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# Industrially Purified Nd Materials Identified by Distinct Mass-Dependent Isotopic Composition

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Rare earth elements (REEs) are considered emerging anthropogenic pollutants. Anthropogenic lanthanum, cerium, samarium, and gadolinium alone, or excess of all the REEs have already been reported in the environment. In addition, it is only a matter of time for neodymium (Nd) of anthropogenic origin to be reported disseminated in the environment, given its growing demand for new technologies and its use in permanent magnets of wind turbine. So far, only in a few cases was the addition of anthropogenic Nd detected in soils and sediments by the measurements of REE concentrations. For this reason, we propose to use the Nd isotopic composition to help the distinction of pollution. The isotopic tracing of Nd using variations in the abundance of  $^{143}\text{Nd}$  from the radioactive decay of  $^{147}\text{Sm}$  (Nd-radiogenic composition) is one option. Here, we expand the Nd isotopic fingerprinting by the investigation of the stable Nd isotopic composition expressed as  $\delta^x\text{Nd}$ , the relative permil (‰) deviation from the isotopic composition of the pure Nd JNdi-1 reference standard. The measurement of  $\delta^x\text{Nd}$  used a MC-ICPMS (multi-collector inductively coupled plasma mass spectrometry) with sample-standard bracketing technique, allowing the determination of precise and accurate Nd isotopic variations. Our results show that Nd-magnets (Neo) and man-made purified Nd materials are not significantly different on average (respectively,  $\delta^{148}\text{Nd}$  of  $-0.105 \pm 0.023$  and  $-0.120 \pm 0.141\text{‰}$ ). More importantly, they are different from terrestrial rocks ( $\delta^{148}\text{Nd}$  of  $-0.051 \pm 0.031\text{‰}$ ). Moreover, the Nd-radiogenic composition of Neo can be highly variable, even when they come from a single supplier. In addition, the study of all Nd stable isotopic compositions demonstrates that irrespective of their natural origin (witnessed by their Nd-radiogenic composition), all Nd from rocks and man-made materials are related by mass-dependent isotopic fractionation laws. We also have defined a parameter, the  $\Delta^{148-150}\text{Nd}'$ , allowing the distinction of thermodynamic isotopic fractionation (the  $\Delta^{148-150}\text{Nd}'$  is invariant) from kinetic isotopic fractionation (the  $\Delta^{148-150}\text{Nd}'$  is negatively correlated with the  $\delta^{148}\text{Nd}$ ). Such covariation is observed for anthropogenic materials that could be seen as small deficit in  $^{150}\text{Nd}$  (around 5 ppm/‰/amu), but too small to be consistent with nuclear field effect. On the other hand, the anthropogenic material defines a covariation in the  $\Delta^{148-150}\text{Nd}'$ - $\delta^{148}\text{Nd}$  space in full agreement with the theoretical expectation from mass-dependent kinetic isotopic fractionation. The mass-dependent fractionation of Nd by chromatographic separation is also consistent with a kinetic

isotopic fractionation. The purification of Nd from other light REEs by industrial processes involves chromatographic separation and, therefore, is likely to produce anthropogenic Nd with low values for  $\delta^{148}\text{Nd}$  associated with high values for  $\Delta^{148-150}\text{Nd}'$ . Both are resolvable with current MC-ICPMS technology and could be useful to trace incoming anthropogenic pollution in the environment. In soils, the combination of low values for  $\delta^{148}\text{Nd}$  with high values for  $\Delta^{148-150}\text{Nd}'$  is likely to be an unambiguous pollution signal from the degradation in the environment of Neo or other industrial products, especially if this is associated with an Nd-radiogenic composition inconsistent with the surrounding rocks and soils. In contrast, the industrial residue of Nd purification could be characterized by high  $\delta^{148}\text{Nd}$  with low values for  $\Delta^{148-150}\text{Nd}'$ , and the leak or the discharge of such residue could also be unambiguously distinguished.

**Keywords:** pollutant, rare earth elements, neodymium, isotopes, permanent magnets, mass dependent fractionation

## INTRODUCTION

The neodymium (Nd) is one of the rare earth elements (REEs) used in industry for various applications (e.g., metallurgy, battery alloys, and ceramics) but overwhelmingly (70%) in permanent magnets (Dutta et al., 2016). Nd-magnets (Neo) contain 20–35% of Nd and are present in new technologies (CD, DVD, or computer hard drive). By far, the increasing use of Neo is linked to the current energy transition. The wind turbine requires 40–200 kg of Nd per MW (Moss et al., 2011; Shaw and Constantinides, 2012), while the electric car and electric bike can even have a greater share in Neo consumption in the future (Brown, 2016). By 2,035, neodymium demand may be almost 40% of the total demand of REEs compared with the 20% in 2010 (Alonso et al., 2012). In addition, Neo is not currently recycled and might not be in the near future (Yang et al., 2017; Diehl et al., 2018).

Anthropogenic contaminations by REEs have already been reported in continental waters, for gadolinium (Gd), lanthanum (La), samarium (Sm), and cerium (Ce) (e.g., Kulaksiz and Bau, 2013 and reference therein; Hissler et al., 2015). In the environment, anthropogenic Nd has been reported in sediment near industrial activity of REE ore deposits (e.g., Elbaz-Poulichet and Dupuy, 1999; Shynu et al., 2011) and reprocessing (e.g., Oliveira et al., 2007; Sanders et al., 2013; Wen et al., 2013; Cánovas et al., 2018). The increasing industrial processing and exponential rise of REE mine production (Haxel et al., 2002) will create a more preminent source of Nd pollution. In addition, the fragility and susceptibility to corrosion for Neo (e.g., Sagawa et al., 1987) will likely generate another, although more widespread, source of anthropogenic Nd in the environment. The ecotoxicology of REEs is debated, but high REEs levels in the environment have been linked to negative consequences in plants, on animals, and microorganisms (e.g., Gwenzi et al., 2018). Thus, the growing demand associated to environmental vulnerability of some REE industrial products strongly suggest that anthropogenic Nd can be considered as an emerging pollutant in the environment (Gwenzi et al., 2018). The use of radiogenic isotopic composition of Nd (the variable excess of  $^{143}\text{Nd}$  relative to all the other

stable isotopes of Nd that is related to the decay of the long-life radioactive  $^{147}\text{Sm}$ ) has revealed the transfers of Nd from pollution induced by industrial activity to animals (Bosco-Santos et al., 2018). In natural waters, Nd, like all the other REEs, is present at ppt level, and by analogy with Gd (Tepe et al., 2014; Merschel et al., 2015), the use of the concentration difference can be a sufficient tool to identify anthropogenic Nd contamination. So far, all REEs (e.g., Hao et al., 2016) or specific REEs, but not Nd, have been detected in continental waters. In soils and sediments, Nd concentrations are, in most cases, above the ppm level (Freslon et al., 2014 and references therein), making anthropogenic Nd contamination more difficult to detect by the use of the REEs concentration only (e.g., Olmez et al., 1991). Recent studies have focused on polluted river sediments and soils, and only the presence of anthropogenic Gd has been demonstrated by the measurement of REE concentrations alone (da Silva et al., 2018; Altomare et al., 2020).

Here, we propose to expand the isotopic tracing of Nd using variations in the abundance of  $^{143}\text{Nd}$  from the radioactive decay of  $^{147}\text{Sm}$  (e.g., Piepgras et al., 1979; Biscaye et al., 1997; Frank, 2002; Lahd Geagea et al., 2008; Li et al., 2009; Bosco-Santos et al., 2018) by the investigation of the isotopic composition of Neo. However, the radiogenic isotopic composition of Nd in soils can be highly variable, even in one location (e.g., Viers and Wasserburg, 2004), and so far, only industrial pollution has been traced with variations in the abundance of  $^{143}\text{Nd}$  in soils (e.g., Steinmann and Stille, 1997). Therefore, we also propose the measurement of the mass-dependent Nd isotopic signatures as a new tool to better distinguish anthropogenic from natural Nd.

The study of stable Nd isotope variations is recent. Analysis of commercial Nd oxide reagents of high purity (Wakaki and Tanaka, 2012) shows that Nd stable isotopic variations could be inherited from the source materials or be caused by isotope fractionation during the industrial purification of Nd from REEs ores. The latter is further suggested since the stable Nd isotopic compositions of various geological reference materials and terrestrial samples showed only very small natural variations (Ma et al., 2013; Ohno and Hirata, 2013; Saji et al., 2016; McCoy-West et al., 2017, 2020a,b). In this study, we report the stable

**TABLE 1** | Source of the purified Nd.

Sample	Material	Source
Jndi-1	Solution	Tanaka et al., 2000
AR	Solution	Ames-Rennes (Chauvel and Blichert-Toft, 2001)
JM-Nancy	Metal	Johnson Matthey (Henry et al., 1997)
JMC'	Solution	Johnson Matthey
JMC	Solution	Johnson Matthey (Luais et al., 1997)
NIST3135a	Solution	NIST, batch 140527
NNB	Solution	PlasmaCAL SCP SCIENCE, batch S151113011
Nancy-16rees	Solution	Astasol, batch 0001

**TABLE 2** | Type of Nd-magnet (Neo) studied.

Sample	Size (mm)	T max (°C)	Vertical pull (kg)	Coating
N35	3 × 3 × 3	80	0.28	Ni-Cu-Ni
N42	5 × 2 × 0.5	80	0.10	Ni-Cu-Ni
N45	5 × 1 × 1.5	80	0.19	Ni-Cu-Ni
N45H	5 × 5 × 1	120	0.40	Ni-Cu-Ni
N45SH	∅10 × 1.5	150	1.10	Ni-Cu-Ni
N50	5 × 5 × 1.2	80	0.40	Ni-Cu-Ni-Au
N52	∅10 × 2	80	1.60	Ni-Cu-Ni

isotopic variations of Nd affected by anthropogenic processes and investigate the use of the mass-dependent Nd isotopic analysis as a new tool to trace Nd pollution in the environment.

## MATERIALS AND METHODS

### Samples

Six man-made purified Nd samples and seven Nd-magnets (Neo) were selected for this study; in addition to the JNdi-1, a pure Nd solution (Tanaka et al., 2000) used as the reference standard. Man-made purified samples (commercially available) are pure Nd in a solution of dilute HNO<sub>3</sub> that mainly correspond from the dissolution of Nd oxides. Four correspond to Nd-concentration standard solutions: NNB, JMC (Luais et al., 1997), JMC', and NIST 3135a (Table 1). The other two are solutions used for their <sup>143</sup>Nd/<sup>144</sup>Nd ratio: JM-Nancy [J&M in Henry et al. (1997)] and AR [Ames Rennes Nd in Chauvel and Blichert-Toft (2001)]. Also, we used a multi-REEs concentration standard (Nancy-16rees; Table 1) containing the 14 naturally occurring lanthanides, Y and Sc. The seven Neo are all made of Nd<sub>2</sub>Fe<sub>14</sub>B by the Magnet Expert Ltd Company but differ by their specific pull force (Table 2). Their fragility and susceptibility to corrosion (Sagawa et al., 1987) is diminished by Ni-Cu-Ni coating and by increasing the temperature resistivity (Tmax). We choose magnets with distinct pull force and distinct Tmax (Table 2).

### Degree of Purification

We used a Thermo Scientific X-series 2 quadrupole inductively coupled plasma mass spectrometer (ICP-MS) to measure concentrations of La, Ce, praseodymium (Pr), Nd, and Sm in Neo and purified Nd samples. Since all our samples have a high purity of Nd, they were introduced with an Nd concentration of at least 1 ppm to allow the measurement of trace amounts of other REEs. Samples were diluted in 0.5 M HCl with 10 ppb of indium as internal standard. Wash time of 7 min between each measurement allowed full decontamination. At 2σ level, the external reproducibility, calculated from five repeated measurements of the NNB solution is 0.3, 1.5, 1.8, and 5.7 ppt/ppm for La/Nd, Ce/Nd, Pr/Nd, and Sm/Nd ratios, respectively.

### Mass Spectrometry

The variations of the Nd isotopic composition were obtained using a Thermo Scientific Neptune Plus multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS) coupled to an Apex HF desolvating nebulizer with an aspiration rate of 50 μl/min. The nine Faraday cups of the multi-collector were used to measure, in static low-resolution mode, the seven Nd isotopes (<sup>142</sup>Nd, <sup>143</sup>Nd, <sup>144</sup>Nd, <sup>145</sup>Nd, <sup>146</sup>Nd, <sup>148</sup>Nd, and <sup>150</sup>Nd) together with two isotopes of Sm (<sup>147</sup>Sm and <sup>149</sup>Sm), to confirm the lack of Sm isobaric interferences on the <sup>144</sup>Nd, <sup>148</sup>Nd, and <sup>150</sup>Nd.

The standard-sample-standard bracketing technique (e.g., Halicz et al., 1999) has been applied to Nd isotopes. Solutions were introduced at a concentration of 50 ppb of Nd in 2% (by volume) HNO<sub>3</sub>, generating an average <sup>146</sup>Nd beam of 1.3 × 10<sup>-11</sup> A on the central collector. A negligible cross-contamination (<0.8 × 10<sup>-14</sup> A) between the sample and the standard was achieved by aspirating 2% HNO<sub>3</sub> wash solution for 12 min between analyses. Our protocol consists of the measurement of standard and sample isotopes values four and three times, respectively, for 200 s each, allowing the calculation of five brackets, and each value corresponds to their average. Each 200-s measurement consists of 100 s of acquisition of the signal (8.389 s × 12 cycles), repeated twice. A single measurement requires almost 2 h and consumes up to 40 ng of Nd.

Nd stable isotopic compositions are expressed as the permil deviation from the isotopic composition of the JNdi-1 as follows:

$$\delta^m\text{Nd} = \left( \frac{(m\text{Nd}/^{144}\text{Nd})_{\text{sample}}}{(m\text{Nd}/^{144}\text{Nd})_{\text{JNdi-1}}} - 1 \right) \times 10^3$$

where *m* = 145, 146, 148, or 150. Since the intensities of samples and standards were matched within 10% of each other, the delta notation and the bracketing technique reduce any contribution from the cross-contamination and isobaric interferences (e.g., Galy et al., 2001). At 2σ level, the external reproducibility, calculated from 48 repeated measurements of the JNdi-1 standard, is 0.031‰, 0.040‰, 0.071‰, and 0.107‰ for δ<sup>145</sup>Nd, δ<sup>146</sup>Nd, δ<sup>148</sup>Nd, and δ<sup>150</sup>Nd, respectively (Table 3). Previous studies have established that terrestrial Nd stable isotopic compositions tend to follow mass-dependent laws (e.g., Wakaki and Tanaka, 2012; Ma et al., 2013; Ohno and Hirata,

**TABLE 3** | Nd isotopic composition of purified Nd and Neo.

Sample	$\epsilon^{143}\text{Nd}$	$2\sigma$	$\delta^{145}\text{Nd}$	$2\sigma$	$\delta^{146}\text{Nd}$	$2\sigma$	$\delta^{148}\text{Nd}$	$2\sigma$	$\delta^{150}\text{Nd}$	$2\sigma$	$\Delta^{148-150}\text{Nd}'$	$2\sigma$	<i>N</i>
			‰		‰		‰		‰		‰		
<b>Purified Nd</b>													
Jndi-1	-10.20	0.35	0.001	0.031	0.003	0.040	0.008	0.071	0.014	0.107	-0.001	0.042	48
AR	-12.98	0.33	-0.030	0.030	-0.064	0.045	-0.134	0.087	-0.195	0.140	-0.002	0.043	19
JM-Nancy	-29.40	0.29	0.052	0.022	0.097	0.027	0.175	0.034	0.279	0.071	-0.012	0.051	10
JMC'	-6.99	0.27	-0.196	0.040	-0.392	0.033	-0.783	0.078	-1.158	0.079	-0.001	0.047	11
JMC	-6.97	0.28	-0.244	0.039	-0.497	0.024	-1.011	0.062	-1.503	0.061	0.005	0.046	14
NIST3135a	-3.67	0.28	-0.045	0.045	-0.092	0.060	-0.202	0.127	-0.286	0.174	-0.009	0.043	14
NNB	-9.02	0.30	-0.029	0.033	-0.062	0.038	-0.131	0.072	-0.180	0.099	-0.009	0.045	45
<b>Neo</b>													
N35	-19.09	0.21	-0.028	0.030	-0.069	0.005	-0.117	0.042	-0.209	0.026	0.024	0.026	3
N42	-21.22	0.21	-0.030	0.052	-0.051	0.041	-0.128	0.073	-0.141	0.079	-0.033	0.064	4
N45	-22.39	0.30	-0.045	0.042	-0.069	0.059	-0.105	0.083	-0.158	0.132	0.002	0.013	3
N45H	-20.52	0.20	-0.026	0.042	-0.056	0.026	-0.133	0.048	-0.151	0.048	-0.031	0.016	3
N45SH	-12.25	0.15	-0.018	0.012	-0.019	0.021	-0.052	0.046	-0.040	0.030	-0.025	0.052	4
N50	-18.82	0.56	-0.025	0.045	-0.051	0.027	-0.127	0.064	-0.173	0.096	-0.010	0.029	3
N52	-17.19	0.26	-0.029	0.039	-0.041	0.034	-0.074	0.123	-0.116	0.149	0.004	0.038	4

2013; Saji et al., 2016; McCoy-West et al., 2017), implying that the largest variations should be displayed by  $\delta^{150}\text{Nd}$  followed by  $\delta^{148}\text{Nd}$ . However, some of the literature data have been acquired using a double-spike method or MC-ICPMS that prevented the study of  $\delta^{150}\text{Nd}$ . Thus, in the following, we will discuss the  $\delta^{148}\text{Nd}$ . In addition, we also introduce the  $\Delta'$  notation to calculate the deviation from the thermodynamic mass-dependent behavior of two stable isotope ratios (Young and Galy, 2004). Here, it is applied to  $^{148}\text{Nd}/^{144}\text{Nd}$  and  $^{150}\text{Nd}/^{144}\text{Nd}$  with:

$$\Delta^{148-150}\text{Nd}' = 10^3 \times \text{Ln} \left( \frac{10^3 \delta^{148}\text{Nd}}{10^3} \right) - \beta \times 10^3 \\ \times \text{Ln} \left( \frac{10^3 \delta^{150}\text{Nd}}{10^3} \right)$$

where  $\beta$  is the exponent relating the thermodynamic fractionation factors for two isotope ratios (Young et al., 2002) and has a maximum value of 0.6756 for  $^{148}\text{Nd}/^{144}\text{Nd}$   $^{150}\text{Nd}/^{144}\text{Nd}$  using the latest accepted atomic masses of Nd isotopes (Audi et al., 2017) and their reduced masses including molecular masses tending toward infinity (Hayles et al., 2017). At  $2\sigma$  level, the external reproducibility of  $\Delta^{148-150}\text{Nd}'$ , calculated from 48 repeated measurements of the JNdi-1 standard, is 0.042‰ (Table 3).

We also measured the radiogenic signature of  $^{143}\text{Nd}$ , expressed as  $\epsilon^{143}\text{Nd}$  with the CHUR (chondritic uniform reservoir) for reference (DePaolo and Wasserburg, 1976) such as:

$$\epsilon^{143}\text{Nd} = \left( \frac{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{sample}}}{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}}} - 1 \right) \times 10^4$$

using  $^{143}\text{Nd}/^{144}\text{Nd}$  ratios normalized to  $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$  (Wasserburg et al., 1981) by the exponential law, and to the JNdi-1 ratio  $^{143}\text{Nd}/^{144}\text{Nd} = 0.512115$  (Tanaka et al., 2000), and using a true bracketing linear correction following Wilson et al. (2012).

## Chemical Treatment

Neo was dissolved at ambient temperature in 4 ml of concentrated distilled  $\text{HNO}_3$  under extractor hood. After dilution with de-ionized water and evaporation, an aliquot containing 2  $\mu\text{g}$  of Nd in 2 M  $\text{HNO}_3$  was taken for chemical separation of Nd from all the other elements contained in Neo. Indeed, their structural formula is  $\text{Nd}_2\text{Fe}_{14}\text{B}$ , and they often contain some Dy and other elements as traces (e.g., Sagawa et al., 1987). Nd purification is required since the accurate measurement of stable isotopic variations by MC-ICPMS can be disturbed by isobaric interferences and matrix effects (e.g., Galy et al., 2001). Our chemical protocol adapted the chromatographic separation used for the measurement of  $\epsilon^{143}\text{Nd}$  (Pin and Zalduegui, 1997). Since the Ln-resin produced mass-dependent fractionation of Nd (Wakaki and Tanaka, 2012; Ohno and Hirata, 2013; Saji et al., 2016), we calibrated the volume corresponding to the collection of Nd in order to recover 100% of Nd, and avoid any isotopic bias. A 100% recovery was achieved in three steps. First is the use of a column filled with 1.6 ml of Tru-resin 50–100  $\mu\text{m}$  that removed all major and trace elements from REEs in 2 M  $\text{HNO}_3$ . The addition of 4.5 ml of ultrapure water (>18 M $\Omega$ .cm, MilliQ Plus system) released all the REEs from the Tru-resin directly into a second column composed of a bed of 0.6 ml of AG1 X8 resin 200–400 mesh above 3.2 ml of Ln-resin 50–100  $\mu\text{m}$ . The second step consisted of collecting all Nd and some other REEs by the addition of 2.5 ml of 6 M HCl. After evaporation and dilution in 0.2 ml of 0.27 M HCl, the third separation consisted of loading onto another column, with an internal diameter of 4.0 mm, composed of a bed of 0.6 ml of AG1

X8 resin 200–400 mesh above 3.2 ml of Ln-resin 50–100  $\mu\text{m}$  that separated Nd from La, Sm, Eu, and all the heavy REEs. The full elution of Nd required 4 ml of 0.27 M HCl. Regularly, the JNdi-1 standard followed the same chemistry procedure to validate the lack of stable isotopic fractionation by this protocol.

Unfortunately, the purification of Nd from light REEs (Ce and Pr) would have required a different chemical protocol (e.g., Rehkamper et al., 1996), and the occurrence of up to 40% of the Ce and Pr initially present in the sample and still present after the purification of Nd on Ln-resin (e.g., McCoy-West et al., 2020a) might induce inaccuracy in the  $\delta^{148}\text{Nd}$  due to matrix effects. Since the average Ce/Nd and Pr/Nd mass ratios of supracrustal rocks are 2.46 and 0.27, respectively (e.g., McLennan, 2001), and that soils can see relative enrichment by a factor of 0.5–5 of these ratios (e.g., Braun et al., 1998; Ramos et al., 2016), the incomplete purification of Nd could lead to Ce/Nd  $\leq 5$  and Pr/Nd  $\leq 0.6$  in the Nd fraction. Fortunately, using our protocol, the addition of Pr (up to 0.7 Pr/Nd mass ratio) or Ce (up to 5 Ce/Nd mass ratio) to the NNB solution had no effect on the  $\delta^{148}\text{Nd}$  measurement during the MC-ICPMS analysis (**Supplementary Figure 1** and **Supplementary Table 1**).

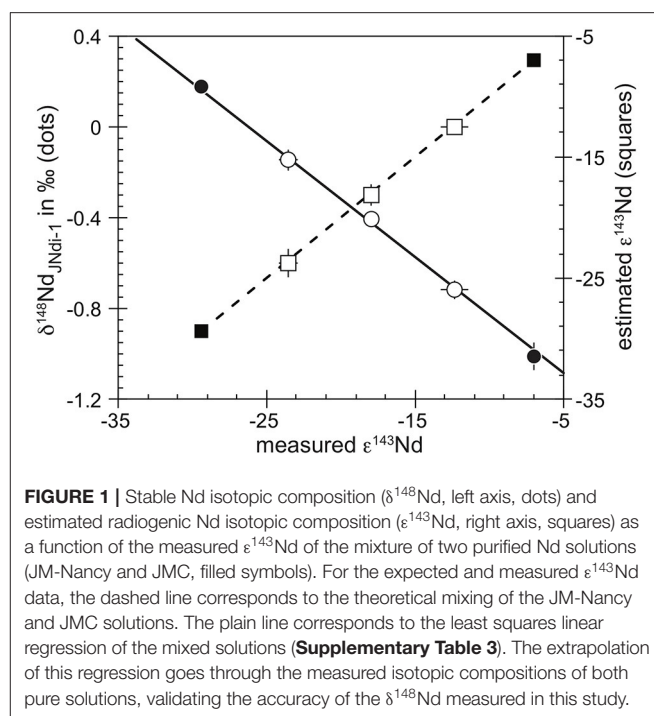
The mass-dependent fractionation of Nd by chromatographic separation (Wakaki and Tanaka, 2012; Ohno and Hirata, 2013; Saji et al., 2016) has been further tested using pure Nd solutions (NNB and JMC) and the multi-REE solution (Nancy-16rees). Pure Nd solution JMC (3  $\mu\text{g}$ ) and of the multi-REEs solution Nancy-16Rees and 1  $\mu\text{g}$  of pure Nd solution of NNB were evaporated and dissolved in 0.2 ml of 0.27 M HCl. Then, each solution was loaded onto a column, with an internal diameter of 4.0 mm, composed of a bed of 0.6 ml of AG1 X8 resin 200–400 mesh above 3.2 ml of Ln-resin 50–100  $\mu\text{m}$ . An eluate of 0.27 M HCl was added to the column, and the total volume of eluate and corresponding amount of collected Nd are reported in **Supplementary Table 2**. For the test with 1  $\mu\text{g}$  of Nd of NNB, only four fractions were separated. For the two tests with 3  $\mu\text{g}$  of Nd, 10 fractions were collected (**Supplementary Table 2**).

## RESULTS

### Accuracy of the Data

The accuracy of radiogenic data can be validated for two solutions already studied (AR and JM-Nancy) since their  $\epsilon^{143}\text{Nd}$  of  $-12.98 \pm 0.33$  ( $2\sigma$ ,  $N = 19$ ) and  $-29.40 \pm 0.29$  ( $2\sigma$ ,  $N = 10$ ), respectively (**Table 3**), are consistent with literature values of  $-13.21 \pm 0.25$  and  $-29.53 \pm 0.47$ , respectively (Henry et al., 1997; Chauvel and Blichert-Toft, 2001). The  $\epsilon^{143}\text{Nd}$  of the JM-Nancy (Henry et al., 1997; this study) is more than 21  $\epsilon$  units lower than the JM Nd used by Wakaki and Tanaka (2012). Such solutions were produced by the dissolution of pure Nd metal, and this huge difference likely reflects the use of different source materials by the Johnson-Matthey Company to produce Nd metal. Thus, these two JMs can be considered as two distinct samples.

The accuracy of the stable isotopic compositions presented in this study has been validated by the standard addition method. JM-Nancy and JMC solutions were mixed in known proportions. The variable mixing proportion, calculated by weight, allowed the calculation of an estimated  $\epsilon^{143}\text{Nd}$ . When the propagation of



**FIGURE 1** | Stable Nd isotopic composition ( $\delta^{148}\text{Nd}$ , left axis, dots) and estimated radiogenic Nd isotopic composition ( $\epsilon^{143}\text{Nd}$ , right axis, squares) as a function of the measured  $\epsilon^{143}\text{Nd}$  of the mixture of two purified Nd solutions (JM-Nancy and JMC, filled symbols). For the expected and measured  $\epsilon^{143}\text{Nd}$  data, the dashed line corresponds to the theoretical mixing of the JM-Nancy and JMC solutions. The plain line corresponds to the least squares linear regression of the mixed solutions (**Supplementary Table 3**). The extrapolation of this regression goes through the measured isotopic compositions of both pure solutions, validating the accuracy of the  $\delta^{148}\text{Nd}$  measured in this study.

mixing uncertainties is taken into account, the estimated  $\epsilon^{143}\text{Nd}$  agrees with the measured  $\epsilon^{143}\text{Nd}$  of the mix solutions (**Figure 1**). Such agreement and the small uncertainties associated with the measured  $\epsilon^{143}\text{Nd}$  suggested the use of the measured  $\epsilon^{143}\text{Nd}$  as a more precise measurement of the mixing proportion. The linear correlation between the measured  $\delta^{148}\text{Nd}$  and  $\epsilon^{143}\text{Nd}$  of the mixing is not offset from values of the pure JM-Nancy and JMC solutions (**Figure 1**) and supports the accurate determination of the stable isotopic variation of Nd with our protocol. Only one of our studied solutions was already measured against the JNdi-1 in the literature, the NIST3135a, with a  $\delta^{148}\text{Nd}$  of  $-0.04 \pm 0.11$  ( $2\sigma$ ,  $N = 11$ , Ma et al., 2013). At  $2\sigma_{\text{mean}}$  level, this value is different from the  $\delta^{148}\text{Nd}$  of  $-0.20 \pm 0.13$  ( $2\sigma$ ,  $N = 14$ , **Table 3**) of NIST3135a reported in this study. However, the accuracy of our measurements has been validated by the standard addition method, and thus, a  $\delta^{148}\text{Nd}$  of  $-0.20\text{‰}$  for NIST3135a is more accurate.

### Stable and Radiogenic Nd Isotopic Variations

For the radiogenic compositions, except N35 and N50, all Neo have different  $\epsilon^{143}\text{Nd}$ , with a total range of around 10  $\epsilon$  units (**Table 3**). The purified Nd samples have an even greater range (almost 26  $\epsilon$  units) in  $\epsilon^{143}\text{Nd}$ . The purified Nd samples present a range of 1.19‰ in  $\delta^{148}\text{Nd}$  associated with a  $\Delta^{148-150}\text{Nd}'$  very close to 0 (**Table 3**), in agreement with the previous findings of variable stable isotopic compositions of pure Nd metal and solutions (Wakaki and Tanaka, 2012; Ma et al., 2013; Ohno and Hirata, 2013; Saji et al., 2016; McCoy-West et al., 2020a). On the contrary, the  $\delta^{148}\text{Nd}$  of the Neo is rather constant, with an average value of  $-0.105 \pm 0.023\text{‰}$ , ( $2\sigma_{\text{mean}}$ ,  $N = 7$ ,

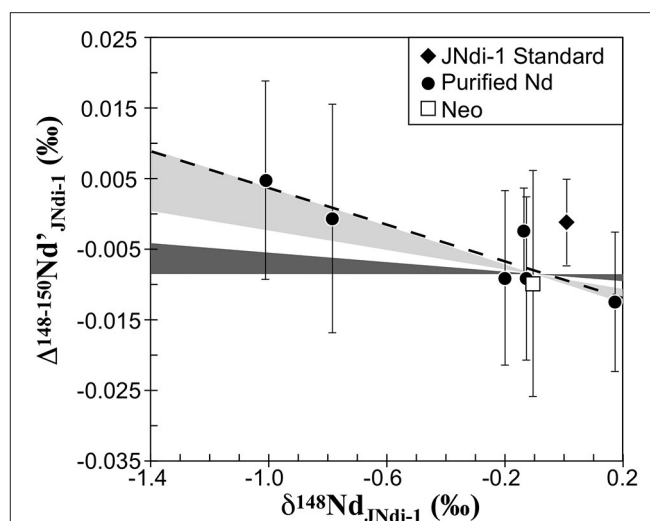
**Table 3**) despite variable sources of Nd exhibited by variable  $\epsilon^{143}\text{Nd}$  (**Table 3**). The average  $\Delta^{148-150}\text{Nd}'$  of anthropogenic materials (purified Nd and Neo) is  $-0.008 \pm 0.009\text{‰}$  ( $2\sigma_{\text{mean}}$ ,  $N = 13$ ). So, industrially purified Nd have 1) distinct stable isotopic composition from JNdi-1, 2) stable isotopic compositions in agreement with mass-dependent fractionations, and 3) a significant spread in their  $\delta^{148}\text{Nd}$  (**Table 3**). However, there is no correlation between the  $\delta^{148}\text{Nd}$  and the degree of purification (relative abundance of La, Ce, Pr, and Sm to Nd) or the  $\epsilon^{143}\text{Nd}$  of the purified Nd samples (**Table 3** and **Supplementary Table 3**). In addition, the Neo has a greater level ( $\sim 3$  orders of magnitude, **Supplementary Table 3**) of other REEs than the purified Nd samples (**Supplementary Table 3**).

A detailed description of the mass-dependent fractionation of Nd by chromatographic separation is provided in the **Supplementary Material**. In short, the purified Nd fractions obtained by chromatographic separation present a range of 0.72‰, 1.11‰, and 1.49‰ in  $\delta^{148}\text{Nd}$  for NNB, JMC, and Nancy-16rees, respectively (**Supplementary Table 2**). The first fractions are enriched in heavy isotopes, while the last fractions are enriched in light isotopes, but all fractions are characterized by a  $\Delta^{148-150}\text{Nd}'$  very close to 0, implying a mass-dependent isotopic fractionation between the  $(\text{Nd}^{3+})-(\text{Cl}^-)_3$  complex in solution and Nd bound to the di(2-ethylhexyl) orthophosphoric acid (HDEHP) of the Ln-resin. So, for anthropogenic materials and chromatographic isotopic fractionation (**Table 3** and **Supplementary Table 2**), the  $\Delta^{148-150}\text{Nd}'$  is always close to 0. In detail, however, a significant correlation is found between the  $\Delta^{148-150}\text{Nd}'$  and the  $\delta^{148}\text{Nd}$  of purified Nd samples (**Figure 2**). Such correlation becomes significant when the number of repeat analyses is  $> 10$  (**Table 3**), allowing reduced uncertainties. It suggests that Neo is on the same trend, while JNdi-1 is outside the trend. In addition, the three different tests of chromatographic isotopic fractionation (**Supplementary Table 2**) are also consistent with a negative covariation between  $\Delta^{148-150}\text{Nd}'$  and  $\delta^{148}\text{Nd}$ , although with poorer precision related to a smaller number of repeat analyses.

## DISCUSSION

### Anthropogenic Signature

The significant difference in the radiogenic isotopic compositions of Neo (10  $\epsilon$  units) and purified Nd samples ( $\sim 26$   $\epsilon$  units) suggests that their Nd originate from different batches if not from different REE ores. Therefore, the natural source of REEs is diverse for the set of studied industrially purified Nd materials (**Table 3**). The  $\epsilon^{143}\text{Nd}$  has proven to be a useful tool to infer anthropogenic pollution from industrial sites to soils (e.g., Steinmann and Stille, 1997) and even to animals (Bosco-Santos et al., 2018) because the industrial process or storage of REEs was efficient enough to mix variable ore sources or used only one source. Here, we show that Neo from one single supplier can have large variation in their  $\epsilon^{143}\text{Nd}$ , and increasing the range of supplier would likely widen the range of the radiogenic signature of Neo. Moreover, soils can have a heterogeneous  $\epsilon^{143}\text{Nd}$  ( $> 8$   $\epsilon$  units; Viers and Wasserburg, 2004). So, in the case of an



**FIGURE 2** | The  $\Delta^{148-150}\text{Nd}'$  as a function of the  $\delta^{148}\text{Nd}$  for anthropogenic material. The error bar corresponds to  $2\sigma_{\text{mean}}$ . The dashed line corresponds to the least squares linear regression of the purified Nd. The shaded areas represent the theoretical domain for a kinetic mass-dependent isotopic fractionation (light gray) and thermodynamic mass-dependent isotopic fractionation (dark gray). The least squares linear regression of the purified Nd is in close agreement with a kinetic mass-dependent isotopic fractionation. The JNdi-1, also a purified Nd, has been excluded from the relationship (see text).

**TABLE 4** | Stable Nd isotopic fingerprint of natural and anthropogenic material.

Material	Reference	$\delta^{148}\text{Nd}$ ‰	$2\sigma_{\text{mean}}$	$\Delta^{148-150}\text{Nd}'$ ‰	$2\sigma_{\text{mean}}$	<i>N</i>
Purified Nd	This study	-0.348	0.368	-0.005	0.005	6
Purified Nd	This study and [1]	-0.120	0.141	nd		22
Neo	This study	-0.105	0.023	-0.010	0.016	7
Anthropogenic material	This study	-0.217	0.176	-0.008	0.009	13
Anthropogenic material	This study and [1]	-0.116	0.109	nd		29
Terrestrial rocks	[2]	-0.053	0.016	nd		44
Terrestrial rocks	[3]	-0.051	0.031	nd		58

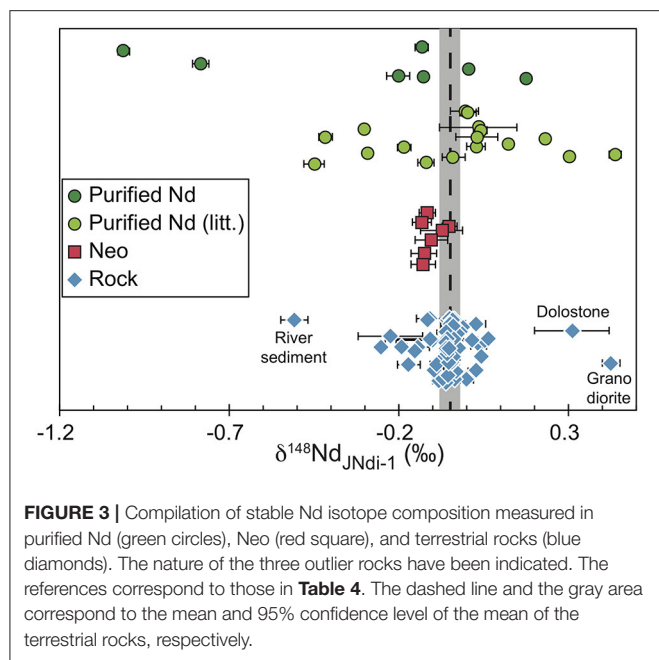
[1]: Wakaki and Tanaka, 2012; Ma et al., 2013; Ohno and Hirata, 2013; Saji et al., 2016; McCoy-West et al., 2020a.

[2]: McCoy-West et al., 2017, 2020a,b.

[3]: Ma et al., 2013; Ohno and Hirata, 2013; McCoy-West et al., 2017, 2020a,b. Nd, not determined.

anthropogenic pollution of soils by Neo, the  $\epsilon^{143}\text{Nd}$  alone could be inconclusive.

There is no relationship between the radiogenic and stable isotopic compositions of anthropogenic materials. Such lack of relationship has already been reported for terrestrial rocks (McCoy-West et al., 2017, 2020b). So, variations in the natural source of Nd cannot explain the range of 1.19‰ in  $\delta^{148}\text{Nd}$  of purified Nd samples. Moreover, when the literature data are included (**Table 4** and **Figure 3**), the  $\delta^{148}\text{Nd}$  of purified



Nd samples has a range and an average of 1.45‰ and  $-0.120 \pm 0.141\%$  ( $2\sigma_{\text{mean}}$ ,  $N = 22$ ), respectively. This is not greatly different from the range and average of the subset of anthropogenic Nd samples (purified Nd and Neo taken together) studied here. In addition, the average stable isotopic composition for both the Neo and the purified Nd materials are similar, with a  $\delta^{148}\text{Nd}$  around  $-0.1\%$  (**Table 4**).

The range and average value of the  $\delta^{148}\text{Nd}$  for natural terrestrial samples is more difficult to determine since the large majority of the data reported  $\delta^{146}\text{Nd}$  (e.g., McCoy-West et al., 2017) or  $\delta^{145}\text{Nd}$  (Saji et al., 2016), with only few reporting  $\delta^{148}\text{Nd}$  (Ma et al., 2013; Ohno and Hirata, 2013). However, in some cases, the  $\delta^{148}\text{Nd}$  has been measured simultaneously to the  $\delta^{146}\text{Nd}$  and those two are related by the linear relationship of  $\delta^{148}\text{Nd} = 2.00037 \times \delta^{146}\text{Nd}$  (McCoy-West et al., 2020a). Using this, the  $\delta^{148}\text{Nd}$  of terrestrial rocks has an average of  $-0.051 \pm 0.031\%$  ( $2\sigma_{\text{mean}}$ ,  $N = 58$ , Ohno and Hirata, 2013; McCoy-West et al., 2017, 2020a,b; Ma et al., 2013; **Table 4**). Some small differences between data produced in different laboratories have been reported (e.g., McCoy-West et al., 2020a), but the average  $\delta^{148}\text{Nd}$  of rock samples, estimated here, is not different from a smaller but self-consistent dataset (**Table 4**, McCoy-West et al., 2020a,b; McCoy-West et al., 2017). In addition, three samples, one granodiorite, one river sediment (Ma et al., 2013), and one dolostone (Ohno and Hirata, 2013) are outliers (excluding those returns  $2\sigma_{\text{mean}}$  reduced to 0.017‰ with  $N = 55$ ) on the terrestrial dataset (**Figure 3**). Consequently, on average, there is a difference of  $\sim 0.05\%$  between the  $\delta^{148}\text{Nd}$  of anthropogenic materials and terrestrial rocks, with the average anthropogenic materials enriched in light isotopes (**Table 4**). In addition, anthropogenic materials are characterized by a far greater spread in the  $\delta^{148}\text{Nd}$  than terrestrial rocks (**Figure 3**).

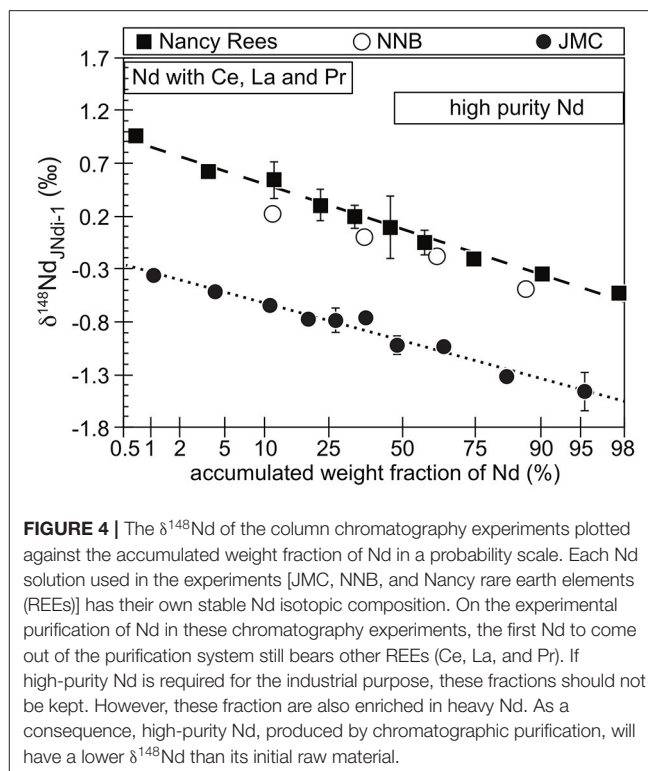
## Nature of the Stable Nd Isotopic Variations in Anthropogenic Materials

All terrestrial materials, despite a diverse origin exhibited by their variable  $\epsilon^{143}\text{Nd}$ , are related by mass-dependent partitioning of isotopes (e.g., Wakaki and Tanaka, 2012; Ma et al., 2013; Ohno and Hirata, 2013; Saji et al., 2016; McCoy-West et al., 2017). So, the enrichment in light isotopes in anthropogenic materials by comparison with terrestrial rocks is likely to be related to an isotopic fractionation during the purification of Nd from the other REEs. Cation exchange is used to obtain individual lanthanides because it is one of the most successful tools to obtain these elements with a high degree of purity (e.g., Spedding et al., 1956; Powell, 1964; Kolodynska and Hubicki, 2012). Several cation exchange resins with various chemical protocols exist to separate the REEs that might be different from one Nd man-made sample to another. The industrial protocols are likely to be not unique and also to include several steps. This might explain the lack of correlation between the degree of purification and the  $\delta^{148}\text{Nd}$  of the purified Nd samples (**Table 3** and **Supplementary Table 3**). In addition, the degree of impurities in the Neo are far greater ( $\sim 3$  orders of magnitude, **Supplementary Table 3**) than for the purified Nd samples, but the impurities could be added like Gd (e.g., Yang et al., 2017) or could be the result of a lower degree of purification of the Nd used in the Neo. So the amount of impurities in our studied man-made samples is likely to be not a straightforward proxy for the method of purification of Nd on a first instance.

However, Ln-resin produces mass-dependent fractionation of Nd (Ohno and Hirata, 2013; Saji et al., 2016), and a detailed study of such fractionation gives a general sense of mass-dependent fractionation of Nd by most industrial processes. For anthropogenic materials and chromatographic isotopic fractionation, the  $\Delta^{148-150}\text{Nd}'$  is correlated with the  $\delta^{148}\text{Nd}$  (**Figure 2** and **Supplementary Table 2**). By definition of  $\Delta^{148-150}\text{Nd}'$ , its variation implies that the mass-dependent fractionation of Nd has not been achieved by a thermodynamic equilibrium process, if the studied material has a common origin (in our case, all materials have been made from terrestrial Nd). Instead, the mass-dependent fractionation of Nd by kinetic processes would induce a linear negative correlation between  $\Delta^{148-150}\text{Nd}'$  and  $\delta^{148}\text{Nd}$  (**Figure 2**). Only JNdi-1 is outside the trend and using the y-intercept of the  $\Delta^{148-150}\text{Nd}'$ - $\delta^{148}\text{Nd}$  linear relationship (**Figure 2**), the JNdi-1 data would be consistent with an excess of 9 or 29 ppm of  $^{148}\text{Nd}$  or  $^{144}\text{Nd}$ , respectively, or a deficit of 14 ppm of  $^{150}\text{Nd}$  with respect to all the other anthropogenic materials studied here. Such offset of the standard can have different origin (purification, mixing, ...) and has already been reported for other isotopic systems (e.g., Mg; Tipper et al., 2008). The negative covariation (**Figure 2**) implies a small excess of  $^{150}\text{Nd}$  associated with the enrichment in heavy isotopes by kinetic mass-dependent fractionation. Using the slope of  $\Delta^{148-150}\text{Nd}'$ - $\delta^{148}\text{Nd}$  (**Figure 2**), we can estimate that the excess of  $^{150}\text{Nd}$  is around 20 ppm for a rise in  $\delta^{148}\text{Nd}$  of 1‰, so  $\sim 5$  ppm/‰/amu. This is almost 2 orders of magnitude smaller than the enrichment in  $^{150}\text{Nd}$  of 395 ppm/‰/amu that could be related to nuclear field effect (Saji

et al., 2016). However, the  $\Delta^{148-150}\text{Nd}'$  corresponds to the deviation from a thermodynamic mass-dependent fractionation (hence, the maximum value of 0.6756 for  $\beta$ ). Also, other values for  $\beta$  are possible. For instance, the minimum value for thermodynamic equilibrium is 0.6734 using molecular masses of  $^{148}\text{Nd-M}$ ,  $^{150}\text{Nd-M}$  and  $^{144}\text{Nd-M}$  with M a macromolecule with a mass tending toward infinity (Hayles et al., 2017). The absolute minimum for  $\beta$  (0.6666) is reached when kinetic isotopic fractionation is considered (Young et al., 2002). In that case, it would generate a negative relationship between  $\Delta^{148-150}\text{Nd}'$  and  $\delta^{148}\text{Nd}$ . The field defined in such space by all possible  $\beta$  (0.6666–0.6711) characterizing kinetic isotopic fractionation (Figure 2) is consistent with the slope defined by anthropogenic materials (excluding JNdI-1). A common kinetic isotopic fractionation for the purified metal, solutions, and Neo (Figure 2) suggests that, irrespective of the industrial source of anthropogenic materials (Tables 1, 2), a common process is likely to fractionate Nd isotopes during its industrial purification. The effect of kinetic isotopic fractionation is, however, too small to explain the excess of  $^{150}\text{Nd}$  reported previously (Saji et al., 2016). The discrepancy between the two studies is likely to result from the different treatments of the data collected by MC-ICPMS. Nuclear field effect appears in purified Nd samples and chromatographic isotopic fractionation after several corrections of the data, including some parameterization (Saji et al., 2016), or this could be an analytical artifact, already reported in MC-ICPMS (e.g., Newman et al., 2009; Xu et al., 2015). In this study, no correction or parameterization of the data has been applied, suggesting that previous report of nuclear field effect on purified Nd samples might be the result of a mathematical artifact.

The three different tests of chromatographic isotopic fractionation (Supplementary Table 2) are also consistent with a negative covariation of  $\Delta^{148-150}\text{Nd}'$  and  $\delta^{148}\text{Nd}$ , although with poorer precision related to a smaller number of repeat analyses. However, the  $\delta^{148}\text{Nd}$  of the fractions of chromatographic separation correlate well with the accumulated eluted Nd on a probability scale (Figure 4) and consistent with previous findings (Wakaki and Tanaka, 2012). So, chromatographic tests are consistent with the concept of theoretical plates (e.g., Glueckauf, 1955, 1958, Supplementary Material). This implies that chemical equilibrium is reached at each theoretical plate along the column and is associated with isotopic enrichment by liquid chromatography. The size of the Ln-resin column in our experimental technique, and the interpretation of the elution curves, led to a number of theoretical plates in the column around 100 (Supplementary Material). Such small number associated to the time of the elution—typically a few hours—is enough to reach a chemical equilibrium between the Nd bound to the di(2-ethylhexyl) orthophosphoric acid (HDEHP) of the Ln-resin and dissolved Nd in HCl solution. However, this is not enough to reach an isotopic equilibrium since the isotopic data are more consistent with kinetic isotopic fractionation. In such case, and by analogy with the observations on these tests of chromatographic isotopic fractionation, the common industrial process leading to a kinetic isotopic fractionation of



**FIGURE 4** | The  $\delta^{148}\text{Nd}$  of the column chromatography experiments plotted against the accumulated weight fraction of Nd in a probability scale. Each Nd solution used in the experiments [JMC, NNB, and Nancy rare earth elements (REEs)] has their own stable Nd isotopic composition. On the experimental purification of Nd in these chromatography experiments, the first Nd to come out of the purification system still bears other REEs (Ce, La, and Pr). If high-purity Nd is required for the industrial purpose, these fractions should not be kept. However, these fraction are also enriched in heavy Nd. As a consequence, high-purity Nd, produced by chromatographic purification, will have a lower  $\delta^{148}\text{Nd}$  than its initial raw material.

anthropogenic materials studied here (Figure 2) could be the chromatographic purification of REEs. For the  $^{148}\text{Nd}/^{144}\text{Nd}$  ratio, the isotopic fractionation factor between the  $(\text{Nd}^{3+})(\text{Cl}^{-})_3$  complex in aqueous solution and the complex Nd-HDEHP is  $0.999969 \pm 0.000004$  for the  $^{148}\text{Nd}/^{144}\text{Nd}$  ratio (Supporting Material). Per atomic mass unit, this is roughly half of the isotopic fractionation factor between the two complexes of Nd with  $\alpha$ -hydroxyisobutyric acid and sulfonic acid (value of  $0.999964 \pm 0.000003$  for the  $^{146}\text{Nd}/^{144}\text{Nd}$  ratio, Wakaki and Tanaka, 2012). Consequently, the separation of Nd from other REEs by cation-exchange resins is consistent with an equilibration with the resin at each theoretical plate, but a kinetic effect is likely to dominate the isotopic shift. In addition, we can see that with different kinds of REE complexes, we obtain the same systematic of mass-dependent Nd isotopic fractionation: the heavier isotopes fall at the beginning of the elution, together with the tail of the lighter-than-Nd REEs (Ce and Pr, Figure 4). The industrial use of Nd generally requires high purity of Nd (>99%), and a full separation of Nd from light REEs is difficult to achieve (e.g., Rehkamper et al., 1996; Pin and Zaldugui, 1997; Ohno and Hirata, 2013). An easy way to obtain high-purity Nd is to collect only the eluted fraction where other LREEs are not present. In that case, it seems that high-purity Nd will be enriched in light isotopes (Figure 4) by a kinetic mass-dependent isotopic fractionation. In particular, this might explain the enrichment in light Nd isotopes for the Neo compared with the average of terrestrial rocks (Figure 3) associated with the significant

presence of Pr (Supplementary Table 3), the REEs that can be found in higher abundance in the Nd fraction after a chromatographic separation (e.g., Pin and Zalduegui, 1997). Also, this hypothesis could explain the enrichment of Nd in light isotopes of many purified Nd samples by comparison with terrestrial rocks (Table 4). The far greater spread in the  $\delta^{148}\text{Nd}$  of anthropogenic materials than in the  $\delta^{148}\text{Nd}$  of terrestrial rocks could correspond to the variability in the industrial process in terms of (1) purity achieved and (2) isotopic fractionation factor dependent on temperature and ligands. Moreover, the industrial purification of Nd might correspond to several steps of purification, enhancing the isotopic fractionation by a Rayleigh-type distillation. In consequence, we propose that an anthropogenic Nd pollution in the environment could be identified by the shift toward more negative  $\delta^{148}\text{Nd}$  values than the range of natural terrestrial samples. More detailed investigations are needed to define precisely the  $\Delta^{148-150}\text{Nd}'$  of natural terrestrial samples, but geological processes are likely to be characterized by near-equilibrium isotopic fractionation implying that the  $\Delta^{148-150}\text{Nd}'$  of anthropogenic materials would be higher than the  $\Delta^{148-150}\text{Nd}'$  of natural terrestrial samples. In that case, the combination of  $\delta^{148}\text{Nd}$  and  $\Delta^{148-150}\text{Nd}'$  values would be a very distinctive fingerprint of anthropogenic Nd pollution. In particular, soils with the combination of low values for  $\delta^{148}\text{Nd}$  with high values for  $\Delta^{148-150}\text{Nd}'$  are likely to be polluted by the degradation in the environment of Neo or other industrial products, especially if this is associated with an  $\varepsilon^{143}\text{Nd}$  inconsistent with the  $\varepsilon^{143}\text{Nd}$  of surrounding rocks and soils. In addition, the industrial residue of Nd purification is likely to be characterized by high  $\delta^{148}\text{Nd}$  with low values for  $\Delta^{148-150}\text{Nd}'$ , and the leak or discharge of such residue could also be unambiguously distinguished.

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## DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author/s.

## AUTHOR CONTRIBUTIONS

AG conceived the study. NB carried out the lab analysis, data processing, and initial interpretation. AG wrote the paper with significant input from NB. All authors contributed to the article and approved the submitted version.

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## SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fenvc.2021.596928/full#supplementary-material>

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**Conflict of Interest:** The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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