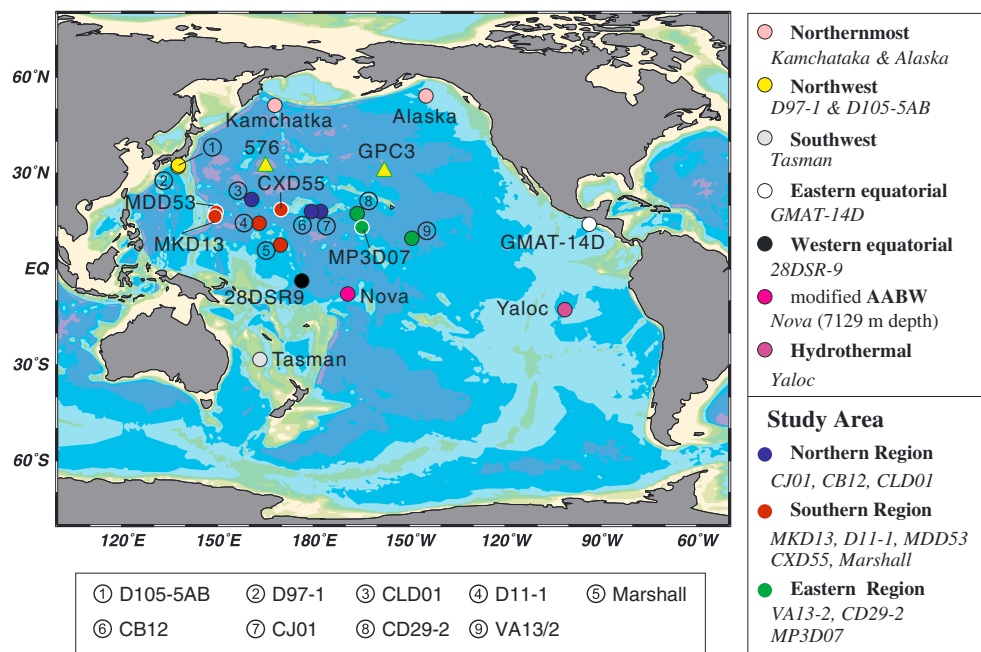


Figure 1. Locations of the studied ferromanganese crusts marked with white edge (MKD13, MDD53, CXD55, MP3D07) together with previously published samples [Ling *et al.*, 1997, 2005; Frank *et al.*, 1999a; van de Flierdt *et al.*, 2003, 2004a, 2004b; Chu *et al.*, 2006], DSDP 86 site 576A, and sediment core LL44-GPC3 [Godfrey, 2002; Pettke *et al.*, 2002]. For convenience of discussion, the marginal crusts were classified into different regions (the northernmost [van de Flierdt *et al.*, 2003], northwest [Chu *et al.*, 2006], southwest [van de Flierdt *et al.*, 2004a], eastern equatorial [Frank *et al.*, 1999a], western equatorial [Chu *et al.*, 2006], modified Antarctic Bottom Water [van de Flierdt *et al.*, 2004a], and hydrothermally influenced water masses near the East Pacific Rise [van de Flierdt *et al.*, 2004b]). In particular, the central North Pacific crusts were also classified according to the geographical locations (red: southern; region; blue: northern region; green: eastern region). CXD55 was grown on a seamount at the Wake Island Passage which was an important channel of northward moving deep water masses [Kawabe and Fujio, 2010], and CXD55 was included in the southern region based on its Pb isotope signature.

that the leachable component of Asian dust likely dominated central North Pacific deep water Pb budgets in the Quaternary. Further, the trends of Pb isotopic compositions of the central North Pacific seawater crusts were shown to be similar to those of the silicate dust fraction of north Pacific sediment cores LL44 GPC3 and DSDP site 576 (Figure 1) [Godfrey, 2002; Ling *et al.*, 2005] supporting that dust may have been the main source of central North Pacific deep water Pb over the entire Cenozoic. However, the silicate dust Pb isotope record reveals distinct mismatches with the ferromanganese crust records. For example, the dust $^{208}\text{Pb}/^{204}\text{Pb}$ record in GPC3 and site 576 prior to 45 Ma was different from the crusts both in the patterns and in the absolute Pb isotopic values. Given that the strong increase in dust flux did not result in a noticeable shift of Pb isotopes in the North Pacific over the last 3 Ma, Pettke *et al.* [2002] argued against the above “dust scenario”, although it has recently been suggested [Willenbring and von Blanckenburg, 2010] that the Quaternary increase in sediment mass accumulation may not

have been as significant as previously thought. It has been proposed that atmospheric aerosol Pb from circum Pacific island arc volcanic exhalations contributed significantly to the dissolved Pb isotope composition of the North Pacific [Pettke *et al.*, 2002]. Following this idea, Klemm *et al.* [2007] argued that the volcanic aerosol Pb flux, which is effectively and globally mixed in the stratosphere, is large enough to control the Pb isotopic composition of central North Pacific deep water. The similarity between the pre-anthropogenic Pb isotope composition of the leachable fraction of Chinese loess and that of central North Pacific hydrogenous ferromanganese crust records was interpreted to be controlled by the common stratospheric volcanic aerosol deposition [Klemm *et al.*, 2007]. Nevertheless, it was recently argued that airborne transport and water mass transport of Pb cannot be distinguished because efficient equatorial water mass mixing may homogenize the dissolved Pb isotope signatures [Meynadier *et al.*, 2008]. The decrease of $^{206}\text{Pb}/^{204}\text{Pb}$ of the crusts during the early Cenozoic was inferred to have

resulted from the crusts moving away from hot spot volcanic activities with radiogenic Pb isotope inputs, whereas afterward, the crusts have been under the influence of the highly homogenized “equatorial band” [Meynadier *et al.*, 2008].

[6] In summary, all the above studies emphasized the apparent homogeneity of the Pb isotope signatures extracted from crusts and largely neglected potential isotope provinciality among different regions of the central North Pacific. In this study, we have investigated potential sources of Pb including circum Pacific arcs, atmospheric deposition, seamount volcanic activities, and hydrothermal inputs. A systematic provinciality of Pb isotopes is revealed in the light of newly obtained Pb isotope results from four ferromanganese crusts.

2. Materials and Methods

[7] To obtain an extended and more detailed picture of the Pb isotope evolution (and Nd isotope evolution for comparison) of deep waters in the central North Pacific, we analyzed two new ferromanganese crusts from the western Pacific seamounts near the Mariana arc (MDD53, 17°26′34″N, 150°17′18″E, water depth 2700m, thickness about 121 mm; MKD13, 16°51′8″N, 149°47′55″E, water depth 1530m, thickness about 80 mm) and the other two from central North Pacific seamounts (CXD55, 19°52′06″N, 172°53′54″E, water depth 1961m, thickness about 85 mm; MP3D07, 13°20′58″N, 165°25′26″W, water depth 2860m, thickness about 90 mm), which grew on basaltic hyaloclastite substrates (Figure 1).

[8] Profiles of samples with typical weights of 5–10 mg were taken from each crust. The digestion method and column chemistry for the purification of Pb and Nd followed Ling *et al.* [2005]. The Nd and Pb isotope data and detailed analytical and mass spectrometric information are provided in supporting information. For analysis of element contents, the crusts were cut perpendicular to growth layers and polished to obtain continuous profile of Co, Mn, Fe, Si, Al, P, Cu, Ni, and Ca using the electron microprobe (JXA-8100) at Nanjing University. We used an empirical Co constant flux method to date these crusts (see supporting information for details).

3. Results

[9] Applying the Co constant flux method to the Co data of the corresponding crusts, ages of 84.8 Ma,

35.8 Ma, 44.8 Ma, and 30.0 Ma were estimated for the analyzed bottom layers at depths of 121.0 mm, 48.3 mm, 80.0 mm, and 83.2 mm of crusts MDD53, CXD55, MP3D07, and MKD13, respectively (Figure A1 in supporting information).¹ The Pb and Nd isotope compositions and their corresponding ages are presented in Table A1 and Figure A2 in supporting information (see also Figure 2).

[10] In crust MDD53, $^{206,207,208}\text{Pb}/^{204}\text{Pb}$ dropped from ~18.85 to ~18.60, from ~15.68 to ~15.62, and from ~38.9 to ~38.64, respectively, around 45 Ma, and then slightly increased afterward. The crust CXD55 only shows a gentle decrease from about 60 Ma to 40 Ma, which suggests that this crust is not old enough at its base to cover the major early Cenozoic Pb isotope shift. The other two crusts (MKD13, MP3D07) analyzed in this study did not record the early Cenozoic radiogenic Pb isotope signatures. In particular, MP3D07 has systematically lower $^{207,208}\text{Pb}/^{204}\text{Pb}$ than other crusts before about 20 Ma and higher $^{206}\text{Pb}/^{204}\text{Pb}$ afterward.

[11] Neodymium isotope compositions of all the crusts, on the other hand, became more radiogenic over time. Interestingly, crusts MDD53 and MKD13 are from locations geographically close to each other but at significantly different water depths. The Nd isotope signatures of the deeper water depth crust MDD53 are somewhat less radiogenic than MKD13, while there are no systematic differences in their Pb isotope records.

4. Discussion

4.1. A Comparison Between the New Records and Published Data

[12] Published North Pacific crusts D11-1 and CD29-2 (Figure 1) were dated using the ^{10}Be method [Ling *et al.*, 1997], later the Co-method [Frank *et al.*, 1999b], as well as Os [Klemm *et al.*, 2005] and Tl [Nielsen *et al.*, 2009] isotope stratigraphy, and thus have more reliable ages. These two crusts, with locations over 3000 km apart from each other, show a marked decrease in $^{208,206}\text{Pb}/^{204}\text{Pb}$ in the early Cenozoic albeit at different amplitudes (Figure 2). A previous study on crusts CJ01, CB12, and CLD01 also confirmed this overall trend [Ling *et al.*, 2005]. In this regard, the trend of Pb isotope compositions as a function of age (i.e., Pb isotope “stratigraphy”) of central North Pacific crusts is well constrained. The general consistency

¹All supporting information can be found in the online version of this article.

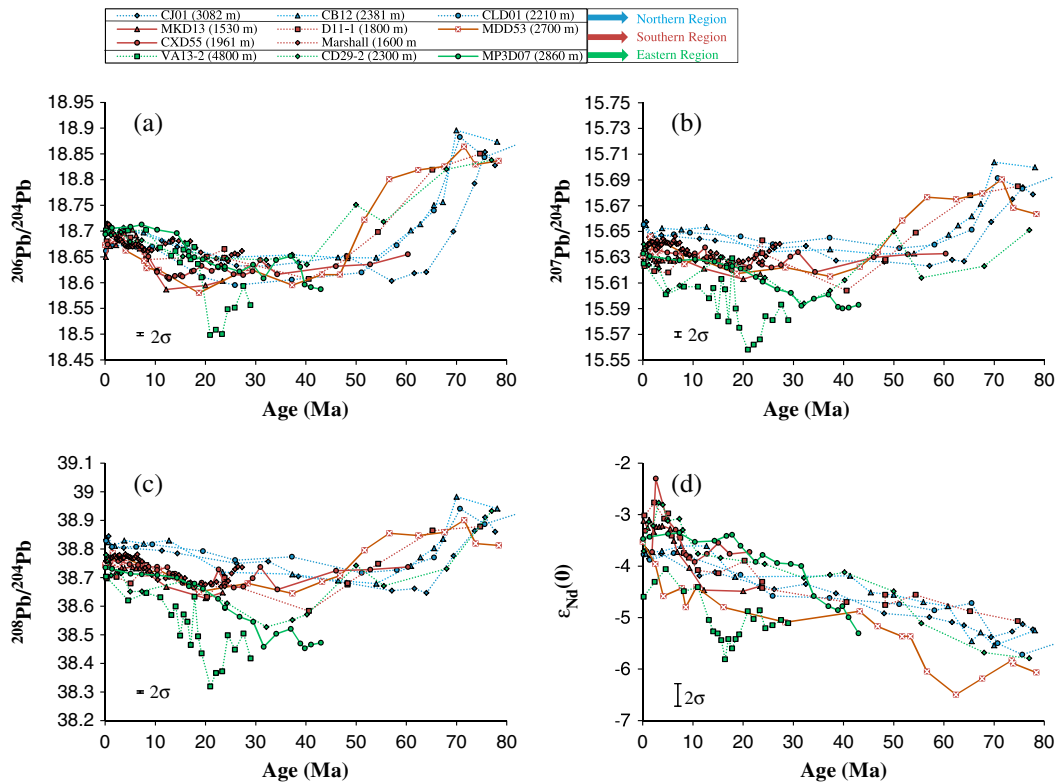


Figure 2. Comparison between data obtained in this study and published records of the central North Pacific ferromanganese crusts: (a) $^{206}\text{Pb}/^{204}\text{Pb}$, (b) $^{207}\text{Pb}/^{204}\text{Pb}$, (c) $^{208}\text{Pb}/^{204}\text{Pb}$, and (d) ϵ_{Nd} time series. Data sources: CJ01, CLD01, CB12 [Ling et al., 2005]; CD29-2, D11-1 [Ling et al., 1997], age model [Nielsen et al., 2009]; VA13-2 [Ling et al., 1997], age model [Frank et al., 1999b]; and Marshall [van de Flierdt et al., 2004a].

of the new Pb isotopic evolution trends with published data (Figure 2) thus supports the reliability of age models of the new crusts (MDD53, MKD13, CXD55, and MP3D07).

[13] Evidently, the systematic Pb isotope differences between different crust records at particular ages, for example around 30 Ma (Figure 2), cannot be the result of dating uncertainties because Pb isotope signatures similar to the unradiogenic minima of the central Pacific crusts (MP3D07, CD29-2, and VA13-2) were not recorded by the western North Pacific crusts at any time (Figures 2b and 2c). The Nd isotope compositions of CXD55 were only measured for the last 20 Myr, and the results are well comparable to those of crust CD29-2 from the eastern North Pacific. Moreover, the new radiogenic Nd isotope record of MP3D07 resembles that of neighboring crust CD29-2 over the last 30 Myr but prior to that was less radiogenic at ϵ_{Nd} values as negative as -5 .

[14] While the ϵ_{Nd} evolution of MKD13 (water depth = 1530 m) is similar to that of the nearby crust D11-1 from a similar water depth (water

depth = 1700 m, Figure 2), MDD53 (water depth = 2700 m) differs from its neighboring shallow crust MKD13 by its systematically less radiogenic Nd isotope compositions over the last 10 Myr (Figure A2). These crusts may have been under the influence of different water masses within the deep western boundary current system [Kawabe and Fujio, 2010; Hu et al., 2012], yet Pb isotope compositions of MDD53 are not distinctively different from MKD13 (Figure A2). In contrast to Pb isotopes, the ϵ_{Nd} signatures of the studied crusts do not show distinct regional distributions (Figure 2). The differences in the evolutions of Nd and Pb isotopes thus support that Pb isotope signatures are less sensitive to ocean circulation than Nd in the central North Pacific due to the much shorter residence time of Pb than that of Nd.

4.2. Geographic Control on the Pb Isotopic Evolution in Central North Pacific Deep Water Over the Cenozoic

[15] The Pb isotope evolution of central North Pacific deep water (Figure 2) had a turning

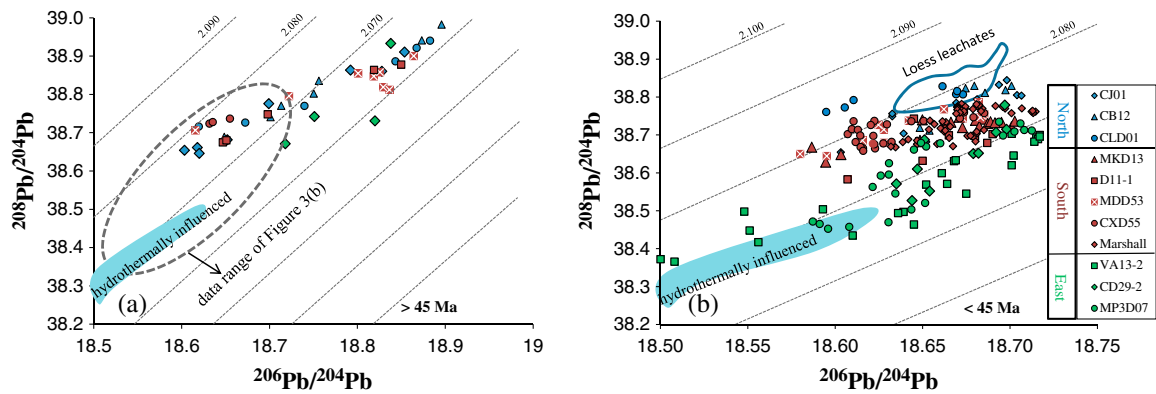


Figure 3. Plot of $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ showing Pb isotopes of the central North Pacific crusts (a) before and (b) after about 45 Ma. Pb isotope data of crusts besides the new ones in this study are from *Ling et al.* [1997, 2005], *David et al.* [2001], and *van de Flierdt et al.* [2004a]. The data of hydrothermally influenced crust Yaloc [van de Flierdt et al., 2004a] which overlap with the oldest part of VA13/2 are also shown for comparison. Loess leachate data were obtained using 0.25 M HCl [Ling et al., 2005] or 10% acetic acid [Jones et al., 2000] as the leaching solution. The dashed lines denote ratios of $^{208}\text{Pb}/^{206}\text{Pb}$.

point roughly at 45 Ma, which corresponded to paleolocations of the crusts near the equator (Figure A3). Moreover, the data obtained in this study together with published records reveal that the spatial distribution of the Pb isotope signatures actually shows a clear provinciality in the central North Pacific, in particular after about 45 Ma (Figure 3). Therefore, for convenience of the discussion, we divide the Pb isotope evolution into two periods at this turning point: the early Cenozoic (>45 Ma) and the late Cenozoic (from 45 Ma to the present).

4.2.1. Inputs From South American Continent as the Main Sources of Radiogenic Pb in the Early Cenozoic

[16] During the latest Cretaceous and early Cenozoic period (e.g., older than 45 Ma), all the crusts were located in the low-latitude Southern Hemisphere and there was no direct deep water exchange between the high southern latitude Pacific, Indian, and Atlantic basins since the Tasman gateway and Drake passage were not opened by then (Figures A3c and A3d) [Lyle et al., 2008]. In this continental configuration and with the prevailing greenhouse conditions, modeling studies [e.g., Huber and Caballero, 2003; Huber et al., 2004] have predicted the existence of a closed sub-Antarctic gyre circulation system in the South Pacific constrained by the Australian, Antarctic, and southernmost South American continents, while the westward middle to low latitude surface currents could directly transport material from the South American coastal area. On the other hand, the formation of deep water in this polar area during the early

Cenozoic is still controversial [e.g., Huber and Sloan, 2001, von der Heydt and Dijkstra, 2006]. For example, while Huber and Sloan [2001] clearly showed that there was no Antarctic deep/bottom water formation under the Eocene greenhouse conditions, the simulation by von der Heydt and Dijkstra [2006] implied that deep water formation was likely to occur if allowing different initial conditions. In both cases, however, the northward transport of the southern high latitude abyssal water was clearly much weaker than at present. Therefore the oceanic environments both in the surface and the deep ocean favored the transport of Pb from the South American coastal area (i.e., the Andean arc) to the locations of the crusts at that time, rather than from the high southern latitude Antarctic or Australian continents.

[17] The Pb isotope composition of the circum-Pacific arcs may also reveal important information on the Pb sources of these crusts during this period (Figure 4). It is noteworthy that the isotopic distribution representing the different arcs shown in Figure 4 likely changed in the geologic past, as the arc production histories in different areas have varied [e.g., Kaiho and Saito, 1994; Hall, 2002; Jicha et al., 2009]. Overall, the Pb isotope compositions of the different arcs each show a wide range of compositions but largely overlap. Thus, it is not possible to distinguish Pb contributions from each arc based on their Pb isotope signatures. Of all the Pacific arcs, the Andean arc is characterized by higher $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ for a given $^{206}\text{Pb}/^{204}\text{Pb}$ and thus plotted at the upper end of the $^{207}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$ diagram, which likely reflects contamination with continental crust during generation of the magmas,

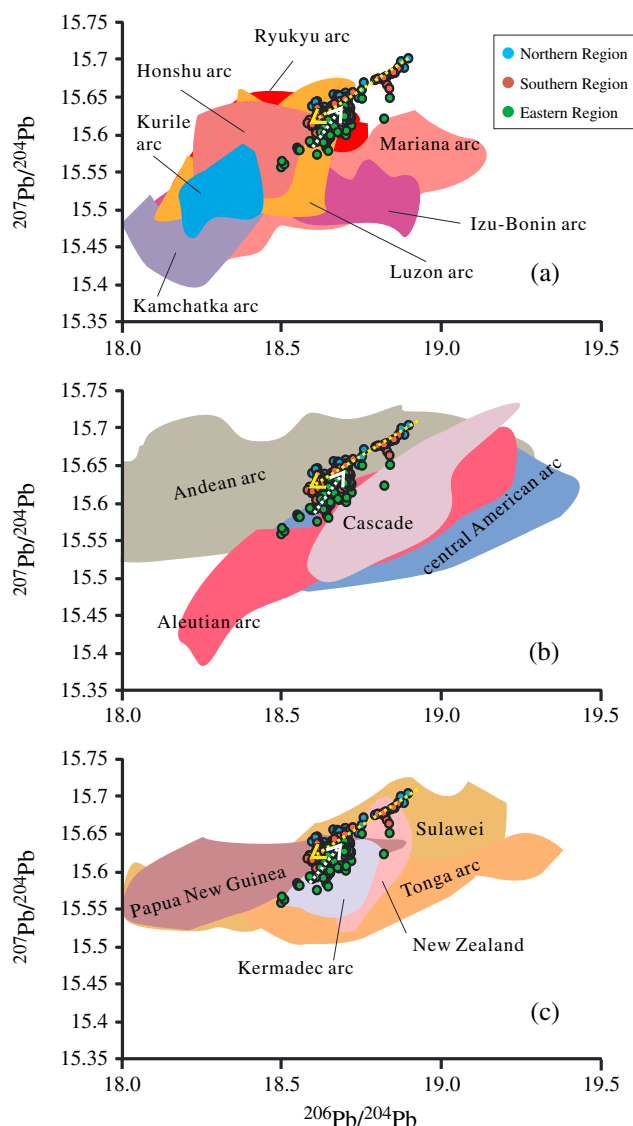


Figure 4. Comparison of Pb isotope signatures recorded by the central North Pacific crusts with those of potential source rocks of the circum Pacific arcs in $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ space: (a) northwestern arcs, (b) northern and eastern arcs, and (c) southwestern arcs. The fields representing the arcs were constructed using the GEOROC geochemical database. A plot in $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ space would give comparable relations (not shown, e.g., *van de Flierdt et al.* [2003]). The yellow arrows denote the trend of the Pb isotope evolution of North Pacific deep water prior to about 45 Ma. The white arrows denote the slight reversing trend after about 20 Ma.

while the Northwest Pacific arcs generally have lower $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ (Figure 4).

[18] Therefore, the Andean weathering inputs are the most likely source of radiogenic Pb isotope signatures for the locations of the ferromanganese crusts at that time. Consequently, the decrease of $^{206,207,208}\text{Pb}/^{204}\text{Pb}$ through the early Cenozoic most likely reflects a reduced contribution from the Andean arc when the crusts moved toward the North Pacific, possibly accompanied by a shift of end-member Pb isotope compositions of the Andean arc.

[19] In addition, volcanic activity of central Pacific seamounts is not expected to have contributed significant amounts of radiogenic Pb to Pacific deep water over the early Cenozoic, given that the late Quaternary Pb isotope distribution in the North Pacific recorded in the surface layers of ferromanganese crusts shows no apparent provincialities related to hotspot volcanism [e.g., *Frank, 2002, Klemm et al., 2007*]. In addition, we compiled Pb isotope data of central North Pacific seamounts (GEOROC database) and compared them to the crust data in $^{207}\text{Pb}/^{204}\text{Pb}$ - $^{206}\text{Pb}/^{204}\text{Pb}$ space (Figure 5). The

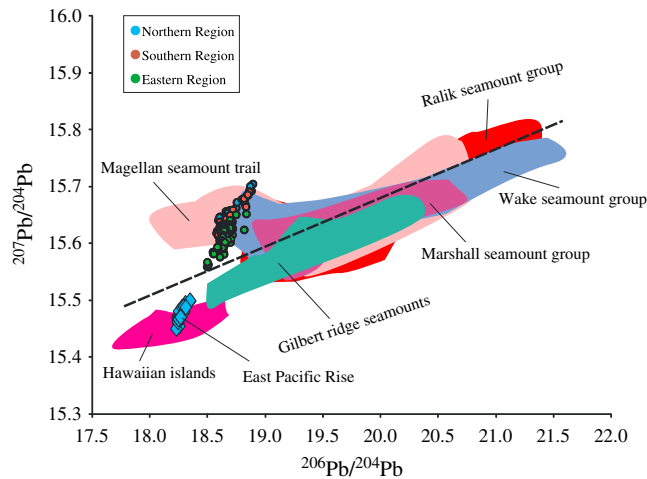


Figure 5. Plot of $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, showing Pb isotope compositions of the central North Pacific crusts, central North Pacific seamounts (GEOROC geochemical database), as well as the hydrothermal inputs which are represented by basalt samples from the modern East Pacific Rise at 10°N (Sims *et al.* [2002]; e.g., see discussion of van de Flierdt *et al.* [2004b]). The circles represent all Pb isotope data of the central North Pacific crusts. The dashed line represents the overall slope of seamount Pb isotopes. Note that the apparent trend of the crust data toward the hydrothermal field and Hawaiian islands is mainly due to the unradiogenic Pb isotope data recorded in the three crusts from the eastern region between about 45 and 20 Ma.

seamounts indeed have overall highly radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ signatures. However, the gentle slope of Pb isotope compositions of the seamounts in Figure 5 implies that the seamounts were highly unlikely predominant sources of Pb for the crusts in the early Cenozoic. Moreover, the least radiogenic values of the crusts appear to point to the Hawaiian Islands' isotopic range (Figure 5). However, the crusts did not show a more Hawaii-like Pb isotopic signal as they moved closer to the islands over the last 45 Myr, which supports that contributions from Hawaiian rocks have not been an important source of Pb.

4.2.2. The Late Cenozoic Record

[20] The Pb isotope compositions of North Pacific deep water at the locations of the crusts in the late Cenozoic show a clear provinciality (Figure 3b), whereby the period of time between 45 and 20 Ma represented the largest differences. In general, the deep Pacific Pb isotope compositions can be explained by the background arc-derived Pb signal, superimposed by potential local sources (e.g., dust dissolution, hydrothermal input, and northward transport of circumpolar water). The deep waters acquired their arc-derived Pb isotope signature due to gyre wide mixing in dissolved form [e.g., von Blanckenburg and Igel, 1999] and possibly deposition-dissolution of arc-derived volcanic aerosols [e.g., Pettke *et al.*, 2002].

[21] For the northern and southern region crusts, the Pb isotope compositions were relatively stable during

this period (Figure 2). As these crusts moved into the North Pacific, the Pb input from western Pacific arcs and possibly Asian dust dissolution became progressively more important. For example, the western Pacific arcs (which are characterized by low $^{206}\text{Pb}/^{204}\text{Pb}$) were able to supply large amounts of Pb with unradiogenic isotope signatures consistent with the evolution trend of the central North Pacific crusts (e.g., Papua New Guinea, Luzon arc, and Honshu arc; Figures 4a and 4c). Given the Pb isotope compositions were within the range of the Andean arc, the Andean arc may still constitute an important source of Pb which, however, is expected to have become progressively less important as the crust locations were moving away over time (Figure A3).

[22] In contrast, hydrothermal input (e.g., from East Pacific Rise; Figure 5) exerted a prominent influence on the eastern crust locations, in particular the deeper sites (VA13-2; Figure 3b) during about 45–20 Ma. This is supported by (1) the lower part of VA13-2 characterized by marked dominance of goethite, indicating enhanced hydrothermal influence coinciding with the most unradiogenic Pb isotope compositions [Frank *et al.*, 1999b]. (2) Eastern crust locations have always been remote from any major direct continental inputs. Even if they received Pb from the American arcs, such fluxes must have been minor given that the isotopic signals of these arcs cannot serve as a suitable unradiogenic mixing end-member (Figure 4b). (3) The hydrogenous-hydrothermal ferromanganese crust from the Bauer Basin (crust Yaloc, Figure 1)

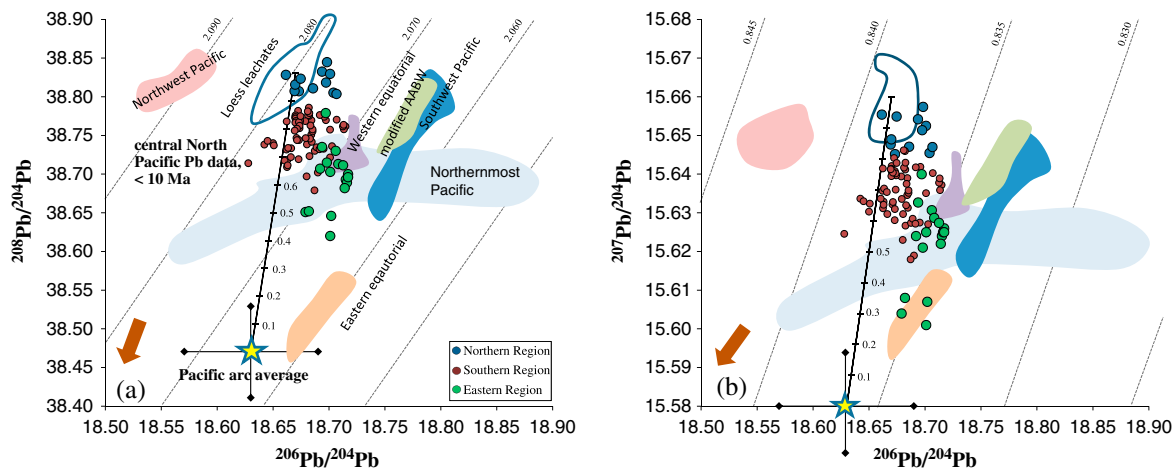


Figure 6. Plot of (a) $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ and (b) $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ showing Pb isotopes of the central North Pacific deep water of the past 10 Ma. For comparison, Pb isotope compositions of water masses around the central North Pacific were also plotted to investigate the potential mixing relationships of the different water masses (see Figure 1 for locations and data sources). Loess leachate data are the same as in Figure 3, with average $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ of 18.67 ± 0.014 , 15.66 ± 0.014 , and 38.83 ± 0.036 , respectively ($n = 14$). The average signature of all Pacific arcs shown in Figure 4 gives $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ of 18.63 ± 0.30 , 15.58 ± 0.052 , and 38.47 ± 0.30 , respectively ($n = 3828$, yellow star). The 1 standard deviation error bars of the yellow stars take into account of the reduction of standard deviations of the source rocks (here we assume a factor 5) due to gyre wide circulation and mixing [von Blanckenburg and Igel, 1999]. Due to the large uncertainties of exact Pb sources, the mixing lines (solid) which are constructed based on the above two end-members (average loess leachates and average Pacific arcs) are only for an illustrative purpose. The dashed lines denote ratios of $^{208}\text{Pb}/^{206}\text{Pb}$ (Figure 6a) and $^{207}\text{Pb}/^{206}\text{Pb}$ (Figure 6b). The brown arrows indicate the position of the hydrothermal Pb end-member which is far outside the range of this figure (e.g., $^{206}\text{Pb}/^{204}\text{Pb}$: 18.25–18.35; $^{207}\text{Pb}/^{204}\text{Pb}$: 15.45–15.50; $^{208}\text{Pb}/^{204}\text{Pb}$: 37.60–37.90 [Sims et al., 2002]).

[van de Flierdt et al., 2004b] in the southeast Pacific clearly has part of Pb derived from hydrothermal activities. And the distribution of unradiogenic Pb isotope signatures of VA13-2, CD29-2, and MP3D07 (Figure 3) together with Yaloc forms a well-defined mixing line reaching the hydrothermal end-member (East Pacific Rise; Figure 5). Therefore, during the period between about 20 and 45 Ma, enhanced hydrothermal activity may have supplied hydrothermal Pb over a regional scale in the central Pacific. Though speculative, enhanced hydrothermal activity was likely associated with the remarkably high seafloor half-spreading rate (>7 cm/yr) of the eastern East Pacific Rise during this period of time [Conrad and Lithgow-Bertelloni, 2007].

[23] Since about 20 Ma, the Pb isotope compositions of the central North Pacific crusts have followed a reversed trend toward more radiogenic signatures, which is represented by small increases in 206 , 207 , $^{208}\text{Pb}/^{204}\text{Pb}$ (Figure 2). The $^{208}\text{Pb}/^{204}\text{Pb}$ of the deep waters at the eastern Pacific crust locations shows a more distinct increase, and consequently an apparent homogenization trend of Pb isotope signatures

(Figure 2). To discuss the evolution of Pb sources at these crust locations during the late Cenozoic, a comparison with the corresponding Nd isotope evolution is helpful. If Nd isotopes are a reliable paleocurrent tracer in the North Pacific, the general increase of ϵ_{Nd} in the North Pacific deep waters at the crust locations (Figure 2d) would suggest that the unradiogenic southern component water has gradually lost its relative influence. Therefore, the reversed trend in Pb isotope signatures over the past 20 Myr cannot be explained by increasing Southern Ocean influence.

[24] Instead, the shift to more radiogenic Pb isotope compositions probably involves proximal input without significantly affecting Nd isotopes which have a longer residence time. To better understand the controlling factors, we compiled Pb isotope compositions of different water masses around the central North Pacific over the last 10 Myr (Figure 6). Given that the hydrothermal end-member field is far away from the studied Pb isotope distribution shown in Figure 6, we infer that hydrothermal influence has been minimal for the central North Pacific deep water over the latest several million years. The Pb isotope

data of deep waters obtained from Izu-Bonin back arc ferromanganese crusts (age <5 Myr) [Chu *et al.*, 2006] represent a northwestern back-arc marginal signal which is distinct from central Pacific deep water [cf. Peate *et al.*, 2009]. The distribution of the central North Pacific Pb isotopes thus does not indicate the importance of marginal northwest Pacific inputs. In contrast to Nd isotopes, the Pb isotope distribution of central North Pacific deep water can also not be explained by mixing between Northernmost Pacific waters and any of the water masses from the south or equatorial Pacific (Figure 6). This is actually not surprising. Due to the sluggish circulation in the North Pacific deep water and the short residence time of Pb, Pb isotopes in the North Pacific are expected to behave highly non-conservative. Thus, Pb isotope signatures of these water masses may have been altered by local inputs during long distance transport. Rather, Pb derived from dust dissolution is likely an important contributor to account for the observed central North Pacific Pb isotope distribution (Figure 6). Obviously, the unradiogenic input from the different arcs is still necessary to explain the provinciality of the Pb isotopes over the last 10 Myr. Therefore Asian dust input could not dominate Pb source for central North Pacific crust locations, despite the fact that silicate deposition in the North Pacific has been dominantly of Asian dust origin [e.g., Nakai *et al.*, 1993; Weber *et al.*, 1996]. It is worthy to note that the abrupt increase of Asian dust flux to the central north Pacific over the last 10 Myr [Kyte *et al.*, 1993] has not been reflected by a notable shift in the Pb isotope compositions of central North Pacific deep water. This is, however, not in contradiction to Asian dust dissolution having been an important source of Pb for the central North Pacific in the last 10 Myr, considering that (a) a recent study suggested that the overall global Quaternary increase in sediment mass accumulation rates, in particular in the central North Pacific may not have been as significant as previously thought [Willenbring and von Blanckenburg, 2010], and (b) more importantly, regardless of the preservation effects, circum Pacific volcanic activity has experienced a similarly abrupt enhancement in the last 10 Myr [Kaiho and Saito, 1994; Straub and Schmincke, 1998; Prueher and Rea, 2001; Jicha *et al.*, 2009]. Thus, it is likely that Pacific arc-derived Pb inputs have also markedly increased in the last 10 Myr.

[25] A mass balance calculation indicates that more than 50% of the Pb in the central North Pacific may

have originated from dust dissolution during the Quaternary (Figure 6). Here we take the background arc Pb isotope composition as the average of Pacific arcs. Interestingly, most of the water mass signatures point to such a background arc-signal. The exception are the marginal Northwest Pacific back-arc water masses [Chu *et al.*, 2006] and the Northernmost Pacific with its closed deep circulation cell [van de Flierdt *et al.*, 2003], in which abundant local supplies of Pb have completely masked the background Pb signal. Note however that a mixing line (Figure 6) drawn only based on dust and the background arc-derived Pb isotope signal seems to be an over-simplification (as the data points deviate from such a two end-member mixing line) which may thus overestimate the dust contribution. In comparison, the oceanic Pb isotope modeling of an earlier study [Henderson and Maier-Reimer, 2002] only gave an estimation of about 10% of dust-derived Pb in the present central North Pacific deep water. The offset between our estimation and the earlier modeling study may be attributed to: (a) a lower estimation of dissolvable fraction of Pb in dust in the earlier modeling study. Henderson and Maier-Reimer [2002] assumed that 8% of the Pb was released from dust to the seawater based on Al solubility but acknowledged that particle surface coatings rich in Pb were not taken into account. Our leaching experiment (see Table A2, about 3.5 ppm leached Pb out of 20 ppm Pb of bulk Chinese loess samples) indicated that Pb is enriched in the Fe-Mn oxides which results in a solubility of Pb from dust on the order of about 17%. (b) The oversimplification of boundary sources in Henderson and Maier-Reimer [2002]. Twenty-four percent of the global Pb influx was assumed to be supplied via the point source of the East China Sea. As a consequence, it may severely underestimate the contribution of dust in this area (i.e., the central North Pacific). (c) Inaccurate end-member estimations in our study, which are unfortunately hard to be improved due to the largely overlapping Pb isotope signatures of different sources. (d) Crusts incorporated Pb during glacial periods when the dust flux was much higher than at present [Chadwick *et al.*, 1999].

4.3. Evaluating the Role of Stratospheric Volcanic Aerosol Deposition on the North Pacific Pb Isotope Evolution

[26] Following the above discussion, we suggest that the similarity of the evolution trends of Pb isotopes at different locations in the North Pacific

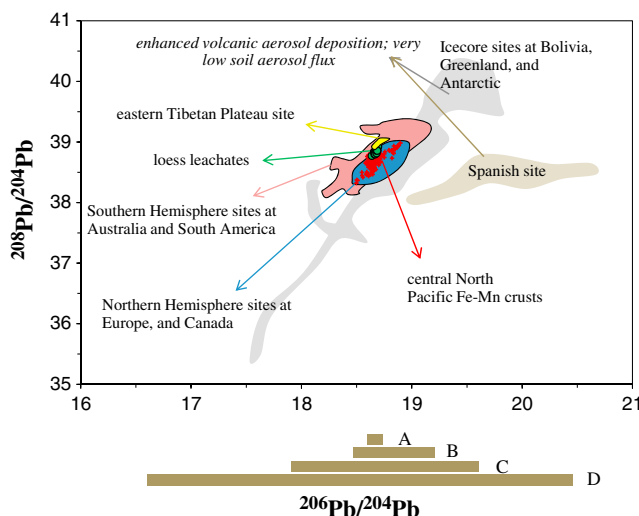


Figure 7. Plot of $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ showing the Pb isotope signature of the direct atmospheric aerosol deposition from worldwide ombrotrophic peat bogs as well as ice-core sites. Peat bog and ice core data were compiled by [Kylander *et al.*, 2010] and are shown together with the latest results of Ferrat *et al.* [2012]. The solid bars below illustrate the late Quaternary $^{206}\text{Pb}/^{204}\text{Pb}$ range of central North Pacific (A) [Frank, 2002], global ocean (B) [Frank, 2002], Pacific arcs (C) (this study), and continental rocks (D) [Kylander *et al.*, 2010]. Note that the gray shades (Spanish site and the ice core sites) are characterized by enhanced deposition of volcanic aerosol deposition but with extreme Pb isotope compositions (e.g., $^{206}\text{Pb}/^{204}\text{Pb} > 20.0$ or < 18.0).

was mainly a result of the source transition from radiogenic Andean arc input to overall less radiogenic western Pacific arcs, hydrothermal inputs, as well as Asian dust dissolution, when these crusts moved from South Pacific to central north Pacific gyre as a consequence of plate movement from the early to the late Cenozoic.

[27] However, the late Quaternary $^{206}\text{Pb}/^{204}\text{Pb}$ ratios recorded in the Fe-Mn crusts or nodules (Figure 7, solid bar B) was suggested to be relatively homogeneous (18.7 ± 0.1) in all ocean basins except the North Atlantic [Klemm *et al.*, 2007]. In particular, there is no significant difference in $^{206}\text{Pb}/^{204}\text{Pb}$ between the North and South Pacific. Considering the large variability of continental rocks (Figure 7, solid bar D), it was suggested that globally mixed volcanic aerosol flux may have been the dominant source for Pacific deep water over the Cenozoic [Klemm *et al.*, 2007]. Moreover, besides the insolubility of silicates, the Pb signatures of the dust silicates have not matched those of seawater since the late Eocene [Klemm *et al.*, 2007]. Rather, the similarity between the Pb isotope compositions of the dust leachates and the central North Pacific deep water was inferred to result from a common atmospheric component (globally homogenized volcanic aerosol from the stratosphere) that had been added to both the loess and the central Pacific Ocean [Klemm *et al.*, 2007].

4.3.1. North Pacific Pb Isotope Distribution in the Late Quaternary Unlikely Controlled By Well-Mixed Stratospheric Volcanic Aerosol Deposition

[28] Here we argue that the stratosphere volcanic aerosol is likely to be overestimated and that Pb isotope compositions in the central North Pacific cannot be regarded as predominantly reflecting stratosphere volcanic aerosol deposition.

[29] First, the Southern Hemisphere Pacific Ocean is characterized by a long-term dust flux about 2 orders of magnitude lower than the Northern Hemisphere [Chadwick *et al.*, 1999] and is located far away from major continents (except glaciated Antarctica), which should be the most likely place to record a dominating well-mixed volcanogenic aerosol flux than the central North Pacific. But this was actually not observed in previous studies given that in contrast to Nd isotopes, the spatial and temporal Pb isotope variability in the Southern Ocean has been relatively high, most likely due to the influence of water mass mixing [Abouchami and Goldstein, 1995; Frank *et al.*, 2002].

[30] Second, the relatively small range of $^{206}\text{Pb}/^{204}\text{Pb}$ ratios recorded in oceanic Fe-Mn crusts during the late Quaternary does not support an overwhelming and globally homogenized atmospheric source. The ombrotrophic

peat bogs and ice cores, which receive the nutrients and trace metals almost exclusively from atmospheric dry or wet deposition [Kylander *et al.*, 2010; Ferrat *et al.*, 2012], reveals that atmospheric dust of both hemispheres (excluding the gray shades with enhanced volcanic aerosol deposition in Figure 7) is comparable with the global ocean in terms of $^{206}\text{Pb}/^{204}\text{Pb}$ range during the late Quaternary (Figure 7, solid bar B). Evidently, the peat bog records are not the result of globally “well mixed” volcanogenic flux deposition as discussed in previous studies [Kylander *et al.*, 2010; Ferrat *et al.*, 2012]. Rather, world-wide peat bogs receive their Pb deposition mainly from local or regional continental dust supplies [Kylander *et al.*, 2010]. In contrast, volcanogenic-contaminated records often showed extreme isotope signatures (Figure 7, gray shades) [Kylander *et al.*, 2010].

[31] In particular, the eastern Tibetan Plateau peat bog records are very similar to the loess leachates, e.g., with $^{206}\text{Pb}/^{204}\text{Pb}$ range of about 18.65–18.8, $^{206}\text{Pb}/^{204}\text{Pb}$ range of about 15.65–15.70, and somewhat higher $^{208}\text{Pb}/^{204}\text{Pb}$ range of 38.90–39.10 [Ferrat *et al.*, 2012], for which local source (e.g., Chinese deserts) mixing relationships have been well established. Around the Pacific, volcanic arcs have $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of about 18.63 ± 0.30 ($n = 3828$). Von Blanckenburg and Igel [1999] modeled the lateral mixing and advection of Pb isotopes in an ocean basin typical of Pacific size. The mixing via ocean currents may reduce the standard deviation of the Pb isotope signatures (Figure 7, solid bar C) by a factor of about 5 when Pb enters from marginal areas to the open ocean deep water, which may have homogenized the arc-derived Pb signatures creating the observed Pacific variability (Figure 7, solid bar A).

[32] Therefore, we suggest that the apparent small range of Pb isotope signatures of both loess leachates and the central North Pacific deep waters cannot have mainly resulted from atmospheric deposition of volcanic aerosol-derived Pb [Klemm *et al.*, 2007], but local sources were obviously in most cases more important.

4.3.2. Trace Element Patterns of the Chinese Loess Leachates

[33] Another aspect regarding the role of the stratospheric volcanic aerosol deposition is related to the origin of Pb in the easily mobilizable component (i.e., carbonates and Fe-Mn oxides) of the dust

particles, which is investigated by the leaching experiments on loess samples collected from different regions of the Chinese Loess Plateau (see supporting information for the procedure and results). The method applied is similar to the leaching of marine sediments [Piotrowski, 2005; Gutjahr *et al.*, 2007] allowing extraction of the authigenic seawater-derived fraction of the particles.

[34] The leachable component of Chinese loess in principle could be composed of carbonates and oxides of various origins. The results show that Pb leached during the de-carbonation step only accounted for 1–20% (Table A2) of the total leachates, indicating that the Fe-Mn (hydro) oxides are the main host phase of leachable Pb. The Fe-Mn (hydro)oxides coatings of dust were previously referred to as “pre-formed oxides” and were suggested to exchange with seawater [Bayon *et al.*, 2004]. Interestingly, trace metals of desert varnish (fine coating of Fe-Mn oxihydroxides on rock surfaces typically observed in arid environments) were suggested to be mainly derived from aqueous leaching of dust particles [e.g., Jones, 1991; Thiagarajan and Lee, 2004]. The agreement between trace element patterns of loess leachates and desert varnish (Figure A4, e.g., mid-REE enrichment, relative enrichment of particle reactive elements like Co, Ni, Pb, V, and REEs over HFSE (immobile), Rb and Sr (high solubility)) supports that their trace metals have similar origin (i.e., aqueous leaching from silicate minerals). Moreover, although Pb is clearly enriched in the Fe-Mn phase compared with the upper continental crust (UCC), there is no indication that Pb is dominated by volcanogenic deposition, as volatile and particle reactive Pb is not distinctively more enriched than the other particle reactive but much less volatile elements (Co, Ni) in the leachable component [e.g., Taran *et al.*, 1995]. Although the trace element patterns cannot constrain the origin of leachable unradiogenic Pb isotopes due to the lack of strictly distinct end-member compositions, it lends additional support to the inference that dust leachable unradiogenic Pb isotope compositions do not reflect predominant volcanic-derived volatile Pb deposition.

[35] As the ultimate sources of the soil-derived dust aerosol may have undergone several sedimentation cycles since the weathering of the primary crystalline rocks (i.e., very old soil), the less radiogenic signatures of the Fe-Mn oxides

than the residue silicates [Jones *et al.*, 2000; Ling *et al.*, 2005] might result from the time-integrated effect of lower Th/Pb and U/Pb in the leachable oxides than the solid residues. Nevertheless, a dedicated future study is needed in order to precisely understand the cause of the less radiogenic Pb isotope compositions in the dust leachates.

5. Conclusions

[36] Radiogenic Pb isotopes can be used to trace ocean circulation only at locations where local inputs have been insignificant compared to the Pb transported by advection. In many cases, such conditions are not met because of the very short residence time of Pb. Therefore, changes in the dissolved Pb isotope composition in deep water masses over time will mainly reflect the history of local external inputs. This is even evident in the Pb isotope evolution of central North Pacific deep water, which is far away from direct coastal inputs.

[37] Despite the fact that they are located in the same gyre system, the North Pacific records can be classified geographically based on significant Pb isotope provincialities. Different sources and transport mechanisms have accounted for Pb isotope signatures delivered to the central North Pacific throughout the Cenozoic. We propose that South American coastal inputs predominantly supplied radiogenic Pb to the crusts in the latest Cretaceous and early Cenozoic through wind or lateral current transport. Since approximately 45 Ma, inputs from erosion of other Pacific arcs (especially the western Pacific arcs) have become more important in order to explain the observed isotope distribution. However, the quantitative contribution of Pb from particular island arcs cannot be distinguished based on Pb isotopes alone. During about 45–20 Ma, enhanced hydrothermal input notably affected the Pb isotopes of the eastern region ferromanganese crusts. Dissolution of Asian dust and loess has been a resolvable component since about 20 Ma, when the Pb isotope evolution showed a slightly reversed trend compared to the early Cenozoic. Previously proposed stratospheric volcanic aerosol deposition could contribute Pb to the North Pacific which was nevertheless not sufficient to erase the observed Pb isotope provincialities in different areas covered by North Pacific deep water.

Acknowledgments

[38] We are grateful to the two anonymous reviewers whose constructive and insightful comments greatly improved the manuscript. T. Yang and W. Pu are thanked for providing technical support during Pb and Nd isotope measurement. This study was funded by the Chinese Association for Research of Oceanic Mineral Resources (DY-115-01-2-2) and a Doctoral Station Grant of the Education Ministry of China.

References

- Abouchami, W., and S. L. Goldstein (1995), A lead isotopic study of circum-Antarctic manganese nodules, *Geochim. Cosmochim. Acta*, *59*(9), 1809–1820.
- Abouchami, W., S. L. Goldstein, S. J. G. Galer, A. Eisenhauer, and A. Mangini (1997), Secular changes of lead and neodymium in central Pacific seawater recorded by a Fe-Mn crust, *Geochim. Cosmochim. Acta*, *61*(18), 3957–3974.
- Basak, C., E. E. Martin, and G. D. Kamenov (2011), Seawater Pb isotopes extracted from Cenozoic marine sediments, *Chem. Geol.*, *286*(3–4), 94–108.
- Bayon, G., C. R. German, K. W. Burton, R. W. Nesbitt, and N. Rogers (2004), Sedimentary Fe–Mn oxyhydroxides as paleoceanographic archives and the role of aeolian flux in regulating oceanic dissolved REE, *Earth Planet. Sci. Lett.*, *224*(3–4), 477–492.
- Chadwick, O. A., L. A. Derry, P. M. Vitousek, B. J. Huebert, and L. O. Hedin (1999), Changing sources of nutrients during four million years of ecosystem development, *Nature*, *397*(6719), 491–497.
- Christensen, J. N., A. N. Halliday, L. V. Godfrey, J. R. Hein, and D. K. Rea (1997), Climate and ocean dynamics and the lead isotopic records in Pacific ferromanganese crusts, *Science*, *277*(5328), 913–918.
- Chu, N. C., C. M. Johnson, B. L. Beard, C. R. German, R. W. Nesbitt, M. Frank, M. Bohn, P. W. Kubik, A. Usui, and I. Graham (2006), Evidence for hydrothermal venting in Fe isotope compositions of the deep Pacific Ocean through time, *Earth Planet. Sci. Lett.*, *245*(1–2), 202–217.
- Conrad, C. P., and C. Lithgow-Bertelloni (2007), Faster seafloor spreading and lithosphere production during the mid-Cenozoic, *Geology*, *35*(1), 29–32.
- David, K., M. Frank, R. K. O’Nions, N. S. Belshaw, and J. W. Arden (2001), The Hf isotope composition of global seawater and the evolution of Hf isotopes in the deep Pacific Ocean from Fe-Mn crusts, *Chem. Geol.*, *178*(1–4), 23–42.
- Ferrat, M., D. J. Weiss, S. F. Dong, D. J. Large, B. Spiro, Y. B. Sun, and K. Gallagher (2012), Lead atmospheric deposition rates and isotopic trends in Asian dust during the last 9.5 kyr recorded in an ombrotrophic peat bog on the eastern Qinghai-Tibetan Plateau, *Geochim. Cosmochim. Acta*, *82*, 4–22.
- Frank, M. (2002), Radiogenic isotopes: Tracers of past ocean circulation and erosional input, *Rev. Geophys.*, *40*(1), 1001, doi:10.1029/2000RG000094.
- Frank, M., B. C. Reynolds, and R. K. O’Nions (1999a), Nd and Pb isotopes in Atlantic and Pacific water masses before and after closure of the Panama gateway, *Geology*, *27*(12), 1147–1150.
- Frank, M., R. K. O’Nions, J. R. Hein, and V. K. Banakar (1999b), 60 Myr records of major elements and Pb–Nd isotopes from hydrogenous ferromanganese crusts:

- Reconstruction of seawater paleochemistry, *Geochim. Cosmochim. Acta*, 63(11-12), 1689–1708.
- Frank, M., N. Whiteley, S. Kasten, J. R. Hein, and K. O’Nions (2002), North Atlantic deep water export to the Southern Ocean over the past 14 Myr: Evidence from Nd and Pb isotopes in ferromanganese crusts, *Paleoceanography*, 17(2), doi:10.1029/2000PA000606.
- Godfrey, L. V. (2002), Temporal changes in the lead isotopic composition of red clays: Comparison with ferromanganese crust records, *Chem. Geol.*, 185(3-4), 241–254.
- Gutjahr, M., M. Frank, C. H. Stirling, V. Klemm, T. van de Fliedert, and A. N. Halliday (2007), Reliable extraction of a deepwater trace metal isotope signal from Fe-Mn oxyhydroxide coatings of marine sediments, *Chem. Geol.*, 242(3-4), 351–370.
- Hall, R. (2002), Cenozoic geological and plate tectonic evolution of SE Asia and the SW Pacific: Computer-based reconstructions, model and animations, *J Asian Earth Sci.*, 20(4), 353–431, Pii S1367-9120(01)00069-4.
- Henderson, G. M., and K. W. Burton (1999), Using (234U/238U) to assess diffusion rates of isotope tracers in ferromanganese crusts, *Earth Planet. Sci. Lett.*, 170(3), 169–179.
- Henderson, G. M., and E. Maier-Reimer (2002), Advection and removal of 210Pb and stable Pb isotopes in the oceans: A general circulation model study, *Geochim. Cosmochim. Acta*, 66(2), 257–272.
- Hu, R., T.-Y. Chen, and H.-F. Ling (2012), Late Cenozoic history of deep water circulation in the western North Pacific: Evidence from Nd isotopes of ferromanganese crusts, *Chinese Sci. Bull.*, doi:1-10, 10.1007/s11434-012-5322-9.
- Huber, M., H. Brinkhuis, C. E. Stickley, K. Doos, A. Sluijs, J. Warnaar, S. A. Schellenberg, and G. L. Williams (2004), Eocene circulation of the Southern Ocean: Was Antarctica kept warm by subtropical waters?, *Paleoceanography*, 19(4).
- Huber, M., and L. C. Sloan (2001), Heat transport, deep waters, and thermal gradients: Coupled simulation of an Eocene Greenhouse Climate, *Geophys. Res. Lett.*, 28(18), 3481–3484.
- Huber, M., and R. Caballero (2003), Eocene El Niño: Evidence for robust tropical dynamics in the “hothouse”, *Science*, 299(5608), 877–881.
- Jicha, B. R., D. W. Scholl, and D. K. Rea (2009), Circum-Pacific arc flare-ups and global cooling near the Eocene-Oligocene boundary, *Geology*, 37(4), 303–306.
- Jones, C. E. (1991), Characteristics and origin of rock varnish from the hyperarid coastal deserts of northern Peru, *Quaternary Res.*, 35(1), 116–129.
- Jones, C. E., A. N. Halliday, D. K. Rea, and R. M. Owen (2000), Eolian inputs of lead to the North Pacific, *Geochim. Cosmochim. Acta*, 64(8), 1405–1416.
- Kaiho, K., and S. Saito (1994), Oceanic crust production and climate during the last 100 Myr, *Terra Nova*, 6(4), 376–384.
- Kawabe, M., and S. Fujio (2010), Pacific Ocean Circulation Based on Observation, *Journal of Oceanography*, 66(3), 389–403.
- Klemm, V., S. Lévassieur, M. Frank, J. R. Hein, and A. N. Halliday (2005), Osmium isotope stratigraphy of a marine ferromanganese crust, *Earth Planet. Sci. Lett.*, 238(1–2), 42–48.
- Klemm, V., B. Reynolds, M. Frank, T. Pettke, and A. N. Halliday (2007), Cenozoic changes in atmospheric lead recorded in central Pacific ferromanganese crusts, *Earth Planet. Sci. Lett.*, 253(1-2), 57–66.
- Kylander, M. E., J. Klaminder, R. Bindler, and D. J. Weiss (2010), Natural lead isotope variations in the atmosphere, *Earth Planet. Sci. Lett.*, 290(1-2), 44–53.
- Kyte, F. T., M. Leinen, G. Ross Heath, and L. Zhou (1993), Cenozoic sedimentation history of the central North Pacific: Inferences from the elemental geochemistry of core LL44-GPC3, *Geochim. Cosmochim. Acta*, 57(8), 1719–1740.
- Ling, H. F., K. W. Burton, R. K. O’Nions, B. S. Kamber, F. von Blanckenburg, A. J. Gibb, and J. R. Hein (1997), Evolution of Nd and Pb isotopes in Central Pacific seawater from ferromanganese crusts, *Earth Planet. Sci. Lett.*, 146(1-2), 1–12.
- Ling, H. F., S. Y. Jiang, M. Frank, H. Y. Zhou, F. Zhou, Z. L. Lu, X. M. Chen, Y. H. Jiang, and C. D. Ge (2005), Differing controls over the Cenozoic Pb and Nd isotope evolution of deepwater in the central North Pacific Ocean, *Earth Planet. Sci. Lett.*, 232(3-4), 345–361. doi:10.1016/j.epsl.2004.12.009.
- Lyle, M., J. Barron, T. J. Bralower, M. Huber, A. O. Lyle, A. C. Ravelo, D. K. Rea, and P. A. Wilson (2008), Pacific ocean and Cenozoic evolution of climate, *Rev. Geophys.*, 46(2).
- Meynadier, L., C. Allegre, and R. K. O’Nions (2008), Plate tectonics, radiogenic isotopic tracers and paleoceanography; the case of the manganese crusts in the Pacific, *Earth Planet. Sci. Lett.*, 272(3-4), 513–522.
- Nakai, S., A. Halliday, and D. Rea (1993), Provenance of dust in the Pacific Ocean, *Earth Planet. Sci. Lett.*, 119(1-2), 143–157.
- Nielsen, S. G., S. Mar-Gerrison, A. Gannoun, D. LaRowe, V. Klemm, A. N. Halliday, K. W. Burton, and J. R. Hein (2009), Thallium isotope evidence for a permanent increase in marine organic carbon export in the early Eocene, *Earth Planet. Sci. Lett.*, 278(3-4), 297–307.
- Peate, D. W., L. Falkena, and A. J. R. Kent (2009), Pb isotope variations in hydrogenetic Fe-Mn crusts from the Izu-Bonin fore-arc, *Chem. Geol.*, 258(3-4), 288–298.
- Pettke, T., A. N. Halliday, and D. K. Rea (2002), Cenozoic evolution of Asian climate and sources of Pacific seawater Pb and Nd derived from eolian dust of sediment core LL44-GPC3, *Paleoceanography*, 17(3), doi:10.1029/2001PA000673.
- Piotrowski, A. M. (2005), A high resolution record of ocean circulation during the last glacial cycle from neodymium isotopes, Ph.D. thesis, Columbia University.
- Prueher, L. M., and D. K. Rea (2001), Tephrochronology of the Kamchatka-Kurile and Aleutian arcs: Evidence for volcanic episodicity, *J. Volcanol. Geoth. Res.*, 106(1-2), 67–84.
- Schaule, B. K., and C. C. Patterson (1981), Lead concentrations in the northeast Pacific: Evidence for global anthropogenic perturbations, *Earth Planet. Sci. Lett.*, 54(1), 97–116.
- Sims, K. W. W., et al. (2002), Chemical and isotopic constraints on the generation and transport of magma beneath the East Pacific Rise, *Geochim. Cosmochim. Acta*, 66(19), 3481–3504, doi:10.1016/s0016-7037(02)00909-2.
- Straub, S. M., and H. U. Schmincke (1998), Evaluating the tephra input into Pacific Ocean sediments: Distribution in space and time, *Geol. Rundsch.*, 87(3), 461–476.
- Taran, Y. A., J. W. Hedenquist, M. A. Korzhinsky, S. I. Tkachenko, and K. I. Shmulovich (1995), Geochemistry of magmatic gases from Kudryavy Volcano, Iturup, Kuril Islands, *Geochim. Cosmochim. Acta*, 59(9), 1749–1761.
- Thiagarajan, N., and C. T. A. Lee (2004), Trace-element evidence for the origin of desert varnish by direct aqueous atmospheric deposition, *Earth Planet. Sci. Lett.*, 224(1-2), 131–141.
- van de Fliedert, T., M. Frank, A. N. Halliday, J. R. Hein, B. Hattendorf, D. Gunther, and P. W. Kubik (2003), Lead isotopes in North Pacific deep water—Implications for past



- changes in input sources and circulation patterns, *Earth Planet. Sci. Lett.*, 209(1-2), 149–164.
- van de Flierdt, T., M. Frank, A. N. Halliday, J. R. Hein, B. Hattendorf, D. Guenther, and P. W. Kubik (2004a), Deep and bottom water export from the Southern Ocean to the Pacific over the past 38 million years, *Paleoceanography*, 19(1), doi:10.1029/2003PA000923.
- van de Flierdt, T., M. Frank, A. N. Halliday, J. R. Hein, B. Hattendorf, D. Gunther, and P. W. Kubik (2004b), Tracing the history of submarine hydrothermal inputs and the significance of hydrothermal hafnium for the seawater budget—A combined Pb-Hf-Nd isotope approach, *Earth Planet. Sci. Lett.*, 222(1), 259–273.
- von der Heydt, A., and H. A. Dijkstra (2006), Effect of ocean gateways on the global ocean circulation in the late Oligocene and early Miocene, *Paleoceanography*, 21(1).
- von Blanckenburg, F., and H. Igel (1999), Lateral mixing and advection of reactive isotope tracers in ocean basins: Observations and mechanisms, *Earth Planet. Sci. Lett.*, 169(1-2), 113–128.
- von Blanckenburg, F., R. K. O'Nions, and J. R. Hein (1996), Distribution and sources of pre-anthropogenic lead isotopes in deep ocean water from Fe-Mn crusts, *Geochim. Cosmochim. Acta*, 60(24), 4957–4963.
- Weber, E. T., R. M. Owen, G. R. Dickens, A. N. Halliday, C. E. Jones, and D. K. Rea (1996), Quantitative resolution of eolian continental crustal material and volcanic detritus in North Pacific surface sediment, *Paleoceanography*, 11(1), 115–127.
- Willenbring, J. K., and F. von Blanckenburg (2010), Long-term stability of global erosion rates and weathering during late-Cenozoic cooling, *Nature*, 465(7295), 211–214.
- Wu, J. F., R. Rember, M. B. Jin, E. A. Boyle, and A. R. Flegal (2010), Isotopic evidence for the source of lead in the North Pacific abyssal water, *Geochim. Cosmochim. Acta*, 74(16), 4629–4638.