Vanadium isotopic fractionation during the formation of marine ferromanganese crusts and nodules

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Abstract

Vanadium (V) isotopes can be significantly fractionated during the delivery, cycling, and burial to the ocean. The utilization of V isotopes might provide a useful geochemical tracer for the evolution of the oceans. This study provides the first detailed investigation of V isotopes in ferromanganese (Fe-Mn) crusts and nodules, which are widely distributed in the modern oxic ocean. Our results show a large variability of V isotope compositions in Fe-Mn crusts and nodules with a $\delta^{51}V$ range from $-0.89$ to $-1.65\%_e$, much greater than current analytical uncertainty ($\pm 0.10\%_e$, 2 SD). Therein, the most recent layers of hydrogenetic Fe-Mn crust and hydrogenous nodules have a narrower V isotope range ($-0.89\%_e$ to $-1.25\%_e$), with no correlation to their collection location or water depth. Thus, our results suggest a relatively homogeneous V isotope composition of marine hydrogenetic Fe-Mn crusts and nodules, with an average $\delta^{51}V_o$ of $-1.05 \pm 0.16\%_e$ (2 SD). The hydrogenetic Fe-Mn crusts and nodules are depleted in $^{51}V$ compared with the recently reported seawater value ($0.2 \pm 0.15\%_e$) by $-1.2 \pm 0.2\%_e$ (2 SD). This can be explained by isotope fractionation during the adsorption of V onto Fe-Mn oxyhydroxides. The various $\delta^{51}V$ in Fe-Mn nodules ($-0.98\%_e$ to $-1.65\%_e$) might be caused by diagentic precipitation of V from pore fluids with lighter isotope composition compared to seawater, thus driving a negative V isotope shift recorded in Fe-Mn nodules with a diagentic imprint. Additionally, a depth profiles across an Fe-Mn crusts reveals systematic changes in $\delta^{51}V$ from $-1.04 \pm 0.13\%_e$ (2 SD) in upper layers to $1.32 \pm 0.06\%_e$ (2 SD) in lower layers representing the relatively older deposition. The observed $\delta^{51}V$ depth profiles might record the changes of V isotope composition of seawater. The proposed temporal variations of $\delta^{51}V$ in seawater could be controlled by the isotope fractionation and fluxes of various V sources and sinks to the ocean that is likely related to the global redox state of the oceans. Another potential interpretation of this isotopic shift in the crusts could be related to the modification of the primary V isotope signature due to diagentic remobilization and reorganization. However, there is no obvious evidence that definitively documents a diagentic control or signal. This study highlights the burial of V with Fe-Mn oxyhydroxide as an important control on the V isotope composition of seawater, and the potential application of Fe-Mn crusts to track the temporal V isotope variations of seawater.

$\delta^{51}V$ (2 SD)

Keywords: Paleoceanography; Marine Fe-Mn oxyhydroxides; Mineral adsorption; V mass balance

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1. INTRODUCTION

Vanadium is a redox-sensitive element with two geologically long-lived stable isotopes, $^{50}\text{V}$ ($-0.25\%$) and $^{51}\text{V}$ ($-99.75\%$). With recent advances of chemical purification and high-precision measurement using multi-collector inductively-coupled-plasma mass-spectrometry (MC-ICP-MS), the small natural isotopic variations for vanadium can be analytically resolved (Nielsen et al., 2011, 2016; Prytulak et al., 2013, 2017; Schuth et al., 2017; Ventura et al., 2015; Wu et al., 2018, 2019; Xue et al., 2018), documenting that V isotopes can be significantly fractionated in both high- and low-temperature processes.

Vanadium is among the most abundant trace metal elements in seawater, with concentrations between $\sim$30 and 40 nmol/kg ($\sim$1.5–2.0 µg per L; e.g. Collier, 1984; Jeandel et al., 1987; Shiller and Boyle, 1987). The residence time of V has been calculated to be between $\sim$50 to 100 thousand years (kyrs) in modern seawater (Emerson and Huested, 1991; Morford and Emerson, 1999, 2004). Data from the deep ocean suggest that V is uniformly distributed, while surface minima of V have been observed in dozens of vertical surface seawaters profiles in the Pacific Ocean (Collier, 1984; Ho et al., 2018). Additionally, recent work, albeit only from small datasets, suggests that the deep ocean seawater is isotopically homogeneous with $\delta^{51}\text{V}_{\text{seawater}}$ of $0.20 \pm 0.15\%$e (Wu et al., 2019) and more positive than most silicate rocks ($-0.9$ to $-0.5\%e$, Prytulak et al., 2013; Wu et al., 2016, 2018; Qi et al., 2019), and river water (Schuth et al., 2019).

The speciation and behavior of V are controlled by the Eh, pH, and V concentrations in seawater. The main species of V in oxic seawater are highly soluble pentavalent vanadate (e.g. HVO$_2^-$ and H$_2$VO$_3^-$; Lewan and Maynard, 1982). Vanadate tends to be adsorbed on the surface of iron (Fe) and manganese (Mn) oxyhydroxides or clay minerals, which is a dominate sink of V in modern seawater (Elderfield and Schultz, 1996, Morford and Emerson, 1999). Under mildly reducing conditions, pentavalent vanadate tends to be reduced to tetravalent vanadyl (e.g. VO$_{2+}$, VO(OH)$_2^-$) by organic compounds. Vanadyl is less soluble than vanadate and readily adsorbed onto settling particles (Breit and Wanty, 1991). Under strongly reducing conditions, vanadyl can be further reduced to trivalent species (e.g. V(OH)$_3^-$) through reactions with sulfate in the water column or pore water (Wanty and Goldhaber, 1992). Trivalent V is highly insoluble in seawater and tends to precipitate as solid oxyhydroxides (Wehrli and Stumm, 1989).

Theoretical calculation predicts that V isotopes can be fractionated during the uptake and accumulation of V in marine sediments (Wu et al., 2015), which is likely controlled by variations in the redox state and surface adsorption (e.g. Algeo and Maynard, 2004; Huang et al., 2015; Morford and Emerson, 1999). Recent studies of V isotope compositions of crude oils have revealed large V isotope fractionation up to $\sim$2%, likely reflecting the depositional redox conditions of the petroleum source rock and the post-burial modification such as maturation and/or biodegradation (Ventura et al., 2015; Gao et al., 2018). In addition, the redox potential of V(V)-V(IV) couple is close to that of Fe(III)-Fe(II) in seawater (e.g. Bonatti et al., 1971; Piper and Calvert, 2009), which suggests that V sequestration from the water column under reducing conditions does not require free hydrogen sulfide (Breit and Wanty, 1991; Morford and Emerson, 1999; Algeo and Maynard, 2004). Thus, V isotope systematics can be used to trace ocean redox variations, especially the variations of anoxic but non-sulfidic seafloor area at local and/or global scales. Despite the potential application of V isotopes as a paleo-redox proxy, the lack of $^{51}$V data in marine materials restricts the understanding of the controlling mechanisms of V isotope fractionation in marine sediments.

Ferromanganese oxyhydroxide deposit is globally distributed throughout the marine seafloor (e.g. Hein and Koschinsky, 2014, and references therein) and is an important oceanic sink for many trace metals (e.g. Koschinsky and Hein, 2003; Barling and Anbar, 2004; Rehkämper and Nielsen, 2004). In addition, scavenging of V tooxic sediment by the adsorption of V onto hydrogenetic Fe–Mn oxyhydroxides is one of the dominate mechanisms for removing V from the well-oxygenated modern ocean (Morford and Emerson, 1999). Thus, to build a mass balance framework for V isotopes, it is important to constrain the natural isotope fractionation of V during incorporation into Fe–Mn oxyhydroxides. The $\delta^{51}$V values of two marine Fe–Mn nodules NOD-P ($-1.65 \pm 0.06\%e$) and NOD-A ($-0.99 \pm 0.10\%e$) have previously been reported (Wu et al., 2016), suggesting that large V isotope fractionation could occur during the formation of Fe–Mn oxyhydroxides. Comparing this result with the recently reported V isotope composition of seawater ($0.20 \pm 0.15\%e$; Wu et al., 2019) implies that Fe–Mn deposits are significantly depleted in $^{51}$V relative to seawater. Theoretical calculations show that the light V isotope ($^{50}$V) is preferentially adsorbed on the surface of Fe oxyhydroxides (Wu et al., 2015), which could explain the V isotope offset between natural Fe–Mn deposits and seawater. But the limited data of $^{51}$V for natural Fe–Mn deposits do not allow for further testing of this hypothesis. In addition, a preliminary estimation of the V isotope mass balance for the oceans was made based on the seawater V isotope data and marine Fe–Mn nodules, implying that burial of V with Fe–Mn oxyhydroxides precipitation could be an important isotopically light sink in the modern ocean (Wu et al., 2019).

Marine Fe–Mn precipitates throughout the oceans are generally classified as hydrogenetic, diagenetic, or hydrothermal deposits (e.g. Hein et al., 1997; Bau et al., 2014). Such classification reflects their discrete formation environment and respective modes of accretion. Moreover, they exhibit distinct differences both in terms of appearance, mineralogy, growth rates and trace element composition (e.g., Glasby, 2006). Therein, hydrogenetic Fe–Mn precipitates could form as crusts and nodule aggregations (e.g. Glasby, 2006), or as micro-nodules and ferromanganese coatings on other sediment grains in the pelagic sediments (e.g., Dunlea et al., 2015). Their formation is
attributed to the direct precipitation and aggregation of colloidal material from ambient seawater (Dymond et al., 1984). In comparison, diagenetic Fe-Mn precipitates are typically formed as nodules and grow at the sediment-water interface of pelagic sediments (Dymond et al., 1984). The growth and trace-metal composition of diagenetic nodules are largely controlled by early diagenetic processes within the sediments with the contribution of metals from the sediment porewaters (e.g., Calvert and Price, 1977; Dymond et al., 1984; Jung and Lee, 1999). Considering that Fe-Mn nodules could form by hydrogenetic or diagenetic precipitation, or a combination (Hein et al., 1997), systematic studies of V isotopic compositions of Fe-Mn deposits are necessary for better understanding V isotope fractionation in the Fe-Mn nodules associated with sequestration of V from seawater and/or pore fluids (Wu et al., 2016).

In this study, we present spatiotemporal variations of $^{51}$V in Fe-Mn crusts, and investigate the controlling factors of V isotope variations in Fe-Mn nodules. Hydrogenetic Fe-Mn crusts mainly consist of Fe-Mn oxyhydroxides that precipitate directly from ambient seawater. Thus, the V isotope investigation of modern Fe-Mn crusts is helpful for understanding the V isotope fractionation during the adsorption of V on the Fe–Mn oxyhydroxides. In addition, because of the slow growth rates of hydrogenic Fe-Mn crusts (1–10 mm/Myr; Hein et al., 2000; Glasby, 2006), they have been applied as archives of past chemical and isotopic compositions for many elements to better constrain deep seawater records (e.g., Nd, Fe, Ni, Tl) (Ling et al., 1997; Frank et al., 1999; Nielsen et al., 2009; Gall et al., 2013; Horner et al., 2015; Gueguen et al., 2016). Thus, we also investigated the depth profiles of V isotopes in one Fe-Mn crust. The major and trace element concentrations of these marine Fe-Mn crusts and nodules were also analyzed to constrain their genetic types. The goals of this study are to investigate: (1) isotope fractionation due to the removal of V via adsorption onto Fe-Mn crusts from seawater, (2) the mechanism for V isotope variations in Fe-Mn nodules, and (3) the potential utility of Fe-Mn crusts as archives for deep seawater V isotope compositions and its implications on the reconstruction of paleo-environmental changes.

2. SAMPLE SELECTION AND PREPARATION

The Fe-Mn crusts and nodules studied here were collected at 2013 from three seamounts or guyots at the West Pacific Ocean using the Chinese manned submersible Jiaolong during DY125-31 cruise. Samples were from Caiwei Guyot (155° E, 15° N) and Caiqi Guyot (154° E, 15° N) from the Magellan Seamount cluster, and Weiyuan Seamount (154° W, 9° N) from Clarion-Clipperton Fe-Mn Nodule Zone (C-C zone) (Fig. 1, Table 1) at water depths of 1720–4420 m, 2000–2400 m and 5200 m, respectively. The samples studied here were obtained from the surface of the seafloor to avoid the potential diagenetic process that have occurred post burial (e.g., Heller et al., 2018). All samples are Fe-Mn crusts and nodules. Some samples are from the surface layer of the ferromanganese crust to study the spatial variations of V isotope of ‘recently’ or near modern precipitated ferromanganese crust (Table 2). Furthermore, some Fe-Mn crust samples (Table 2) were sawed perpendicular to growth layers, which best represents a stratigraphic record of ocean chemistry.

Vanadium isotopic compositions of two USGS international standards NOD-P-1 and NOD-A-1 were previously reported in (Wu et al., 2016). NOD-P-1 was collected from the Pacific Ocean (14°50’ N, 124°28’ W, Clarion-Clipperton Fe-Mn Nodule Zone) at a depth of 4,300 meters, and NOD-A-1 was collected from the Atlantic Ocean along the Blake Plateau (31° 02’ N, 78° 22’ W) at a depth of 788 meters (Flanagan and Gottfried, 1980). The data of these two Fe-Mn nodule standards are discussed with other samples in this work.

3. ANALYTICAL METHODS

3.1. Whole-rock major and trace elements

The collected Fe-Mn crust and nodule samples were first cleaned by ultrasonication with deionized water and then dried in an oven at 105°C for six hours. Then samples were powdered using an agate mortar and pestle until the sample passed through a 200 mesh sieve. Prior to powdering, crust samples were cut into layers using a hacksaw with a vertical thickness of 1–3 cm. Nodule samples with diameters of 2–5 cm were cut in half from center prior to powdering. Whole-rock major and trace element measurements of Fe-Mn crusts and nodules were conducted at the ALS Laboratory Group in Guangzhou, China (http://www.alsglobal.net.cn/). The sample powders were combined with lithium borate flux and fused in a furnace at ~1000°C. The resulting melt was then cooled and dissolved in nitric acid and hydrochloric acid. This solution was then analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) for major elements measurements. For trace element measurements, the powders were digested with a mixture of perchloric, nitric and hydrofluoric acids, and then dissolved with dilute hydrochloric acid. The prepared solutions were then analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Several standard reference materials were analyzed to access accuracy, precision and reproducibility for major (GBW07107 and GBW07108) and trace (GBM908-10, GBM908-5, MRGeo08, OREAS 90) elements measurements, respectively. The results are shown in Table S1. Analytical accuracy and precision are better than ±2% for major elements and better than ±5% for the elements discussed here. The major and trace element compositions of Fe-Mn crusts and nodules are listed in Table 2.

3.2. Vanadium isotope analyses

Approximately 10–20 mg of sample powders containing 5–10 μg of V were digested for V isotope analysis. Samples were first treated with aqua regia. After evaporation to dryness, samples were dissolved with a 3:1 (v/v) mixture of concentrated HF and HNO₃ to digest the remaining oxide
and silicate phases. Then, samples were dried and further treated with aqua regia and concentrated HNO₃ and dried down in between each step. All the samples were finally dissolved in 1 mL of 1 M HNO₃ for ion-exchange chromatography. The details of the V chemical purification protocol and isotopic measurement procedure are described in great details in Wu et al. (2016). Briefly, V was purified with a multistep ion-exchange procedure by coupling cation- and anion-exchange columns. The cation resin AG50W-X12

Table 1
Location of the ferromanganese crusts and nodules samples.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Cruise No.</th>
<th>Type</th>
<th>Water depth (mbsl)</th>
<th>Longitude</th>
<th>Latitude</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weiyuan seamount</td>
<td>Dive64A OR512-121T</td>
<td>Crust</td>
<td>5200</td>
<td>154°17.8' W</td>
<td>9°59.8' N</td>
</tr>
<tr>
<td></td>
<td>Dive64A OR512-141T</td>
<td>Nodule</td>
<td>5200</td>
<td>154°17.8' W</td>
<td>9°59.8' N</td>
</tr>
<tr>
<td></td>
<td>Dive64A OH200-111T(2)</td>
<td>Nodule</td>
<td>5200</td>
<td>154°17.8' W</td>
<td>9°59.8' N</td>
</tr>
<tr>
<td></td>
<td>Dive64A OH200-111T(3)</td>
<td>Nodule</td>
<td>5200</td>
<td>154°17.8' W</td>
<td>9°59.8' N</td>
</tr>
<tr>
<td></td>
<td>Dive68 OH200-011T(1)</td>
<td>Nodule</td>
<td>5100</td>
<td>153°3.7' W</td>
<td>6°44.6' N</td>
</tr>
<tr>
<td></td>
<td>Dive68 OH200-011T(2)</td>
<td>Nodule</td>
<td>5100</td>
<td>153°3.7' W</td>
<td>6°44.6' N</td>
</tr>
<tr>
<td>Caiwei Guyot</td>
<td>Dive69 OJ121-111T</td>
<td>Crust</td>
<td>4420</td>
<td>155°24.0' E</td>
<td>15°25.8' N</td>
</tr>
<tr>
<td>Dive70A OJ112-112T</td>
<td>Crust</td>
<td>1954–2230</td>
<td>155°33.0' E</td>
<td>15°55.2' N</td>
<td></td>
</tr>
<tr>
<td>Dive70B OJ113-211T</td>
<td>Crust</td>
<td>2350–2500</td>
<td>155°33.0' E</td>
<td>15°55.2' N</td>
<td></td>
</tr>
<tr>
<td>Dive70C OJ111-314T</td>
<td>Crust</td>
<td>2350–2500</td>
<td>155°33.0' E</td>
<td>15°55.2' N</td>
<td></td>
</tr>
<tr>
<td>Dive71 OJ112-011T</td>
<td>Crust</td>
<td>1720</td>
<td>155°25.2' E</td>
<td>15°52.8' N</td>
<td></td>
</tr>
<tr>
<td>Caiqi Guyot</td>
<td>Dive73 OJ110-012T</td>
<td>Crust</td>
<td>2000–2400</td>
<td>154°58.2' E</td>
<td>15°9.0' N</td>
</tr>
<tr>
<td>Dive73 OJ110-021T</td>
<td>Crust</td>
<td>2000–2400</td>
<td>154°58.2' E</td>
<td>15°9.0' N</td>
<td></td>
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<td>Dive73 OJ110-033T</td>
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<td>Dive73 OJ120-011T</td>
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<td>154°58.2' E</td>
<td>15°9.0' N</td>
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<tr>
<td>Dive73 OJ120-021T</td>
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<td>2000–2400</td>
<td>154°58.2' E</td>
<td>15°9.0' N</td>
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</tr>
<tr>
<td>Nod-P</td>
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<td>4300</td>
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<td>14°50' N</td>
<td></td>
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<tr>
<td>Nod-A</td>
<td>Nodule</td>
<td>788</td>
<td>78°22' W</td>
<td>31°2' N</td>
<td></td>
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</table>

Fig. 1. Map showing the locations of Fe-Mn crusts and nodules samples. Black stars show sample locations. Also shown is the range of depositional depths in meters below sea-level (mbsl) for the samples. More details of sample location and description are in Table 1.
<table>
<thead>
<tr>
<th>Type</th>
<th>Section</th>
<th>$\delta^{18}$V</th>
<th>2 SD</th>
<th>n</th>
<th>Si wt.%</th>
<th>Al wt.%</th>
<th>Mn wt.%</th>
<th>Fe wt.%</th>
<th>P wt.%</th>
<th>Li ppm</th>
<th>V ppm</th>
<th>Co ppm</th>
<th>Ni ppm</th>
<th>Cu ppm</th>
<th>Zn ppm</th>
<th>Mn/Fe</th>
</tr>
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<td><em>Wenian Seamount</em></td>
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<tr>
<td>Dive64A OR512-121T</td>
<td>Crust</td>
<td>Bulk</td>
<td><strong>-1.04</strong></td>
<td>0.08</td>
<td><strong>7</strong></td>
<td><strong>5.74</strong></td>
<td>1.65</td>
<td><strong>19.5</strong></td>
<td><strong>20.3</strong></td>
<td>0.29</td>
<td><strong>11</strong></td>
<td><strong>719</strong></td>
<td><strong>1530</strong></td>
<td><strong>2520</strong></td>
<td><strong>2230</strong></td>
<td><strong>532</strong></td>
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<td>Bulk</td>
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<td>0.01</td>
<td><strong>3</strong></td>
<td><strong>8.38</strong></td>
<td>2.86</td>
<td><strong>24.6</strong></td>
<td><strong>8.3</strong></td>
<td>0.24</td>
<td><strong>118</strong></td>
<td><strong>456</strong></td>
<td><strong>2220</strong></td>
<td><strong>9863</strong></td>
<td><strong>5810</strong></td>
<td><strong>838</strong></td>
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<tr>
<td>Dive64A OH200-111 T(2)</td>
<td>Nodule</td>
<td>Bulk</td>
<td><strong>-1.31</strong></td>
<td>0.03</td>
<td><strong>3</strong></td>
<td><strong>7.98</strong></td>
<td>3.16</td>
<td><strong>23.2</strong></td>
<td><strong>10.6</strong></td>
<td>0.20</td>
<td><strong>63</strong></td>
<td><strong>483</strong></td>
<td><strong>2250</strong></td>
<td><strong>8000</strong></td>
<td><strong>5140</strong></td>
<td><strong>704</strong></td>
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<tr>
<td>Dive64A OH200-111 T(3)</td>
<td>Nodule</td>
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<td><strong>-1.33</strong></td>
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<td><strong>3</strong></td>
<td><strong>6.51</strong></td>
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<td><strong>82</strong></td>
<td><strong>517</strong></td>
<td><strong>2440</strong></td>
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<td>0.05</td>
<td><strong>3</strong></td>
<td><strong>6.18</strong></td>
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<tr>
<td><em>Caiwei Guyot</em></td>
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<td><strong>3</strong></td>
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was applied to remove Fe, Ti, and other main matrix elements (e.g., Al, Ca, Mn, and Cr). Then AG1-X8 (200–400 mesh) chloride-form anion resin was used to further remove residual matrix and isobaric elements (e.g., K, Na, Mg, and trace amount of Cr). The total procedural blank is less than 2 ng, thus is negligible compared with the loaded amount of V (5–10 μg). The V yields of the total chemical procedures are >99%. Vanadium isotopic ratios were measured using a sample-standard bracketing method on a Thermo Scientific Neptune plus Multi-Collector Inductively Coupled Plasma-Mass Spectrometer (MC-ICP-MS) at the University of Science and Technology of China (USTC) using an Aridus II desolvating nebulizer (CETAC Technologies) for sample introduction. Measurements were performed at medium-resolution mode (resolution ΔM/M > 4000) to discern the isotope of target elements from isobaric interfering molecular species such as 36Ar14N+, 36Ar16O+, and 38Ar14N+ (Nielsen et al., 2016; Wu et al., 2016). A 100Ω amplifier was used to monitor the signal of 51V. The typical sensitivity of 51V was ~150 V/ppm. All sample and standard solutions were introduced into the instrument with a V concentration of 0.8 ppm to reduce matrix effects, producing enough signal intensity of 51V (~300 mV) for high-precision analyses. Although our chemical procedure should ensure quantitative removal of Cr and Ti, we simultaneously measured 49Ti and 53Cr to accurately correct any potential interferences of 50Ti and 50Cr on 51V. Sample-standard bracketing method was applied to calibrate instrument mass discrimination effects, using the aliquots of the Alfa Aesar (AA) V standard solution made and distributed by Nielsen et al. (2011) and Prytulak et al. (2011) as the bracketing solution. Vanadium isotopic data are reported in a δ notation of per mil compared to this AA V standard (δ51V = ([51V/50V]sample / [51V/50V]AA − 1) × 1000 ‰).

The data quality of V isotope analyses was monitored using a variety of in-house standards, international reference materials, and duplicated samples. The δ51V values of the nodule standards are –1.57 ± 0.09‰ (2 SD, n = 4, NOD-P) and –0.98 ± 0.01‰ (2 SD, n = 3, NOD-A), within analytical error of previously reported values (Table 2) (NOD-P: –1.65 ± 0.06‰, n = 10 and NOD-A: –0.99 ± 0.10‰, n = 19, Wu et al., 2016). The reproducibility of in-house standards and duplicated samples for V isotope analyses are always better than 0.10‰ (2 SD).

### 4. RESULTS

The Fe-Mn crust and nodule samples show enrichment of Mn, Fe and trace transition metal (such as V, Co, Ni, Cu, and Zn) compared to Pacific Ocean pelagic clays and average upper continental crust (Bishoff et al., 1979; Rudnick and Gao, 2003) (Table 2). Therein, the nodule samples from Weiyuan Seamount have Mn/Fe ratios from 2 to 6, Cu + Ni contents from ~1 wt.% to 2.8 wt.%, these values are much higher than that of crust samples from Weiyuan Seamount and Caiwei and Caiqi Guyot, which have Mn/Fe ratios lower than 2 and Cu + Ni contents lower than 0.7 wt.% (Table 2). The nodule samples from Weiyuan Seamount also have lower V contents (400–
500 ppm) compared with the crust samples collected at a nearby locality (719 ppm) (Table 2). All the crusts and nodules in this work have V/Al ratios of 15.3–211.7 (×10⁻³), higher than at least an order of magnitude than that of average Pacific Pelagic Clay (1.3 × 10⁻³ Bioggis et al., 1979) and upper continental crust (1.2 × 10⁻³ Rudnick and Gao, 2003) (Table 2). Some Fe-Mn crust samples collected from Caiwei Guyot and Caiqi Guyot show evidence for phosphatization with high concentrations of P (1.48–6.42 wt.%) and Ca (5.47–18.6 wt.%) relative to other samples (Ca < 3 wt.% and P < 1 wt.%) (Table 2).

The δ¹⁵N of the studied Fe-Mn crusts and nodules range from ~0.89‰ to ~1.63‰ (Table 2), much lower than the seawater values (0.20 ± 0.15‰, Wu et al., 2019). For the samples from Weiyuan Seamount, where both Fe-Mn crusts and nodules were collected, the δ¹⁵N of nodule samples (~1.33‰ to ~1.63‰) are significantly lower than that of the crust sample (~1.04‰) (Table 1).

5. DISCUSSION

5.1. Geochemistry and genesis of the Fe-Mn crusts and nodules

Marine Fe-Mn crusts and nodules are distinguished by their morphology and form by different genesis. Fe-Mn crusts are mainly of hydrogenetic origin that precipitate directly from ambient cold seawater (e.g. Hein et al., 1997), with growth rate less than ~10 mm/Ma (Glasby, 2006). The formation of Fe-Mn crusts can be influenced by the hydrothermal fluids near hot-spot volcanoes, active volcanic arcs, and spreading centers (Hein et al., 1997). In contrast, Fe-Mn nodule formation can be characterized as either hydrogenetic or diagenetic genesis, or by a combination of both processes (Hein et al., 1997). Diagenetic precipitation occurs near the sediment-seawater interface, under the influence of sub-oxic pore fluids from the sediment column underneath (Hein and Koschinsky, 2014), with growth rate of ~10–100 mm/Ma (Glasby, 2006). The difference in deposition modes for Fe-Mn can result in various sources of major and minor metals (Bau et al., 2014). Marine Fe-Mn crusts and nodules also display diverse morphological, mineralogical, and chemical properties (Halbach et al., 1981). Under diagenetic conditions, 10 Å manganates (buserite and todorokite) formed as the main Mnoxyhydroxide phase (Atkins et al., 2014). Because of the large tunnel-structure of todorokite, cations like Ni, Cu, and Zn that are mobilized from the sediment during oxic diagenesis tend to be incorporated into its crystal structures (Glasby, 2006). Diagenetic and transitional Fe-Mn nodules can also incorporate significant amounts of Li from seawater into the 10 Å manganates (buserite and todorokite, Jiang et al., 2007). In addition, diagenetic Fe-Mn nodules generally have higher Mn/Fe ratios relative to the hydrogenous crusts and nodules (Hein et al., 1997). This is because manganese and iron reduction processes do not occur simultaneously in the diagenetic sequence, and the environmental conditions that are typical for diagenetic Fe-Mn nodule growth occur in zones where upward migration of reduced Mn²⁺ in the pore water start to become re-

oxidized (Kuhn et al., 2017). This causes Mn-Fe elemental fractionation within diagenetic layers of manganese nodules with higher Mn/Fe ratio (Wegorzewski and Kuhn, 2014). Considering that marine Fe-Mn crusts and nodules could form by several processes, we will first discern the genesis of these Fe-Mn crust and nodule samples based on their geochemical features.

All the Fe-Mn crust samples in this study are located in Bonatti’s field of hydrogenetic growth on the ternary diagram of (Ni + Cu + Co) × 10-Fe-Mn (Fig. 2), showing that they are hydrogenetic in origin without influence of hydrothermal overprinting (Bonatti, 1972; Menendez et al., 2019). The thick Fe-Mn nodules show a dual structure with distinct geochemical features between the upper portion (younger non-phosphatized layers) and the underlying lower portion (older phosphatized layers). Therein, the older phosphatized layers of the Fe-Mn crusts have been impregnated with carbonate fluorapatite (CFA) with enrichments of phosphorus (Table 2) during episodes of phosphatization in the late Eocene through middle Miocene (Hein et al., 1993, 2000).

The studied Fe-Mn nodule samples are located in Bonatti’s field of hydrogenic, diagenesis, and mixed growth (Fig. 2). Therein, the Mn/Fe ratios of Fe-Mn crust and nodules from Weiyuan seamount (C-C zone) are also positively correlated with Cu + Ni (also Zn) and Li concentrations (Fig. 3). The Weiyuan crust sample shows the lowest Mn/Fe, Li and Cu + Ni concentrations among all samples from Weiyuan seamount and is within the range of other crust samples from West Pacific (Fig. 3). Taking this crust sample as the hydrogenous endmember of Weiyuan Fe-Mn crusts and nodules, the correlation trend between the Mn/Fe and the metals shown in Fig. 3 may indicate that various extents of diagenesis could influence the chemical compositions of Fe-Mn nodules. The reference material NOD-P, which was also collected from the C-C

![Fig. 2. Ternary diagram with Mn, Fe, and (Co + Ni + Cu) × 10 for all Fe-Mn crusts and nodules of this study. Dashed black lines define different fields, corresponds to hydrogenic growth, diagenetic growth, mixed growth, and hydrothermal evolution (with fields modified from Bonatti, 1972 and Menendez et al., 2019). All the crust samples in this study are in the hydrogenic area of the ternary diagram while the nodule samples distribute in hydrogenic, diagenetic and mixed areas.](image-url)
zone, also fits this trend between Mn/Fe and trace metals (Fig. 3). In contrast, the geochemical features of NOD-A (Mn/Fe ratio, Cu, Ni, and Zn contents) are similar to the hydrogenous Fe-Mn crust although it shows an enrichment in Li. The NOD-A nodule is also located in Bonatti’s field of hydrogenetic growth on the ternary diagram of \( (\text{Ni} + \text{Cu} + \text{Co}) / \text{Fe-Mn} \) (Fig. 2). Thus, we conclude that the studied Fe-Mn nodules from the C-C zone (Weiyuan seamount and NOD-P) are mainly influenced by diagenesis and should be considered as diagenetic nodules, while NOD-A is more likely from a hydrogenetic nodule that is not significantly affected by diagenetic imprint.

In the discussion below, we will first discuss the fractionation of V isotope between hydrogenic Fe-Mn crusts/nodules and seawater with the results of non-phosphatized crust samples and hydrogenic nodule sample NOD-A. Then, we will discuss if/how diagenetic formation influences the V isotope composition of marine Fe-Mn nodules with the results of diagenesis nodule samples. Lastly, we will investigate the possibility to apply Fe-Mn crusts as archives to record paleo-ocean V isotope variations, by discussing the controlling of the V isotope variations for the depth profile of Fe-Mn crusts.

5.2. The control of V isotope fractionation in the hydrogenic Fe-Mn crusts and nodules

Due to the slow growth rate of hydrogenous Fe-Mn crusts, the accumulation history could be over many millions of years thus the measured isotope values are an integration of several million years. Although the age data for these samples are not exactly known, the non-phosphatized upper layers of these Fe-Mn crust samples from equatorial Pacific were thought to have formed during the Miocene likely younger than 10–17 million years old (Hein et al., 1993; Hyeong et al., 2013; Nishi et al., 2017). The non-phosphatized layers of these Fe-Mn crust samples are characterized by limited V isotope variations, with \( \delta^{51}\text{V} \) values between \(-0.89\%e\) and \(-1.25\%e\) (Table 2 and Fig. 4). The Mn/Fe ratios and V concentrations of these Fe-Mn crust samples do not document clear correlations with \( \delta^{51}\text{V} \) (\( R^2 = 0.34 \) for Mn/Fe vs \( \delta^{51}\text{V} \) and \( R^2 = 0.00 \) for V vs \( \delta^{51}\text{V} \), Fig. 4). The hydrogenous Fe-Mn nodule, NOD-A, also has a \( \delta^{51}\text{V} \) value \((-0.99\%e\) similar to the Fe-Mn crust samples \((-0.89\%e\) to \(-1.25\%e\). In addition, there is no clear \( \delta^{51}\text{V} \) difference for samples collected at various water depths below 500 m (Fig. 5) or from different ocean seamounts. The limited variation of \( \delta^{51}\text{V} \) in these hydrogenous Fe-Mn crusts and nodules regardless of their elemental geochemistry, location and depositional water-depth implies that \( \delta^{51}\text{V} \) in younger non-phosphatized hydrogenetic ferromanganese crusts and nodules are uniform throughout the oceans, with an average of \(-1.05 \pm 0.16\%e\) (2 SD, n = 22).

Hydrogenetic Fe-Mn crusts and nodules grow by incorporation of Fe- and Mn-oxyhydroxide precipitates from seawater and scavenge dissolved trace elements from the water column. Considering the long residence time of V (50–100 kyr) relative to the circulation time of the ocean (\( \approx 2 \) kyr) and the homogeneous V concentrations of deep seawater (Collier, 1984; Ho et al., 2018; Jeandel et al., 1987; Shiller and Boyle, 1987), it is highly likely that V in the deep ocean is well mixed. It is also suggested that V isotopic composition of open ocean seawater is homogeneous across major ocean basins albeit with limited data, with \( \delta^{51}\text{V} \) of \( 0.20 \pm 0.15\%e \) (Wu et al., 2019). Thus, \( \delta^{51}\text{V} \) in near modern Fe-Mn crusts and nodules are systematically fractionated by \(-1.2 \pm 0.2\%e \) (2 SD) from the starting seawater values.

A possible mechanism for the V isotopic offset between seawater and hydrogenous Fe-Mn crusts and nodules is the isotope fractionation during the adsorption of V on the surface of the Fe-Mn oxyhydroxide. Theoretical calculation

Fig. 3. Mn/Fe ratios versus Li (a), Cu + Ni (b), and V (c) in Fe-Mn crusts and nodules samples. All the nodule samples except NOD-A in this study are from C-C zone. The area and dotted line in (b) also show the variation and hyperbolic regression curve of Ni + Cu against Mn/Fe for the diagenesis nodules from the C-C zone (after Halbach et al., 1981). The crusts and nodules show obviously chemical distinctions.
suggests that V isotope fractionation could occur among V species with different valence states and coordinated environment (Wu et al., 2015). In an oxic and a weakly alkaline (pH = 7–8) ocean, V is mainly present as V(V), which forms vanadate oxyanion in natural seawater (e.g., Peacock and Sherman, 2004). Vanadium isotope fractionation between vanadate oxyanion species (HVO$_4^{2-}$ and H$_2$VO$_4$) may be negligible because they have the same coordinated environ-

Fig. 4. Mn/Fe ratios (a) and V (b) versus $\delta^{51}$V in Fe-Mn crusts and nodules samples. The Mn/Fe ratio and V concentrations of Fe-Mn crust samples show no clear correlation with $\delta^{51}$V ($R^2 = 0.34$), while the $\delta^{51}$V of the deep-water diagenetic nodules display a negative correlation with Mn/Fe ratio ($R^2 = 0.85$).

Fig. 5. Vanadium isotope variation in the non-phosphatized upper layers of Fe-Mn crusts and hydrogenetic Fe-Mn nodule NOD-A in relation to water depth. The yellow area shows estimated average $\delta^{51}$V of near modern hydrogenetic Fe-Mn crusts and nodules and its error with two standard deviations (2 SD) of multiple measurements of the samples.

suggests that V isotope fractionation could occur among V species with different valence states and coordinated environment (Wu et al., 2015). In an oxic and a weakly alkaline (pH = 7–8) ocean, V is mainly present as V(V), which forms vanadate oxyanion in natural seawater (e.g., Peacock and Sherman, 2004). Vanadium isotope fractionation between vanadate oxyanion species (HVO$_4^{2-}$ and H$_2$VO$_4$) may be negligible because they have the same coordinated environ-

The current model of the marine mass balance for V in ocean suggests that authigenic enrichment of V in oxic sediment accounts for about half of the total burial flux of V from modern oceans (Morford and Emerson, 1999). Dunlea et al (2015) also shows that pelagic sediments from sites across the South Pacific Gyre have higher V/Al than typical continental material. They further ascribe the enrichment of authigenic V in the pelagic sediments to the accumulation of V with Fe-Mn oxyhydroxide sediment components and/or oxyhydroxide coatings on pre-existing particles in the water column (Dunlea et al., 2015). In this case, V isotope composition of Fe-Mn oxyhydroxide components in pelagic sediment should also be lower than that of seawater by about $-1.2 \pm 0.2\%e$. Oxic removal via sorption could thus drive the V isotope composition of seawater heavy relative to the source flux. This conclusion further
proves previous model of oceanic V isotope mass balance which suggests that the deposition and burial of sediments under oxic conditions is an important mechanism for removing light $^{50}$V from seawater (Wu et al., 2019).

5.3. Vanadium isotope variations in the diagenetic Fe-Mn nodules

Deep-sea diagenetic Fe-Mn nodules have uniformly lighter V isotope compositions than hydrogenetic Fe-Mn crusts (Table 2). Furthermore, the $\delta^{51}$V of the deep-water diagenetic nodules display a negative correlation with Mn/Fe ($R^2 = 0.85$, Fig. 4). This relationship indicates that nodules with a strong diagenetic signature (e.g., high Mn/Fe) also have more negative $\delta^{51}$V. The shift of V isotope compositions with intensified diagenetic imprint could reflect: (1) phase transition of Fe-Mn oxyhydroxide by diagenetic alteration, which altered the mineralogy and V isotope composition of the original hydrogenetic minerals, or (2) isotope fractionation caused by the release of V along with Fe-Mn oxyhydroxide reduction and dissolution in sub-oxic porewaters and their transportation and deposition to form diagenetic Fe-Mn nodules.

It is well known that marine Fe-Mn crusts and nodules with different genesis show mineralogical diversity. Hydrogenic Fe-Mn crusts are mainly composed of phyllomanganate (birnessite and vernadite) and ferric oxyhydroxides, while diagenetic Fe-Mn nodules are mainly comprised of 10 Å manganates (buserite and todorokite) (e.g., Glasby, 2006). The principal Mn oxyhydroxide minerals in different types of Fe-Mn oxyhydroxide crusts and nodules have distinctive structure that control the surface adsorption behaviors and crystal-chemistry of various elements (e.g., Li, Ni; Jiang et al., 2007; Peacock, 2009). It is well known that V isotope fractionation varies with mineralogy during mineral adsorption (e.g. Goldberg et al., 2009). Thus, V isotope variations of nodules might be the result of the structural diversity between main Mn oxyhydroxide phases of hydrogenetic crusts (birnessite and vernadite) and diagenetic nodules (10 Å manganates). However, the nodule sample NOD-A has a $\delta^{51}$V value similar to hydrogenic Fe-Mn crust, although the high Li abundance (Fig. 3) may only be accommodated in the crystal structures of large tunnel-structures found in todorokite (Jiang et al., 2007). Thus, it is difficult to explain the V isotope composition of NOD-A if we regard the mineralogy of the Mn oxyhydroxide as the main control on the variation of V isotopes in diagenetic ferromanganese nodules. On the other hand, the concentrations of transition metals (Cu, Zn, and Ni) and the REE pattern both indicate that NOD-A is derived from seawater rather than pore fluids (Bau et al., 2014). In comparison, the correlation between transition metal contents (such as Cu, Ni, Zn and V) and Mn/Fe ratios in Fe-Mn crusts and nodules from Weiyuan seamount (Fig. 3) indicate the various contributions of pore fluids. Thus, the negative correlation between V isotope variations in Fe-Mn nodules and Mn/Fe ratios is more likely controlled by source contribution (seawater vs. pore fluids) during their formation rather than a mineralogical control.

Pore fluids are considered as the most important source of metals for diagenetic Fe-Mn nodules (e.g., Dymond et al., 1984). The variations of Ti isotope compositions in diagenetic nodules were explained by the adsorption of Ti from pore fluids in a closed-system reservoir of limited size (Rehkämper et al., 2002). To test whether this mechanism can also explain the observed V isotope variations in diagenetic nodules, we use a batch closed system model to test V isotope fractionation during adsorption. The model is similar to the Ti isotope model used in Rehkämper et al. (2002). Diagenetic Fe-Mn nodule growth mainly occurs in zones where the upward migration of reduced Mn$^{2+}$ pore fluids are re-oxidized (Kuhn et al., 2017). Considering that the redox potential of $V$(V)-$V$(IV) couple is close to that of Fe(III)-Fe(II) and lower than that of Mn(IV)-Mn(II) in seawater (e.g. Bonatti et al., 1971; Piper and Calvert, 2009), it is highly unlikely the reduction of pentavalent V species and related isotope fractionation could largely occur in zones where there is Mn$^{2+}$ transportation and deposition. We thus consider adsorption of V on the surface of Mn oxyhydroxides as the dominant process to control V isotope fractionation within pore fluid and thus the fractionation factor $\alpha$ is set at 0.9988 based on our inferred V isotope fractionation between hydrogenic Fe-Mn crusts and seawater. The partition coefficient of V between Fe-Mn oxyhydroxide and pore fluid ($K_{Fe-Mn \text{ oxyhydroxide/fluid}}$) is set at $3.5 \times 10^5$ based on the estimation from the V contents in seawater and Fe-Mn crusts, which is close to the estimated distribution coefficients of V between manganese oxyhydroxides and seawater by a previous study ($5.7 \times 10^5$, Takematsu et al., 1985). The main purpose of this model is to provide a first approximation to the concentration and isotope variations of V during closed-system adsorption. We set the initial concentration to seawater-like values of $c_{V_{10}} = 35 \text{nM}$ (Jeandel et al., 1987; Ho et al., 2018), and tested the model varying different initial value of $\delta^{51}V_{10}$ between seawater (0.20‰) and hydrogenic ferromanganese crusts and nodules (−1.05‰) endmember. Also, the growth and trace-metal composition of diagenetic-type precipitates is largely controlled by the diffusivity of pore fluids from underlying sediments (Calvert and Price, 1977; Dymond et al., 1984). Thus, it is reasonable to assume that the $\delta^{51}$V of pore fluids are between the endmember values of seawater and hydrogenic ferromanganese crusts and nodules. The assumed seawater composition may underestimate the V concentration of pore fluids given the remobilization of V with Mn and Fe recycling during early diagenesis, which will cause an increase of V concentration within pore fluids (Shaw et al., 1990; Morford et al., 2005). However, the direction of the trend lines of the modeling results will not change with the variations of initial composition and is not dependent on either of these assumptions. The results of these calculations are summarized and compared with the analytical data in Fig. 6. The model shows that the nodules with more diagenetic deposition from pore fluids (i.e. high Mn/Fe ratio and low V concentration) should have more positive $\delta^{51}$V value. Such a trend contradicts our data (Fig. 6). Thus, it is unlikely that the V isotope variations in diagenetic nodules can be completely explained by varying the proportion of V adsorption in a closed-system reservoir.
Instead, the range of $\delta^{51}V$ of the Fe-Mn crusts and nodules from Weiyuan seamount can be most easily explained by a mixing of hydrogenetic and diagenetic endmembers. Therein, the V content (719 ppm) and $\delta^{51}V(1.04\%)$ of the crust samples from C-C zone are used as the hydrogenetic endmember, representing water column supplied V, and the V content (406 ppm) and $\delta^{51}V(1.63\%)$ of the nodules from C-C zone with the highest Mn/Fe ratio are used as the diagenetic endmember, representing sediment pore water supplied V. Mixing between such endmembers does reproduce the observed variations in $\delta^{51}V$ (Fig. 6). Such mixing processes may be appropriate for deep-sea nodules, since the diagenetic metals are likely supplied episodically during the stirring of bottom sediments along with the continuous supply of hydrogenous metal ions to form the Fe-Mn nodules (Jung and Lee, 1999). The diagenetic endmember $\delta^{51}V$ value might reflect the isotopic fractionation that occurred during diffuse/transportation of V in the pore water and its scavenging by diagenetic Fe-Mn oxyhydroxide afterwards. Further studies of pore water analyses providing sedimentary profiles are necessary to better understand V isotope fractionation during early diagenesis.

### 5.4. Depth profile of V isotope variations in Fe-Mn crusts

The depth profile of crusts from Caiwei guyot (such as Dive70B OJ113-211T) displays a negative V isotope shift in the deeper and thus older portions of the Fe-Mn crusts (Fig. 7). It is noteworthy that the older portions of the Fe-Mn crusts are imprinted by phosphatization with high Ca and P contents, with the replacement of carbonate in Fe-Mn crust pore space by carbonate fluorapatite (CFA) (e.g. Hein et al., 1993). The CFA imprint on the primary crust material could modify the bulk composition of the crust. Previous leaching experiment showed that the CFA phase in Fe-Mn crust contains negligible V (Koschinsky and Hein, 2003). Thus, the primary V isotope composition in the Fe-Mn crust might not be modified during phosphatization, if such a process only results from the admixture of CFA to the primary crust material. Some studies also suggest that phosphatization of Fe-Mn crusts occurred under less-oxidizing conditions (Koschinsky and Halbach, 1995; Nishi et al., 2017). Previous study shows that the phosphatized layers display more abundant Ni, Cu, and Zn, higher Mn/Fe ratio and lower Co concentrations relative to non-phosphatized layers in the Fe-Mn crust profile (Nishi et al., 2017). Such geochemical features are suggested to indicate that phosphatized layers formed under less-oxidizing conditions due to diagenetic influence (Nishi et al., 2017). Thus, it is possible that the post-depositional phosphatization altered the original V isotope compositions. However, not all the studied phosphatized layers in the crust profiles show isotope deviation and the layer with the highest phosphorus content (6.42 wt.%) has a $\delta^{51}V$
value (−0.98 ± 0.07‰) indistinguishable from the overlying younger layers (−1.08‰ to −0.97‰; Fig. 7). In addition, the phosphatized layers with lighter δ34V values do not document an enrichment of Ni, Cu or Zn, although they have higher Mn/Fe ratios (1.76–2.03) than all the layers except one (1.32–1.65) with “modern” δ34V values (Fig. 7 and Table 2). Thus, it seems unlikely that V isotope variations of the Fe-Mn crust profile could be simply explained as the results of diagenetic deposition along with phosphatization. Partial reduction and dissolution of the Fe-Mn oxyhydroxide phases might also occur under less-oxidizing condition, which could result in the diagenetic remobilization and reorganization of elements within the Fe-Mn crusts (Koschinsky et al., 1997). Although no obvious evidence of such diagenetic modification is found in our samples, we cannot definitively rule out its potential influence on the V isotope documents in the phosphatized layers, which needs further study.

It is also possible that the V isotope variations observed in the sample Dive70B OJ113-211T are primary. If this is the case, the V isotope shift in the Fe-Mn crust profile might reflect the variation of the isotope fractionation factor between seawater and Fe-Mn crust over time with an invariant seawater isotope composition. The isotope fractionation factor might vary due to external parameters such as temperature, salinity or pH. Because Fe-Mn oxyhydroxides only form under oxic conditions, the dominant V species was likely vanadate when the phosphatized layers formed. Thus, the variations of isotope fractionation cannot be explained by the change of V species in seawater. The temperature change in the deep ocean would be minimal and thus also unlikely to change the isotope fractionation. In addition, it is difficult to ascribe the isotope variations to only mineralogical controls, as previously discussed. Thus, it is most likely that the V isotope variations in the depth profile of Fe-Mn crust are not caused by the changes in isotope fractionation factor.

Alternatively, the observed V isotope variations of the Fe-Mn crust profile might reflect the evolving seawater V isotope compositions. These temporal changes could record a global signal due to the relatively long residence time of V isotope compositions. These temporal changes could record the evolution of isotope fractionation factors in the Fe-Mn oxyhydroxides of the Fe-Mn crusts and nodules exhibiting large V isotope variations with average value of −1.05 ± 0.16‰ (2 SD), regardless of sampling location and water depth. Such results imply a relatively homogeneous V isotope composition of marine hydrogenic Fe-Mn crusts and nodules. The hydrogenic Fe-Mn crusts and nodules are depleted in δ34V compared with seawater. This offset is potentially the result of isotope fractionation during the adsorption of V onto Fe-Mn particles with fractionation factor of −1.2 ± 0.2‰ (2 SD). Thus, burial of V with Fe-Mn oxyhydroxides precipitation is an important isotopically light sink in the modern ocean.

6. SUMMARY

We conducted the first systematic V isotope analyses of Fe-Mn crusts and nodules exhibiting large V isotope variations from which we conclude the following:

(1) The younger non-phosphatized layers of hydrogenic Fe-Mn crust and hydrogenous Fe-Mn nodules have limited V isotope variations with average value of −1.05 ± 0.16‰ (2 SD), regardless of sampling location and water depth. Such results imply a relatively homogeneous V isotope composition of marine hydrogenic Fe-Mn crusts and nodules.

(2) The hydrogenic Fe-Mn crusts and nodules are depleted in δ34V compared with seawater. This offset is potentially the result of isotope fractionation during the adsorption of V onto Fe-Mn particles with fractionation factor of −1.2 ± 0.2‰ (2 SD). Thus, burial of V with Fe-Mn oxyhydroxides precipitation is an important isotopically light sink in the modern ocean.

(3) Fe-Mn nodules have large V isotope variations with δ34V values ranging between −0.98‰ to −1.65‰. This variability can be explained by the variable contribution of V from diagenetic and hydrogenic precipitation. Because these diagenetic nodules are affected by the chemistry within the underlying sediment, they may not record the primary seawater V isotope signature.
(4) Vanadium isotope variations are observed in the depth profile of a Fe-Mn crusts. Although we cannot definitively rule out the possibility that diagenetic remobilization and reorganization in the phosphatized layers modify the primary V isotope signature. However, if the observed $\delta^{51}V$ depth profiles record V isotope seawater variations, this is likely controlled by the redox-related seawater V mass balance. Thus, our results imply that the $\delta^{51}V$ records of hydroxrous Fe-Mn crusts can provide insights into ancient ocean chemistry.

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APPENDIX A. SUPPLEMENTARY MATERIAL

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REFERENCES


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