

Nickel isotopic composition of the mantle

Louise Gall^{a,b}, Helen M. Williams^c, Alex N. Halliday^b, Andrew C. Kerr^d

^aCIRES, University of Colorado, Boulder, CO–80309, USA

^bDepartment of Earth Sciences, University of Oxford, Oxford OX1 3JA, UK

^cDepartment of Earth Sciences, Durham University, Durham DH1 3LE, UK

^dSchool of Earth and Ocean Sciences, Cardiff University, Cardiff CF10 3AT, UK

Abstract

This paper presents the first detailed study of Ni isotope variations in mantle rocks of different types and origins. Ultramafic rocks display a relatively large range in $\delta^{60}\text{Ni}$ (permil deviation in $^{60}\text{Ni}/^{58}\text{Ni}$ relative to the NIST SRM 986 Ni isotope standard) from 0.15‰ to 0.36‰, with olivine-rich rocks such as dunite and olivine cumulates showing lighter isotope compositions than komatiite, lherzolite and pyroxenite. In order to understand these variations mineral separates from peridotite xenoliths have also been analysed. Olivine and orthopyroxene mineral separates display light $\delta^{60}\text{Ni}$ whereas clinopyroxene and garnet are isotopically heavy. This indicates that peridotite whole-rock $\delta^{60}\text{Ni}$ are a function of variations in mineralogy, suggesting that melts will have $\delta^{60}\text{Ni}$ that is dominated by variations in residual mantle and cumulate mineralogy. Based on fertile peridotite xenoliths and Phanerozoic komatiite samples it is concluded that the upper mantle has a relatively homogeneous Ni isotope composition, with our best estimate of $\delta^{60}\text{Ni}_{\text{mantle}}$ being $0.23 \pm 0.06\text{‰}$ (2 s.d.). Given that >99% of the Ni in the silicate Earth is located in the mantle, this also defines the Ni isotope composition of the bulk silicate Earth. This value is nearly identical to that of new measurements of a suite of chondrites and iron meteorites (mean $\delta^{60}\text{Ni} = 0.26 \pm 0.12\text{‰}$ and $0.29 \pm 0.10\text{‰}$, respectively) showing that the BSE is chondritic with respect to its Ni isotope

composition, with little to no Ni mass-dependent isotope fractionation resulting from core formation.

1. Introduction

Nickel is a first-row transition metal that, under mantle melting conditions, behaves as a strongly compatible element. The Earth's upper mantle have a mean Ni concentration of 2000 $\mu\text{g/g}$, which means this reservoir contains >99% of the silicate Earth's Ni inventory (McDonough and Sun, 1995; Palme and O' Neill, 2014). In mantle derived rocks Ni is primarily concentrated in olivine, the dominant silicate mineral in the upper mantle. In Mg-rich mantle olivine Ni^{2+} substitutes for Mg^{2+} in octahedral coordination, leading to olivine Ni concentrations of 3000 g/g (e.g. Sato, 1977; Stosch, 1981; Deer et al., 1982; Witt-Eickschen and O'Neill, 2005). Spinel is the only other mineral that can accommodate similar amounts of Ni, also predominantly in octahedral coordination (Stosch, 1981; Witt-Eickschen and O'Neill, 2005). However, as the modal abundance of spinel in upper mantle lithologies is <5%, its impact on the mantle Ni budget is minor. Orthopyroxene is the second most common mineral in the upper mantle and can hold smaller, but significant, amounts of Ni (<1000 $\mu\text{g/g}$), substituting into octahedral coordination space for Mg or Fe in the orthopyroxene lattice structure (Stosch, 1981; Deer et al., 1982; Witt-Eickschen and O'Neill, 2005). Nickel can also be found in lower concentrations (<500 $\mu\text{g/g}$) in clinopyroxene and garnet, also situated in octahedral coordination in both minerals (Witt-Eickschen and O'Neill, 2005). Mineral inclusions in diamond have provided a glimpse of the mineral composition of the lower mantle. Here Ni is generally concentrated in ferropericlase, the most abundant mineral, where it is present in amounts of 1–2.5 wt.% (Kaminsky, 2012). Nickel has also been found in its native form in many samples, which potentially is due to disproportionation of magnesio-wüstite into bridgmanite which produces Fe-Ni metal (Frost et al., 2004; Wade and Wood, 2005; Williams et al., 2012).

Nickel stable isotopes are a relatively new geochemical tracer that has not been evaluated in detail in terrestrial high-temperature environments. A number of studies have attempted to quantify the degree of Ni isotope variation in igneous rocks, including mantle derived materials (Cameron et al., 2009; Steele et al., 2011; Gall et al., 2012, 2013; Gueguen et al., 2013; Chernozhkin et al., 2015; Ratié et al., 2015; Estrade et al., 2015). However, most of this data are limited to rock standards or reference materials, and no systematic Ni stable isotope study of mantle rocks has been published. Other work on Ni stable isotopes in high-temperature environments has focused on meteorites (Cook et al., 2007; Moynier et al., 2007; Steele et al., 2011, 2012) and magmatic sulphide ore bearing bodies (Hofmann et al., 2014). Published data determines the range of $\delta^{60}\text{Ni}$ (the permil deviation in $^{60}\text{Ni}/^{58}\text{Ni}$ relative to the NIST SRM 986 Ni isotope standard) for mantle rocks to lie between -0.1‰ and 0.3‰. This study intend to investigate this, for this environment, surprisingly large variation in isotope composition. Our aim is to better define the Ni isotope composition of the mantle by presenting data from peridotite and komatiite samples of widely different origins, as well as mantle mineral separate data, and discussing these in context with published whole-rock data as well as new data from this study. Finally we aim to compare the isotope composition of the Bulk Silicate Earth (i.e. the mantle) to that of meteorites, to estimate the impact of core formation on the Ni isotope system on Earth. For this also chondrite and iron meteorite data is presented as well as compared to existing data on these types of samples.

2. Sample selection

2.1. Mantle xenoliths, peridotites and mineral separates

The ultramafic xenoliths used for this study are from the Neogene volcanic province in Northern Tanzania, a part of the eastern Rift Valley of East Africa. Most of the studied samples were collected from the Lashaine volcano, an area that has been well studied due to its carbonatite lavas and the presence of ultramafic xenoliths similar to those from kimberlites (e.g. Dawson et al., 1970; Cohen et al., 1984; Dawson, 2002). The analysed samples comprise two garnet lherzolites (BD730

and BD1355), three spinel harzburgites (BD774, BD822 and BD1542) and one alkaline pyroxenite (BD744). The garnet peridotites consist of varying proportions of red to purple garnet, emerald green clinopyroxene, orthopyroxene and magnesium-rich olivine (Fo_{90} for olivine from BD730), the latter without any signs of serpentinisation (Dawson et al., 1970). The spinel peridotites contain a much higher percentage of olivine (80-90 vol.% compared to 50-65 vol.% in the garnet peridotites) and lower amounts of orthopyroxene (5-12 vol.% versus 20-40 vol.% in the garnet peridotites), but similar amounts of clinopyroxene (1-3 vol.% only in both groups) (Dawson et al., 1970; Reid et al., 1975; Rhodes and Dawson, 1975). The pyroxenite sample consists of rounded iron-rich olivine (Fo_{84}), opaque phases (mainly chromite and magnetite), and clinopyroxene, surrounded by mica (Dawson and Smith, 1972). A kimberlite hosted garnet lherzolite xenolith from the Balfontain Mine in South Africa (e.g. Cardwell and Dawson, 1970) and a dunite from the Appalachian peridotite massif in Jackson County, N. Carolina, USA (e.g. Kulp and Brobst, 1954; Stueber, 1969), were also analysed as comparison to the volcanic xenoliths from Tanzania. The latter samples were both provided by the Natural History Museum in London. We have also analysed the USGS reference materials DTS-1 and PCC-1 for their Ni isotope compositions. The reference sample PCC-1 is a partially serpentinized harzburgite from the Cazadero ultramafic massif, California, USA (Flanagan, 1967, 1969; Barnes and O'Neil, 1969) and DTS-1 is a dunite sample from the Twin Sisters Mountain, Washington, USA (Flanagan, 1967, 1969; Ragan, 1963).

In addition to whole rock mantle xenoliths we have analysed mineral separates from mantle xenoliths from of the Cameroon Line. The analysed samples here come from four xenoliths collected from four different volcanic centres along the Cameroon Line. The analysed mineral separates consist of olivine, orthopyroxene (two samples each from two different spinel lherzolites; C235A, C273Q and P13), clinopyroxene (one separate from spinel lherzolite P13 and one from harzburgite N12) and garnet (one sample, a megacryst from harzburgite N12). The three spinel lherzolites analysed contains 45-65 vol.% olivine, 25-35 vol.% orthopyroxene, 10-15 vol.% clinopyroxene and <5 vol.% spinel, while the one harzburgite sample contains 55-60 vol.% olivine

and 40-45 vol.% orthopyroxene as well as megacrysts (<5%) of clinopyroxene and garnet (Lee et al., 1996). These mineral separates have previously been analysed for their Fe isotope compositions by Williams et al. (2005), who concluded that the minerals were largely in inter-mineral isotopic equilibrium. This was based on the constant offsets between the different phases from mantle xenoliths and massif samples. The observed differences are also broadly within the range of all other peridotite and pyroxenite xenoliths analysed, supporting that, within error, they represent Fe isotope equilibrium.

2.2. Komatiites

Komatiites are generated by extremely high-degree (35 to 50%) partial melting of the mantle. The occurrence of komatiites is largely restricted to Archean and early Proterozoic terranes, which is considered to reflect the higher ambient mantle temperatures at these times (e.g. Nisbet et al., 1993; Arndt et al., 2008). As large-degree partial melts komatiites approximate the chemical composition of their source, and thus have been used to constrain the composition of the mantle in several studies on Fe isotopes (e.g. Dauphin et al., 2010; Hibbert et al., 2012), on Mo isotopes (Greber et al., 2015) and on Cu isotopes (Savage et al., 2015).

The komatiites of Gorgona Island, Colombia, are the only documented occurrence of a Phanerozoic komatiite (dated at 90 Ma; Walker et al., 1999; Sinton et al., 1998). Being the youngest known example of komatiite these are also the texturally least altered specimens of this rock type available and have been well characterised in previous publications (e.g. Aitken and Echeverría, 1984; Arndt et al., 1997; Kerr et al., 1996; Kerr, 2005). The mineralogy of the Gorgona cumulates and komatiites consists of olivine, plagioclase, pyroxene, Cr-spinel and altered, devitrified glass, with the metamorphic grade not exceeding greenschist facies (Aitken and Echeverría, 1984). Some of the samples analysed in this study have previously been analysed for Fe isotopes by Hibbert et al. (2012).

2.3. Meteorites

For this study nine magmatic iron meteorites from six different meteorite classes were analysed (Negrillos and North Chile, IIA; Charcas and Henbury, IIIA; Sikhote-Alin, IIB; Arispe, IC; Clark County, IIIF; Gibeon and Duel Hill, IVA). Twelve chondrite meteorites from different classes were analysed, of which four were carbonaceous chondrites (Allende, CV3; Murchison, CM2; Orgueil, CI1; Ornans, CO3), two enstatite chondrites (Indarch, EH4; Khaipur, EL6) and six ordinary chondrites (Kernouve, H6; Baratta, H3; Bremervorde, L4; Buderheim, L6; Parnallee, LL3; St. Severin, LL6). All but three meteorites analysed were provided by the Natural History Museum, London; the three remaining meteorites were supplied by the Smithsonian National Museum, Washington D.C.

3. Methods

A comprehensive description of our procedures for Ni separation and isotope analysis can be found in Gall et al. (2012) with only a summary of the most important aspects given here.

All peridotite, komatiite and chondrite samples were dissolved in high-pressure Teflon bombs to assure complete dissolutions of all minerals phases. The samples were weighed into pre-cleaned Savillex high-pressure hexagon-cap vials and a mixture of concentrated HNO₃ and HF (1:5) was added to the powder after which the vial was sealed. The samples were then put in an oven (at 140°C) for two days after which the dissolutions were complete without residue. The mineral separate samples were weighed into pre-cleaned Savillex beakers and dissolved in a 1:5 mixture of concentrated HNO₃ and HF on a hotplate (130°C) overnight. Following digestion, the all silicate samples were dried and treated first with concentrated HNO₃ and then 6 M HCl to remove any remaining fluorides. To remove any contamination on the outer layers of the iron meteorites the solid samples were first polished with SiC paper and cleaned in MQ water, and then leached in cold 6 M HCl for 30 min. This last step was repeated 3 times, after which >90% of the samples still

remained. The cleaned iron meteorites were dissolved in 6 M HCl on a hotplate (120°C) overnight. Following complete dissolution, all samples were evaporated until dry and taken up in 6 M HCl before chromatography. A three stage column chromatographic technique was used to separate Ni from sample matrices, exploiting the ability of Ni to form strong complexes with firstly ammonia and secondly dimethylglyoxime. A final anion exchange cleanup column ensured removal of any Fe possibly remaining in the samples. The full procedural blank from this separation technique was less than 3 ng Ni, which is negligible compared to the amounts of Ni processed per sample (1000-3000 ng). The yield for mantle rocks and meteorites was close to 100%. We used the double-spike technique to ensure that any potential fractionation induced during the separation procedure was corrected for by spiking of all samples prior to chemical separation.

Nickel has five stable isotopes: ^{58}Ni , ^{60}Ni , ^{61}Ni , ^{62}Ni and ^{64}Ni , with the respective abundances of 68.08%, 26.22%, 1.14%, 3.63% and 0.93% Gramlich et al. (1989). A double-spike approach was used here for correction of instrumental mass bias, and, as discussed above, isotopic fractionation during sample processing. The double spike consisted of 25:75 ^{61}Ni : ^{62}Ni and was added to each sample at a sample:spike Ni ratio of 0.4. The purified Ni solutions were analysed using a Nu Plasma II (Nu Instruments) high-resolution multi-collector inductively coupled plasma mass spectrometer (MC-ICPMS) at Oxford University. Sample solutions of 100 ng/g Ni were introduced into the plasma in 0.3 M (2%) HNO_3 using a Nu Instruments DSN desolvator and a PFA concentric nebulizer (Elemental Scientific). Measurements consisted of 40 10-second integrations and baselines were measured by ESA deflection. The possible interference of ^{58}Fe on ^{58}Ni was corrected online through simultaneous measurement of ^{57}Fe . All analyses were performed at medium mass resolution mode (resolving power, $\Delta m/m \sim 3000$) to ensure that any polyatomic interferences were resolved. The mean beam intensity obtained under these conditions were 3 V on mass 58, or around 40 V per ppm Ni. The data reduction procedure of measured isotope ratios followed Siebert et al. (2001).

Most samples analysed during this study were digested twice and all processed solutions were analysed on at least 2 different occasions. Multiple full repeats and analyses of the USGS reference materials PCC-1 (15 individual analyses), BHVO-2 (35 analyses) and SCo-1 (16 analyses) gave a long term external reproducibility of 0.07‰ (2 s.d.) for silicate samples. All Ni isotope ratios reported here are presented as the $^{60}\text{Ni}/^{58}\text{Ni}$ ratio relative to the Ni isotope standard SRM 986 (NIST).

4. Results

All results are available in Table 1-3. The number of replicate analyses, n , for each sample is given in these tables and all uncertainties are reported as 2 standard deviations.

Results of peridotite and komatiite analyses are given in Table 1. The Ni isotope composition of the two USGS peridotite reference materials DTS-1 and PCC-1 were determined to be $-0.08 \pm 0.07\text{‰}$ and $0.14 \pm 0.06\text{‰}$ respectively. Our values for these rock standards are in excellent agreement with previously published data reported by Gueguen et al. (2013) (DTS-1: $-0.07 \pm 0.05\text{‰}$ and PCC-1: $0.12 \pm 0.05\text{‰}$) and Chernonozhkin et al. (2015) (DTS-1: $-0.07 \pm 0.01\text{‰}$ and PCC-1: $0.17 \pm 0.05\text{‰}$). There is a discrepancy with the $\delta^{60}\text{Ni}$ for PCC-1 reported by Cameron et al. (2009), who obtain a value nearly 0.20‰ heavier ($0.34 \pm 0.08\text{‰}$) than the other data. As this heavy value has not been replicated by either this study, Gueguen et al. (2013) or Chernonozhkin et al. (2015) it is not included in the discussion nor in the comparison of new and published data in Fig. 1.

The eight ultramafic samples display $\delta^{60}\text{Ni}$ ranging from 0.15‰ to 0.36‰. The dunite (NHM-1) exhibit the lowest $\delta^{60}\text{Ni}$ having a value of $0.15 \pm 0.07\text{‰}$. Two of the three harzburgite samples also display low values of $0.18 \pm 0.07\text{‰}$ (BD1542) and $0.20 \pm 0.03\text{‰}$ (BD822), while the last harzburgite (BD774) have a relatively high $\delta^{60}\text{Ni}$ of $0.28 \pm 0.06\text{‰}$. The two volcanic lherzolite xenoliths possess slightly higher $\delta^{60}\text{Ni}$ of $0.23 \pm 0.06\text{‰}$ (BD730) and $0.25 \pm 0.06\text{‰}$ (BD1355), with the kimberlite lherzolite xenolith (NHM-2) showing similar $\delta^{60}\text{Ni}$ of $0.22 \pm 0.06\text{‰}$. The single analysed pyroxenite xenolith (BD744) have a significantly higher $\delta^{60}\text{Ni}$ than all other samples:

0.36±0.08‰. The mean $\delta^{60}\text{Ni}$ value of all peridotite xenolith samples is 0.22±0.08‰ (i.e. excluding the pyroxenite and dunite samples).

The Gorgona samples show a similar range in $\delta^{60}\text{Ni}$ compared to the peridotite xenoliths, with $\delta^{60}\text{Ni}$ ranging from 0.15‰ to 0.26‰. The three olivine cumulate samples display lower $\delta^{60}\text{Ni}$ values of 0.15±0.05‰, 0.19±0.04‰ and 0.22±0.04‰ respectively, while the two komatiite samples show slightly higher $\delta^{60}\text{Ni}$ of 0.24±0.06‰ and 0.26±0.07‰.

Results of mineral separate sample analyses are given in Table 2. These analyses reveal that the measured mineral phases have distinctly different $\delta^{60}\text{Ni}$. Olivine range from 0.14±0.05‰ for sample C273Q to 0.17±0.05‰ for P13. Orthopyroxene show much lower values of -0.04±0.04‰ (C235A) and -0.02±0.06‰ (P13). The lherzolite clinopyroxene separate displayed an extremely high $\delta^{60}\text{Ni}$ of 2.83±0.11‰, while the harzburgite clinopyroxene sample is also heavy, though less extreme, at 0.42±0.08‰. The sole garnet analysed showed an intermediate isotopic composition of 0.30±0.06‰.

Results of meteorite analyses are given in Table 3. The Ni isotope composition of eight of the nine iron meteorites analysed show a range in $\delta^{60}\text{Ni}$ from 0.20‰ to 0.36‰, with no systematic variation between different sample groups being visible. The last iron meteorite sample (Duel Hill, IVA) display a significantly lower $\delta^{60}\text{Ni}$ of -0.06±0.06‰. Chondrite meteorites display a range in $\delta^{60}\text{Ni}$ similar to that of iron meteorites. Of the carbonaceous chondrites the CI1 chondrite Orgueil showed the lowest value of 0.18±0.04‰, Allende and Murchison (CV3 and CM2, respectively) possess very similar values of 0.24±0.07‰ and 0.23±0.07‰, respectively, whereas Ornans (CO3) display a slightly higher value of 0.29±0.08‰. The two enstatite chondrites Indarch (EH4) and Khaipur (EL6) display very similar values of 0.28±0.09‰ and 0.29±0.08‰. The most variation in $\delta^{60}\text{Ni}$ within chondrite meteorites is found amongst ordinary chondrites. This group of six samples (two each from the H, L and LL classes) display $\delta^{60}\text{Ni}$ values varying between 0.16±0.05‰ and 0.51±0.07‰.

5. Discussion

5.1. Evidence for mineralogical control on $\delta^{60}\text{Ni}$ variations in mantle rocks

The data from mineral separates demonstrate a significant degree of high temperature Ni isotopic fractionation in mantle rocks. The two orthopyroxene separates are significantly lighter isotopically than the two olivine separates and both olivine and orthopyroxene separates are isotopically light relative to heavy clinopyroxene and garnet (Fig. 1). Nickel is situated in the same position (replacing Mg in octahedral coordination) in all the analysed minerals, therefore their different isotope compositions cannot be due to the crystallographic differences between the minerals. The analyses of all main three silicate phases (olivine, orthopyroxene and clinopyroxene) of the spinel lherzolite sample P13 are especially interesting. Although the co-existing spinel (5% modal mineralogy of sample, Lee et al. (1996); Table 2) was not analysed an approximative isotopic composition of the bulk sample could be calculated to be $\delta^{60}\text{Ni} = 0.25 \pm 0.13\%$ (the comparatively large error on this value reflects the propagation of errors on individual mineral separate analyses). This value is consistent with data from other peridotites. The same mineral separates from sample P13 were also analysed for their Fe isotope composition by Williams et al. (2005) (see supplemental table for $\delta^{57}\text{Fe}$ values), who determined them to be in inter-mineral isotope equilibrium for Fe isotopes. The calculated Fe isotope composition from these mineral separate analyses was determined to be $0.15 \pm 0.18\%$, which also overlaps with mantle $\delta^{57}\text{Fe}$ values (e.g. Dauphas et al., 2009). Furthermore, the trace-element abundances of this sample demonstrate its primitive, unmetasomatised nature (Lee et al., 1996). Therefore, there is no indication that this sample or its calculated bulk isotope composition is anomalous. It is however possible that the extremely heavy isotope composition of the P13 clinopyroxene represent kinetic isotope fractionation rather than equilibrium fractionation. While Fe isotopes do appear to record inter mineral isotope equilibrium for this sample the mass balance of Fe and Ni is very different in mantle rocks, making it possible for kinetic isotope composition to be preserved for Ni isotopes. Considering that the other clinopyroxene analysis (from harzburgite N12; $0.42 \pm 0.08\%$) and the analysis of a pyroxenite

xenolith (BD744; $0.36 \pm 0.08\%$) both also are significantly heavier than all other minerals and bulk rocks, it must be concluded that an isotopically heavy composition for clinopyroxene in mantle rocks is real. If the P13 clinopyroxene does represent equilibrium isotope fractionation the heavy Ni isotope composition of the P13 clinopyroxene separate effectively demonstrates that the potential impact of modal mineralogy on the bulk Ni isotope compositions of mantle rock is significant.

Figure 2 shows the modal mineral abundances of olivine, orthopyroxene and clinopyroxene in the Tanzanian xenolith samples plotted against their whole-rock $\delta^{60}\text{Ni}$. There is a striking positive correlation between whole-rock $\delta^{60}\text{Ni}$ and the modal abundance of clinopyroxene, with the isotopically heaviest sample containing the most clinopyroxene. This figure also shows that the heavy harzburgite (BD774) contains 2-3 times as much clinopyroxene as the other two harzburgite samples. This indicates that, although the majority of Ni in mantle rocks is located in olivine, whole-rock Ni isotope compositions are strongly dependent on the proportion of clinopyroxene. From the very strong preference of clinopyroxene for isotopically heavy Ni (Fig. 1, Table 2) this is entirely understandable.

A compilation of all the available $\delta^{60}\text{Ni}$ data of ultramafic rocks divided according to sample type is also shown in Fig. 1. Previously published data for unaltered peridotite samples are all analyses of the rock reference material PCC-1, DTS-1, DTS-2 (USGS) and JP-1 (GJS) (Steele et al., 2011; Gueguen et al., 2013; Chernonozhkin et al., 2015). The USGS reference sample PCC-1 is a harzburgite (Cazadero ultramafic massif, California) and DTS-1, -2 (Twin Sisters Mountain, Washington) and JP-1 (Horoman dunite, Japan; Imai et al., 1995) are dunites. All these reference materials are from Alpine-type ultramafic massifs, similar to the Appalachian dunite NHM-1 analysed during this study. All the analyses of dunites and most of the harzburgites show these depleted olivine-rich rock types have light Ni isotope compositions relative to lherzolites (Fig. 1). This is entirely consistent with our mineral Ni isotope data. One other possibility is that the low $\delta^{60}\text{Ni}$ signatures of the peridotite massif samples (PCC-1, DTS-1 and -2, JP-1 and NHM-1) reflect secondary alteration processes, such as serpentinization. To evaluate this possibility we have also

plotted published data for serpentinized peridotites in Fig. 1. These samples come from four different locations: the Logatchev hydrothermal field on the mid-Atlantic ridge (Gueguen et al., 2013), the Cerro Matoso laterite deposit, Colombia (Gall et al., 2013), the Barro Alto ultramafic massif, Brazil (Ratié et al., 2015), and the ophiolitic belt in Albania (Estrade et al., 2015). All but one of these samples display $\delta^{60}\text{Ni}$ similar to fresh peridotite xenoliths, varying between 0.09‰ and 0.32‰. This suggests that $\delta^{60}\text{Ni}$ in peridotites is not significantly affected by serpentinization and that such processes cannot be responsible for the large range in $\delta^{60}\text{Ni}$ found in mantle rocks.

Our data demonstrate that whole-rock $\delta^{60}\text{Ni}$ variations likely reflect mineral isotope fractionation effects and indicate the influence this has on bulk cumulate compositions and melt depleted residues. For example, olivine-rich cumulate komatiites from Gorgona display lower $\delta^{60}\text{Ni}$ relative to the primitive komatiite samples from the same suite and dunites and harzburgites appear to be isotopically lighter than lherzolites (Fig. 1). Similarly, if clinopyroxene is isotopically heavy, melt extraction will generate depleted mantle residues with light Ni isotope composition relative to fertile mantle material. This is because of the non-modal nature of partial melting processes and the preferential contribution of clinopyroxene to the melting assemblage. Therefore, a best estimate of the primitive mantle $\delta^{60}\text{Ni}$ may be defined by the composition of the three lherzolites (two from Lashaine volcano and one from a South African kimberlite) and the two Gorgona komatiite samples. This yields a $\delta^{60}\text{Ni}_{\text{mantle}}$ value of $0.23 \pm 0.06\text{‰}$ (mean and 2 s.d. of all measurements of these samples). The calculated bulk rock $\delta^{60}\text{Ni}$ for the fertile lherzolite sample P13 ($0.25 \pm 0.13\text{‰}$) is also in excellent agreement with this narrower $\delta^{60}\text{Ni}$ estimate for the mantle.

Published ^{57}Fe data exist for the Gorgona komatiites (data from Hibbert et al., 2012) the ultramafic reference materials PCC-1, DTS-2 (from Dauphas et al., 2009), DTS-1 and JP-1 (from Poitrasson et al., 2004) and for the mineral separates from spinel lherzolite P13 (from Williams et al., 2005). When these data are plotted against $\delta^{60}\text{Ni}$ a clear positive relationship is observed for all but one of the whole-rock samples ($R^2 = 0.936$; Fig. 3). The isotopically heaviest samples for both Ni and Fe are the komatiites, while olivine-rich cumulates and rocks have lower $\delta^{60}\text{Ni}$ and $\delta^{57}\text{Fe}$

values. The mineral separates (olivine and orthopyroxene) as well as the reconstructed composition of P13 are also plotted in Fig. 3. The calculated composition for this sample ($\delta^{60}\text{Ni}_{\text{P13}} = 0.25 \pm 0.13\text{‰}$ and $\delta^{57}\text{Fe}_{\text{P13}} = 0.15 \pm 0.18\text{‰}$) plots together with the komatiites at the heavier end of the spectrum, another indication of this sample's fertility. The olivine separate from sample P13 plots along the trend next to the Gorgona olivine cumulates. However, the P13 orthopyroxene separate has a very low $\delta^{60}\text{Ni}$ given its relatively high $\delta^{57}\text{Fe}$ and thus does not fall on the trend. On the other hand, the P13 orthopyroxene overlaps with the only whole-rock sample (DTS-1) that does not follow the general trend (Fig. 3), possibly indicating a higher prevalence of orthopyroxene in this sample. The $\delta^{57}\text{Fe}$ of the P13 clinopyroxene separate is heavier than the values for olivine and orthopyroxene (see insert on Fig. 3), although due to its extremely high $\delta^{60}\text{Ni}$ this mineral plots far from the general $\delta^{60}\text{Ni}$ – $\delta^{57}\text{Fe}$ trend seen in Fig. 3. This relationship therefore appears to be controlled by accumulation of isotopically light olivine due to melt extraction or fractional crystallisation. This further supports our observation that $\delta^{60}\text{Ni}$ in mantle rocks is related to sample mineralogy.

5.2. Isotope composition of the BSE, meteorites and Ni isotope fractionation during core formation

Given that >99% of the Ni in the silicate Earth is located in the mantle, our value of $\delta^{60}\text{Ni}_{\text{mantle}}$ of $0.23 \pm 0.06\text{‰}$ is also the best estimate for the BSE. This is in good agreement with the previously suggested value of $0.18 \pm 0.04\text{‰}$ by Steele et al. (2011) and well overlapping with the $0.15 \pm 0.24\text{‰}$ proposed by Cameron et al. (2009), while a third estimate of $0.05 \pm 0.05\text{‰}$ by Gueguen et al. (2013) is significantly lighter than all of these. All these studies however incorporate data for altered mantle and fractionated crustal rocks in their estimates. In contrast, the BSE estimate presented in this study is entirely based on fertile mantle rocks (gt-lherzolite and komatiite). Considering the evidence given for a mineralogical control on the Ni isotope composition, this new

estimate should represent a more accurate evaluation of the mean Ni isotopic composition of the Bulk Silicate Earth.

Our data for chondritic meteorites give this group a mean $\delta^{60}\text{Ni}$ of $0.26\pm 0.12\text{‰}$ (Fig. 4), excluding the significantly heavier sample Bruderheim (0.51‰). This ordinary chondrite has been noted to have large mineralogical variations even in small samples (Duke et al., 1961) making it difficult to be certain that the $\delta^{60}\text{Ni}$ measured here is representative of its actual isotope composition. Especially considering the indications for a mineralogical control of a sample's Ni isotopic composition. Our mean $\delta^{60}\text{Ni}$ value for chondrites is in excellent agreement with published values by Cameron et al. (2009) and Steele et al. (2012), who found $\delta^{60}\text{Ni}$ in chondrites to vary between 0.18‰ and 0.33‰ (Fig. 6).

Comparison of both published chondrite data and those presented in this study with our estimated $\delta^{60}\text{Ni}_{\text{BSE}}$ suggests that the BSE is chondritic with respect to its Ni isotope composition. The mass-dependent Ni isotope data of chondrites from Moynier et al. (2007) and Cook et al. (2007) are not included in this comparison. This is because almost all data from these studies are from measurements of chondrite metal separates and not whole-rock samples. The only exception to this are two measurements of bulk silicate samples in Moynier et al. (2007), one of Allende (CV3 chondrite) and one of Murchison (CM2 chondrite). These data are however significantly lighter (approximately -0.2‰ , Fig. 6) than both ours' and Cameron et al. (2009)'s analyses of the same chondrite samples. This is probably due to the chemical separation technique used by Moynier et al. (2007), from which the Ni yield was only about 80% for silicates. As none of these analyses, nor those of Cook et al. (2007), used the double-spike technique, any stable isotope fractionation relating to chemical processing may not have been corrected for. Additionally, errors on measurements performed in these two studies are significantly larger (estimated $\pm 0.14\text{‰}$ and up to $\pm 0.80\text{‰}$ on $\delta^{60}\text{Ni}$ data from Moynier et al. and Cook et al. respectively; Fig. 6) than for the data presented here or other more recently published data, making comparisons with more precise data difficult.

Our analyses of iron meteorites give a mean $\delta^{60}\text{Ni}$ of $0.29 \pm 0.10\%$, omitting the very light iron meteorite Duel Hill ($-0.06 \pm 0.06\%$). The reason for excluding this sample is its very low concentration of the siderophile elements Ir and W, combined with very high concentrations of chalcophile elements, e.g. Au, As, Cu and Ni (Wasson and Richardson, 2001). This suggests that this iron meteorite may contain a high amount of sulphide. Considering that published data have shown terrestrial sulphides to have very light Ni isotope compositions (as low as -1.03% Gueguen et al., 2013) it is possible that a sulphide component could contribute to Duel Hill's light isotopic composition. Excluding this sample our data for iron meteorites are in very good agreement with published data from Cameron et al. (2009); Steele et al. (2011); Gueguen et al. (2013) and Chernonozhkin et al. (2015). The Ni isotope data from Moynier et al. (2007) and Cook et al. (2007) are, again, spread over a much wider range than any other published data (Fig. 6), although this may in part be due to the wider range of samples, such as nonmagmatic iron meteorites, included in these studies.

It has recently been shown that the BSE has a chondritic stable isotope composition for Mo (Greber et al., 2015) and for Cr (Bonnand et al., 2015) (contrary to earlier suggestions by Hin et al., 2013; Burkhardt et al., 2014; Moynier et al., 2011). On the other hand, the BSE is non-chondritic for Si stable isotopes (ascribed to core formation by Armytage et al., 2011), and also for V isotopes (Prytulak et al., 2013; Nielsen et al., 2014), for reasons that remain unclear. The similarity in mean $\delta^{60}\text{Ni}$ between chondrites, iron meteorites and the BSE indicates that, in the case of Ni isotopes, core formation was not accompanied by any measurable isotope fractionation. This conclusion is entirely consistent with the study by Lazar et al. (2012), based on solid metal-talc Ni isotope fractionation experiments. These authors found that even though the metal appears to be consistently slightly isotopically heavier than the silicate phase, the fractionation factor is minor at core-mantle boundary conditions ($\Delta^{60}\text{Ni} = 0.02\%$ at 2500 K). The authors also noted that metal-silicate isotope fractionation appear to be temperature dependant. When using their expression for this ($\Delta^{62}\text{Ni}_{\text{metal-talc}} = 0.25(\pm 0.02) \times 10^6/T^2 (\pm 2 \text{ s.e.})$) to calculate the fractionation factor at mantle

temperatures $\Delta^{60}\text{Ni}$ varies between 0.04 and 0.09‰ for temperatures from 1400 down to 900°C (Fig. 7). If basing the fractionation factor on our $\delta^{60}\text{Ni}$ data for the BSE and iron meteorites $\Delta^{60}\text{Ni}$ becomes 0.056‰ (± 0.06 ; s.d.), which would correspond to a temperature of at least 1200°C (Fig. 7). The similarity in isotope composition for chondrites and iron meteorites however would imply that iron meteorites were all formed in equilibrium with silicate mantled at high temperatures, with no Rayleigh effects preserved. This supports the concept of iron meteorites as relict planetary cores and not impact melts.

6. Conclusions

1. Our data show that the upper mantle is variable in its Ni isotope composition, with a mean value of 0.23‰.
2. There are systematic variations in $\delta^{60}\text{Ni}$ between different mantle minerals, with olivine and orthopyroxene being significantly lighter than clinopyroxene and garnet, suggesting that mantle rock Ni isotope composition may be controlled by differences in mineralogy caused by cumulate effects due to melt extraction and fractional crystallisation.
3. There is a relationship between $\delta^{57}\text{Fe}$ and $\delta^{60}\text{Ni}$ in ultramafic rocks related to mineralogy, with lighter values of both isotope systems recorded in olivine-rich dunite and harzburgite and heavier values shown in more fertile material.
4. Our best estimate for the $\delta^{60}\text{Ni}_{\text{BSE}}$ is 0.23 ± 0.06 ‰ based solely on lherzolite xenoliths and Phanerozoic komatiites. This is in good agreement with previously suggested values of by Cameron et al. (2009) and Steele et al. (2011) but heavier than the value proposed by Gueguen et al. (2013).
5. Comparison between our BSE value and Ni isotope data for meteorites indicates that the BSE is chondritic and that core formation did not generate any measurable Ni isotope fractionation.

6. Iron meteorites generally display chondritic $\delta^{60}\text{Ni}$, with a mean of $0.29 \pm 0.10\%$. However, Duel Hill is very light ($-0.06 \pm 0.06\%$), which is likely related to a high sulphide component of this sample.

6. Acknowledgements

We are indebted to all those who have supplied samples for this study. The Natural History Museum, London, and the Smithsonian National Museum of Natural History, Washington, are thanked for contributing meteorite samples, the late J.B. Dawson and Richard Herrington for peridotite samples. Thanks to Nick Belshaw, Theodor Krastev and Phil Holdship for their invaluable technical assistance with the analyses. We would like to thank Tim Elliot and Ambre Luguët for their comments on earlier versions of the manuscript. We would also like to thank the editor and three reviewers for their valuable comments and criticisms of the manuscript. We would like to acknowledge funding by the UK Science and Technology Facilities Council and the European Research Council (Starting Grant 306655). Helen Williams acknowledges Advanced NERC Fellowship NE/F014295/2.

References

- Aitken, B. G., Echeverría, L. M., 1984. Petrology and geochemistry of komatiites and tholeiites from Gorgona Island, Colombia. *Contributions to Mineralogy and Petrology* 86 (1), 94–105.
- Armytage, R. M. G., Georg, R. B., Savage, P. S., Williams, H. M., Halliday, A. N., 2011. Silicon isotopes in meteorites and planetary core formation. *Geochimica et Cosmochimica Acta* 75 (13), 3662–3676.
- Arndt, N., Lesher, C. M., Barnes, S. J., 2008. *Komatiite*. Cambridge University Press.
- Arndt, N. T., Kerr, A. C., Tarney, J., 1997. Dynamic melting in plume heads: the formation of Gorgona komatiites and basalts. *Earth and Planetary Science Letters* 146 (1-2), 289–301.
- Barnes, I., O’Niel, J. R., 1969. The Relationship between Fluids in Some Fresh Alpine-Type Ultramafics and Possible Modern Serpentinization. Western United States. *Geol. Soc. America Bulletin* 80, 1947–1960.
- Bonnand, P., Williams, H. M., Parkinson, I. J., J, W. B., Halliday, A. N., 2015. Stable chromium isotopic composition of meteorites and metal-silicate experiments: implications for fractionation during core formation. *Earth and Planetary Science Letters* 435, 14–21.
- Burkhardt, C., Hin, R. C., Kleine, T., Bourdon, B., 2014. Evidence for Mo isotope fractionation in the solar nebula and during planetary differentiation. *Earth and Planetary Science Letters* 391, 201–211.

Cameron, V., Vance, D., Archer, C., House, C. H., 2009. A biomarker based on the stable isotopes of nickel. *Proceedings of the National Academy of Sciences* 106 (27), 10944–10948.

Carswell, D. A., Dawson, J. B., 1970. Garnet peridotite xenoliths in South African kimberlite pipes and their petrogenesis. *Contributions to Mineralogy and Petrology* 25, 163–184.

Chernonozhkin, S. M., Goderis, S., Lobo, L., Claeys, P., Vanhaecke, F., 2015. Development of an isolation procedure and MC-ICP-MS measurement protocol for the study of stable isotope ratio variations of nickel. *Journal of Analytical Atomic Spectrometry* 30, 1518–1530.

Cohen, R. S., O’Nions, R. K., Dawson, J. B., 1984. Isotope geochemistry of xenoliths from East Africa: implications for development of mantle reservoirs and their interaction. *Earth and Planetary Science Letters* 68, 209–220.

Cook, D. L., Wadhwa, M., Clayton, R. N., Dauphas, N., Janney, P. E., Davis, A. M., 2007. Mass-dependent fractionation of nickel isotopes in meteoritic metal. *Meteoritics & Planetary Science* 42 (12), 2067–2077.

Dauphas, N., Craddock, P. R., Asimow, P. D., Bennett, V. C., Nutman, A. P., Ohnenstetter, D., 2009. Iron isotopes may reveal the redox conditions of mantle melting from Archean to Present. *Earth and Planetary Science Letters* 288 (1-2), 255–267.

Dauphas, N., Teng, F.-Z., Arndt, N. T., 2010. Magnesium and iron isotopes in 2.7 Ga Alexo komatiites: Mantle signatures, no evidence for Soret diffusion, and identification of diffusive transport in zoned olivine. *Geochimica et Cosmochimica Acta* 74 (11), 3274–3291.

Dawson, J. B., 2002. Metasomatism and partial melting in upper-mantle peridotite xenoliths from the Lashaine volcano, northern Tanzania. *Journal of Petrology* 43, 1749–1777. Dawson, J. B., Powell, D. G., Reid, A. M., 1970. Ultrabasic Xenoliths and Lava from the Lashaine Volcano, Northern Tanzania. *Journal of Petrology* 11 (3), 519–548.

Dawson, J. B., Smith, J. V., 1972. Alkalic Pyroxenite Xenoliths from the Lashaine Volcano, Northern Tanzania. *Journal of Petrology* 14 (1), 113–131.

Deer, W. A., Howie, R. A., Zussman, J., 1982. *Rock Forming Minerals*, 2nd Edition. Vol. 1A and 2A. Longman.

Duke, M., Maynes, D., Brown, H., 1961. The petrography and chemical composition of the Bruderheim meteorite. *Journal of Geophysical Research* 66 (10), 3557–3563.

Estrade, N., Cloquet, C., Echevarria, G., Sterckeman, T., Deng, T., Tang, Y., Morel, J.-L., 2015. Weathering and vegetation controls on nickel isotope fractionation in surface ultramafic environments (Albania). *Earth and Planetary Science Letters* 423 (C), 24–35.

Flanagan, F. J., 1967. US Geological Survey silicate rock standards. *Geochimica et Cosmochimica Acta* 31, 289–308.

Flanagan, F. J., 1969. US Geological Survey standards II. First compilation of data for the new USGS rocks. *Geochimica et Cosmochimica Acta* 33, 81–120.

Frost, D. J., Liebske, C., Langenhorst, F., A, M. C., 2004. Experimental evidence for the existence of iron-rich metal in the Earth's lower mantle. *Nature* 428, 409–412.

Gall, L., Williams, H., Siebert, C., Halliday, A., 2012. Determination of mass-dependent variations in nickel isotope compositions using double spiking and MC-ICPMS. *Journal of Analytical Atomic Spectrometry* 27, 137.

Gall, L., Williams, H. M., Siebert, C., Halliday, A. N., Herrington, R. J., Hein, J. R., 2013. Nickel isotopic compositions of ferromanganese crusts and the constancy of deep ocean inputs and continental weathering effects over the Cenozoic. *Earth and Planetary Science Letters* 375, 148–155.

Gramlich, J. W., Beary, E. S., Machlan, L. A., Barnes, I. L., 1989. The absolute isotopic composition and atomic weight of terrestrial nickel. *Journal of Research of the National Institute of Standards and Technology* 94 (6), 357.

Greber, N. D., Puchtel, I. S., Nägler, T. F., Mezger, K., 2015. Komatiites constrain molybdenum isotope composition of the Earth's mantle. *Earth and Planetary Science Letters* 421 (C), 129–138.

Gueguen, B., Rouxel, O., Ponzevera, E., 2013. Nickel Isotope Variations in Terrestrial Silicate Rocks and Geological Reference Materials Measured by MC-ICP-MS. *Geostandards and Geoanalytical Research*.

Hibbert, K. E. J., Williams, H. M., Kerr, A. C., Puchtel, I. S., 2012. Iron isotopes in ancient and modern komatiites: Evidence in support of an oxidised mantle from Archean to present. *Earth and Planetary Science Letters* 321-322, 198–207.

Hin, R. C., Burkhardt, C., Schmidt, M. W., Bourdon, B., Kleine, T., 2013. Experimental evidence for Mo isotope fractionation between metal and silicate liquids. *Earth and Planetary Science Letters* 379, 38–48.

Hofmann, A., Bekker, A., Dirks, P., Gueguen, B., 2014. Comparing orthomagmatic and hydrothermal mineralization models for komatiite-hosted nickel deposits in Zimbabwe using multiple-sulfur, iron, and nickel isotope data. *Mineralium Deposita*.

Imai, N., Terashima, S., Itoh, S., Ando, A., 1995. 1994 compilation values for GSJ reference samples, "Igneous rock series". *Geochemical Journal* 29 (1), 91–95.

Kaminsky, F., 2012. Mineralogy of the lower mantle: a review of 'super-deep' mineral inclusion in diamond. *Earth Science Reviews* 110, 127–147.

Kerr, A. C., 2005. La Isla de Gorgona, Colombia: A petrological enigma? *Lithos* 84 (1-2), 77–101.

Kerr, A. C., Marriner, G. F., Arndt, N. T., Tarney, J., Nivia, A., Saunders, A. D., Duncan, R. A., 1996. The petrogenesis of Gorgona komatiites, picrites and basalts: new field, petrographic and geochemical constraints. *Lithos* 37 (2-3), 245–260.

Kulp, J. L., Brobst, D. A., 1954. Notes on the dunite and the geochemistry of vermiculite at the Day Book dunite deposit, Yancey County, North Carolina. *Economic Geology* 49 (3), 211–220.

Lazar, C., Young, E. D., Manning, C. E., 2012. Experimental determination of equilibrium nickel isotope fractionation between metal and silicate from 500°C to 950°C. *Geochimica et Cosmochimica Acta* 86 (C), 276–295.

Lee, D. C., Halliday, A. N., Davies, G. R., Essene, E. J., Fitton, J. G., Temdjim, R., 1996. Melt Enrichment of Shallow Depleted Mantle: a Detailed Petrological, Trace Element and Isotopic Study of Mantle-Derived Xenoliths and Megacrysts from the Cameroon Line. *Journal of Petrology* 37 (2), 415–441.

McDonough, W. F., Sun, S. S., 1995. The composition of the Earth. *Chemical Geology* 120 (3-4), 223–253.

Moynier, F., Blichert-Toft, J., Télouk, P., Luck, J. M., 2007. Comparative stable isotope geochemistry of Ni, Cu, Zn, and Fe in chondrites and iron meteorites. *Geochimica et Cosmochimica Acta* 71, 4365–4379.

Moynier, F., Yin, Q.-Z., Schauble, E., 2011. Isotopic Evidence of Cr Partitioning into Earth's Core. *Science* 331 (6023), 1417–1420.

Nielsen, S. G., Prytulak, J., Wood, B. J., Halliday, A. N., 2014. Vanadium isotopic difference between the silicate Earth and meteorites. *Earth and Planetary Science Letters* 389, 167–175.

Nisbet, E. G., Cheadle, M. J., Arndt, N. T., Bickle, M. J., 1993. Constraining the potential temperature of the Archaean mantle: A review of the evidence from komatiites. *Lithos* 30 (3-4), 291–307.

Palme, H., O' Neill, H. S. C., 2014. Cosmochemical Estimates of Mantle Composition. In: Carlson, R. W. (Ed.), *Treatise on Geochemistry: The Mantle and Core*, 2nd Edition. Elsevier Ltd., Ch. 3.1, pp. 1–38.

Poitrasson, F., Halliday, A. N., Lee, D. C., Levasseur, S., Teutsch, N., 2004. Iron isotope differences between Earth, Moon, Mars and Vesta as possible records of contrasted accretion mechanisms. *Earth and Planetary Science Letters* 223 (3-4), 253–266.

Prytulak, J., Nielsen, S. G., Ionov, D. A., Halliday, A. N., Harvey, J., Kelley, K. A., Niu, Y. L., Peate, D. W., Shimizu, K., Sims, K. W. W., 2013. The stable vanadium isotope composition of the mantle and mafic lavas. *Earth and Planetary Science Letters* 365 (C), 177–189.

Ragan, D. M., 1963. Emplacement of the Twin Sisters dunite, Washington. *American Journal of Science* 261, 549–565.

Ratié, G., Jouvin, D., Garnier, J., Rouxel, O., Miska, S., Guimarães, E., Vieira, L. C., Sivry, Y., Zelano, I., Pelletier, E. M., Thil, F., Quantin, C., 2015. Nickel isotope fractionation during tropical weathering of ultramafic rocks. *Chemical Geology* 402 (C), 68–76.

Reid, A. M., Donaldson, C. H., Brown, R. W., Ridley, W. I., Dawson, J. B., 1975. Mineral chemistry of peridotite xenoliths from the Lashaine volcano, Tanzania. *Physics and Chemistry of the Earth* 9, 525–543.

Rhodes, J. M., Dawson, J. B., 1975. Major and trace element chemistry of peridotite inclusions from the Lashaine volcano, Tanzania. *Physics and Chemistry of the Earth* 9, 545–557.

Sato, H., 1977. Nickel content of basaltic magmas: identification of primary magmas and a measure of the degree of olivine fractionation. *Lithos* 10, 113–120.

Savage, P. S., Moynier, F., Chen, H., Shofner, G., Siebert, J., Badro, J., Puchtel, I. S., 2015. Copper isotope evidence for large-scale sulphide fractionation during Earth's differentiation. *Geochemical Perspectives Letters*, 1, 53–64.

Siebert, C., Nägler, T. F., Kramers, J. D., 2001. Determination of molybdenum isotope fractionation by double-spike multicollector inductively coupled plasma mass spectrometry. *Geochemistry Geophysics Geosystems* 2 (7).

Sinton, C. W., Duncan, R. A., Storey, M., Lewis, J., Estrada, J. J., 1998. An oceanic flood basalt province within the Caribbean plate. *Earth and Planetary Science Letters* 155 (3-4), 221–235.

Steele, R. C. J., Coath, C. D., Regelous, M., Russell, S., Elliott, T., 2012. Neutron-poor Nickel Isotope Anomalies in Meteorites. *The Astrophysical Journal* 758 (1), 59.

Steele, R. C. J., Elliott, T., Coath, C. D., Regelous, M., 2011. Confirmation of mass independent Ni isotopic variability in iron meteorites. *Geochimica et Cosmochimica Acta* 75 (24), 7906–7925.

Stosch, H. G., 1981. Sc, Cr, Co and Ni partitioning between minerals from spinel peridotite xenoliths. *Contributions to Mineralogy and Petrology* 78 (2), 166–174.

Stueber, A. M., 1969. Abundances of K, Rb, Sr and Sr isotopes in ultramafic rocks and minerals from western North Carolina. *Geochimica et Cosmochimica Acta* 33, 543–553.

Wade, J., Wood, B. J., 2005. Core formation and the oxidation state of the Earth. *Earth and Planetary Science Letters* 236, 78–95.

Walker, R. J., Storey, M., Kerr, A. C., Tarney, J., Arndt, N. T., 1999. Implications of ^{187}Os isotopic heterogeneities in a mantle plume: evidence from Gorgona Island and Curaçao. *Geochimica et Cosmochimica Acta* 63 (5), 713–728.

Wasson, J. T., Richardson, J. W., 2001. Fractionation trends among IVA iron meteorites: Contrasts with IIIAB trends. *Geochimica et Cosmochimica Acta* 65 (6), 951–970.

Williams, H., Peslier, A., McCammon, C., Halliday, A., Levasseur, S., Teutsch, N., Burg, J., 2005. Systematic iron isotope variations in mantle rocks and minerals: The effects of partial melting and oxygen fugacity. *Earth and Planetary Science Letters* 235 (1-2), 435–452.

Williams, H. M., Wood, B. J., Wade, J., Frost, D. J., Tuff, J., 2012. Isotopic evidence for internal oxidation of the Earth's mantle during accretion. *Earth and Planetary Science Letters* 321–322, 54–63.

Witt-Eickschen, G., O'Neill, H. S., 2005. The effect of temperature on the equilibrium distribution of trace elements between clinopyroxene, orthopyroxene, olivine and spinel in upper mantle peridotite. *Chemical Geology* 221 (1-2), 65–101.