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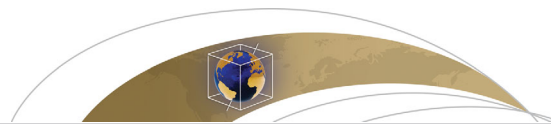
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## RESEARCH ARTICLE

10.1002/2015GC005871

## Key Points:

- $\epsilon$ Nd of foraminifera investigated for the first time in the South China Sea
- Improvement of the extraction of seawater Nd isotopes from marine sediments
- Past hydrological changes in the subtropical Pacific for the last 25 kyr

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## Neodymium isotopic composition in foraminifera and authigenic phases of the South China Sea sediments: Implications for the hydrology of the North Pacific Ocean over the past 25 kyr

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**Abstract**  $\epsilon$ Nd and normalized Rare Earth Elements (REE) patterns of benthic and planktonic foraminifera and Fe-Mn coatings precipitated on sediments have been investigated for the South China Sea (SCS) to (1) assess the reliability of the extraction of past seawater  $\epsilon$ Nd in the SCS and to (2) reconstruct past hydrological changes during the last 25 kyr. Reductively cleaned mono-specific planktonic foraminifera (*Globigerinoides ruber*) and mixed benthic foraminifera in core-top sediments from 1500 to 2400 m display similar  $\epsilon$ Nd values to those of the modern Pacific Deep Water (PDW) ( $\epsilon$ Nd of  $-3.9$  to  $-4.4$ ). Furthermore, the  $\epsilon$ Nd of the reductive cleaning solutions shows similar  $\epsilon$ Nd values to ones obtained on cleaned foraminifera. Combined with PAAS-normalized REE patterns, these results confirm that the oxidative and reductive cleaning procedure applied to foraminifera does not totally remove all of the Fe-Mn coatings and that  $\epsilon$ Nd values yielded by cleaned planktonic foraminifera retain the  $\epsilon$ Nd imprint of the bottom and/or pore water.  $\epsilon$ Nd values obtained from a leaching procedure carried out on the bulk non-decarbonated sediments are comparable to the  $\epsilon$ Nd values of the modern PDW, whereas a similar leaching procedure applied to decarbonated sediments reveals a bias due to contamination with Nd deriving from lithogenic particles. In core MD05-2904, seawater  $\epsilon$ Nd, reconstructed from planktonic foraminifera, indicates that the last glacial period is characterized by lower  $\epsilon$ Nd ( $-5.2 \pm 0.2$  to  $-6.4 \pm 0.3$ ) than the late Holocene ( $-4.1 \pm 0.2$ ). Assuming that Nd input from river does not change strongly the  $\epsilon$ Nd of the PDW of the northern SCS, these  $\epsilon$ Nd variations suggest a higher relative proportions of southern-sourced water in the deep water of the western subtropical Pacific Ocean during the last glacial period.

### 1. Introduction

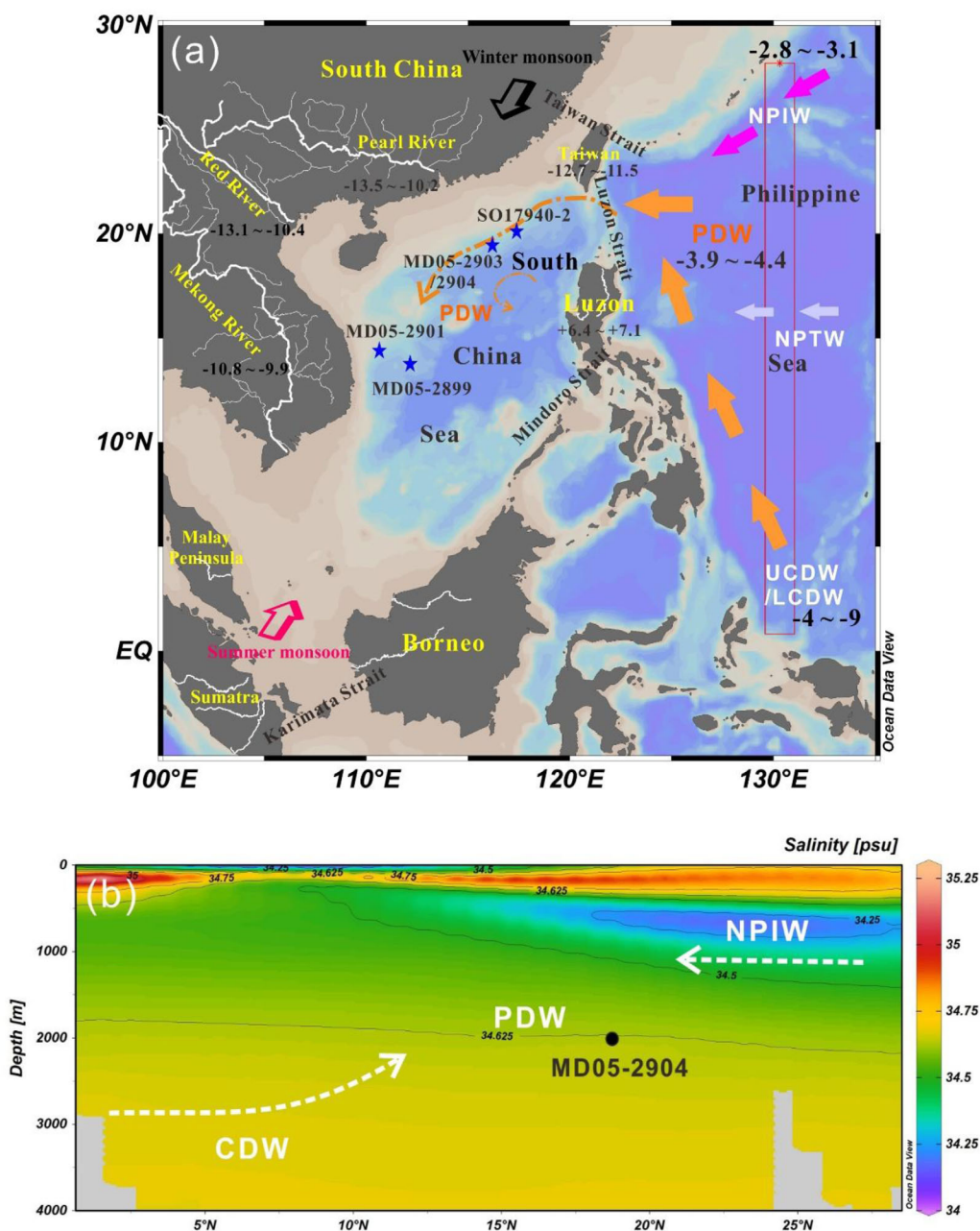
The importance of global ocean circulation for climate variability is now widely recognized [Broecker and Denton, 1990; Rahmstorf, 2002]. The Pacific Ocean plays a key role in global ocean circulation in terms of heat redistribution through surface current flow from the equatorial areas to high latitudes, which in turn changes the carbon storage capacity of the ocean by deep water ventilation or stratification, resulting in significant climatic implications [Matsumoto et al., 2002; Herguera et al., 2010]. Even though it has received increasing attention over recent decades [Talley and Joyce, 1992; Reid, 1997; Talley and Yun, 2001; Siedler et al., 2004; Zenk et al., 2005; Kawabe et al., 2003, 2005, 2006, 2009; Kawabe and Fujio, 2010], the evolution through time of North Pacific Deep Water and North Pacific Intermediate Water (NPDW and NPIW), as well as the penetration of southern-sourced water (SSW) into the North Pacific Ocean, is as yet not well constrained since the last glacial period and is still controversial [Galbraith et al., 2007; Okazaki et al., 2010; Chikamoto et al., 2012; Rella et al., 2012; Jaccard and Galbraith, 2013; Max et al., 2014; Rella and Uchida, 2014].

The spatial distributions of the seawater neodymium (Nd) isotopic composition, expressed here as " $\epsilon$ Nd =  $\left( \frac{^{143}\text{Nd}/^{144}\text{Nd}}{^{143}\text{Nd}/^{144}\text{Nd}}_{\text{CHUR}} - 1 \right) \times 10,000$  (CHUR: Chondritic Uniform Reservoir) [Jacobsen and Wasserburg, 1980]," have been recently established for the Philippine Sea and for the northern part of the SCS. This study highlights that seawater  $\epsilon$ Nd of deep water masses in the Philippine Sea

results from the vertical mixing of the SSW, corresponding to the Upper Circumpolar Deep Water and Lower Circumpolar Deep Water (UCDW and LCDW) characterized by an  $\epsilon_{\text{Nd}}$  value of around  $-6$  to  $-9$  in the Southern Ocean [Piepgras and Wasserburg, 1982; Jeandel, 1993; Carter *et al.*, 2012; Amakawa *et al.*, 2013; Stichel *et al.*, 2012; Rickli *et al.*, 2014; Basak *et al.*, 2015], and the northern-sourced water (NSW), corresponding to the North Pacific Deep Water and North Pacific Intermediate Water (NPDW and NPIW) characterized by  $\epsilon_{\text{Nd}}$  value of  $\sim -4$  to  $-3$  [Piepgras and Jacobsen, 1988; Amakawa *et al.*, 2004, 2009]. In the deep ocean, the only way to alter the initial Nd isotopic composition of water mass is to add Nd with a different  $\epsilon_{\text{Nd}}$  values through riverine and eolian inputs and boundary exchange or by mixing isotopically different water masses [e.g., Lacan and Jeandel, 2001, 2005; Goldstein and Hemming, 2003; Frank, 2002]. The spatial distribution of seawater  $\epsilon_{\text{Nd}}$  in the northern SCS has shown that  $\epsilon_{\text{Nd}}$  of the deep water masses of the SCS below 1500 m is homogenous ( $-3.5 \pm 0.3$  and  $-4.5 \pm 0.4$ ) and similar to that of the deep Philippine Sea at similar and greater water depth ( $-3.6 \pm 0.2$  to  $-4.4 \pm 0.4$ ) [Wu *et al.*, in press]. This implies that the  $\epsilon_{\text{Nd}}$  values of the PDW which enters the northern SCS through the Luzon Strait ( $>2400$  m) is not modified by the exchange process [Wu *et al.*, in press] and that Nd can be considered to faithfully trace water mass provenance and mixing of the Philippine Sea intermediate and deep water masses [Wu *et al.*, in press].

Hence, seawater  $\epsilon_{\text{Nd}}$  record obtained from marine cores from the northwestern margin of the SCS can be considered to have a potential to assess the glacial-interglacial behavior of NSW and SSW in the North Pacific Ocean that has been debated. In this context, it is important to establish a reliable method for  $\epsilon_{\text{Nd}}$  extraction from the SCS marine cores. Recent studies have debated about how to extract seawater  $\epsilon_{\text{Nd}}$  signature from foraminifera and dispersed authigenic Fe-Mn coatings of deep-sea sediments [Bayon *et al.*, 2002; Vance *et al.*, 2004; Piotrowski *et al.*, 2012; Kraft *et al.*, 2013; Tachikawa *et al.*, 2014]. While the Nd isotopic composition obtained from benthic foraminifera can be used to reconstruct bottom  $\epsilon_{\text{Nd}}$  seawater records, the significance of  $\epsilon_{\text{Nd}}$  values obtained from reductively and non-reductively cleaned planktonic foraminifera is still under debate [Vance and Burton, 1999; Vance *et al.*, 2004; Martínez-Botí *et al.*, 2009; Kraft *et al.*, 2013; Pena *et al.*, 2013; Tachikawa *et al.*, 2013, 2014]. Investigation of REE in various phases of foraminifera suggests that approximately 90% of the REE reside in the coating fraction, and the remaining 10% is contained in the foraminifera calcite lattice [Palmer, 1985]. Thus, it has been proposed that  $\epsilon_{\text{Nd}}$  values obtained from the diagenetic Fe-Mn coatings precipitated on foraminiferal shells, primarily correspond to bottom seawater and/or pore water  $\epsilon_{\text{Nd}}$  values [Tachikawa *et al.*, 2013, 2014]. Nevertheless, several other studies suggest that the reductive cleaning procedure can efficiently remove the Fe-Mn coatings precipitated on the planktonic foraminifera and can be used to establish  $\epsilon_{\text{Nd}}$  of surface or subsurface seawater [e.g., Pena *et al.*, 2013; Osborn *et al.*, 2008; Martínez-Botí *et al.*, 2009].

The  $\epsilon_{\text{Nd}}$  seawater record for the late quaternary has been successfully reconstructed from  $\epsilon_{\text{Nd}}$  analyzed on the Fe-Mn oxide fraction leached from sediments collected in certain areas of the ocean [Rutberg *et al.*, 2000; Piotrowski *et al.*, 2004; Gutjahr *et al.*, 2008; Martin *et al.*, 2010]. In some other locations, however, especially close to continental margins under the influence of strong river discharges,  $\epsilon_{\text{Nd}}$  values of sediment leachates do not match the seawater  $\epsilon_{\text{Nd}}$  but appear to be biased by preformed Fe-Mn coatings delivered from rivers [Bayon *et al.*, 2004; Gutjahr *et al.*, 2008]. In addition, the analytical procedures permitting the correct extraction of seawater  $\epsilon_{\text{Nd}}$  from the authigenic phase in bulk sediments are controversial [Bayon *et al.*, 2002; Kraft *et al.*, 2013; Piotrowski *et al.*, 2012]. Recently, Wilson *et al.* [2013] have reassessed the reliability of different approaches to extract Nd isotopes preserved in Fe-Mn coatings. These authors suggest that short leaching times and high sediment/solution ratios allow the extraction of seawater  $\epsilon_{\text{Nd}}$  from sediments and could be considered as a reliable proxy for reconstructing past seawater  $\epsilon_{\text{Nd}}$ . Nevertheless, the analytical procedure needs to be evaluated for each individual site rather than being used as a simple method that can be uniformly applied. In order to reconstruct past seawater  $\epsilon_{\text{Nd}}$  of the SCS, it is necessary to carefully verify that Nd isotopic compositions obtained from sediments and foraminifera are reliable and reflect seawater  $\epsilon_{\text{Nd}}$  signature. Here we have investigated several core-top samples from different parts of the SCS where a vertical gradient of the seawater  $\epsilon_{\text{Nd}}$  has been observed in order to evaluate the reliability of different procedures for the extraction of seawater  $\epsilon_{\text{Nd}}$  from foraminifera and Fe-Mn coatings of detrital particles. Nd values obtained from cleaned and uncleaned foraminifera are compared to seawater  $\epsilon_{\text{Nd}}$  recently measured by Wu *et al.* [in press]. Additionally, we present the Nd isotopic composition of foraminifera collected from sediments of a core located in the northern SCS to reconstruct the hydrology of the western subtropical North Pacific over the past 25 kyr.



**Figure 1.** (a) Sample location map. The main deep water components in the Pacific Ocean have been also reported. LCDW: Lower Circumpolar Deep Water; UCDW: Upper Circumpolar Deep Water; PDW: Pacific Deep Water; NPIW: North Pacific Intermediate Water; NPTW: North Pacific Tropical Water. The  $\delta Nd$  values of the main water masses have been also reported. Schematic deep water flow paths of CDW and NPIW are shown by orange and pink arrows, respectively. The NPTW has been shown in gray arrows. The orange dashed lines schematically denote the pathway of deep water flow from Philippine Sea to the SCS. (b) Latitudinal transect of annual mean salinity along the WOCE Pacific transect [World Ocean Atlas, 2013]. Core MD05-2904 is located in the PDW of the northern SCS that is characterized by similar hydrological parameter ( $T^{\circ}C$ ,  $S$ , and phosphate concentrations) [Gong et al., 1992] to those of the WOCE Pacific transect reported in Figure 1b.

## 2. Hydrological Setting

The SCS is connected in the south with the Sulu and Java Seas through the shallow Mindoro (~200 m) and Karimata Straits (<50 m) and in the north with the East China Sea and Pacific Ocean through the Taiwan Strait (<100 m) and the deep channel of the Luzon Strait (>2400 m), respectively (Figure 1). Numerous studies have been undertaken of deep water circulation in the SCS (below 2000 m) in order to constrain the inflow and the pathway of the PDW into the SCS [Li and Qu, 2006; Qu et al., 2006; Wang et al., 2011; Tian et al., 2006; Zhao et al., 2014]. A vertical sandwich structure of water exchange between the SCS and the North Pacific has been



observed recently in the Luzon Strait that is the only deep connection between the SCS and the North Pacific. During the winter, an inflow of western Pacific water into the SCS occurs in the surface and deep layers while an outflow to the Philippine Sea can be observed at intermediate depth compensating for inflow [Gong *et al.*, 1992; Tian *et al.*, 2006]. Water masses below 2000 m in the SCS are characterized by relatively homogenous physical properties (2.1–2.3°C, 34.59–34.62) similar to those of the PDW observed in the Philippine Sea at around 2000 m [Li and Qu, 2006; Qu *et al.*, 2006; *World Ocean Atlas Data*, 2013]. The PDW, characterized by a low temperature (1.6°C) and high salinity (34.62), sinks in the deep SCS basins immediately after it crosses the Luzon Strait [Wyrki, 1961]. It enhances the vertical mixing (upwelling) and potentially contributes to the upper layer circulation [Tian *et al.*, 2009; Li and Qu, 2006; Qu *et al.*, 2006; Qu, 2002]. These processes facilitate the rapid turnover of the SCS deep water that has been recently estimated at around 30–70 years [Qu *et al.*, 2006; Chang *et al.*, 2010]. The basin-scale oxygen distribution suggests that deep water which enters the SCS is transported north-westward to the northern slope of the SCS and thereafter southward along the western margin of the sea (Figure 1) [Qu *et al.*, 2006; Li and Qu, 2006]. The South China Sea Intermediate Water (SCSIW) (350–1350 m) is characterized by higher salinity than the NPIW observed in the Philippine Sea. This is due to vertical diffusion of the SCSIW with deep water in the SCS [Chen *et al.*, 2001; Xie *et al.*, 2011; Tian *et al.*, 2009]. The intrusion of NPIW has been found to be greater in winter than in summer and is associated with leakage of the Kuroshio Current [Qu *et al.*, 2006; Chen and Huang, 1996]. Mid-depth water exchange in the Luzon Strait also displays seasonal variability. During the winter, there is an inflow of the NPIW into the SCS through the southern part of the Luzon Strait whereas the outflow of the SCSIW to the Philippine Sea is located in the northern part of the Luzon Strait. These water masses flow in an opposite direction during the summer [Tian *et al.*, 2006; Yang *et al.*, 2010; Xie *et al.*, 2011].

Above a depth of 350 m, surface and subsurface circulations in the SCS are mainly controlled by the seasonal reversals of the wind direction during the summer and winter monsoons. This induces a cyclonic surface circulation in winter and an anticyclonic one in summer [Shaw and Chao, 1994; Fang *et al.*, 1998]. The surface North Pacific Tropical Water (NPTW), characterized by high salinity, enters the SCS and is diluted by freshwater discharged by the large Asian rivers, thereby inducing the relatively fresher South China Sea Tropical Water (SCSTW) [Xie *et al.*, 2011].

More recently, Wu *et al.* [in press] showed that below 2000 m  $\epsilon$ Nd values of deep water masses of the Philippine Sea and the northwestern margin of the SCS present a narrow range between  $-3.5 \pm 0.3$  and  $-4.5 \pm 0.4$ , corresponding to the presence of the PDW. In the Philippine Sea, above a depth of around 1000 m, the NPIW is characterized by  $\epsilon$ Nd values that reach  $-2.7 \pm 0.4$  and which are similar to those obtained from the subtropical North Pacific.  $\epsilon$ Nd of the SCSIW is slightly lower (between  $-3.6 \pm 0.3$  and  $-3.9 \pm 0.3$ ) than that of the NPIW due to vertical diffusion with the PDW in the SCS [Wu *et al.*, in press].

### 3. Material and Methods

#### 3.1. Material

The Calypso cores MD05-2899 (13°47.66'N, 112°10.89'E, 2393 m), MD05-2901 (14°22.503'N, 110°44.6'E, 1454 m), MD05-2903 (19°27.31'N, 116°15.06'E, 2047 m), and MD05-2904 (19°27.32'N, 116°15.15'E, 2066 m) were retrieved on the northwestern margin of the SCS during the R/V Marion Dufresne MARCO POLO IMAGES XII Cruise in 2005 (Figure 1 and Table 1).

Four core-top sediments were sampled from each core where Holocene sediments are well identified by preliminary  $\delta^{18}\text{O}$  curves obtained on planktonic foraminifera (unpublished data). These core-top sediments were investigated to represent modern time or at least late Holocene. In addition, seven additional downcore sediment samples were collected in the upper 10 m of core MD05-2904. The age model of core MD05-2904 has been first established by Ge *et al.* [2010] and modified by Wan and Jian [2014]. It is based on 16 C-14 AMS dates obtained from planktonic foraminifera *G. ruber*. On the basis of age model, the eight downcore sediment samples provide snapshots on hydrological conditions of the northern SCS spanning the last 25 kyr (Table 1).

#### 3.2. Analytical Procedures

Thirty milligram of mono-specific planktonic foraminifera *G. ruber*, mixed planktonic foraminifera, and around 8 mg mixed benthic foraminifera, with shell sizes larger than 150  $\mu\text{m}$ , were handpicked under a

**Table 1.** Nd Isotopic Composition, Nd/Ca and Mn/Ca Ratios of Reductively Cleaned Foraminifera and Cleaning Solutions<sup>a</sup>

Core/Station	Latitude	Longitude	Water Depth (m)	Age (kyr)	Sample ID	$\epsilon_{Nd}$	$2\sigma$	Mn/Ca ( $\mu\text{mol/mol}$ )	Nd/Ca ( $\mu\text{mol/mol}$ )
MD05-2903	19.45°N	116.25°E	2047	Core top	Cleaned <i>G. ruber</i>	-4.7	0.2		
				Core top	Cleaned BF	-3.7	0.4		
				Core top	Cleaning solution of <i>G. ruber</i>	-4.3	0.4		
				Core top	Cleaning solution of BF	-4.7	0.4		
MD05-2901	14.28°N	110.74°E	1454	Core top	Cleaned <i>G. ruber</i>	-6.3	0.3		
				Core top	Cleaned BF	-6.9	0.2		
				Core top	Cleaning solution of <i>G. ruber</i>	-7.2	0.2		
				Core top	Cleaning solution of BF	-6.9	0.4		
MD05-2899	13.79°N	112.19°E	2393	Core top	Cleaned <i>G. ruber</i>	-6.6	0.2		
				Core top	Cleaned BF	-5.9	0.3		
				Core top	Cleaning solution of <i>G. ruber</i>	-6.2	0.4		
				Core top	Cleaning solution of BF	-6.0	0.4		
MD05-2904	19.46°N	116.25°E	2066	0.14	Cleaned <i>G. ruber</i>	-4.1	0.2	216	1.12
				0.14	Cleaning solution of <i>G. ruber</i>	-4.1	0.3		
				0.14	Cleaned BF	-4.1	0.4	295	1.98
				0.14	Cleaning solution of BF	-4.8	0.4		
MD05-2904	19.46°N	116.25°E	2066	0.14	Cleaned foraminiferas of mixed species	-4.2	0.3	128	0.62
MD05-2904	19.46°N	116.25°E	2066	0.14	Uncleaned <i>G. ruber</i>	-4.2	0.2	613	1.74
MD05-2904	19.46°N	116.25°E	2066	2.13	Cleaned <i>G. ruber</i>	-4.4	0.3	139	0.79
MD05-2904	19.46°N	116.25°E	2066	2.13	Cleaning solution of <i>G. ruber</i>	-4.2	0.3		
MD05-2904	19.46°N	116.25°E	2066	6.25	Cleaned <i>G. ruber</i>	-4.7	0.2	298	1.37
MD05-2904	19.46°N	116.25°E	2066	6.25	Cleaning solution of <i>G. ruber</i>	-5.0	0.3		
MD05-2904	19.46°N	116.25°E	2066	6.25	Cleaned BF	-4.2	0.5	338	1.38
MD05-2904	19.46°N	116.25°E	2066	6.25	Uncleaned <i>G. ruber</i>	-4.8	0.2	859	1.78
MD05-2904	19.46°N	116.25°E	2066	11.18	Cleaned <i>G. ruber</i>	-5.1	0.2	421	1.16
MD05-2904	19.46°N	116.25°E	2066	11.18	Uncleaned <i>G. ruber</i>	-5.2	0.2	837	1.74
MD05-2904	19.46°N	116.25°E	2066	15.25	Cleaned <i>G. ruber</i>	-6.2	0.3	278	0.90
MD05-2904	19.46°N	116.25°E	2066	15.25	Cleaning solution of <i>G. ruber</i>	-6.4	0.3		
MD05-2904	19.46°N	116.25°E	2066	19.17	Cleaned <i>G. ruber</i>	-6.4	0.3	182	0.77
MD05-2904	19.46°N	116.25°E	2066	19.17	Cleaning solution of <i>G. ruber</i>	-6.1	0.3		
MD05-2904	19.46°N	116.25°E	2066	20.80	Cleaned <i>G. ruber</i>	-5.9	0.2	301	1.49
MD05-2904	19.46°N	116.25°E	2066	20.80	Cleaning solution of <i>G. ruber</i>	-5.6	0.3		
MD05-2904	19.46°N	116.25°E	2066	20.80	Cleaned foraminiferas of mixed species	-5.9	0.3	190	1.60
MD05-2904	19.46°N	116.25°E	2066	22.45	Cleaned <i>G. ruber</i>	-5.6	0.2	375	1.72
MD05-2904	19.46°N	116.25°E	2066	22.45	Cleaning solution of <i>G. ruber</i>	-5.2	0.3		
St8 (D3)	20°2.9'N	117°25'E	5		Seawater	-3.3	0.4		
St8 (D3)	20°2.9'N	117°25'E	2000		Seawater	-4.2	0.4		
St11 (10-JJW-82)	18°30'N	114°15'E	5		Seawater	-5.3	0.4		
St11 (10-JJW-82)	18°30'N	114°15'E	2000		Seawater	-3.5	0.3		
St13 (SEATS)	17°59'N	115°59'E	5		Seawater	-7.0	0.3		
St13 (SEATS)	17°59'N	115°59'E	2000		Seawater	-3.6	0.3		
St15 (10-JJW-55)	14°31'N	111°00'E	5		Seawater	-8.5	0.3		
St16 (10-JJW-46)	11°00'N	111°00'E	5		Seawater	-7.1	0.3		

<sup>a</sup> $\epsilon_{Nd}$  values from seawater samples obtained from Wu et al. [in press] have been also reported for comparisons.

binocular microscope. All of the foraminifera were gently crushed between two glass plates to open all chambers. The calcite fragments were then ultrasonicated for 1 min before pipetting the suspended particles with water to separate the waste. This step was repeated until the water became clear and free of clay. All samples were checked under a binocular microscope to ensure that all particles had been removed. Physically cleaned samples were transferred to centrifuge tubes for the oxidative-reductive cleaning step (foraminifera which underwent this process are hereafter referred to as “cleaned foraminifera”). For the purpose of comparison, three samples were subjected to mechanical cleaning only (hereafter referred to “uncleaned foraminifera”). The oxidative-reductive foraminiferal cleaning procedure used in this study followed that described by Vance and Burton [1999], using 10 mL reductive solution (1 M hydrous hydrazine, 16 M NH<sub>4</sub>OH, 0.25 M citric acid + 16 M NH<sub>4</sub>OH in a ratio of 1:6:3) and 5 ml oxidative solution (0.2 M NaOH and 30% H<sub>2</sub>O<sub>2</sub> in a 1:1 ratio) per sample to more efficiently remove authigenic Fe-Mn coatings. For the reductive step, samples were heated in a water bath at 80°C for 30 min and were ultrasonicated every 2.5 min for 10 s. After transferring the reductive cleaning solution to a centrifuge tube, the cleaned foraminifera were rinsed with Milli-Q water. The analytical procedure for the oxidative step was similar except that samples were ultrasonicated every 10 min for a period of 30 s. All samples, including non-reductively cleaned samples, underwent a weak acid leaching for 5 min in 1 ml 0.001 M HNO<sub>3</sub> with ultrasonication. After the

cleaning step, samples were transferred into a 1.5 ml tube. A 0.5 ml of deionized water was first added to the tube, and then the foraminifera were dissolved using stepwise 100  $\mu$ l nitric acid (0.5 M HNO<sub>3</sub>) until the dissolution reaction stopped. The dissolved samples were centrifuged and the supernatant was immediately transferred to Teflon beakers to prevent the leaching of any possible remaining phases. All of the dissolved foraminifera shell fraction and authigenic fraction contained in the reductive cleaning solution were dried using a hotplate for Nd purification. Element concentrations and REE patterns analysis were performed on a 10% cut of both the dissolved foraminifera shells and the corresponding reductive cleaning solutions collected from core MD05-2904.

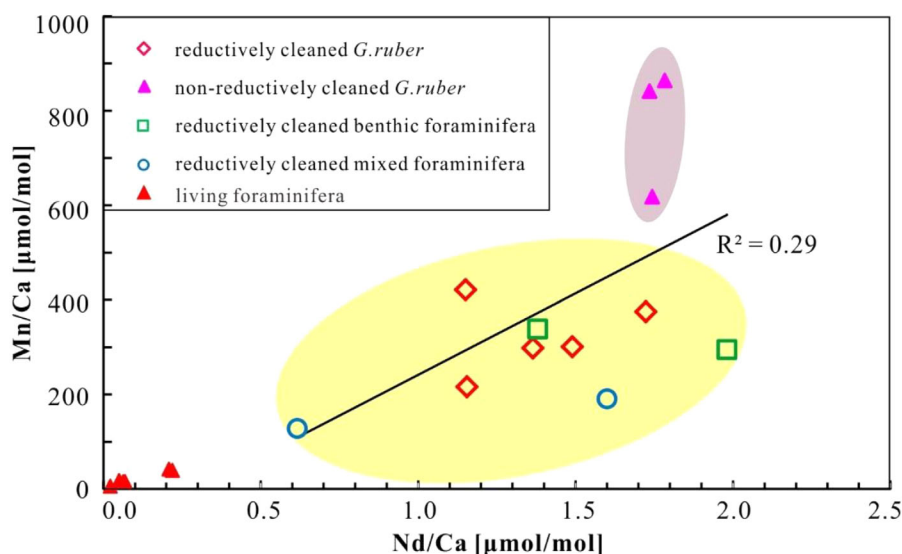
Several studies have been carried out to test the reliability of seawater-derived Nd extraction from bulk sediments involving different leaching procedures [Bayon *et al.*, 2002; Gutjahr *et al.*, 2007; Wilson *et al.*, 2013; Molina-Kescher *et al.*, 2014b]. First, it is recommended to not remove the carbonate fraction of the bulk sediments; second, the leaching time should not be too long; third, the sample size/leachate ratios need to be large [Wilson *et al.*, 2013]. In this study, in order to better constrain the reliability of using bulk sediments leachates to reconstruct past seawater  $\epsilon$ Nd from sediments of the northern SCS, an evaluation was conducted on five samples covering the Holocene and the Last Glacial Maximum (LGM). First, sequential analysis was performed on ground samples of 0.2, 1, and 2 g which were simply rinsed with deionized water and then directly leached with 7 ml 0.02 M hydroxylamine hydrochloride in 25% (v/v) acetic acid (HH solution) for 30 min. Then, five additional samples of 1 g were treated using the same leaching procedure but with a longer leaching time of 1 h. Parallel 1 g samples of sediment were decarbonated using a sodium acetate buffered acetic acid solution, and subjected to 30 min of leaching with 7 mL 0.02 M HH solution in order to assess the possible influence of the decarbonation process. Decarbonated samples of 0.2 g were leached for 30 min, 2 h, and 3 h with 0.02 M HH solution in order to test the influence of leaching times.

Nd was purified from all samples following the analytical procedure described in detail by Copard *et al.* [2010]. In brief, we used TRU-Spec and Ln-Spec resins following the method described in detail by Pin and Santos Zalduegui [1997]. In this method, samples were loaded using 2 ml of 1 M HNO<sub>3</sub> on preconditioned TRU-Spec columns (83 mg portion of TRU-spec). The unwanted cations were eluted using five portions of 0.5 ml of 1 M HNO<sub>3</sub>. The TRU-Spec columns were then placed over the Ln-Spec columns. The light REE were then eluted from the upper (TRU-Spec) column using seven portions of 0.1 ml of 0.05 M HNO<sub>3</sub>. After decoupling from the TRU-Spec columns, La, Ce, and most of the Pr were removed from the Ln-Spec columns using 3.25 ml of 0.25 M HCl. Nd was then eluted with an additional 2.5 ml of 0.25 M HCl.

### 3.3. Ca, Mn, and REE Concentrations and <sup>143</sup>Nd/<sup>144</sup>Nd Analysis

Ca, Mn, and REE concentrations were determined at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) by measuring their isotopes <sup>44</sup>Ca, <sup>55</sup>Mn, and <sup>146</sup>Nd using a Thermo Scientific Inductively Coupled Plasma-Quadrupole Mass Spectrometer (ICP-QMS X Series<sup>®</sup>). The used protocol, previously described by Bourdin *et al.* [2011], is briefly described as follows. Carbonate sample and standard solutions were systematically adjusted to 100 ppm Ca through dilution. This is because (1) high Ca levels need to be avoided as high contents can increase salt deposition on cones and consequently affect ICP-QMS stability and (2) adjusted Ca concentration levels introduced into ICP-QMS at 100  $\mu$ l/min provide a way to control matrix effects due to the presence of Ca. Instrumental calibration, based on the standard addition method, was achieved using multi-elementary standard solutions. The signal drift through the analytical sessions was monitored and corrected by the analysis every nine samples of blank and carbonate standard JcP-1 solutions. Other carbonate standards (JcT-1, ARAG-AK, BAM, and GSR-6) were also regularly analyzed to validate elemental concentrations. When analyzing the REE of the reductive cleaning solution from foraminifera and leachates from bulk sediments, a high-purity REE solution was also measured and additional internal standards (<sup>115</sup>In and <sup>103</sup>Rh) were added to sample and standard solutions. Our measurements were characterized by analytical uncertainties ranging from 5% for the lightest REE to 15% for the heaviest [Bourdin *et al.*, 2011]. The reproducibility of measurements for two repeated samples varied according to the different element to calcium ratios ( $2\sigma$ : 10% for Mn/Ca, 5% for Nd/Ca). The Nd concentrations in blanks are systemically lower than 0.1 ppb, which is negligible compared to the average concentration of 15 ppb  $\pm$  5% measured in samples.

The <sup>143</sup>Nd/<sup>144</sup>Nd ratios were analyzed using the Thermo Fisher Neptune<sup>Plus</sup> Multi-collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS) at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) in Gif-sur-Yvette. The Nd isotopic composition was analyzed at a concentration of 10–15



**Figure 2.** Mn/Ca ratios versus Nd/Ca ratios obtained on reductively cleaned and non-reductively cleaned foraminifera samples (planktonic foraminifera *G. ruber*, benthic foraminifera, and mixed foraminifera) of core MD05-2904. Non-reductively cleaned foraminifera show higher Mn/Ca ratios compared to reductively cleaned foraminifera. Mn/Ca and Nd/Ca ratios obtained from Pomiès *et al.* [2002] for living foraminifera have been reported for comparison.

ppb. The mass-fractionation correction was made by normalizing  $^{146}\text{Nd}/^{144}\text{Nd}$  to 0.7219 and applying an exponential-fractionation correction. During the analytical sessions, every two samples were bracketed with analyses of appropriate Nd standard solutions JNdi-1 and La Jolla characterized by certified values of  $0.512115 \pm 0.000006$  [Tanaka *et al.*, 2000] and  $0.511858 \pm 0.000007$  [Lugmair *et al.*, 1983], respectively. Standard solutions JNdi-1 and La Jolla were analyzed at concentrations similar to those of the samples and we have corrected all of the measurements affected by a machine bias when necessary by using the La Jolla standard. The external reproducibility ( $2\sigma$ ) for time resolved measurement, deduced from repeated measurements of the La Jolla standard and JNdi-1, ranged from 0.2 to 0.4 Epsilon units for various analytical sessions. The analytical error associated to each sample analysis is taken as the external reproducibility of the La Jolla standard for each session. Blank values were  $<100$  pg and can be neglected as they represent less than 1% of the sample Nd analyzed.

## 4. Results

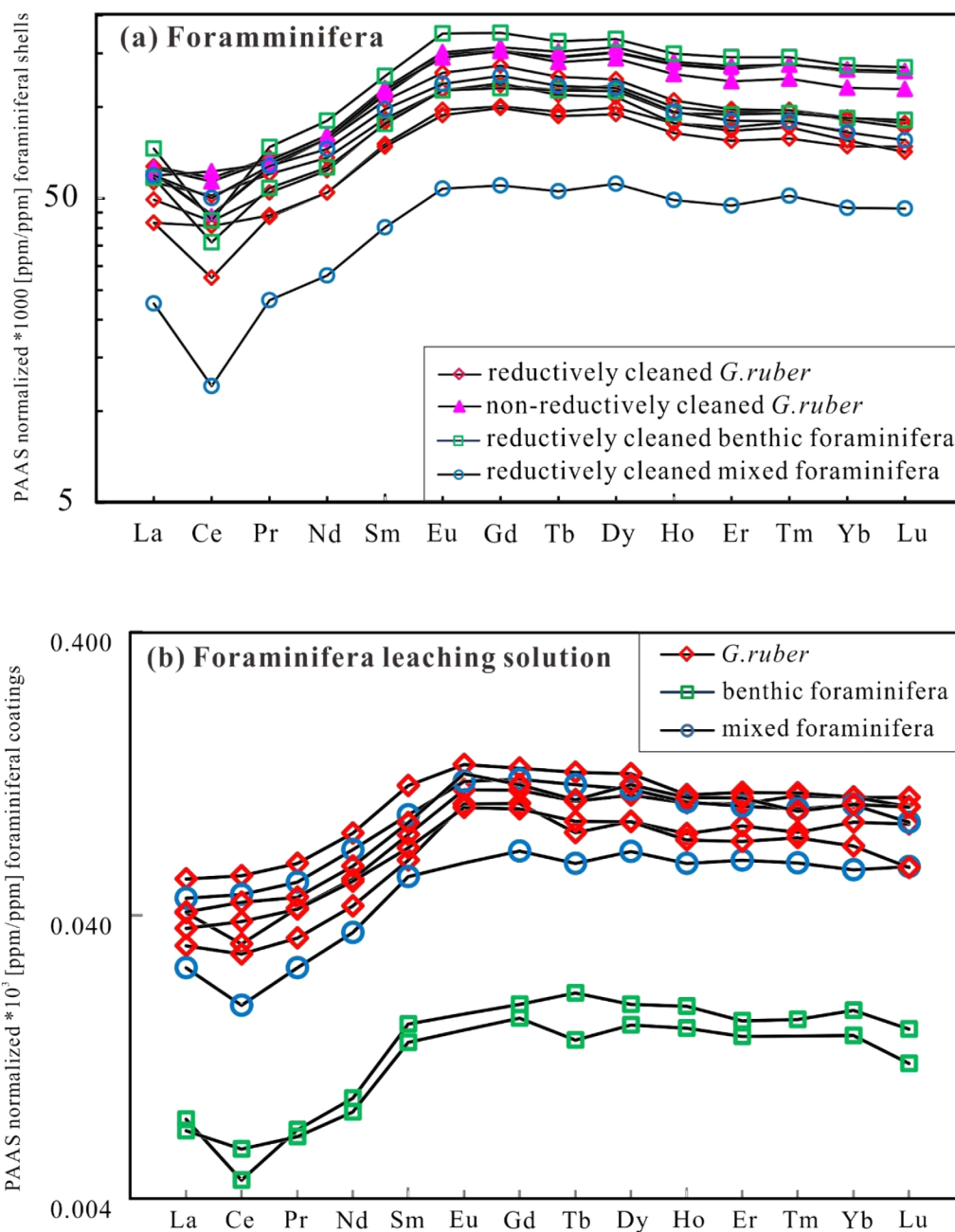
### 4.1. Element/Ca Ratios and REE Concentrations

Ca, Mn, and REE concentrations were measured on dissolved cleaned foraminifera and reductive cleaning solutions in order to evaluate the efficiency of the cleaning procedures. Mn/Ca ratios range from 128 to 421  $\mu\text{mol/mol}$  for cleaned foraminifera and from 613 to 859  $\mu\text{mol/mol}$  for uncleaned foraminifera (Figure 2 and Table 1). Unlike Mn/Ca ratios, Nd/Ca ratios in cleaned foraminifera are randomly distributed from 1.12 to 1.72  $\mu\text{mol/mol}$ , with one exception with very low ratios (0.62  $\mu\text{mol/mol}$ ). Nd/Ca ratios obtained from uncleaned foraminifera are around 1.74–1.78  $\mu\text{mol/mol}$ . Although the uncleaned foraminifera are characterized by higher Mn/Ca ratios, Nd/Ca ratios in cleaned and uncleaned foraminifera display similar ranges of level and are not correlated with Mn/Ca ratios ( $r^2 = 0.29$ ) (Figure 2).

REE concentrations obtained from planktonic and benthic foraminifera and reductive cleaning solutions were normalized to Post-Archean Average Australian Shales (PAAS) [Nance and Taylor, 1976]. All of the PAAS-normalized REE patterns are quite similar and present no or pronounced negative Ce anomalies as well as Middle REE (MREE) enrichment (Figure 3a). This pattern with a negative Ce anomaly, especially for low REE concentration samples, is similar to other published seawater REE patterns in the SCS [Alibo and Nozaki, 2000]. PAAS-normalized REE of reductive cleaning solution shows a clear MREE enrichment (Figure 3b).

REE concentrations were also measured in leachates obtained from bulk non-decarbonated and decarbonated sediments. The PAAS-normalized REE patterns display a MREE enrichment that is independent of the leaching procedures (Figure 4). For bulk non-decarbonated core-top samples (Figures 4a–4d), the REE



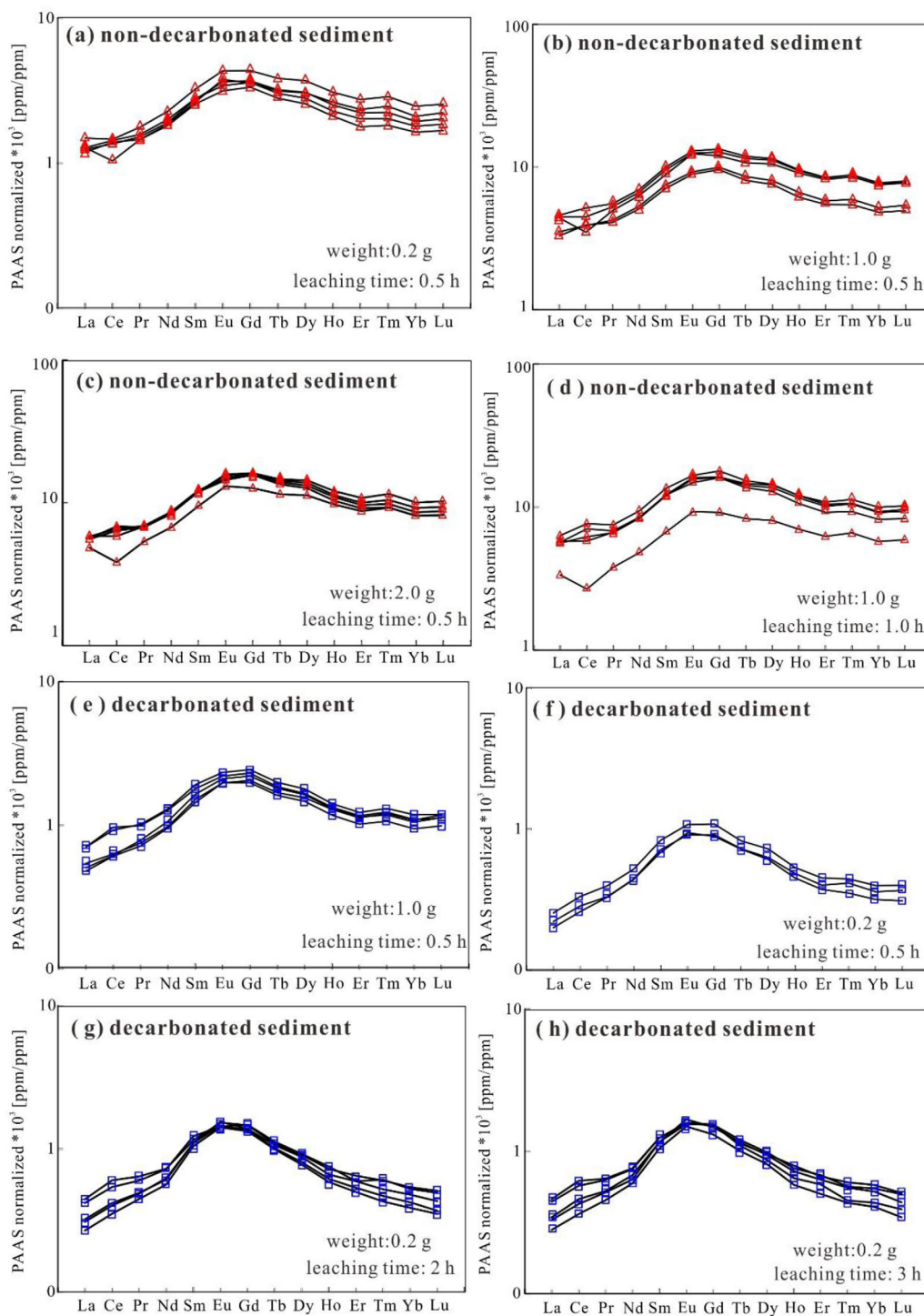


**Figure 3.** (a) PAAS-normalized REE patterns obtained on reductively cleaned and non-reductively cleaned foraminifera samples of core MD05-2904 (planktonic foraminifera *G. ruber*, benthic foraminifera, and mixed foraminifera); (b) PAAS-normalized REE patterns obtained from reductive cleaning solutions.

patterns show moderate negative Ce anomalies regardless of the sample sizes and leaching time. The downcore samples of core MD05-2904 do not present negative Ce anomalies. Leachates of all the decarbonated samples exhibit MREE enrichment with no negative Ce anomalies (Figures 4e–4h).

**4.2.  $\epsilon$ Nd in Foraminifera and Bulk Sediments Leachates**

$\epsilon$ Nd values obtained on mono-specific samples of planktonic foraminifera *G. ruber*, mixed planktonic foraminifera, and mixed benthic foraminifera lie in a narrow range from  $-3.7 \pm 0.4$  to  $-4.7 \pm 0.4$  for the core-top sample from MD05-2903 and from  $-4.1 \pm 0.2$  to  $-4.8 \pm 0.4$  for the core-top sample from MD05-2904 (Table 1). It is worth noting that mean  $\epsilon$ Nd values obtained on foraminifera cleaning solutions are similar or weakly more unradiogenic.  $\epsilon$ Nd values for all foraminifera samples and reductive cleaning solutions from



**Figure 4.** PAAS-normalized REE patterns obtained from sediment leachate solutions of downcore samples from core MD05-2904. (a–d) Results obtained on different size of bulk non-decarbonated sediments (0.2, 1, and 2 g) and different time of leaching (0.5 and 1 h); (e–h) results obtained on different size of decarbonated sediments (0.2 and 1 g) and different time of leaching (0.5, 2, and 3 h).

core-top samples of cores MD05-2899 and MD05-2901 (obtained from a more southern position of the SCS), ranged from  $-5.9 \pm 0.3$  to  $-6.6 \pm 0.2$ , and from  $-6.3 \pm 0.3$  to  $-7.2 \pm 0.2$ , respectively. Consequently,  $\delta\text{Nd}$  values obtained on the same sediment sample from a mono-specific sample of planktonic foraminifer *G. ruber*, mixed planktonic foraminifera, mixed benthic foraminifera, and reductive cleaning solution are more or less in the same range (Table 1) and each core-top sediments shows specific  $\delta\text{Nd}$  values.

In core MD05-2904,  $\epsilon\text{Nd}$  values were analyzed on samples of foraminifera from the Holocene and the late last glacial period.  $\epsilon\text{Nd}$  values of all samples of foraminifera investigated from core MD05-2904 exhibited a wide range from  $-6.4 \pm 0.3$  to  $-4.1 \pm 0.2$  (Table 1 and Figure 5). The late glacial period is characterized, on average, by lower  $\epsilon\text{Nd}$  ( $-5.2 \pm 0.3$  to  $-6.4 \pm 0.3$ ) than the late Holocene ( $-4.1 \pm 0.2$ ). In general,  $\epsilon\text{Nd}$  values obtained for each mono-specific sample of planktonic foraminifera *G. ruber*, mixed planktonic foraminifera, mixed benthic foraminifera, and from the reductive cleaning solution are in agreement within uncertainty (Figure 5b).

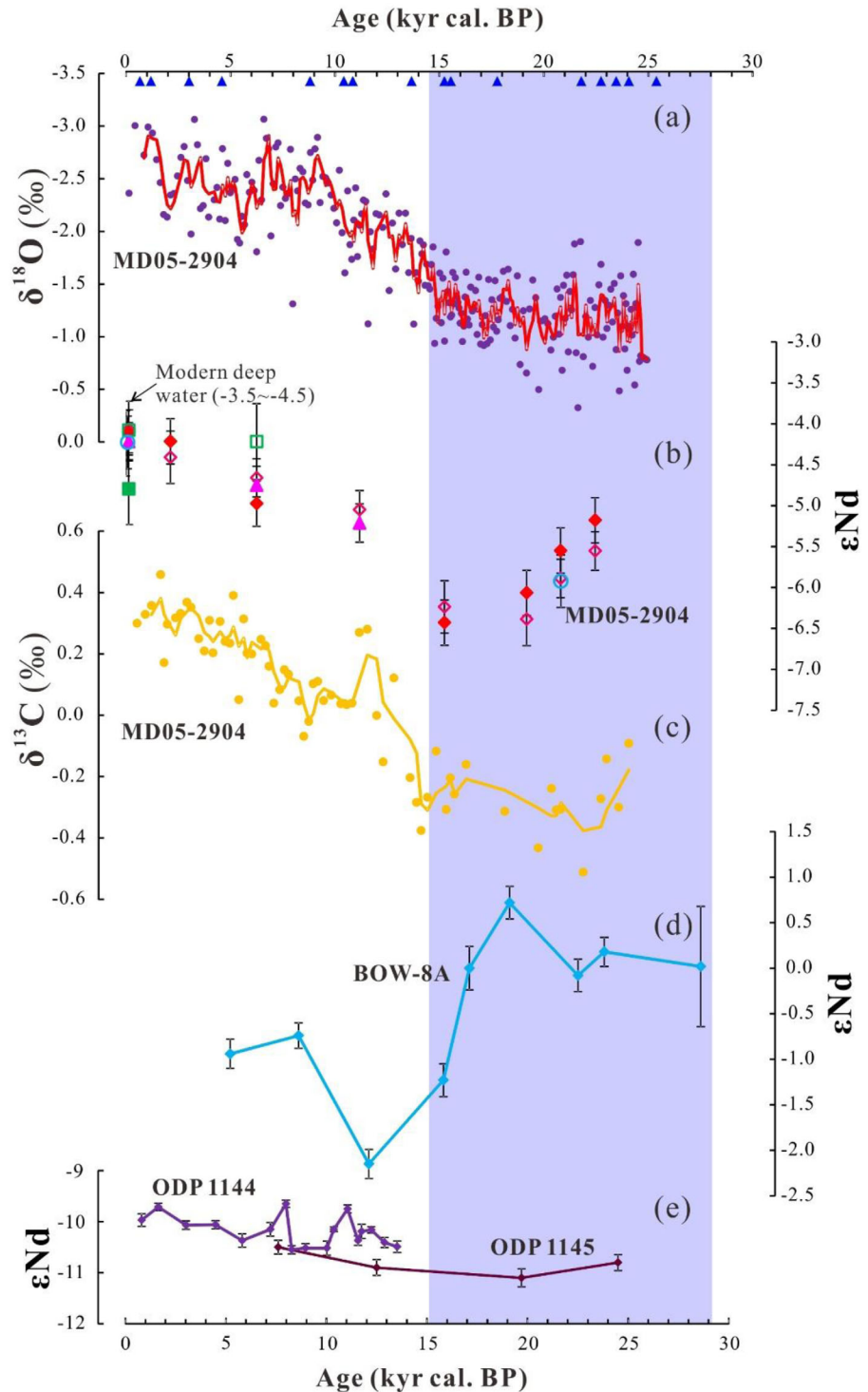
For core MD05-2904,  $\epsilon\text{Nd}$  obtained from HH leachates of decarbonated and non-decarbonated sediments are outlined in Figure 6b and Table 2.  $\epsilon\text{Nd}$  obtained from HH leachates of bulk non-decarbonated sediments vary from  $-6.4 \pm 0.3$  for glacial sediments to  $-4.4 \pm 0.3$  for core-top samples. On the other hand,  $\epsilon\text{Nd}$  obtained from leachates of decarbonated sediments range from  $-7.0 \pm 0.2$  for glacial sediments to  $-5.5 \pm 0.3$  for core-top samples and average values for each age studied here systematically display lower  $\epsilon\text{Nd}$  of around 1.0 Epsilon unit compared to non-decarbonated sediments. For both non-decarbonated and decarbonated sediments,  $\epsilon\text{Nd}$  values are slightly affected by the leaching procedure used in this study. In general, an increase in the leaching time (from 0.5 to 3 h) and a reduction of sample weight (from 1 to 0.2 g) is associated to a significant decrease of the  $\epsilon\text{Nd}$  values (Figure 6 and Table 2).

## 5. Discussion

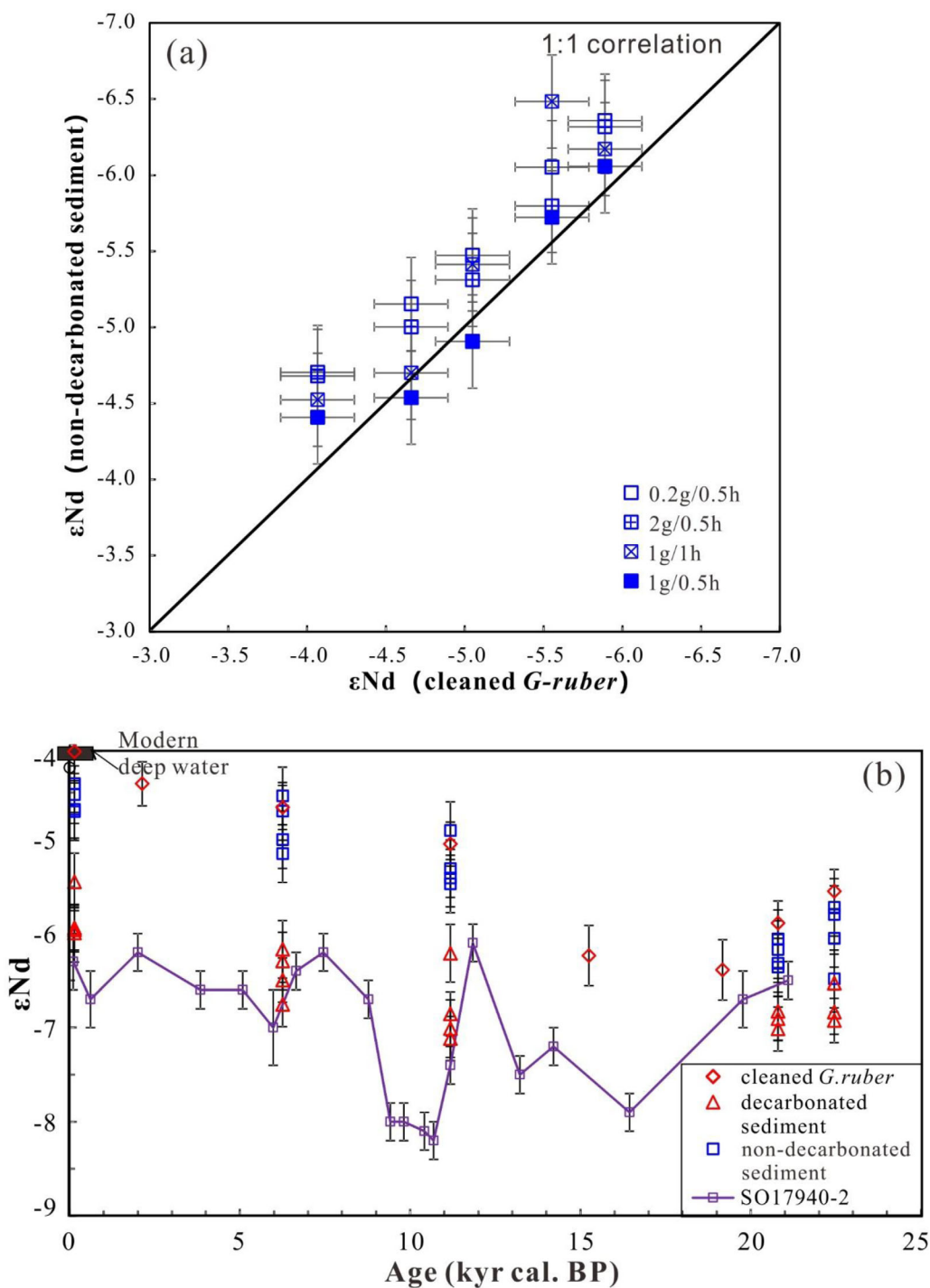
### 5.1. Elemental Ratios and REE Patterns in Foraminifera

The Mn/Ca ratio in foraminifera has been identified as an indicator for early diagenetic Fe-Mn oxides, or Mn-rich carbonates, which precipitated on the foraminiferal carbonate [Boyle, 1983; Pomiès et al., 2002]. The ratio is usually used to monitor the efficiency of reductive cleaning [Boyle, 1983; Pena et al., 2005]. Mn/Ca ratios in the reductively cleaned foraminifera shells (128–421  $\mu\text{mol/mol}$ ) are around 3 times lower than those of the non-reductively cleaned foraminifera samples (613–859  $\mu\text{mol/mol}$ ). However, such values are 10–30 times higher than Mn/Ca ratios obtained from living and nonfossil planktonic foraminifera collected in plankton tows and sediment traps (0.25–15  $\mu\text{mol/mol}$ ) [Pomiès et al., 2002; Martínez-Botí et al., 2009; Roberts et al., 2012]. Similarly, Nd/Ca ratios from cleaned foraminifera (1.15–1.72  $\mu\text{mol/mol}$ ) are much higher than Nd/Ca ratios obtained previously from planktonic foraminifera collected in sediment traps (0.008–0.70  $\mu\text{mol/mol}$ ) [Pomiès et al., 2002; Martínez-Botí et al., 2009] (Figure 2).

Whereas Nd/Ca ratios in both reductively cleaned and uncleaned foraminifera exhibit different values, no linearly decreasing trend from uncleaned samples to cleaned samples was observed (Figure 2). However, all reductively cleaned foraminifera (*G. ruber*, benthic or mixed foraminifera) tend to reveal a weak link between Nd/Ca and Mn/Ca ratios in foraminifera ( $r^2 = 0.29$ ). Palmer [1985] has suggested that around 90% of REE were incorporated into authigenic phases in foraminifera shell. In addition, the distribution of planktonic foraminifera Nd investigated recently at micrometer scale has revealed that Nd concentration in Fe-Mn-rich parts was much higher than in foraminiferal calcite, where Nd distribution was randomly heterogeneous [Roberts et al., 2012; Tachikawa et al., 2013]. The weak link between Nd/Ca and Mn/Ca ratios of cleaned foraminifera observed in our study might also imply that the cleaning procedure used do not totally remove all the Fe-Mn coatings and Nd carried by these authigenic phases. Reductively and non-reductively cleaned foraminifera exhibit similar REE patterns with a moderate to negative Ce anomaly and a MREE enrichment similar to those identified in dissolved foraminifera and fossil fish teeth [Gutjahr et al., 2007; Martin et al., 2010; Kraft et al., 2013]. REE patterns in both the surface and deep water in the SCS [Wu et al., in press], and in other ocean basins, merely display pronounced negative Ce anomaly but no MREE enrichment (Figure 4) [Alibo and Nozaki, 2000; Bayon et al., 2011; Jeandel et al., 2013]. Several hypotheses have been put forward to explain this puzzling feature [Palmer, 1985; Elderfield et al., 1990; Hannigan and Sholkovitz, 2001; Haley et al., 2005]. In general, these authors hypothesize that the MREE enrichment in various dissolved phases is related to fractionated REE incorporated in foraminifera or more truly an overprinted pore water signature during early diagenetic processes. Authigenic phases in marine sediments were suggested to be an important carrier of REE as they contain higher concentrations of REE than foraminiferal tests [Piotrowski et al., 2012; Roberts et al., 2012; Tachikawa et al., 2013]. REE patterns characterized by MREE enrichment have been observed in both pore water and Fe-Mn hydroxide phases [Haley et al., 2004; Surya Prakash et al., 2012]. Here PAAS-normalized REE patterns obtained from cleaned foraminifera and



**Figure 5.** (a)  $\delta^{18}\text{O}$  records obtained from planktonic foraminifera *G. ruber* of core MD05-2904 over the past 25 kyr [Ge et al., 2010; Wan and Jian, 2014]; smooth curve is derived from a three-point average result (red line). Blue triangles show AMS  $^{14}\text{C}$  age control points [Ge et al., 2010; Wan and Jian, 2014]; (b)  $\epsilon\text{Nd}$  values obtained from cleaning solution of *G. ruber* (solid red diamond), reductively cleaned *G. ruber* (empty pink diamond), non-reductively cleaned *G. ruber* (solid pink triangle), reductively cleaned mixed foraminifera (empty light blue circle), reductively cleaned benthic foraminifera (empty green rectangle), and cleaning solution of benthic foraminifera (solid green rectangle).  $\epsilon\text{Nd}$  values of water masses at the similar water depth of core MD05-2904 (2000 m) are reported for comparison; (c)  $\delta^{13}\text{C}$  records obtained from benthic foraminifera *C. wuellerstorfi* of core MD05-2904 [Wan and Jian, 2014]. (d)  $\epsilon\text{Nd}$  records obtained from the authigenic fraction of sediments from core BOW-8A located in the Bering Sea ( $54^{\circ}47'\text{N}$ ,  $176^{\circ}55'\text{E}$ , 884 m) [Horikawa et al., 2010]; (e)  $\epsilon\text{Nd}$  of the decarbonated-fraction of sediments from the ODP Sites 1144 ( $20^{\circ}3.180'$ ,  $117^{\circ}25.133'$ , 2035 m) and 1145 ( $19^{\circ}35.040'$ ,  $117^{\circ}37.868'$ , 3175 m) [Boulay et al., 2005; Hu et al., 2012].



**Figure 6.** (a) Crossplot of  $\epsilon\text{Nd}$  values of non-decarbonated sediment leachates and  $\epsilon\text{Nd}$  values obtained from cleaned planktonic foraminifera *G. ruber*. (b)  $\epsilon\text{Nd}$  values obtained from acid-reductive HH leachates of bulk non-decarbonated and decarbonated sediments of core MD05-2904.  $\epsilon\text{Nd}$  values have been obtained by using HH leaching of 0.2, 1, and 2 g samples of sediments leached for 0.5, 1, 2, and 3 h.  $\epsilon\text{Nd}$  obtained on seawater samples close to the studied site [Wu *et al.*, in press] as well on cleaned planktonic foraminifera *G. ruber* of core MD05-2904 are also reported.  $\epsilon\text{Nd}$  from acid-reductive HH leachates of bulk decarbonated sediments of the core SO17940-2 [Huang *et al.*, 2013] are also reported for comparison.

reductive cleaning solutions are similar (Figures 3a and 3b). Thus, we suggest that MREE enrichment in foraminifera is associated with REE incorporated in authigenic components precipitated on the foraminifera. For the reductive cleaning solutions, PAAS-normalized REE patterns are similar to those of foraminifera shells (Figures 3a and 3b). It can be noted that both cleaned benthic foraminifera (two samples from core



**Table 2.** Nd Isotopic Composition of Bulk Sediment Leachates Measured Along the Gravity Core MD05-2904<sup>a</sup>

Sed. Age (kyr)	Carbonate Treatment	Weight (g)	Leaching Time (min)	$\epsilon$ Nd	2 $\sigma$	$\epsilon$ Nd (Average)
0.14	Non-decarbonated	0.20	30	-4.7	0.3	-4.6
	Non-decarbonated	1.00	30	-4.4	0.3	
	Non-decarbonated	2.00	30	-4.7	0.3	
	Non-decarbonated	1.00	60	-4.5	0.3	
	Decarbonated	0.20	30	-6.0	0.3	
	Decarbonated	0.20	120	-6.0	0.2	
	Decarbonated	0.20	180	-6.0	0.2	
6.25	Non-decarbonated	0.20	30	-5.2	0.3	-4.9
	Non-decarbonated	1.00	30	-4.5	0.3	
	Non-decarbonated	2.00	30	-5.0	0.3	
	Non-decarbonated	1.00	60	-4.7	0.3	
	Decarbonated	0.20	30	-6.0	0.3	
	Decarbonated	0.20	120	-6.5	0.2	
	Decarbonated	0.20	180	-6.8	0.2	
11.18	Non-decarbonated	0.20	30	-5.5	0.3	-5.3
	Non-decarbonated	1.00	30	-4.9	0.3	
	Non-decarbonated	2.00	30	-5.4	0.3	
	Non-decarbonated	1.00	60	-5.3	0.3	
	Decarbonated	0.20	30	-7.1	0.3	
	Decarbonated	0.20	120	-6.9	0.2	
	Decarbonated	0.20	180	-7.1	0.2	
20.80	Non-decarbonated	0.20	30	-6.2	0.3	-6.2
	Non-decarbonated	1.00	30	-6.1	0.3	
	Non-decarbonated	2.00	30	-6.2	0.3	
	Non-decarbonated	1.00	60	-6.1	0.3	
	Decarbonated	0.20	120	-6.9	0.2	
	Decarbonated	0.20	180	-7.0	0.2	
	Decarbonated	1.00	30	-6.8	0.3	
22.45	Non-decarbonated	0.20	30	-6.1	0.3	-6.1
	Non-decarbonated	1.00	30	-5.7	0.3	
	Non-decarbonated	2.00	30	-5.8	0.3	
	Non-decarbonated	1.00	60	-6.5	0.3	
	Decarbonated	0.20	120	-6.9	0.2	
	Decarbonated	0.20	180	-6.8	0.2	
	Decarbonated	1.00	30	-6.5	0.3	

<sup>a</sup><sup>14</sup>C ages were published by Ge et al. [2010] and Wan and Jian [2014].

MD05-2904) and corresponding coating solutions are characterized by slightly lower concentrations in REE and exhibit marked negative Ce anomalies typical of the seawater (Figure 3). This may be due to a less contribution of authigenic phases to REE contents in these benthic foraminifera. In addition,  $\epsilon$ Nd obtained from the reductive cleaning solution is characterized by slightly more negative value (-4.8) compared to the cleaned foraminifera (-4.2), thus suggesting the influence of a small contribution of lithogenic particulate reactivity ( $\epsilon$ Nd = -12).

In summary, we observed here that the chemical cleaning process could not fully remove the Nd related to authigenic phases. Therefore,  $\epsilon$ Nd values obtained in both reductively cleaned and non-reductively cleaned planktonic foraminifera are more likely to be associated with bottom and/or pore water  $\epsilon$ Nd values rather than surface seawater values, being consistent with a recent review [Tachikawa et al., 2014].

### 5.2. REE Patterns in Bulk Sediment Leachate

PAAS-normalized REE patterns of leachates obtained from bulk sediments display MREE enrichment regardless of leaching procedures (Figures 4a–4d), indicating significant contribution of REE from Fe-Mn hydroxides [Haley et al., 2005; Bau and Koschinsky, 2009]. Previous studies have shown that a long leaching time could introduce REE contamination from lithogenic fraction thereby leading to unusual Ce anomalies [Bayon et al., 2002; Gutjahr et al., 2007]. In this study, using identical leaching times, core-top samples display a negative Ce anomaly whereas anomaly was absent for downcore samples (Figures 4a–4d). Moreover, leachates from decarbonated sediments did not display a negative Ce anomaly. Thus, the leaching time

does not seem to be a main factor influencing detrital contribution. REE mobilization has been reported during the early state of diagenesis associated with redox cycling of Fe-Mn oxyhydroxides within surface sediment leading to preferential Ce enrichment in pore water [Elderfield and Sholkovitz, 1987]. Several studies show positive Ce anomalies associated with Fe-Mn oxide after leaching of the easily exchangeable fraction of ferromanganese deposits [Ohta and Kawabe, 2001; Bau and Koschinsky, 2009]. Hence, we suggest that the positive Ce anomalies in some samples here that did not undergo carbonate removal might be due to REE remobilization during the early diagenetic process and that the presence of carbonate could reduce REE extraction from detrital fraction thus avoiding contamination by the residue. Alternatively, decarbonation partially attacks detrital phase, which facilitates REE release from terrigenous fraction.

### 5.3. $\epsilon$ Nd in the Foraminifera and Reductive Cleaning Solutions of Core-Top Samples

$\epsilon$ Nd values determined from cleaned mono-specific samples of planktonic foraminifera (*G. ruber*), cleaned mixed foraminifera, nonreductively cleaned planktonic foraminifera, mixed benthic foraminifera, and associated authigenic phases, all taken from core-top samples from the same site, are characterized by a narrow range (Table 1 and Figure 5).

$\epsilon$ Nd values obtained from core-top samples exhibit variations of at least 2 Epsilon units between the northern and the western middle part of the SCS (Table 1). For cores MD05-2904 and MD05-2903, located in the northern SCS,  $\epsilon$ Nd values varied from  $-4.1 \pm 0.2$  to  $-4.8 \pm 0.4$  and from  $-3.7 \pm 0.4$  to  $-4.7 \pm 0.4$ , respectively. Seawater  $\epsilon$ Nd values at the surface and at depth of both cores obtained from neighboring water stations are reported in Table 1. Benthic and planktonic foraminifera and their associated authigenic phases are similar to those of the deep water of the northern SCS ( $\epsilon$ Nd between  $\sim -4.2 \pm 0.4$  to  $-3.5 \pm 0.3$ ; Table 1) and are significantly different from surface seawater samples ( $\sim -7.0 \pm 0.3$  to  $-5.3 \pm 0.4$ ). For cores MD05-2899 and MD05-2901 in the western middle part of the SCS,  $\epsilon$ Nd values varied from  $-5.9 \pm 0.3$  to  $-6.6 \pm 0.2$  and from  $-6.3 \pm 0.3$  to  $-7.2 \pm 0.2$ , respectively. Although  $\epsilon$ Nd values from deep water are not available for the southern and middle part of the SCS, the reported proximal surface water  $\epsilon$ Nd are more negative ( $\sim -8.5 \pm 0.3$  to  $-7.1 \pm 0.3$ ) compared with the  $\epsilon$ Nd values observed in foraminifera and incorporated authigenic phases [Amakawa et al., 2000; Wu et al., in press] (Table 1). These results confirm that  $\epsilon$ Nd obtained from planktonic foraminifera do not exhibit the imprint of the surface seawater  $\epsilon$ Nd. Taking into consideration that planktonic and benthic foraminifera yield similar  $\epsilon$ Nd values for each of the cores investigated, we can hypothesize that foraminifera have recorded the  $\epsilon$ Nd from bottom water and confirm that the Nd isotopic composition of foraminifera is mainly marked by  $\epsilon$ Nd of authigenic phases as shown by Nd/Ca and Mn/Ca ratios and PAAS-normalized REE patterns. Such results support recent studies [Pomiès et al., 2002; Elmore et al., 2011; Kraft et al., 2013; Tachikawa et al., 2013] suggesting that foraminifera record the Nd isotopic seawater composition of the bottom water. It implies also that seawater  $\epsilon$ Nd values below 1500 m of the western middle part of the SCS are characterized by slightly more negative values than those of the northern SCS, possibly due to the influence of local sources [Wu et al., in press]. Further investigations need to be carried out in the future on seawater  $\epsilon$ Nd of the southern SCS to verify such hypothesis.

### 5.4. Nd Isotopic Composition Discrepancy in Bulk Sediment Leachates for the Last 25 kyr

In core MD05-2904,  $\epsilon$ Nd values obtained from foraminifera samples from the Holocene and the Last Glacial Maximum (LGM) exhibited a large range from  $-6.4 \pm 0.4$  to  $-4.1 \pm 0.2$  (Figure 5 and Table 1). The LGM period is characterized on average by more unradiogenic  $\epsilon$ Nd ( $-5.2 \pm 0.3$  to  $-6.4 \pm 0.4$ ) than the late Holocene ( $-4.1 \pm 0.2$ ). In general,  $\epsilon$ Nd values obtained from mono-specific samples of planktonic foraminifera *G. ruber*, mixed planktonic foraminifera, and mixed benthic foraminifera are similar and suggest that significant changes of seawater  $\epsilon$ Nd have taken place over the past 25 kyr in the northern SCS.

$\epsilon$ Nd values obtained from HH leachates of bulk non-decarbonated sediments from the same core-top samples (MD05-2904), extracted by using different leaching procedures, range from  $-4.4 \pm 0.3$  to  $-4.7 \pm 0.3$  and are similar to modern seawater  $\epsilon$ Nd in the northern SCS at a depth of about 2000 m (between  $-3.5 \pm 0.3$  and  $-4.5 \pm 0.4$ ) [Wu et al., in press]. In addition, there is a good agreement between HH leachates of bulk non-decarbonated sediments and  $\epsilon$ Nd obtained from foraminifera (Figure 6a). For all of the samples that we have investigated, HH leachates of non-decarbonated sediments of 1 g, leached for 0.5 h, yields  $\epsilon$ Nd values closest to those obtained from cleaned *G. ruber* (Figure 6a and Table 2). The results indicate that seawater  $\epsilon$ Nd could be extracted by this leaching procedure for bulk non-decarbonated sediments from our study site.

In contrast,  $\epsilon\text{Nd}$  values obtained from decarbonated sediments from the core-top samples ( $-5.5 \pm 0.3$  to  $-6.0 \pm 0.2$ ) differ from those of deep water in the northern SCS ( $-3.5 \pm 0.3$  to  $-4.5 \pm 0.3$ ) [Wu *et al.*, in press] (Figure 6b and Table 2). For each sample investigated in core MD05-2904, the  $\epsilon\text{Nd}$  values obtained from the decarbonated sediments systematically display values 1.5 Epsilon units lower than non-decarbonated sediments or cleaned *G. ruber*. Such offset in the  $\epsilon\text{Nd}$  values are also observed even if the best condition of HH leaching determined on non-decarbonated sediments (1 g of sample with 0.5 h leaching time) is applied.

For the purposes of comparison, the results of Huang *et al.* [2013], who extracted  $\epsilon\text{Nd}$  from acid-reductive HH leachates of decarbonated sediments of the core SO17940-2 ( $20^{\circ}07.0'N$ ,  $117^{\circ}23.0'E$ ; water depth of 1727 m) bathed in similar water mass to core MD05-2904, are reported in Figure 6b. The  $\epsilon\text{Nd}$  record core SO17940-2 do not show glacial-interglacial changes and  $\epsilon\text{Nd}$  values obtained on the core-top samples ( $-6.3 \pm 0.3$ ) is not consistent with the  $\epsilon\text{Nd}$  range of PDW analyzed in the SCS at same water depth ( $-4.0$  to  $-4.5$ ). The  $\epsilon\text{Nd}$  record of this core is systematically more unradiogenic than the  $\epsilon\text{Nd}$  derived from foraminifera in our study but it is similar to the values obtained from core MD05-2904 using a similar leaching procedure on the decarbonated sediment fraction (0.2 g of sample with 2 h leaching time).

Considering that detrital material of surface sediments around the study sites MD05-2904 and SO17940-2 are characterized by an  $\epsilon\text{Nd}$  of about  $-11$  [Wei *et al.*, 2012; Liu *et al.*, 2015], the negative offset observed in  $\epsilon\text{Nd}$  from HH leachates of decarbonated sediments may be caused by Nd deriving from the lithogenic fraction during the leaching procedure. Nevertheless, the  $\epsilon\text{Nd}$  record obtained by Huang *et al.* [2013] is probably a mixing between lithogenic Nd extracted by the analytical procedure used and seawater  $\epsilon\text{Nd}$  variability that might explain why both  $\epsilon\text{Nd}$  records display quite similar variations particularly between 25 and 15 kyr. The contamination of  $\epsilon\text{Nd}$  from lithogenic fraction, volcanic ash, and/or preformed Fe-Mn oxides has already been discussed in several studies [Bayon *et al.*, 2002; Elmore *et al.*, 2011; Wilson *et al.*, 2013; Kraft *et al.*, 2013]. All of these results support the idea that removing carbonate may promote dissolution of detrital fraction. In contrast, HH leachates of non-decarbonated sediments from the SCS provide bottom water  $\epsilon\text{Nd}$  under certain sample size/solution ratios and leaching times, in agreement with results recently obtained in the Indian Ocean [Wilson *et al.*, 2013].

### 5.5. Hydrological Implications for the Pacific Since the LGM

The large range of  $\epsilon\text{Nd}$  values obtained from foraminifera from core MD05-2904 (between  $-6.4 \pm 0.4$  and  $-4.1 \pm 0.2$ ) reflects major changes in the seawater  $\epsilon\text{Nd}$  during the last 25 kyr (Figure 5b). To understand such  $\epsilon\text{Nd}$  variations, it is necessary to determine the  $\epsilon\text{Nd}$  of the water masses circulating in the northern SCS or, at least, to identify the main potential isotopic mixing end-members involved in the water mass balance. One must also take into account that the Nd isotopic composition of these end-members could be changed since the last glacial period.

The spatial distribution of present seawater  $\epsilon\text{Nd}$  has recently been established for the Philippine Sea and the northern SCS permitting the identification of the  $\epsilon\text{Nd}$  of the main water masses of the SCS and the Philippine Sea. Results show a homogenous Nd isotopic composition for the PDW throughout the northern SCS, similar to the Nd isotopic composition of the PDW in the Philippine Sea ( $\sim -4$ ) [Wu *et al.*, in press]. Any significant modification of the  $\epsilon\text{Nd}$  value of the PDW was detected after it enters the SCS implying a negligible role for the "boundary exchange" process in the northern SCS [Wu *et al.*, in press].

The seawater  $\epsilon\text{Nd}$  on the northwestern margin of the SCS seem to be not strongly influenced by "boundary exchange" [Lacan and Jeandel, 2001, 2005] since the last glacial period because  $\epsilon\text{Nd}$  values of sediments from the northwestern margin of the SCS have not changed drastically over the past 25 kyr. The sedimentary sources along this oceanic margin correspond mainly to the Pearl River and Taiwanese Rivers, which are characterized by similar ranges of  $\epsilon\text{Nd}$  from  $-10.2$  to  $-13.5$  and from  $-11.5$  to  $-12.7$ , respectively [Liu *et al.*, 2007; Wei *et al.*, 2012]. A small contribution of lithogenic material deriving from the volcanic arc of Luzon (mainly smectite), transported by surface and intermediate currents, has been also identified in sediments on the northwestern margin of the SCS [Boulay *et al.*, 2005; Liu *et al.*, 2010]. However, the  $\epsilon\text{Nd}$  distribution of detrital material of surface sediment in the northern SCS presents a narrow value range (from  $-11$  to  $-12$ ) [Wei *et al.*, 2012] implying a strong dilution of the volcanic material by sediments deriving from Taiwanese and Chinese Rivers. Over the last 25 kyr B.P., changes in  $\epsilon\text{Nd}$  of the detrital fraction of the ODP Sites 1144 and 1145, located close to core MD05-2904, are only between  $-9.9$  and  $-11.1$  [Boulay *et al.*, 2005; Hu *et al.*, 2012] (Figure 5e)

that is insufficient to explain the 2 Epsilon Nd unit variations observed in the reconstructed seawater  $\epsilon\text{Nd}$  record obtained from core MD05-2904 (Figure 5b). However, the quantity of sediments transfers to the north-western margin of the SCS since the last glacial period could be also modified by changes of Asian summer monsoon rainfall intensity and by the reworking of the shelf's sediment during low sea level stand [e.g., *Boulay et al.*, 2005]. These processes have the potential to modify sediments transport to the deep water basin and the dissolved Nd input from the Pearl River to the studied site. However, at present days,  $\epsilon\text{Nd}$  values of the PDW along the northwestern margin of the SCS is not modified in nepheloid layers as well as in different part of the northern SCS characterized by contrasted terrigenous fluxes environment [*Wu et al.*, in press]. In addition,  $\epsilon\text{Nd}$  record obtained in core MD05-2904 at low time resolution display a significant decrease of  $\epsilon\text{Nd}$  values between 23 and 15 ka and an increase of  $\epsilon\text{Nd}$  values during the last glacial-interglacial transition until about 7 ka that are not related to any major changes of the shoreline and river mouth position induce by sea level variations. Nevertheless, past seawater  $\epsilon\text{Nd}$  record from the north-western margin of the SCS need to be investigated at a higher time resolution in the further investigation to assess any potential impacts of variations sea level and sediments transfer to the deep basin on the Nd budget of the SCS.

In addition, the modern SCS deep water refresh very rapidly with a resident time estimated between 30 and 70 years [*Qu et al.*, 2006; *Chang et al.*, 2010]. Further, potential change in bottom water residence time in the north-western SCS during LGM might have only negligible effect on seawater  $\epsilon\text{Nd}$  variability because dissolved-particulate interaction is estimated to be very quick (from weeks to months [*Jeandel and Oelkers*, 2015]).

Consequently, assuming that the Nd budget of the northern SCS is not strongly modified since the last glacial time, the large variations of bottom water  $\epsilon\text{Nd}$  values between the LGM ( $-6.4 \pm 0.2$ ) and the Holocene ( $-4.1 \pm 0.2$ ) estimated for core MD05-2904 could be interpreted as indicating a major re-organization of intermediate/deep water circulation in the Pacific during the last deglaciation and/or a major changes of the Nd isotopic composition of water masses (Figure 5b).

With the exception of  $\epsilon\text{Nd}$  values obtained in the Northwest Pacific close to the East China Sea that have been interpreted as being the result of lithogenic input,  $\epsilon\text{Nd}$  values of the modern NPDW, obtained from several water stations in the North Pacific, are generally characterized by radiogenic values of  $\sim -4$  [*Piepgras and Wasserburg*, 1980; *Amakawa et al.*, 2004, 2009]. The  $\epsilon\text{Nd}$  of the glacial NPDW is actually not available. However, in the Bering Sea, *Horikawa et al.* [2010] have shown that  $\epsilon\text{Nd}$  obtained from the authigenic fraction of sediments from core BOW-8A ( $54^{\circ}47'N$ ,  $176^{\circ}55'E$ , 884 m) displays more radiogenic values ( $+0.8$ ) during glacial time than the Holocene ( $-2$ ) (Figure 5d). This has been interpreted as being the result of enhanced vertical mixing of the NPIW with surface water displaying a high radiogenic Nd isotopic composition strongly influenced by sediment from the volcanic margin of the Bering Sea (Aleutian Arc and Kamchatka Peninsula) [*Horikawa et al.*, 2010]. Such variations in the  $\epsilon\text{Nd}$  of the NPIW observed in the subarctic region would have had a remarkable influence, through vertical mixing, on the Nd isotopic signature of the glacial NPDW and would have produced a more radiogenic glacial NPDW in the North Pacific. In addition, during glacial times, it has been shown by modeling and various proxies such as ventilation age changes that glacial NPDW could be produced in different areas of the North Pacific [*Okazaki et al.*, 2010; *Rae et al.*, 2014]. However, as seawater  $\epsilon\text{Nd}$  of the upper layer of the North Pacific range from  $\sim -2.8$  to  $-4.5$  [*Amakawa et al.*, 2004, 2009], the glacial NPDW need to stay through time a radiogenic end-member and cannot explain the negative  $\epsilon\text{Nd}$  values of the glacial seawater obtained from core MD05-2904.

Present-day  $\epsilon\text{Nd}$  values of AAIW and CDW (SSW) in the south Pacific range from  $-6$  to  $-8.5$  and from  $-8$  to  $-9$  [*Molina-Kescher et al.*, 2014a; *Carter et al.*, 2012; *Amakawa et al.*, 2013]. The SSW and particularly the AAIW are strongly modified in the North Pacific by dilution with NPDW and NPIW [*Piepgras and Jacobsen*, 1988] and by boundary exchange or exchange with volcanic particulates derived from numerous volcanic areas [*Amakawa et al.*, 2009; *Grenier et al.*, 2013]. The  $\epsilon\text{Nd}$  values of the SSW during glacial periods is poorly constrain but a shift toward more radiogenic values was identified during the HS1 for the AAIW in cold-water corals ( $\sim -6.5$ ) of the Drake Passage [*Robinson and van de Flierdt*, 2009] and during the LGM for deep-sea cores collected at different water depth from the Chatham Rise (continental slope basin East of New Zealand) [*Noble et al.*, 2013]. This study indicates a glacial LCDW  $\epsilon\text{Nd}$  of around  $-5.6$  corresponding to an offset up to  $\sim 0.8$   $\epsilon\text{Nd}$ -units more radiogenic than those obtained for glacial deep water on core MD05-2904 ( $-5.2 \pm 0.3$  to  $-6.4 \pm 0.3$ ) and for South Atlantic and equatorial Indian ( $\epsilon\text{Nd} = -6.4$  to  $-7.4$ ) [*Piotrowski et al.*, 2004, 2009]. However, as seawater  $\epsilon\text{Nd}$  at the Chatham Rise are influenced by the signature of the NPDW and could be modified locally by boundary exchange or exchange with volcanic particles derived

from New Zealand's North Island, further investigations are necessary to constrain the Nd isotopic composition of the glacial UCDW and LCDW. Nevertheless, the glacial  $\epsilon\text{Nd}$  values of the SSW (AAIW and CDW) in the southern Pacific is less radiogenic compared to the Holocene of about more than 1  $\epsilon\text{Nd}$ -units reflecting a reduced export of NADW due to re-organization of the Atlantic meridional overturning circulation, which was propagated throughout the glacial Southern Ocean [Piotrowski *et al.*, 2004, 2009]. The modification of the CDW in the North Pacific by boundary exchange or exchange with volcanic particulates derived from numerous volcanic areas has been observed for surface and intermediate water masses [Grenier *et al.*, 2013], but are not well documented for deep water masses of the southern Philippine Sea that could contribute significantly to the upper layer by vertical mixing. The modifications of the  $\epsilon\text{Nd}$  values of the glacial CDW during northward penetration are also not available for the LGM.

Nevertheless, assuming that the glacial CDW ( $-7$ ) was not fully modified from the Southern Ocean to the Philippine Sea during the last glacial period, the seawater  $\epsilon\text{Nd}$  record obtained from core MD05-2904 could reflect a modification of the proportions of the NSW (NPIW/NPDW) and the SSW (CDW) in the Philippine Sea (Figure 5b). The LGM, characterized by unradiogenic  $\epsilon\text{Nd}$  values compared to those of the Holocene, would imply a retreat of the NSW (NPIW/NPDW) to the north and/or a higher propagation of the SSW (CDW) to the north compared to the modern situation, which is characteristic of the late Holocene period (last 6 kyr) (Figure 5b). Such interpretation needs to be confirmed by further investigation of  $\epsilon\text{Nd}$  record in the western equatorial Pacific to determine the Nd isotopic composition of the glacial CDW in the southern Philippine Sea.

Previous studies have suggested that NPIW formation was more intense during the last glacial period [Rella *et al.*, 2012; Max *et al.*, 2014] or during the cold event HS1 in the subarctic Pacific [Okazaki *et al.*, 2010; Chikamoto *et al.*, 2012; Jaccard and Galbraith, 2013]. According to compilation of radiocarbon records in the North Pacific combined with modeling simulation, it has been suggested that the formation of NPIW could even extend to a depth of 3600 m [Okazaki *et al.*, 2010; Rae *et al.*, 2014]. The simulated deep water pathways spread southward along the western margin of the North Pacific, forming a simple western boundary deep current system that can reach the Philippine Sea and the northern SCS [Okazaki *et al.*, 2010; Wan and Jian, 2014].

However, such a scenario, implying a higher proportion of NSW during the LGM, is not supported by the seawater  $\epsilon\text{Nd}$  record from core MD05-2904 that in contrast implies a higher proportion of SSW (Figure 5b). It was suggested that deep Pacific Ocean is isolated from the upper one at the boundary around 2000 m [Matsumoto *et al.*, 2002; Keigwin, 1998]. In addition, on the basis of the  $\delta^{13}\text{C}$  record obtained from benthic foraminifera in cores from the subarctic region, there is no evidence for enhanced NPDW formation during the glacial period [Max *et al.*, 2014]. In agreement with the seawater  $\epsilon\text{Nd}$  record of core MD05-2904, all of these observations suggest that deep water formation in the North Pacific (NPDW) during the LGM was probably no greater than it is today.

Numerous studies have shown that, during the last glacial period, a slowdown of the NADW formation occurred which is associated with a reduction in its propagation to the South Atlantic [Oppo and Fairbanks, 1987; Duplessy *et al.*, 1988; Labeyrie *et al.*, 1996; Curry and Oppo, 2005]. Benthic-planktonic foraminifera  $^{14}\text{C}$  age difference in the North Atlantic increased greatly in the last glacial period compared to the present suggesting a decreased ventilation rate or changes in the proportions of northern-sourced water (NSW) and southern-sourced water (SSW) [Keigwin and Schlegel, 2002; Keigwin, 2004; Robinson *et al.*, 2005]. Furthermore, deep water  $\epsilon\text{Nd}$  values obtained from the Atlantic Ocean and the Southern Ocean for the last glacial period are characterized by more radiogenic values than the Holocene implying a higher proportion of southern-sourced water (SSW) relative to northern-sourced water (NSW) [Rutberg *et al.*, 2000; Piotrowski *et al.*, 2004, 2005, 2012; Robinson and van de Flierdt, 2009; Roberts *et al.*, 2010; Skinner *et al.*, 2013; Böhm *et al.*, 2015]. Despite the poor level of documentation regarding past seawater changes in the Indian and Pacific Oceans, available studies indicate an enhanced northward propagation of the SSW during glacial periods [Piotrowski *et al.*, 2009; Basak *et al.*, 2010; Pena *et al.*, 2013]. Studies undertaken on sediment cores from the equatorial Indian Ocean show positive excursions of past seawater  $\epsilon\text{Nd}$  values, associated with lower  $\delta^{13}\text{C}$ , during glacial periods [Piotrowski *et al.*, 2009; Wilson *et al.*, 2012] suggesting more pronounced northward intrusion of SSW. The seawater  $\epsilon\text{Nd}$  record obtained from core MD05-2904 confirms the presence of a higher proportion of SSW in the western subtropical Pacific during the last glacial period than during the late Holocene. However, this higher contribution of the CDW need to be confirmed by further investigation permitting to establish the seawater  $\epsilon\text{Nd}$  record of the western equatorial Pacific (south



Philippine Sea) in order to constrain for the western Pacific Ocean the North-South Nd isotopic gradient of the CDW during glacial time.

## 6. Conclusion

Neodymium isotopic compositions ( $\epsilon\text{Nd}$ ) extracted from cleaned and uncleaned benthic and planktonic foraminifera, and Fe-Mn coatings precipitated on sediments, have been investigated for the first time in the SCS. The results are compared to modern seawater  $\epsilon\text{Nd}$  to (i) assess the reliability of extraction of past seawater  $\epsilon\text{Nd}$  from such an archive and to (ii) establish past circulation changes in deep water masses in the western subtropical Pacific over the past 25 kyr.

PAAS-normalized REE patterns, Mn/Ca, and Nd/Ca ratios obtained from reductively/non-reductively cleaned foraminifera and reductive cleaning solutions used for extracting Nd from associated authigenic phases in foraminifera shells reveal that the reductive cleaning process cannot remove the authigenic contaminants completely. Comparison of Nd isotopic compositions analyzed for various species of foraminiferal calcite tests and authigenic phases are quite similar and indicate that  $\epsilon\text{Nd}$  obtained from cleaned and uncleaned foraminifera are overprinted by Nd deriving from authigenic Fe-Mn coatings precipitated on foraminifera. Therefore, the Nd isotopic composition of both reductively cleaned and non-reductively cleaned foraminifera reflect the bottom and/or pore water  $\epsilon\text{Nd}$  and can be used as a useful tracer to reconstruct past seawater changes for deep ocean.

In contrast, the interpretation of Nd isotopic composition in bulk sediment leachates is more complicated. Although Nd isotopic composition obtained from acid-reductive HH leachates of bulk non-decarbonated sediment exhibits similar  $\epsilon\text{Nd}$  values to those of foraminifera and bottom water (for core-top samples), partial dissolution of lithogenic fractions has been observed when acid-reductive HH leaching is carried out on decarbonated sediments.

The  $\epsilon\text{Nd}$  record obtained from core MD05-2904 displays large variations in seawater  $\epsilon\text{Nd}$  values between the LGM ( $-6.4 \pm 0.3$ ) and the Holocene ( $-4.1 \pm 0.2$ ), implying a modification of Nd inputs from rivers and/or a re-organization of the circulation in the western subtropical Pacific. The first hypothesis is not supported by the distribution of seawater  $\epsilon\text{Nd}$  obtained in the northern part of the SCS [Wu *et al.*, in press]. However, further investigations, based on a high time resolution  $\epsilon\text{Nd}$  record, need to be carried out in future in order to assess any potential impacts of sea level and Asian monsoon rainfall variations on sediments transfer to the deep basin of the SCS and the Nd budget of the SCS. We have proposed that these variations reflect a modification of the relative proportions of the NSW ( $\epsilon\text{Nd}$  around  $-4$ ) and the SSW ( $\epsilon\text{Nd}$  around  $-8$ ) due to vertical mixing in the Philippine Sea. The unradiogenic glacial seawater  $\epsilon\text{Nd}$  values obtained in core MD05-2904 could imply a slowdown of NPDW (and NPIW) ventilation and/or a higher propagation of the CDW to the north compared to the late Holocene (last 6 kyr) (Figure 5). This interpretation imply to hypothesis that glacial CDW have not be fully modified by boundary exchange or exchange with volcanic particulates from volcanic arc of the western Pacific margin. Further analysis of  $\epsilon\text{Nd}$  values of deep water masses from the southern part of the Philippine Sea and on marine core from the western subtropical Pacific needs to be realized to better constrain the Nd isotopic composition of the CDW at present time and during the last glacial period.

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