



# Equilibrium nickel isotope fractionation in nickel sulfide minerals

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Received 6 October 2016; accepted in revised form 15 October 2017

## Abstract

Nickel is an important element on Earth, and a major element in the Earth's core, and plays important roles in many geological and biological systems. As an important sink of Ni, Ni sulfides are closely concerned with Ni migration in magma systems and the genesis and evolution of magmatic sulfide deposits. Ni isotopes of Ni sulfides may be a powerful geochemical tracer in magmatic processes and evolution of magmatic sulfide deposits. However Ni isotope fractionation factors of sulfides remain poorly known, which makes the applications of Ni isotopes to geological problems associated with sulfides difficult. In this study, the first-principles methods are used to compute Ni isotope fractionation parameters of polydymite (Ni<sub>3</sub>S<sub>4</sub>), heazlewoodite (Ni<sub>3</sub>S<sub>2</sub>), millerite (NiS), godlevskite (Ni<sub>9</sub>S<sub>8</sub>) and vaesite (NiS<sub>2</sub>). The reduced partition function ratios of <sup>60</sup>Ni/<sup>58</sup>Ni ( $10^3 \ln \beta_{60-58}$ ) for these minerals decrease in the order of polydymite > heazlewoodite > millerite > godlevskite > vaesite. Ni isotope fractionations in these Ni sulfides show an approximately linear dependence on the average Ni–S bond lengths, and have a significant negative correlation with the average Ni–Ni bond lengths. Furthermore, a change in Fe/Ni ratio can also lead to Ni isotope fractionation, and with substitution Fe for Ni, the reduced partition function ratios of <sup>60</sup>Ni/<sup>58</sup>Ni decrease.

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**Keywords:** Ni isotopes; Equilibrium isotope fractionation; Sulfides; Density functional theory

## 1. INTRODUCTION

Nickel plays important roles in modern technology and industry, where it is mainly utilized for nickel steel (~46%), nonferrous alloy and superalloy (~34%), electroplating (~14%), and others (~6%) (Kuck, 2012). As a typical transition metal, Ni displays a mixture of ferrous and nonferrous metal properties (Aromaa, 2011), and plays special roles in some cases. It is a biologically-active element (Ragsdale, 2009) which is necessary for the biological reactions related to some geological processes (Ragsdale, 2007; Gall et al., 2012), and its evolution is closely concerned with the Earth's geochemistry (Zamble et al., 2017). As one of

the essential trace elements for some organisms (Rawlins et al., 2012), it could help us understand organic-rich sedimentary environments and be used as a tracer for crude oils (Lewan, 1984; Porter et al., 2014). It is a compatible element in magma systems, and plays important roles in the origin and evolution of mantle derived magmas (Song et al., 2009). Concentrations of Ni differ widely from the Earth's core to crust. Ni is present at about 5.35 wt.% in the core, 0.19 wt.% in the lower mantle, 0.20 wt.% in the upper mantle (Javoy et al., 2010), 88 µg/g in the lower continental crust, 33.5 µg/g in the middle continental crust, and 47 µg/g in the upper continental crust (Rudnick and Gao, 2014). The concentrations of Ni are also very different in different kinds of rocks. It is present at about 2000 mg/kg in ultrabasic rock, 130–140 mg/kg in basic rock, 50–70 mg/kg in shale, and 2–5 mg/kg in granite, sandstone and

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limestone (Reiman and De Caritat, 1998). The world's known Ni resources are very large, with approximately 60% in laterites and 40% in Ni sulfide deposits (Kuck, 2006).

Magmatic Ni sulfide deposits are closely related to ultramafic or mafic magmatism derived from the mantle (Naldrett, 2013). These deposits formed when immiscible sulfides segregated from host magmas which became saturated in sulfides, and then concentrated chalcophile elements from the silicate magmas (Naldrett, 2013). In magmatic Ni sulfide deposits, Ni sulfide minerals are very common. Several thermodynamically stable Ni sulfide phases are known, including millerite (NiS), polydymite (Ni<sub>3</sub>S<sub>4</sub>), heazlewoodite (Ni<sub>3</sub>S<sub>2</sub>), vaesite (NiS<sub>2</sub>) and godlevskite (Ni<sub>9</sub>S<sub>8</sub>) (Kerestedjian et al., 2007; Guillaume et al., 2008). Among them, millerite, vaesite, polydymite, and heazlewoodite are the most common Ni sulfides (Guillaume et al., 2008).

Because of their fundamental properties, industrial applications, and the close relation with Ni migration in magma systems, Ni sulfides have received considerable attention. Industrial interest has focused on nickel sulfide semiconductors for applications, such as solar cells (Kloprogge et al., 1993), supercapacitors (Du et al., 2014), rechargeable lithium batteries (Wang et al., 2007b), and photocatalysts (Meng et al., 2014). For Ni migration in magma systems, studies of Ni sulfides mainly focused on ore metal budgets and partitioning in the genesis and differentiation of magma (Li and Audétat, 2015), the diffusion of Ni from Ni-rich sulfides to give rise to anomalously high Ni content in olivine (Ishimaru and Arai, 2008), and formation of Ni sulfide deposits affected by the influence of crustal contamination on primary magma (Evans et al., 2000). In addition, Fe-Ni sulfides were likely to play crucial roles in the origin of life (e.g., Huber and Wächtershäuser, 1997; Huber et al., 2003).

Nickel has five stable isotopes, <sup>58</sup>Ni, <sup>60</sup>Ni, <sup>61</sup>Ni, <sup>62</sup>Ni, and <sup>64</sup>Ni, with relative abundances of 68.0769%, 26.2231%, 1.1399%, 3.6345%, and 0.9256%, respectively (Gramlich et al., 1989). Ni isotope analysis has shown potential for geological and planetary applications (Chernonozhkin et al., 2015). Ni isotope variations in extraterrestrial and terrestrial materials, including iron meteorites, chondrites, methanogens, Ni-sulfide-mineralised komatiites, igneous and mantle derived rocks, oceanic metalliferous deposits, continental sediments, organic-rich sediments, ferromanganese crusts, seawater, river water, soil, fly ash, smelting slags, and so on, have been reported in many studies (Moynier et al., 2007; Cook et al., 2008; Cameron et al., 2009; Gall et al., 2013; Gueguen et al., 2013; Cameron and Vance, 2014; Hofmann et al., 2014; Porter et al., 2014; Ratié et al., 2015, 2016; Gueguen et al., 2016). These studies have shown that Ni isotope signatures vary greatly depending on environmental conditions and Ni isotopes can be fractionated at high temperature. Early studies on Ni isotopes were primarily concentrated in extraterrestrial samples to help understand Ni isotope variations in the early solar system and planetary processes (e.g., Morand and Allègre, 1983; Moynier et al., 2007). Ni isotopes could also potentially

become useful geochemical tools to investigate the early life on the Earth (Cameron et al., 2009, 2012). Recently, Ni isotopes were utilized for tracing the weathering processes of continental rocks (Estrade et al., 2015; Ratié et al., 2015), the composition of ancient seawater (Wasylenko et al., 2015) and Ni cycling on the Earth (Ratié et al., 2015). In magmatic systems, Ni isotopes could potentially be applied as powerful tools to investigate high temperature processes (Lazar et al. 2012; Gueguen et al., 2013). Thus Ni isotopes could provide very useful tools for investigating many fundamental problems.

For interpreting isotope variations in natural systems, it is indispensable to determine the equilibrium isotope fractionation factors by laboratory experiments or theoretical calculations. Their temperature dependence is important to estimate the temperature of many geological processes (e.g., Lazar et al., 2012). Moreover, these factors are essential geochemical parameters for identifying isotopic equilibrium (e.g., Young et al., 2015). But for Ni isotopes, there are only a few studies providing the equilibrium fractionation factors. Fujii et al. (2011) studied equilibrium Ni isotope fractionations between some species which are connected with the modern and ancient oceans using laboratory experiments and theoretical calculations. Lazar et al. (2012) used the three-isotope method to investigate equilibrium Ni isotope fractionation between Ni-metal and Ni-talc in the temperature range of 500–950 °C under 8–13 kbar. Fujii et al. (2014) studied equilibrium Ni isotope fractionations in the inorganic species which are connected with the geochemical and biological environments based on density functional theory. Wasylenko et al. (2015) studied experimentally the equilibrium Ni isotope fractionation between solution and solid during adsorption of Ni onto ferrihydrite. Ni isotope fractionation factors obtained in these studies could be helpful for understanding the isotope variations of Ni observed in natural systems. Excepting the experimental work of Lazar et al. (2012), which could be applied in magmatic systems, the other three studies were related to surface waters. Ni isotope fractionation parameters relevant to numerous important geological processes have never been studied.

As far as we know, neither experimental calibrations nor theoretical calculations have been performed to determine the equilibrium Ni isotope fractionation factors in sulfide minerals. Laboratory experiments are challenging in that isotope exchange reactions may take a long time to reach equilibrium at low temperature, while at high temperature, thermal and chemical diffusion may cause kinetic fractionation (Richter et al., 2003, 2009; Huang et al., 2010). First-principles calculations could provide an important and useful tool for computing the fractionation factors of various stable isotopes between minerals (e.g., Méheut et al., 2007, 2009, 2010; Blanchard et al., 2009; Kowalski and Jahn, 2011; Schauble, 2011; Huang et al., 2013, 2014; Feng et al., 2014; Liu et al., 2014, 2015, 2016; Méheut and Schauble, 2014; Wu et al., 2015; Ducher et al., 2016; Qin et al., 2016). By adopting this method, we calculate equilibrium Ni isotope fractionation factors of undoped Ni sulfide minerals, and also calculate equilibrium Ni isotope fractionation factors of millerite, vaesite and

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