Theoretical and experimental investigation of nickel isotopic fractionation in species relevant to modern and ancient oceans

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Abstract

Nickel plays a central role as an enzyme co-factor in the metabolism of methanogenic Archaea. Methanogens can fractionate Ni isotopes during assimilation, opening the possibility of using the stable isotopic composition of Ni as a biomarker. However, other sources of Ni isotopic variations need to be evaluated before one can establish Ni isotopes as an unambiguous tracer of methanogenesis in the rock record. Equilibrium exchange of Ni between the different species present in the ocean is a potential source of isotopic fractionation. Through controlled laboratory experiments and theoretical calculations, we quantify equilibrium Ni iso fractionation between different species relevant to the modern and ancient ocean: Ni(H 2O) 6 2+, Ni(H2O)18 2+, NiOH(H 2O)5 +, Ni(OH) 2(H2O)4, NiCl(H 2O)5 +, cis-NiCl2(H2O)4, trans-NiCl2(H2O)4, NiHS(H 2O)4 +, Ni(H-O)2(H2O)4, NiSO4(H2O)4, NiHCO3(H2O)4 +, NiCO3(H2O)4, and organic ligands (crown ether and oxalic acid). The magnitude of ligand-controlled Ni isotopic fractionation, approximately 1.25‰/amu (2.5‰ for the 60Ni/58Ni ratio), is similar to that previously measured in cultures of methanogenic Archaea.

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1. INTRODUCTION

Microbial activity can fractionate non-traditional stable isotopes, opening the possibility of using those variations to trace life in past geologic environments (e.g., Beard et al. 1999; Mandernack et al. 1999; Croal et al. 2004; Crosby et al. 2005; Balci et al. 2006; Cameron et al. 2009). However, abiotic processes can also impart measurable isotopic fractionations and should not be overlooked. Owing to its ubiquity in rocks and minerals, its complex redox chemistry, and its central role in biochemistry, Fe has received much attention in both experimental and theoretical studies (see Dauphas and Rouxel, 2006; Johnson et al., 2008, for some reviews).

Although Ni is less abundant than Zn, Cu or Fe in organisms, it plays a major role in some key enzymes such as the methyl-coenzyme M reductase found in methanogenic Archaea (Thauer, 1998), the Ni-containing superoxide dismutase that protects some photosynthetic organism from oxidative stress (Dupont et al., 2008), and it may be necessary for assimilation of nitrogen from urea in phytoplankton (Price and Morel, 1991). In the ocean, Ni shows a characteristic nutrient profile, however, its depletion in surface waters is not as drastic as it is for other metals (e.g., Sclater et al., 1976; Bruland, 1980; Bruland and Lohan, 2003).
It has been speculated that Ni could have played a central role in controlling the evolution of redox conditions at Earth’s surface. Konhauser et al. (2009) measured a decrease in the Ni concentration of banded iron formations at 2.7 Gyr ago, associated with a decrease in the occurrence of ultramafic magmatism. They argued that such decrease might have triggered the “Great Oxidation Event” on Earth. With less Ni, methanogens could not have released as much methane and, through a cascade of events, this would have contributed to a major increase in the oxygen level in the atmosphere.

Cameron et al. (2009) showed that Ni isotopes could be fractionated by methanogenic Archaea, which preferentially assimilate light Ni isotopes while the residual growth medium in all experiments and in the cell biomass from the non-methanogenic control organism (P. calidifontis) shows essentially no isotopic fractionation. The fractionation of up to 1.46‰ for 60Ni/58Ni ratio (~0.7‰/amu) in methanogens is much larger than any effect measured in extraterrestrial samples, terrestrial basalts, or continental sediments (e.g., 0.15 ± 0.24‰; Cook et al., 2007; Moynier et al., 2007; Cameron et al., 2009). While this first foray into Ni isotopic biogeochemistry is encouraging, other sources of Ni isotopic variations need to be evaluated before one can use Ni isotopes as unambiguous tracers of methanogenesis in ancient rocks.

For example, exchange of Ni between the different species present in the ocean represents a potential source of isotopic fractionation. Nickel is distributed in the modern ocean between inorganic species (e.g., Ni2+, NiCl+, NiCl2, NiCO3, NiHCO3, and NiSO4) and some organic ligands (denoted L) of unspecified nature (Turner et al., 1981; Byrne et al., 1988; Donat et al., 1994; Saito et al., 2004; Turner and Martino, 2006; Vraspir and Butler, 2009). Turner et al. (1981) calculated the speciation of dissolved Ni in seawater in the absence of organic ligand and found the following proportions, Ni2+ (47%), NiCl+ and NiCl2 (34%), NiCO3 and NiHCO3+ (14%). In presence of an organic ligand, NiL can dominate (e.g., Turner and Martino, 2006). It is worth noting that in the ancient ocean, the speciation could have been different and it is unknown if organic ligands were present. Thermodynamic calculations for Proterozoic and Archean oceans, give NiHS+ as the dominant species under certain conditions (Saito et al., 2003).

In this study, we have investigated both theoretically and experimentally the isotopic fractionation of Ni between some of the major species present in the modern and ancient oceans: Ni(H2O)62+, Ni(H2O)82+, Ni(OH)H2O5+, Ni(OH)H2O4+, Ni(OH)H2O3+, cis-NiCl3(H2O)4+, trans-NiCl3(H2O)4+, NiHS(H2O)5+, NiHS(H2O)4+, NiSO42−, NiHCO32−, and NiCO32−.

It is difficult to assess the degree of Ni isotopic fractionation associated with organic ligands found in natural systems. As a first order approach, we performed equilibration experiments with a synthetic ligand (a crown ether, dicyclohexano-18-crown-6, DC18C6) and performed computations for Ni complexation with oxalic acid (C2H2O4).

The equilibrium isotopic fractionations were calculated for the different Ni complexes present in solution by using the reduced partition function ratio (RPFR or β factors) of the different isotopologues (Urey, 1947; Bigeleisen and Mayer, 1947). The RPFR of the hydrated Ni ion, chloride, hydrogen sulfide, and oxalate can be calculated from thermodynamic data and structural data (Frisch et al., 2003), which is not the case of Ni coordinated with the crown ether (Ni–DC18C6). The RPFR of the Ni–DC18C6 complex are estimated from the isotopic fractionation factor obtained in an isotopic exchange experiment. Two sets of experiments at different HCl concentrations (4.7 and 8.5 mol/L, M) were performed to test the effect of speciation on Ni isotopic fractionation.

2. METHODS

2.1. Computational methods

Orbital geometries, vibrational frequencies, Gibbs free energies of aqueous Ni(II) species were computed using density functional theory (DFT) as implemented by the Gaussian 03 code (Frisch et al., 2003). The DFT method employed here is a hybrid density functional consisting of Becke’s three-parameter non-local hybrid exchange potential (B3) (Becke, 1993) with Lee–Yang and Parr (LYP) (Lee et al., 1988) non-local functionals. The 6-311+G(d,p) basis set, which is an all-electron basis set, was chosen for H, C, O, S, Cl, and Ni. For the solvation effect, CPCM continuum solvation method (CPCM: conductor-like polarizable continuum model) was used.

The contribution of the nuclear volume was estimated by using the numerical multiconfigurational Dirac–Coulomb Hartree–Fock (MCDCHF) method, which was implemented in the four-component relativistic atomic program package GRASP2K (Jönsson et al., 2007). The electronic structures of Ni0 ([Ar]3d84s2) and Ni2+ ([Ar]3d6) were calculated. Vibrational, solvent, dynamic correlation, magnetic Breit interaction, and quantum electrodynamics effects were neglected. The Fermi statistical distribution function was adopted as a finite nucleus model. Root mean square radii reported in the literature (Fricke and Heilig, 2004) were used in the calculation. The default values in GRASP2K were adopted for the other conditions or parameters (Jönsson et al., 2007; Abe et al., 2008).

2.2. Extraction experiments and isotopic analyses

Dicyclohexano-18-crown-6 (DC18C6) (over 97% purity) was a product of Fluka Chemie GmbH. Nickel dichloride (hydrated, 99.95% purity) was a product of Sigma–Aldrich, Co., Inc. Hydrochloric acid, in which the Ni impurity was certified to be less than 2.2 ppt, was purchased from Kanto Chemical, Co., Inc. Other chemicals were reagent grade from Wako Pure Chemical Industries, Ltd.

Nickel dichloride was dissolved in HCl to make solutions ranging from 0.8 to 1.8 M Ni(II) in 3.8–8.5 M HCl. The organic phase was diluted in chloroform to make a solution of 0.2 M DC18C6. A 1 mL aqueous solution and a 10 mL organic solution were mixed in a glass vial with a magnetic stirrer, and the glass vial was sealed. The proportion of the two phases was chosen based on the reported
The species of Ni(II) in HCl medium in the laboratory experiment are Ni^{2+}, NiCl^+, and NiCl_2, which are related through the following stepwise reactions,

\[ \text{Ni}^{2+} + \text{Cl}^- \rightleftharpoons \text{NiCl}^+ \]  
\[ \text{NiCl}^+ + \text{Cl}^- \rightleftharpoons \text{NiCl}_2 \]

Fig. 1 shows the mole fractions of Ni species estimated by using the apparent stability constants \( K_1 \) and \( K_2 \) of reactions 1 and 2 (Bjerrum, 1988). The formation of the nickel chloride species is possible in conditions of elevated acidity.

The extraction reaction of Ni(II) with the macrocyclic ligand may be written as,

\[ \text{NiCl}^- + L \rightleftharpoons \text{NiLCl}_2^- \]

where \( L \) stands for DC18C6. The distribution ratio \( D \) is rewritten with moralities as,

\[ D = \frac{\sum \left[ \text{Ni}^{n+} \right]_{\text{org}}}{\sum \left[ \text{Ni}^{n+} \right]_{\text{aq}}} \approx \frac{\left[ \text{NiLCl}_2^- \right]}{\left[ \text{Ni}^{2+} \right] + \left[ \text{NiCl}^+ \right] + \left[ \text{NiCl}_2^- \right]} \]

Measured \( D \) values are shown in Fig. 2 as a function of HCl molarity. The \( D \) values are smaller than 10^{-4} and show an increase with acidity. The fitted \( D \) values based on Eq. (5) are shown together as a dotted curve. The results can be fitted with \( K_{\text{ex}} = 0.00084 \). Small misfit between calculated and experimental data (Fig. 2) may be due to the lack of precise activity coefficients of Ni(II) species in highly concentrated HCl solutions.

The isotope separation factor \( x_m \), between the aqueous and the organic phases, is defined as:

\[ x_m = \frac{\sum \left[ ^{58}\text{Ni} \right] / \sum \left[ ^{60}\text{Ni} \right]_{\text{org}}}{\sum \left[ ^{58}\text{Ni} \right] / \sum \left[ ^{60}\text{Ni} \right]_{\text{aq}}} \]

### 3. RESULTS AND DISCUSSION

#### 3.1. Isotope fractionation of Ni in solvent extraction

The species of Ni(II) in HCl medium in the laboratory experiment are Ni^{2+}, NiCl^+, and NiCl_2, which are related through the following stepwise reactions,

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where the superscript \( m \) indicates the mass of a particular isotope \((m = 60, 61 \) or \( 62 \)). \((\Sigma^{60}\text{Ni}/\Sigma^{64}\text{Ni})_{\text{org}} \) and \((\Sigma^{60}\text{Ni}/\Sigma^{64}\text{Ni})_{\text{aq}} \) are the isotopic ratios of \(^{60}\text{Ni}/^{64}\text{Ni} \) measured in the organic and aqueous phases, respectively, summed over all the species present in each phase. Because of the very small value of \( D \) (Fig. 2), most Ni stays in the aqueous phase and the \(^{60}\text{Ni}/^{64}\text{Ni} \) ratio of the starting material (hydrated NiCl\(_2\)) can be substituted for \((\Sigma^{60}\text{Ni}/\Sigma^{64}\text{Ni})_{\text{aq}} \). For example, with \( D = 10^{-4} \) and \( x_m = 1.001 \) a shift of \( -0.0001\% \), for the \(^{60}\text{Ni}/^{64}\text{Ni} \) ratio of the aqueous phase relative to the starting material would be expected. The isotope enrichment factor is defined as \( x_m - 1 \). Because \( x_m \approx 1 \), \( x_m - 1 \approx \ln x_m \). In the present paper, we use the \( \delta \) notation,

\[
\delta^{60}\text{Ni} = \left( \frac{^{60}\text{Ni}}{^{64}\text{Ni}} \right)_{\text{species/phase}} \left( \frac{^{60}\text{Ni}}{^{64}\text{Ni}} \right)_{\text{initial}} - 1 \times 1000
\]  

(7)

Because the Ni isotopic composition of the aqueous phase remains almost unchanged, \( \delta^{60}\text{Ni} \) of the organic phase is similar to \( 10^3 \ln x_m \). It should be noted that in studies on Ni isotope fractionation in natural systems, \( \delta^{60}\text{Ni} \) is referenced to a standard like SRM-986. In the present study, \( \delta^{60}\text{Ni} \) corresponds to the difference in Ni isotopic composition between the organic phase and the starting material (aqueous phase). The \( \delta^{60}\text{Ni} \) values obtained are shown in Table 1. At both acidities (3.8 and 8.5 M), the organic phase is enriched in the lighter isotopes.

The classic theory of chemical isotope fractionation is based on mass-dependent isotopic differences in vibrational energies of isotopologues (Urey, 1947; Bigeleisen and Mayer, 1947). The isotope enrichment factor is proportional to \( \delta m/m' \), where \( \delta m = m - m' \) with \( m \) and \( m' \) the masses of two isotopes (prime represents the light isotope). The conventional theory of mass-dependent fractionation was expanded by Bigeleisen (1996) to take into account the nuclear field shift effect,

\[
\ln z = \frac{hc}{kT} v_{Is}a + \frac{1}{2} \left( \frac{h}{2\pi mkT} \right)^2 \frac{\delta m}{m} \frac{v}{m} b
\]  

(8)

where \( v_{Is} \) is the nuclear field shift, \( a \) the nuclear field shift scaling factor, \( b \) the scaling factor for the conventional mass-dependent effect, \( h \) the Plank constant, \( c \) the light velocity, \( k \) the Boltzmann constant, and \( T \) the temperature. The nuclear field shift effect was identified as the cause of the mass-independent isotope fractionation in chemical exchange reactions (Bigeleisen, 1996; Nomura et al., 1996; Fujii et al., 2009a). The nuclear field shift results from differences in nuclear size and shape of different isotopes (Fricke and Heilig, 2004; King, 1984). Different isotopes have the same number of protons, but they do not have the same distribution of protons in space. The nuclear charge distribution, which is usually represented as the mean-square charge radius \( \langle r^2 \rangle \), is affected by the number of neutrons in the nucleus. The nuclear charge distribution produces an electric field, and its variation from one isotope to another shifts the atomic energy levels, also displacing the electronic molecular states. The nuclear field shift is not mass-dependent but is strongly related to the neutron configuration of the nucleus.

The nuclear field shift is proportional to the isotopic difference in the mean-square charge radius, \( \delta \langle r^2 \rangle \) (King, 1984). \( \langle r^2 \rangle \) of \(^{60}\text{Ni} \) increases with mass number, but the relationship, \( \delta \langle r^2 \rangle \) vs. \( \delta m/m' \) does not follow a simple straight line (Fricke and Heilig, 2004). In order to identify a possible relationship between \( \delta^{60}\text{Ni} \) and \( \delta \langle r^2 \rangle \), the mass dependent component was removed by using the exponential law of mass fractionation (Albarède et al., 2004; Russell et al., 1977, 1978). This normalization is effective for revealing the mass-independent component of the isotopic variations (Fujii et al., 2009b,c, 2010). The results of the equilibration experiments with DC18C6 are displayed in Fig. 3. Plots of \( \delta^{60}\text{Ni} \) vs. \( \delta m/m' \) (Fig. 3b and c) show similar profiles to \( \delta \langle r^2 \rangle \) vs. \( \delta m/m' \) (Fig. 3a). However, considering the large uncertainties in Fig. 3b and c, we cannot resolve the presence of a nuclear field shift effect in Ni isotopes.

Recent quantum chemical studies have adopted finite nucleus models into \textit{ab initio} methods (Schauble, 2007; Abe et al., 2008a,b, 2010). Nuclear field shift effects have been documented for Hg, Tl, and U redox reactions. Since the electron density at the nucleus is larger for \( s \)-orbital, the presence or absence of \( s \)-electrons may cause a larger

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**Table 1**

Isotopic fractionation of nickel during exchange experiments between HCl medium and a macrocyclic complex (see text for details). Ni bound to the organic ligand is systematically lighter than Ni dissolved in HCl.

<table>
<thead>
<tr>
<th>[HCl]/M</th>
<th>( \delta^{60}\text{Ni} )</th>
<th>( \delta^{61}\text{Ni} )</th>
<th>( \delta^{62}\text{Ni} )</th>
<th>( \delta^{63}\text{Ni} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.7</td>
<td>-1.72 ± 0.08</td>
<td>-2.40 ± 0.17</td>
<td>-3.37 ± 0.16</td>
<td>-1.9 ± 2.4</td>
</tr>
<tr>
<td>8.5</td>
<td>-1.50 ± 0.10</td>
<td>-2.17 ± 0.26</td>
<td>-2.96 ± 0.21</td>
<td>-7.2 ± 1.1</td>
</tr>
</tbody>
</table>

Errors are \( 2\sigma \).
the isotope pair $^{61}\text{Ni}/^{58}\text{Ni}$ by using the exponential law (Albarède et al., 2004). Errors are the same as those shown in Table 1. (a) Normalized $^{61}\text{Ni}/^{58}\text{Ni}$ values and relative $\delta\langle r^2\rangle$ values (Fricke and Heilig, 2004) are normalized to the isotope pair $^{61}\text{Ni}/^{58}\text{Ni}$ by using the exponential law (Albarède et al., 2004). Errors are the same as those shown in Table 1. (a) Normalized $\delta\langle r^2\rangle$. (b) Normalized $\delta^{60}\text{Ni}$ values for the $[\text{HCl}]=4.7\text{M}$ experiment. (c) Normalized $\delta^{60}\text{Ni}$ for the $[\text{HCl}]=8.5\text{M}$ experiment.

Table 2

<table>
<thead>
<tr>
<th>Mass number</th>
<th>$\langle r^2 \rangle_{1/2}/\text{fm}^2$</th>
<th>Ni$^{2+}$ total energy/a.u.</th>
<th>Ni$^0$ total energy/a.u.</th>
<th>Nuclear field shift effect$/10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>58</td>
<td>3.776</td>
<td>$-1518.51221333$</td>
<td>$-1519.36507200$</td>
<td>0.000</td>
</tr>
<tr>
<td>60</td>
<td>3.813</td>
<td>$-1518.51209952$</td>
<td>$-1519.36495812$</td>
<td>-0.076</td>
</tr>
<tr>
<td>61</td>
<td>3.823</td>
<td>$-1518.51208658$</td>
<td>$-1519.36492716$</td>
<td>-0.096</td>
</tr>
<tr>
<td>62</td>
<td>3.842</td>
<td>$-1518.51200958$</td>
<td>$-1519.36486813$</td>
<td>-0.136</td>
</tr>
<tr>
<td>64</td>
<td>3.860</td>
<td>$-1518.51195343$</td>
<td>$-1519.36481194$</td>
<td>-0.173</td>
</tr>
</tbody>
</table>

* The nuclear field shift effect is calculated by $\ln K_{ii} = (\delta E(Ni^0) - \delta E(Ni^{2+}))/kT$ at $T = 285\text{K}$. Energy of photons of 1 a.u. is equal to $2.1947 \times 10^7\text{cm}^{-1}$ or $3.4597 \times 10^{-18}\text{J}$.

nuclear field shift effect. In the present study, the total electronic energies at the ground states of Ni$^0$ [(Ar)3$d^8$] and Ni$^{2+}$ [(Ar)3$d^9$] were calculated for different isotopes with different nuclear charge radii. The root mean square radii ($\langle r^2 \rangle_{1/2}$) reported in the literature (Fricke and Heilig, 2004) were used in the calculation. The results of those calculations are shown in Table 2 in atomic units (a.u.). As an example, the nuclear field shift effect in the Ni$^0$–Ni$^{2+}$ redox reaction was estimated (Table 2). The estimated magnitude is much smaller than experimentally documented Ni isotope fractionation in aqueous systems (Cameron et al., 2009; this study). This suggests that the isotopic fractionation of Ni originates from mass differences rather than a nuclear field shift effect.

3.2. $\beta$-Factors of Ni species

The isotope enrichment factor due to the intramolecular vibrations can be evaluated from the RPFR (Bigeleisen and Mayer, 1947), $(s'/s)f$,

$$\ln(s'/s)f = \sum \ln b(u'_i) - \ln b(u_i)$$

(9)

where

$$\ln b(u_i) = \ln u_i + u_i/2 + \ln(1 - e^{-u_i})$$

(10)

and

$$u_i = hv_i/kT$$

(11)

and $v$ stands for vibrational frequency. The subscript $i$ stands for the $i$th molecular vibrational level with primed variables referring to the light isotopologue. The isotope enrichment factor due to the molecular vibration can be evaluated from the frequencies ($v$) summed over all the different modes. $(s'/s)f$ is equivalent to the $\beta$ notation commonly encountered in geochemistry.

3.2.1. Nickel ion

Extensive structural studies of Ni($H_2O)_6^{2+}$ have been carried out (Caminiti et al., 1977; Neilson and Enderby, 1978; Sandstrom, 1979; Magini, 1981; Magini et al., 1982; Waizumi et al., 1992a,b, 1999). In order to evaluate the strength of mass-dependent effects, quantum chemical calculations of the vibrational energies of the hydrated Ni(II) species were performed. Because of the excellent convergence of the reaction energies of Ni(II) species, using a basis set higher than 6-311+G(d,p) is recommended (Rulíšek and Havlas, 1999). For our quantum chemical calculations, we therefore selected the basis set 6-311+G(d,p). The hydrated Ni(II) species is generally thought to be present as octahedral Ni($H_2O)_6^{2+}$. The calculated bond length of Ni–O and the literature values are reported in Table 3. The Ni–O bond length obtained is identical to the value determined with the same basis set (Rulíšek and Havlas, 1999), and the value agrees with experimental data (Caminiti et al., 1977;
−ΔH_{hyd} = −ΔE_b + ΔE_{el} + nΔH_{vap} + ΔnRT − ΔE(Cp)
−ΔE_{el} + ΔE_{red} + ΔE_{geom} \tag{12}

ΔE_b is the total binding energy of the gas phase cluster [Ni(H_2O)_6]^{2+}. ΔE_{el} represents the solvation free energy of Ni(H_2O)_6^{2+}. This term, which contains the entropic contribution to the solvation free energy for the continuum dielectric part, was neglected. ΔH_{vap} is the heat of vaporization of water, which is 10.50 kcal/mol (Lide, 2008). The ΔE(Cp) term arises from the difference in heat capacity of the components of the system, which corresponds to a small correction of ~1 kcal/mol at 298 K (Li et al., 1996). ΔE_{geom} is the difference in vibrational zero-point energy in forming clusters. ΔE_{red} is a correction due to relativistic effects for metal centers, and ΔE_{geom} is a correction due to geometry relaxation for H_2O during the formation of the clusters. The last three terms tend to cancel out (a few kcal/mol) (Li et al., 1996), and these corrections were not included in our calculation. The calculated value of ΔH_{hyd} is shown in Table 5. The hydration enthalpy of metal cations has been determined by thermochemical methods (Rosseinsky, 1965; Smith, 1977; Marcus, 1985), and literature values are shown for comparison. The ΔH_{hyd} value obtained agrees well with a value reported by Rosseinsky (1965). Li et al. (1996) showed that, for divalent cations, even small cluster models like Ni(H_2O)_6^{2+} can reproduce ΔH_{hyd}^{2+}. Based on the validity of the calculation of Ni(H_2O)_6^{2+}, ln β was determined by using Eqs. (9)–(11). The ln β values

Table 3
Bond length determined for Ni(H_2O)_6^{2+}.

<table>
<thead>
<tr>
<th>Method(^a)</th>
<th>Bond, Ni-O/Å</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>2.086</td>
<td>This work</td>
</tr>
<tr>
<td>DFT(^b)</td>
<td>2.073(4.464)</td>
<td>This work</td>
</tr>
<tr>
<td>DFT</td>
<td>2.002</td>
<td>Wazuzumi et al. (1992b)</td>
</tr>
<tr>
<td>DFT</td>
<td>2.087</td>
<td>Rudolph and Pye (1999)</td>
</tr>
<tr>
<td>XRD</td>
<td>2.05–2.06</td>
<td>Caminiti et al. (1977)</td>
</tr>
<tr>
<td>XRD(^b)</td>
<td>2.069</td>
<td>Magini (1981)</td>
</tr>
<tr>
<td>XRD(^d)</td>
<td>2.056–2.072</td>
<td>Magini et al. (1982)</td>
</tr>
<tr>
<td>ND(^e)</td>
<td>2.07–2.10</td>
<td>Neilson and Enderby (1978)</td>
</tr>
<tr>
<td>EXAFS</td>
<td>2.07</td>
<td>Sandstrom (1979)</td>
</tr>
</tbody>
</table>

\(^a\) DFT (density functional theory), XRD (X-ray diffraction), ND (neutron diffraction), EXAFS (extended X-ray absorption fine structure).
\(^b\) 12 H_2O were arranged in the second hydration sphere.
\(^c\) Ni–O bond length for hydration waters in the second hydration sphere is shown in parentheses.
\(^d\) Solutions contain Ni(H_2O)_6\(^{2+}\) (n = 0, 1, and 2).
\(^e\) D_2O was used.

Table 4
Totally symmetric vibrational frequencies of Ni(II) aqua-complexes.

<table>
<thead>
<tr>
<th>Hydration number n</th>
<th>Method</th>
<th>Frequency (^{a}) (cm(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>DFT</td>
<td>347</td>
<td>This work</td>
</tr>
<tr>
<td>18</td>
<td>DFT</td>
<td>394</td>
<td>This work</td>
</tr>
<tr>
<td>−</td>
<td>Raman(^a)</td>
<td>390</td>
<td>Edwards and Knowles (1992)</td>
</tr>
<tr>
<td>−</td>
<td>Raman(^b)</td>
<td>395</td>
<td>Bickley et al. (1993)</td>
</tr>
</tbody>
</table>

\(^a\) Sample was a solution of Ni(II) formate.
\(^b\) Sample was a solution of Ni(II) malonate.

Table 5
Hydration enthalpy of Ni(H_2O)_6^{2+}.

<table>
<thead>
<tr>
<th>Hydration number n</th>
<th>ΔH_{hyd}/kcal/mol</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>515</td>
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<tr>
<td>18</td>
<td>538</td>
<td>This work</td>
</tr>
<tr>
<td>−</td>
<td>518</td>
<td>Rosseinsky (1965)</td>
</tr>
<tr>
<td>−</td>
<td>503</td>
<td>Smith (1977)</td>
</tr>
<tr>
<td>−</td>
<td>502</td>
<td>Marcus (1985)</td>
</tr>
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</table>

Table 6
Logarithm of the reduced partition function, ln β, for isotope pair \(^{60}\)Ni/\(^{60}\)Ni.

<table>
<thead>
<tr>
<th>Species</th>
<th>ln β at 285 K/(^{60})Ni</th>
<th>ln β at 298 K/(^{60})Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(H_2O)_6^{2+}</td>
<td>5.909</td>
<td>5.432</td>
</tr>
<tr>
<td>Ni(H_2O)_6^{2+}</td>
<td>6.576</td>
<td>6.046</td>
</tr>
<tr>
<td>NiOH(H_2O)_5^{2+}</td>
<td>6.209</td>
<td>5.715</td>
</tr>
<tr>
<td>Ni(OH)_2(H_2O)_4</td>
<td>6.044</td>
<td>5.569</td>
</tr>
<tr>
<td>NiCl(H_2O)_5^{2+}</td>
<td>5.771</td>
<td>5.305</td>
</tr>
<tr>
<td>cis-NiCl_2(H_2O)_4</td>
<td>5.250</td>
<td>4.825</td>
</tr>
<tr>
<td>trans-NiCl_2(H_2O)_4</td>
<td>5.213</td>
<td>4.787</td>
</tr>
<tr>
<td>Ni(H_2O)_3^{3+}</td>
<td>5.175</td>
<td>4.756</td>
</tr>
<tr>
<td>Ni(H_2O)_3^{3+}</td>
<td>6.472</td>
<td>4.395</td>
</tr>
<tr>
<td>NiSO_4(H_2O)_3</td>
<td>6.242</td>
<td>5.877</td>
</tr>
<tr>
<td>NiHCO_3(H_2O)_4^{2+}</td>
<td>6.295</td>
<td>5.787</td>
</tr>
<tr>
<td>NiCO_3(H_2O)_4</td>
<td>6.308</td>
<td>5.989</td>
</tr>
<tr>
<td>Ni-crown complex</td>
<td>4.177</td>
<td>3.859</td>
</tr>
<tr>
<td>Ni(C_2O_4)_3^{2−}</td>
<td>6.392</td>
<td>5.872</td>
</tr>
<tr>
<td>Ni(C_2O_4)_3^{2−}</td>
<td>4.660</td>
<td>4.275</td>
</tr>
</tbody>
</table>

\(^a\) Estimated as ln β = 4.177 × \((\frac{\nu}{\nu_0})^{3}\).
at 285 and 298 K for the isotope pair \(^{58}\text{Ni} - ^{60}\text{Ni}\) are shown in Table 6. The temperature dependence of \(\ln \beta\) is shown in Fig. 4 in the temperature range of 273–423 K (0–150 °C). The variation of \(\ln \beta\) within this temperature range is \(-4\%\). The \(\ln \beta\) value of hydrated \(\text{Ni}^{2+}\) using only the first coordination sphere was 5.432\(\%\) (298 K), while setting the second hydration sphere increased \(\ln \beta\) by ca. 6.046\(\%\) at 298 K. It should be noted that, in studies on Fe isotope fractionation, some difficulties to reproduce experimental data from theoretical calculations have been reported (Anbar et al., 2005; Domagal-Goldman et al., 2008; Hill et al., 2009). It is of interest that, for trivalent cations like \(\text{Fe}^{3+}\), a larger cluster model including second coordination sphere may shift the theoretical estimate closer to the experimental result (Table 6).

### 3.2.2. Nickel hydroxide

The structure of the first Ni hydrosulfide product \(\text{Ni(OH)}_2\) was calculated using a cluster model (Li et al., 1996). That of the second hydrosulfide product \(\text{Ni(OH)}_2\) was calculated as a point symmetry (trans-) geometries of both \(\text{Ni(OH)}_2\) species were shown in Table 7. The \(\ln \beta\) values at 285 and 298 K are shown in Table 6. The \(\ln \beta\) values of \(\text{cis-}\) and \(\text{trans-}\) \(\text{NiCl}_2\) species are similar (4.825\(\%\) and 4.787\(\%\) at 298 K), which suggests that the structural details of \(\text{NiCl}_2\) species do not have a large influence on the Ni isotopic fractionation. The nickel chloride relevant to the ocean chemistry may be \(\text{NiCl}^+\) with \(\ln \beta = 5.305\%\) at 298 K.

### 3.2.3. Nickel chloride

The structure of \(\text{NiCl}(\text{H}_2\text{O})_5^+\) was calculated. The bond lengths converged to values of 2.11–2.13 Å (Ni–O) and 2.29 Å (Ni–Cl) (Table 7), but unfortunately structural data of pure \(\text{NiCl}(\text{H}_2\text{O})_5^+\) is not available for comparison. The structure of \(\text{NiCl}_2\) can be in \(\text{cis-}\) and \(\text{trans-}\) geometries (Mizuno, 1961; Kleinberg, 1969; Agulló-Rueda et al., 1987; Waizumi et al., 1992b; Ptasiewicz-Bak et al., 1999). Structural studies on \(\text{NiCl}_2\) crystals indicated that \(\text{cis-NiCl}_2\) was the dominant species (Waizumi et al., 1992b; Ptasiewicz-Bak et al., 1999), while other studies found that \(\text{trans-NiCl}_2\) was dominant (Mizuno, 1961; Kleinberg, 1969; Agulló-Rueda et al., 1987). Therefore, the geometries of both \(\text{cis-}\) and \(\text{trans-}\) \(\text{NiCl}_2\) species were calculated. The bond lengths of the optimized structures are shown in Table 7. Though the result of our calculation for the Ni–O bond length of \(\text{cis-NiCl}_2\) is slightly longer compared to literature data, the other Ni–O and Ni–Cl bond lengths are acceptable. The Gibbs free energies at 298 K were also calculated. The calculation was performed with and without solvation (hydration). The results are shown in Table 8. Without solvation, \(\text{cis-NiCl}_2\) is more stable than \(\text{trans-NiCl}_2\), while \(\text{trans-NiCl}_2\) is more stable than \(\text{cis-NiCl}_2\) if solvation is included.

The \(\ln \beta\) values at 285 and 298 K are shown in Table 6. The \(\ln \beta\) values of \(\text{cis-}\) and \(\text{trans-}\) \(\text{NiCl}_2\) species are similar (4.825\(\%\) and 4.787\(\%\) at 298 K), which suggests that the structural details of \(\text{NiCl}_2\) species do not have a large influence on the Ni isotopic fractionation. The nickel chloride relevant to the ocean chemistry may be \(\text{NiCl}^+\) with \(\ln \beta = 5.305\%\) at 298 K.

### 3.2.4. Nickel sulfide

According to the reported stability constants (Saito et al., 2003; Al-Farawati and van den Berg, 1999), the formation of nickel sulfide species is possible in conditions of

![Fig. 4. Temperature dependence of \(\ln \beta\). Using \(\ln \beta\) values at 298 K (Table 6), \(\ln \beta (T) = \ln \beta (298) \times (298/T)^\gamma\) was calculated. The calculated \(\ln \beta (T)\) values are shown as functions of \(1/T^2\). (a) Inorganic species (b) organic species and carbonates.](image-url)
Ni(HS)₂(H₂O)₄ were 2.41–2.42 Å (Ni–S) and 2.17–2.18 Å (Ni–Cl) of Ni chlorides (see Table 7). This suggests that the weaker ligand bond distances of Ni sulfides are longer than those of Ni chlorides.

The calculated bond lengths for NiHS(H₂O)₅ are 2.329 Å (Ni–S) and 2.13–2.15 Å (Ni–O), while those for trans-NiCl₂(H₂O)₄ are 2.10, 2.38, and Magini (1961) studies.

Species Method Bond, Ni–O/Å Bond, Ni–Cl/Å Reference
NiCl₂(H₂O)₄ XRD 2.056–2.072 2.43–2.468 Waizumi et al. (1999)
NiCl₂(H₂O)₄ ND 2.05 2.359 Kleinberg (1969)
NiCl₂(H₂O)₄ DFT 2.108–2.109 2.347 This work
NiCl₂(H₂O)₄ XRD 2.10 2.38 Mizuno (1961)
NiCl₂(H₂O)₄ DFT 2.11–2.13 2.289 This work
NiCl₂(H₂O)₄ CPCM: conductor-like polarizable continuum model.

Species Solvation G\text{hartree} G/kcal/mol ΔG/kcal/mol
cis None −2734.709375 −1716057.48 −1.91
trans None −2734.706336 −1716055.57 None
trans CPCM −2734.765972 −1716093.00 3.12
trans CPCM −2734.770484 −1716096.12

CPCM: conductor-like polarizable continuum model.

The structure of NiCO₃ was also computed as a single nickel atom in aqueous solutions. The crystal structures of anhydrous and hydrous NiSO₄ show the presence of NiSO₄(H₂O)₅ and NiSO₄(H₂O)₄ in sulfate solutions. At 298 K, NiSO₄(H₂O)₅ is predominant compared to NiSO₄(H₂O)₄ (Bechtold et al., 1978). The calculated structure of NiSO₄(H₂O)₅ agreed with a structural model proposed by Magini (1979) (see model b' reported on FeSO₄(H₂O)₅). The calculated bond lengths as well as the literature data are reported in Table 9. The calculated ln β value at 298 K is 5.877% (Table 6), which is 1.1–1.5% larger than those of Ni sulfides.

3.2.6. Nickel carbonate
Chemical behavior of Ni aqueous carbonates is less known (Hummel and Curti, 2003; Baeyens et al., 2003, and references therein). To our knowledge, structural data of monomers of NiHCO₃⁺ and NiCO₃ in aqueous solutions are not available. There are several crystallographic studies on polynuclear Ni complexes in metallocarbonate systems (for example, Wikstrom et al., 2010, and references therein), in which CO₃²⁻ acts as monodentate and/or bidentate ligands to Ni complexes. Here, we treated CO₃²⁻ as the bidentate ligand to Ni²⁺ and computed NiHCO₃⁺ as NiHCO₃(H₂O)₂⁺ according to a core structure of Ni carbonate complexes (see "coordination mode d" of Fig. 2 by Escuer et al., 1996). The structure of NiCO₃ was also computed as NiCO₃(H₂O)₄, in which H⁺ is dissociated from NiHCO₃(H₂O)₄. The ln β values of nickel carbonate complexes are compiled in Table 6. The ln β values (298 K) for NiHCO₃(H₂O)₄ and NiCO₃(H₂O)₄ were calculated to be 5.877% and 5.989% respectively. These are larger than those of Ni chlorides and sulfides, and are similar to that of sulfate.
of $\ln b$ between aqueous and organic phases, $\ln b$ was estimated. The analysis gives $\ln b$ for nickel monooxalate, $\text{NiC}_2\text{O}_4(\text{H}_2\text{O})_2$, and trans-$\text{NiCl}_2(\text{H}_2\text{O})_4$, the relative abundance of these species at each HCl molarity, and the measured $\delta^{60}$Ni fractionation between aqueous and organic phases, $\ln b$ of the Ni–DC18C6 complex was estimated. The analysis gives $\ln b = 4.177^{\circ}$ (Table 6) at 285 K, which is equivalent with $\ln b = 3.859^{\circ}$ at 298 K. In our experiment, the difference of $\ln b$ between the Ni–DC18C6 complex and other species (Ni$^{2+}$, NiCl$^+$, and NiCl$^2$) is measured as $\delta$Ni. As shown in Table 6, the difference in $\ln b$ is in the order of $\text{Ni}^{2+} > \text{NiCl}^+ > \text{NiCl}_2$. This suggests that the magnitude of $\delta$Ni decreases by promoting the complexion of Ni$^{2+}$ with Cl$^-$. Hence, it is natural that we observed smaller isotope fractionation at higher acidity as shown in Table 1.

### 3.2.7. Nickel macrocyclic compound

Some lipids in the archaeabacteria (Woese and Fox, 1977) have the structure of macrocyclic tetraether (Kushwaha et al., 1981). The isotopic fractionation of metals in macrocyclic compounds is hence of interest. Here, we estimate $\ln b$ of the Ni–DC18C6 complex in our chemical exchange experiment.

By using $\ln b$ (285 K) of Ni($\text{H}_2\text{O})_6^{2+}$, NiCl($\text{H}_2\text{O})_3^+$, and trans-$\text{NiCl}_2(\text{H}_2\text{O})_4$, the relative abundance of these species at each HCl molarity, and the measured $\delta^{60}$Ni fractionation between aqueous and organic phases, $\ln b$ of the Ni–DC18C6 complex was estimated. The analysis gives $\ln b = 4.177^{\circ}$ (Table 6) at 285 K, which is equivalent with $\ln b = 3.859^{\circ}$ at 298 K. In our experiment, the difference of $\ln b$ between the Ni–DC18C6 complex and other species (Ni$^{2+}$, NiCl$^+$, and NiCl$^2$) is measured as $\delta$Ni. As shown in Table 6, the difference in $\ln b$ is in the order of $\text{Ni}^{2+} > \text{NiCl}^+ > \text{NiCl}_2$. This suggests that the magnitude of $\delta$Ni decreases by promoting the complexion of Ni$^{2+}$ with Cl$^-$. Hence, it is natural that we observed smaller isotope fractionation at higher acidity as shown in Table 1.

### 3.2.8. Nickel carboxylate

The carboxyl group is a major functional group in humic acids (Schnitzer and Skinner, 1965) that control the reactions between cations and organic matters in groundwater. In seawater, it is known that reactions between amino acids, CO$_2$, and carbonates, can make soluble carbamino carboxylates (Neuberg et al., 1957). To enhance the knowledge on Ni isotope fractionation in reactions with organic ligands, we calculated $\ln b$ for nickel monooxalate, NiC$_2$O$_4(\text{H}_2\text{O})_4$, dioxalate (bisoxalate), Ni(C$_2$O$_4$)$_2(\text{H}_2\text{O})_2$, and trioxalate (trisoxalate), Ni(C$_2$O$_4$)$_3^-$, by the same quantum chemical calculations as described above. The molecular structures were computed based on published structural models (Krylov et al., 1976; Bickley et al., 1991). Only one trans-diaqua-bisoxalatobisnickel crystal structure, Ni(C$_2$O$_4$)$_2$($\text{H}_2\text{O})_2$, is available in the literature for dipotassium bisoxalatonicel, K$_2$[Ni(C$_2$O$_4$)$_2($H$_2$O)$_2$]-4H$_2$O (Román et al., 1993). The Ni–O bond lengths were reported to be 2.016 or 2.050 Å (C$_2$O$_4$) and 2.086 Å (H$_2$O). Our calculated Ni–O bond lengths are 2.038 Å (C$_2$O$_4$) and 2.224 Å (H$_2$O). The calculated Ni–O bond length is in good agreement with the crystal data for C$_2$O$_4$$.^2^$. The intramolecular vibrations of K$_2$[Ni(C$_2$O$_4$)$_2($H$_2$O)$_2$]-4H$_2$O was analyzed by Raman spectrometry (Bickley et al., 1991). Measurement of the symmetrical Ni–O ring stretch of Ni(C$_2$O$_4$)$_2$ gave a value of 583 cm$^{-1}$, which is in good agreement with our calculation of 560 cm$^{-1}$. The calculated $\ln b$ values are reported in Table 6. Complexation with C$_2$O$_4$ induces a decrease in $\ln b$, i.e., NiC$_2$O$_4(\text{H}_2\text{O})_4$ (6.348$^{\text{circ}}$) > Ni(C$_2$O$_4$)$_2$($\text{H}_2$O)$_2$ (5.872$^{\text{circ}}$) > Ni(C$_2$O$_4$)$_2$ (4.275$^{\text{circ}}$) at 298 K. In $\ln b$ of Ni oxalates is larger than that of Ni–compound. This may be due to the stronger electron affinity of oxalate ions to Ni$^{2+}$ (Watters and DeWitt, 1960) than that of oxygen donors of DC18C6.

### Table 9

<table>
<thead>
<tr>
<th>Species or media</th>
<th>Method</th>
<th>Bond, Ni–O/Å</th>
<th>Bond, Ni–S/Å</th>
<th>Bond, S–O/Å</th>
<th>Angle, Ni–S–O/°</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO$_4$(H$_2$O)$_3$</td>
<td>DFT</td>
<td>2.06–2.08$^a$</td>
<td>3.07</td>
<td>1.45–1.59</td>
<td>118</td>
<td>This work</td>
</tr>
<tr>
<td>1 M NiSO$_4$ + 2.88 M H$_2$SO$_4$</td>
<td>XRD</td>
<td>2.126</td>
<td>–</td>
<td>1.51$^b$</td>
<td>–</td>
<td>Caminiti (1982)</td>
</tr>
<tr>
<td>2 M NiSO$_4$</td>
<td>XRD</td>
<td>2.063</td>
<td>–</td>
<td>1.50$^b$</td>
<td>–</td>
<td>Caminiti (1982)</td>
</tr>
<tr>
<td>2 M NiSO$_4$</td>
<td>XRD</td>
<td>2.068</td>
<td>3.49</td>
<td>1.50$^b$</td>
<td>–</td>
<td>Licheri et al. (1984)</td>
</tr>
<tr>
<td>2 M NiSO$_4$</td>
<td>XRD</td>
<td>2.070</td>
<td>–</td>
<td>1.51$^b$</td>
<td>–</td>
<td>Licheri et al. (1984)</td>
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<tr>
<td>2 M NiSO$_4$</td>
<td>XRD</td>
<td>2.059</td>
<td>–</td>
<td>1.49$^b$</td>
<td>–</td>
<td>Caminiti (1986)</td>
</tr>
<tr>
<td>1.5 M NiSO$_4$ + 3.0 M H$_2$SO$_4$</td>
<td>XRD</td>
<td>2.059</td>
<td>–</td>
<td>1.51$^b$</td>
<td>–</td>
<td>Caminiti (1986)</td>
</tr>
<tr>
<td>Li$_2$SO$_4$</td>
<td>–$^c$</td>
<td>2.06$^c$</td>
<td>3.2–3.35$^c$</td>
<td>1.49$^c$</td>
<td>130–140$^c$</td>
<td>Caminiti (1986)</td>
</tr>
<tr>
<td>NiSO$_4$</td>
<td>XRD</td>
<td>1.99</td>
<td>3.13$^d$</td>
<td>1.53</td>
<td>125$^d$</td>
<td>Dimaras (1957)</td>
</tr>
<tr>
<td>NiSO$_4$</td>
<td>XRD</td>
<td>2.06</td>
<td>3.20$^d$</td>
<td>1.60</td>
<td>121$^d$</td>
<td>Dimaras (1957)</td>
</tr>
<tr>
<td>NiSO$_4$6H$_2$O</td>
<td>ND</td>
<td>2.02–2.10</td>
<td>–</td>
<td>1.48–1.46</td>
<td>–</td>
<td>O’connor and Dale (1966)</td>
</tr>
<tr>
<td>NiSO$_4$7H$_2$O</td>
<td>XRD</td>
<td>2.031–2.078</td>
<td>–</td>
<td>1.464–1.471</td>
<td>–</td>
<td>Pattanaik et al. (2007)</td>
</tr>
<tr>
<td>NiSO$_4$nH$_2$O</td>
<td>EXAFS</td>
<td>2.05</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ Ni–O bond length for the nearest O atom of SO$_4^{2-}$ in the first coordination sphere of Ni was converged to be 1.99 Å.

$^b$ Calculated from O–O distance of SO$_4^{2-}$ as it is the regular tetrahedron.

$^c$ Estimation for Ni sulfate.

$^d$ Calculated from lattice parameters.

### 3.3. Implications for Ni isotope systematics in the modern and ancient oceans

For all Ni species, the temperature dependence of $\ln b$ (Fig. 4) is estimated by using the relationship $\ln b (T) = \ln b (298) \times (298/T)^2$ with the $\ln b$ values at 298 K compiled in Table 6. The variation of $\ln b$ among inorganic species at 298 K is 1.7$^\text{circ}$ (Fig. 4a), while that among organic species at 298 K is 2.5$^\text{circ}$ (Fig. 4b). It is clear that exchange reactions between simple inorganic and organic ligands can create isotope fractionation reaching ~2.5$^\text{circ}$. This range encompasses the isotopic fractionation measured by Cameron et al. (2009) in methanogenic Archaea ($\delta^{60}$Ni up to...
Because of very low concentration,\[\text{Cl}^-\]in Archaean ocean. Marks show those in modern ocean.

For modern ocean, pH, \[\text{Cl}^-\]proposed by Walker (1983). Free \[\text{SO}_4^{2-}\]
the standard redox potential of reaction 17 at pH 8.22 (a typical modern seawater condition, Macleod et al., 1994) is estimated to be \(-0.29\) V in standard hydrogen electrode potential (Pourbaix, 1974). This is much smaller than \(E_h = 0.5\) V for typical modern seawater (Macleod et al., 1979), and hence the formation of \(\text{NiSH}^+\) is not considered.

To estimate the composition of Ni species and isotope fractionation between these, an appropriate combination of stability constants for reactions, 1 and 13–16 must be selected from literature data. Temperature of the modern ocean is around 291 K (global mean sea surface temperature), while that of the Archean has been reported to be up to 343 K (Robert and Chaussidon, 2006). Though the temperature difference affects the speciation and isotopic calculation, as a first approximation, we estimate them at a standard temperature, 298 K. The selected log \(K\) values are

\[\log K(\text{NiCl}^+) = 0.72\] (Turner et al., 1981), \(\log K(\text{NiOH}^+) = -9.86\) (Turner et al., 1981), \(\log K(\text{NiSO}_4^2-) = 0.9\) (Byrne et al., 1988), \(\log K(\text{NiHCO}_3^-) = 1.59\), and \(\log K(\text{NiCO}_3^-) = 3.57\) (Smith and Martell, 1976). These constants were determined for ionic strength \(I = 0.7\) M by using reported data (Zhorov et al., 1976). It should be noted that the \(K(\text{NiCl}^+)\) value used here is higher than that for HCl system (Bjerrum, 1988), while \(K(\text{NiSO}_4^2-)\) used here is smaller than the reported values obtained in laboratory experiments (Wasylkiewicz, 1990; Tsierezos and Molinou, 2000; Chen et al., 2005, and references therein). The uncertainty of \(K(\text{NiHCO}_3^-)\) and \(K(\text{NiCO}_3^-)\) is discussed in detail by Hummel and Culti (2003).

To guide future work in Ni isotope systematics, we have calculated the speciation and the isotopic fractionation of Ni in the Archean and modern oceans (Fig. 5). Our calculations do not take into account the presence of organic ligands with strong affinities for Ni. We predict the isotopic composition of the main species of Ni in condition relevant the Archean ocean.


\[
\begin{align*}
\text{Ni}^{2+} + \text{H}_2\text{O} & \rightleftharpoons \text{NiOH}^+ + \text{H}^+ \quad (13) \\
\text{Ni}^{2+} + \text{SO}_4^{2-} & \rightleftharpoons \text{NiSO}_4^- \\
\text{Ni}^{2+} + \text{HCO}_3^- & \rightleftharpoons \text{NiHCO}_3^- \\
\text{Ni}^{2+} + \text{CO}_3^{2-} & \rightleftharpoons \text{NiCO}_3^- 
\end{align*}
\]

and reaction 1 for \(\text{NiCl}^+\) are considered. For a seawater condition, \([\text{Ni}^{2+}]\) \(\sim 10^{-8}\) M and pH \(\sim 8\), higher order hydrolysis and polymerization (Baes and Mesmer, 1976; Hummel and Culti, 2003, and references therein), e.g., \(\text{Ni(OH)}_3^-, \text{Ni(OH)}_2^2-, \text{Ni}_2\text{OH}_3^-,\) and \(\text{Ni}_3\text{OH}_4^{4+}\), may be insignificant. Also higher order complexations of chloride and sulfate are not considered. Though there is a redox reaction between sulfide and sulfate ions as,

\[\text{H}_2\text{O} + \text{Ni}^{2+} + 2\text{SO}_4^{2-} \rightarrow \text{NiSO}_4^4\text{H}_2\text{O} + 2\text{H}^+\]

the activity coefficients of all species were set to be unity as a diluted system. (b) Isotope fractionations of Ni species compared to the naturally occurring isotope ratios. \(\delta^{60}\text{Ni}\) was estimated by using concentrations of Ni species shown in Fig. 5a and the in \(\beta\) values at 298 K shown in Table 6. Curves show estimated \(\delta^{60}\text{Ni}\) values of Ni species in Archaean ocean. Marks show those in modern ocean.
For the Archean ocean, the total concentration of Ni(II) was set to be 9 nM (Konhauser et al., 2009). Concentrations of H^+, SO_4^{2-}, HCO_3^-, and CO_3^{2-}, were read from Fig. 2 of Walker (1983). [OH^-] was estimated from [H^+] and the ion product of water at 298 K, −log K_W = 13.995 (Lide, 2008). Because of a very low expected concentration (Walker, 1983), [Cl^-] was not included in the speciation calculation.

For the modern ocean, the total concentration of Ni(II) was set to be 9 nM (Konhauser et al., 2009), and pH 8.22, m(Cl^-) = 0.55 mol/kg, and m(HCO_3^-) = 0.0020 mol/kg (Macleod et al., 1994) were used. [OH^-] was estimated from pH and the ion product of water (Lide, 2008). [CO_3^{2-}] was estimated using an equation given by Walker (1983) and log P(CO_2) = −3.44 (read from a figure by Macleod et al., 1994).

Concentrations of Ni species as functions of carbon dioxide partial pressure are plotted in Fig. 5a. For the modern ocean, our calculation results in mole fractions of Ni^[2+], NiCl^[+] (20%), NiCl^0 (57%), NiCO_3^[+] (19%), NiHCO_3^[+] (2%), and NiSO_4 (2%). Considering our simplified calculation, our results are in fairly good agreement with the results of Turner and Martinho (2006).

As an example for the condition of Archean ocean, at log P(CO_2) = −1, the mole fractions of Ni species are: Ni^[2+] (68%), NiCO_3^[+] (5%), NiHCO_3^[+] (24%), and NiSO_4 (3%). This indicates that the major species of Ni(II) in the Archean ocean would be hydrated Ni^[2+] and Ni carbones. Fig. 5b shows δ^{66}Ni for each Ni species. Heavier isotopes are fractionated in the order of NiCO_3 > NiSO_4 > NiHCO_3^[+] > NiOH^[+], whereas the inverse effect occurs in Ni^[2+] (and NiCl^[+]). This is the same order of ln β (Table 6). For example, NiCO_3 is enriched in heavy isotopes by ~0.6‰ compared to Ni^[2+].

Experimentally and theoretically, we have demonstrated that ligand exchange reactions can create Ni isotope fractionation of ~1.25‰/amu (2.5‰ for the δ^{66}Ni/δ^{59}Ni ratio). Therefore Ni isotope geochemistry might be used to trace the speciation of Ni in the ancient ocean.

4. CONCLUSION

In this study, we have investigated both theoretically and experimentally the isotopic fractionation of Ni at equilibrium between several species (hydrated Ni^[2+], hydroxides, chlorides, sulfides, sulfate, and carbonates) and organic ligands (crown ether and oxalic acid). The isotopic effect of the distribution of Ni between ligands relevant to the modern and ancient ocean chemistry is ~1.25‰/amu (2.5‰ for the δ^{66}Ni/δ^{59}Ni ratio), which is of the same magnitude as the isotopic fractionation created by methanogenic Archaea. Therefore, isotopic fractionation during the distribution of Ni between different species should not be neglected for the interpretation of the Ni isotopic record of sedimentary rocks.

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REFERENCES


Isotope fractionation of nickel 481


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