Extinct Radionuclides in the Early Solar System: The Initial Solar System

Abundance of ⁶⁰Fe from Angrites and Unequilibrated Ordinary Chondrites and

²⁶Al-²⁶Mg Chronology of Ungrouped Achondrites

by

Lev Spivak-Birndorf

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Approved September 2012 by the Graduate Supervisory Committee:

Meenakshi Wadhwa, Chair Richard Hervig Francis Timmes Lynda Williams Ariel Anbar

ARIZONA STATE UNIVERSITY

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ABSTRACT

The presence of a number of extinct radionuclides in the early Solar System (SS) is known from geochemical and isotopic studies of meteorites and their components. The half-lives of these isotopes are short relative to the age of the SS, such that they have now decayed to undetectable levels. They can be inferred to exist in the early SS from the presence of their daughter nuclides in meteoritic materials that formed while they were still extant. The extinct radionuclides are particularly useful as fine-scale chronometers for events in the early SS. They can also be used to help constrain the astrophysical setting of the formation of the SS because their short half-lives and unique formation environments yield information about the sources and timing of delivery of material to the protoplanetary disk. Some extinct radionuclides are considered evidence that the Sun interacted with a massive star (supernova) early in its history.

The abundance of ⁶⁰Fe in the early SS is particularly useful for constraining the astrophysical environment of the Sun's formation because, if present in sufficient abundance, its only likely source is injection from a nearby supernova. The initial SS abundance of ⁶⁰Fe is poorly constrained at the present time, with estimates varying by 1-2 orders of magnitude. I have determined the ⁶⁰Fe-⁶⁰Ni isotope systematics of ancient, well-preserved meteorites using highprecision mass spectrometry to better constrain the initial SS abundance of ⁶⁰Fe. I find identical estimates of the initial ⁶⁰Fe abundance from both differentiated

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basaltic meteorites and from components of primitive chondrites formed in the Solar nebula, which suggest a lower ⁶⁰Fe abundance than other recent estimates.

With recent improved meteorite collection efforts there are more rare ungrouped meteorites being found that hold interesting clues to the origin and evolution of early SS objects. I use the ²⁶Al-²⁶Mg extinct radionuclide chronometer to constrain the ages of several recently recovered meteorites that sample previously unknown asteroid lithologies, including the only know felsic meteorite from an asteroid and two other ungrouped basaltic achondrites. These results help broaden our understanding of the timescales involved in igneous differentiation processes in the early SS.

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Chapter 1

INTRODUCTION TO EXTINCT RADIONUCLIDES

BACKGROUND

Meteorites that formed in the early Solar System preserve evidence for the former presence of several short-lived radionuclides with $t_{1/2} < \sim 100$ Ma (e.g., ¹⁰Be, ²⁶Al, ⁵³Mn, ⁴¹Ca, ⁶⁰Fe, ¹²⁹I, ¹⁴⁶Sm, ¹⁸²Hf) that have since decayed to undetectable levels. While these radionuclides are now extinct, their existence in the early Solar System can be inferred from excesses of their daughter isotopes measured in mineral phases and bulk samples of ancient meteorites. This was first demonstrated with the observation of excess ¹²⁹Xe in a chondrite, which was inferred to result from the decay of the extinct radionuclide ¹²⁹I (Reynolds 1960), a product of supernova nucleosynthesis. Later results showing an association of the excess ¹²⁹Xe with stable ¹²⁷I, serving as a proxy for the now extinct ¹²⁹I, supported the idea that ¹²⁹I was incorporated into meteorites when it was still extant and decayed in situ (Jeffery and Reynolds 1961). Since the discovery of ¹²⁹I the existence of a number of other extinct radionuclides in the early Solar System has been inferred from isotopic studies of meteorites (e.g., Russell et al. 2001). Stable and very long-lived radioactive nuclides that are synthesized in massive stars could have formed at any time since the beginning of the universe before being incorporated into the Solar System. In contrast, the presence of extinct radionuclides that are the products of stellar nucleosynthesis in meteorites can provide constraints on the time of formation of the elements that were incorporated into the Solar System because they would have completely decayed

if they were created too long before the Sun (e.g., Schramm and Wasserburg 1970). Extinct radionuclides are produced in a variety of stellar environments and can therefore also provide important information about the types of stars that contributed material to the early Solar System and the astrophysical setting in which the Sun formed (e.g. Huss et al. 2009).

Chronometers based on the decay of extinct radionuclides are also critical to resolving the timescales of geologic processes in the early Solar System as recorded by meteorites, such as condensation of rocky material, accretion and differentiation of planetesimals, and their subsequent processing (e.g. Kita et al. 2005; Nyquist et al. 2009a). This is because the very short half-lives of extinct radionuclides allow for high-precision determination of meteorite ages with uncertainties of ~ 1 Ma or less. These chronometers can only provide relative age differences for early Solar System objects and must be anchored to a long-lived absolute chronometer, among which only the ²⁰⁷Pb-²⁰⁶Pb chronometer has high enough precision to be suitable for this purpose. A critical requirement for the use of extinct radionuclide chronometers is that the parent nuclide was originally homogeneously distributed in the early Solar System. Differences in the initial abundances of extinct radionuclides inferred for various objects will therefore reflect only their formation time and not the preservation of originally heterogeneous distribution of the radionuclide in the early Solar System (e.g. Nyquist et al. 2009).

Two of the extinct radionuclides that were present in the early Solar System, 26 Al ($t_{1/2} = 0.73$ Ma) and 60 Fe ($t_{1/2} = 2.62$ Ma), may have also played an

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integral role in the evolution of planets and asteroids to their current states. It has been suggested that energy from the decay of ²⁶Al (Urey 1955) and/or ⁶⁰Fe (Kohman and Saito 1954) could have possibly been the primary heat source(s) for melting and differentiating small planetesimals that were not large enough to reach melting temperatures through accretion heating or the decay of long-lived radionuclides. A substantial portion of this thesis focuses on ⁶⁰Fe and ²⁶Al, thus additional background information on these two extinct radionuclides is described in the following sections of this chapter.

THE ²⁶Al-²⁶Mg SYSTEM

The second extinct radionuclide that was found to be present in the early Solar System was ²⁶Al. Its existence was inferred from excesses of its daughter product, ²⁶Mg, that were correlated with ²⁷Al/²⁴Mg ratios in Ca-Al-rich refractory inclusions (CAIs) from the primitive Allende carbonaceous chondrite (Lee et al. 1976). More precise data soon followed for mineral separates from an individual Allende CAI, demonstrating an internal ²⁶Al-²⁶Mg isochron for the object that corresponded to an initial ²⁶Al/²⁷Al ratio of ~5 × 10⁻⁵ at the time it formed in the Solar nebula (Lee et al. 1977). Numerous measurements of the ²⁶Al-²⁶Mg systematics of CAIs since then have shown that pristine samples have initial ²⁶Al/²⁷Al ratios of ~5 × 10⁻⁵ when they condensed from the solar nebula (MacPherson et al. 1995, 2012; Jacobsen et al. 2008). Ca-Al-rich inclusions are likely the first solids to condense from the Solar nebula and their absolute ²⁰⁷Pb-²⁰⁶Pb age (Amelin et al. 2002; Bouvier and Wadhwa 2010) is commonly considered to be the age of Solar System. As such, the abundance of ²⁶Al present in CAIs when they formed can be considered the Solar System initial abundance.

Models of galactic chemical evolution (GCE) suggest that the abundances of r-process radionuclides (¹²⁹I, ²⁴⁴Pu, ²⁴⁷Cm) can be explained by steady-state production in massive stars and ejection into in the interstellar medium (ISM) over the lifetime of the galaxy, provided there was a period of free-decay of ~100 Ma between the nucleosynthesis of these isotopes and their incorporation into the Solar System (e.g., Nittler and Dauphas 2006; Brennecka et al 2010a). In contrast, the initial abundance of ²⁶Al inferred from CAIs implies that fresh nucleosynthetic material was added to the Solar System from a stellar source just prior to its formation, because the very short-lived ²⁶Al would have been completely extinct after the free-decay interval required by other longer-lived radionuclides if it had been produced in the same steady-state GCE processes (e.g., Lee et al. 1976; Nittler and Dauphas 2006, Wasserburg 2006). Direct measurements of gamma-rays from the decay of ²⁶Al also indicate background levels in the ISM that are lower than that inferred for the Solar nebula from meteoritic abundances (Diehl et al. 2006), implying a different source for this nuclide. This important finding implies a close association of massive stars with the protosolar molecular cloud and/or young Sun; such an association could even have triggered the formation of the Solar System through the collapse of the molecular cloud induced by shock waves from a nearby supernova explosion (Cameron and Truran 1977). The abundance of other extinct-radionuclides in the early Solar System are also critical to questions about the association of the Sun

with massive stars and will be further addressed in this thesis in subsequent sections about 60 Fe.

If ²⁶Al was homogenously distributed in the early Solar System. then it can potentially be used as a powerful chronometer for resolving fine-scale differences in the formation time of meteorites and components within them. Whether or not ²⁶Al was homogeneously distributed in the early Solar System can also provide information about its sources and formation mechanisms, as well as those of other extinct radionuclides. If ²⁶Al was delivered into a dynamic and turbulent solar nebula from a single external stellar source, it is likely to be well mixed and homogeneously distributed in the early Solar System, and thus could be useful as a chronometer. In contrast, if ²⁶Al was formed in the early Solar System by energetic particle irradiation during a brief active phase of the Sun, its distribution would not be expected to be homogenous and would reflect the abundance and distribution of target materials at that time and the duration of the irradiation event(s), complicating its use as a chronometer (Lee et al. 1998). The source(s) of ²⁶Al and other extinct radionuclides therefore has broader implications for understanding the history of the Sun's interaction with massive stars (Lee et al. 1998). The ²⁶Al-²⁶Mg chronometer has been applied to numerous early-formed components in primitive meteorites, such as CAIs and chondrules, revealing important information about their relative formation times and the evolution of these Solar System materials (e.g., Kita et al. 2005; Kita and Ushikubo 2012). As previously mentioned, the heat from ²⁶Al decay might also have been responsible for melting small planetesimals (Urey 1955; Lee et al.

1976), though the important connection of establishing the presence of extant ^{26}Al in later formed differentiated meteorites has only recently been possible with advances in analytical techniques (e.g., Srinivasan et al. 1999; Nyquist et al. 2009a; Spivak-Birndorf et al. 2009; Wadhwa et al. 2009). This thesis focuses in part on utilizing these sensitive measurement techniques to investigate the timescales of planetesimal differentiation in the early Solar System with ²⁶Al-²⁶Mg chronometry of a number of ungrouped differentiated meteorites that represent crustal samples of previously unknown asteroids or possibly new lithologies from a known parent body. Specifically, the goal of this work is to determine if ²⁶Al was present, and in what abundance, at the time that these unique meteorites formed. Therefore, this work helps to address questions about the timing of planetesimal differentiation and the formation of various rock types on different parent bodies in the early Solar System. The presence and abundance of ²⁶Al in a variety of differentiated meteorites could also have implications for its potential as a heat source for the melting and differentiation asteroids. The question of ²⁶Al homogeneity in the early Solar System is also addressed by comparing the ²⁶Al-²⁶Mg relative ages of meteorites with absolute Pb-Pb ages to see if they are concordant.

THE ⁶⁰Fe-⁶⁰Ni SYSTEM

As described briefly in the previous section, the presence of very shortlived radionuclides such as ²⁶Al in the early Solar System raises intriguing

questions about the origins of these isotopes and possible connections with nearby massive stars when the Sun formed. The initial Solar System abundance of ⁶⁰Fe is an important constraint for addressing these questions because of the particular conditions under which it is formed. Although ²⁶Al is abundantly produced in massive stars, including during supernovae explosions (Timmes et al. 1995), it is also possible to create ²⁶Al by energetic particle irradiation of gas or dust, as might have occurred around an early active phase of the Sun (e.g., Chaussidon and Gounelle 2006). The detection of the extinct radionuclide ¹⁰Be in CAIs is thought to be evidence of energetic particle irradiation in the early Solar System because this isotope is only produced by this process and is not formed by stellar nucleosynthesis (McKeegan et al. 2000). However, it is also possible that the ¹⁰Be delivered to the early Solar System originated as galactic cosmic rays that were trapped in the molecular cloud core that collapsed to form the Sun (Desch et al., 2004). Spallation reactions caused by energetic particle irradiation in the early Solar System might therefore not be required to explain ¹⁰Be in CAIs, which could have implications for the contribution of this process to the production of other extinct radionuclides such as ²⁶Al. Nevertheless, the Solar System initial abundance of ²⁶Al may reflect more than one nucleosynthetic source, making the necessity of a nearby reservoir of fresh stellar material somewhat ambiguous. On the other hand, neutron-rich ⁶⁰Fe cannot be produced by particle irradiation and is only made in abundance in massive stellar environments such as supernovae (Lee et al. 1998). Because of its short half-life and conditions required for nucleosynthesis, a high Solar System initial abundance of ⁶⁰Fe would therefore be

strong evidence of interaction with a stellar source just prior to the formation of the Sun.

As with ²⁶Al, the first evidence for the presence of ⁶⁰Fe in the early Solar System was found in CAIs, inferred from excesses of its daughter nuclide, ⁶⁰Ni (Birck and Lugmair 1988). However, nucleosynthetic anomalies on the other isotopes of Ni in CAIs (Birck and Lugmair 1988; Quitté et al. 2007; Bizzarro et al. 2007) make it difficult to interpret the anomalies in 60 Ni as resulting solely from the decay of ⁶⁰Fe. While CAIs cannot be used to directly determine the initial Solar System ⁶⁰Fe abundance, it is possible to estimate this value indirectly from the initial ⁶⁰Fe/⁵⁶Fe ratio determined for an object that has a well-defined age relative to CAIs based on other chronometers. The first unambiguous evidence of *in situ* decay of extant ⁶⁰Fe in the early Solar System was found in basaltic eucrites. Specifically, different bulk samples of individual eucrites record ⁶⁰Ni excesses that are correlated with Fe/Ni ratios (Shukolyukov and Lugmair 1993a,b). Eucrites are well suited to the detection of small enrichments of radiogenic ⁶⁰Ni from ⁶⁰Fe because they have very high Fe/Ni ratios due to the preferential sequestration of Ni over Fe into the core when the howardite-eucritediogenite (HED) parent body differentiated (Shukolyukov and Lugmair 1993a,b). The 60 Fe/ 56 Fe ratio inferred at the time of eucrite formation could then be used to indirectly estimate the Solar System initial abundance of ⁶⁰Fe using the known age difference between their formation and the formation of CAIs based on other chronometers (Shukolyukov and Lugmair 1993a). However, the ⁶⁰Fe-⁶⁰Ni systematics of the eucrites showed some evidence of disturbances (Shukolyukov

and Lugmair 1993a,b) that may reflect their complicated thermal histories involving subsolidus equilibration and impact brecciation (e.g. Metzler et al. 1995).

In the last decade there have been several investigations of the initial Solar System ⁶⁰Fe abundance using a variety of meteorite samples and analytical techniques (Mostefaoui et al. 2005; Tachibana et al. 2006; Mishra et al. 2010; Quitté et al. 2010; Tang and Dauphas 2012; Telus et al. 2012). Studies of components in the least equilibrated ordinary chondrites using *in situ* measurement techniques yield estimates of the initial Solar System ⁶⁰Fe/⁵⁶Fe of $\sim 10^{-7}$ to $\sim 10^{-6}$ (Mostefaoui et al. 2005; Tachibana et al. 2006; Mishra et al. 2010; Telus 2012). In contrast, studies of the ⁶⁰Fe-⁶⁰Ni systematics of differentiated meteorites and individual chondrules using bulk chemical techniques provide lower estimates of the initial Solar System ⁶⁰Fe/⁵⁶Fe of $\sim 10^{-8}$ (Quitté et al. 2010; Tang and Dauphas 2012). It is clear from these conflicting results that the initial Solar System ⁶⁰Fe abundance is not well established and requires further investigation.

A major goal of this thesis is to better constrain the initial ⁶⁰Fe abundance using high-precision measurements of differentiated meteorites and components from unequilibrated ordinary chondrites (UOC). Specifically, this thesis focuses on the ⁶⁰Fe-⁶⁰Ni systematics of the angrites, including bulk samples and the internal systematics of the quenched angrite D'Orbigny. The angrites are promising samples to help constrain the initial Solar System ⁶⁰Fe abundance. They have high Fe/Ni ratios (Quitté et al. 2010) due to the formation of a core on

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their parent body, ancient and well-defined ages relative to CAIs (Amelin 2008a,b; Brennecka and Wadhwa 2012; Spivak-Birndorf et al. 2009; Kleine et al. 2012) and show evidence of rapid crystallization with little to no later disturbance (Mittlefehldt et al. 2002; Floss et al. 2003), meaning they should record their original ⁶⁰Fe-⁶⁰Ni systematics. This thesis also includes a study of the ⁶⁰Fe-⁶⁰Ni systematics of individual chondrules separated from some of the least metamorphosed UOC, measured using high-precision bulk chemical analytical techniques. These measurements can be compared to in situ analyses of the same types of chondrules to help clarify the discrepancy in initial Solar System ⁶⁰Fe estimates provided by the various techniques applied to different samples. Precisely constraining the initial abundance and distribution of ⁶⁰Fe in the early Solar System has important implications for the nucleosynthetic sources that contributed to the protosolar molecular cloud, as well as the question of whether the decay of ⁶⁰Fe was an important heat source for differentiating small planetesimals.

Chapter 2

THE ABUNDANCE OF ⁶⁰FE IN THE EARLY SOLAR SYSTEM: EVIDENCE FROM ANGRITES AND CHONDRULES FROM UNEQUILIBRATED ORDINARY CHONDRITES

INTRODUCTION

Meteorites preserve evidence for the former presence of a number of short-lived ($t_{1/2} \le 100$ Ma) radionuclides in the early Solar System that are now extinct (e.g., Kita et al. 2005). Constraining the abundances of these extinct radionuclides at the beginning of the Solar System can provide insight on the nucleosynthetic sources and processes that contributed material to the Solar nebula. The abundance of some extinct radionuclides at the beginning of the Solar System can be accounted for by inferred galactic background levels (i.e., the abundance inherited by the Solar nebula from the interstellar medium; Huss et al. 2009). Other extinct radionuclides are considered too abundant in the early Solar System to be explained by this process alone and require additional input either from a nearby stellar source, such as a supernova, or from spallation reactions induced by cosmic rays (Huss et al. 2009). Most of the extinct radionuclides that are thought to be overabundant in the early Solar System can potentially be produced by both nucleosynthesis in stars and energetic particle interactions (Chaussidon and Gounelle 2006), making it difficult to distinguish between these sources. However, 60 Fe (t_{1/2} = 2.62 Ma; Rugel et al. 2009) is only efficiently produced by stellar nucleosynthesis, not by irradiation (Lee et al. 1998), and its abundance in the early Solar System can therefore yield particularly strong

constraints on the sources of other extinct radionuclides and the astrophysical environment in which the Sun formed.

The most accurate and precise estimates of the age of the Solar System are based on the radiometric ages of the first solids to form in the Solar nebula, calcium-aluminum rich inclusions (CAIs; Amelin et al. 2010; Bouvier and Wadhwa 2010). The amount of a given extinct radionuclide present at the time of CAI formation can therefore be considered to be the initial Solar System abundance. Estimates of the initial Solar System abundances of many of the extinct radionuclides such as ²⁶Al, ⁴¹Ca and ¹⁸²Hf, are determined from measurements of CAIs or the minerals within them (e.g., MacPherson et al. 1995; Sahijpal et al. 1998; Burkhardt et al. 2008). This is not the case for ⁶⁰Fe because CAIs have nucleosynthetic Ni isotope anomalies that prevent clear interpretation of the ⁶⁰Fe-⁶⁰Ni isotope systematics (Birck and Lugmair 1988; Quitté et al. 2007; Bizzarro et al. 2007). Since the initial Solar System abundance of ⁶⁰Fe cannot be clearly determined directly from CAIs, it is estimated from other Solar System objects that have evidence for extant ⁶⁰Fe and a known time of formation relative to CAIs (e.g., Shukolyukov and Lugmair 1993a; Mostefaoui et al. 2005; Tachibana et al. 2006; Quitté et al. 2010; Tang and Dauphas 2012). However, the initial Solar System ⁶⁰Fe abundance is still poorly constrained, with significant disagreement among the estimates provided by investigations of different types of meteorites using various analytical techniques. Studies of minerals in the matrix and chondrules of primitive chondrites using *in situ* analytical techniques provide estimates of the initial Solar System ${}^{60}\text{Fe}/{}^{56}\text{Fe}$ ratio ranging from about 10^{-7} to 10^{-6} (Mostefaoui et al. 2005; Tachibana et al. 2006; Mishra et al. 2010). Studies of bulk samples and mineral separates from basaltic meteorites (eucrites and angrites) yield a lower initial 60 Fe/ 56 Fe ratios of $\sim 10^{-8}$ (Shukolyukov and Lugmair 1993a,b; Quitté et al. 2010; Tang and Dauphas 2012).

The D'Orbigny angrite is an ancient basaltic meteorite that cooled quickly and experienced minimal alteration since it formed in the early Solar System (Mittlefehldt et al. 2002; Floss et al. 2003). It is therefore likely that different radiometric chronometers closed simultaneously when D'Orbigny crystallized and have not been subsequently reset. The ancient age of D'Orbigny and the time of formation after CAIs are known precisely from the absolute ²⁰⁷Pb-²⁰⁶Pb ages of these objects (Amelin 2008a; Bouvier and Wadhwa 2010). D'Orbigny also preserves evidence for the presence of a number of extinct radionuclides at the time it crystallized (i.e., ²⁶Al, ⁵³Mn and ¹⁸²Hf; Glavin et al. 2004; Markowski et al 2007; Spivak-Birndorf et al. 2008; Kleine et al. 2012). As such, D'Orbigny is a promising target to search for evidence of live ⁶⁰Fe with the potential to yield a robust estimate of the initial Solar System ⁶⁰Fe/⁵⁶Fe ratio.

While internal mineral isochrons can provide information on the age of an individual meteorite, "whole-rock" isochrons using bulk samples of different meteorites from a common parent body can help constrain the timing of widespread elemental fractionation associated with events such as core formation and mantle differentiation (Shukolyukov and Lugmair 2007; Kleine et al. 2012). For example, while plutonic angrites formed several Ma after quenched angrites such as D'Orbigny (Amelin 2008a; Brennecka and Wadhwa 2012), the ⁵³Mn-⁵³Cr

systematics of bulk angrite samples suggest that the sources of the various angrites differentiated in the mantle of the parent body early in its history and are preserved at the scale of individual meteorites (Shukolyukov and Lugmair 2007). Quitté et al. (2010) recently reported an apparent ⁶⁰Fe-⁶⁰Ni isochron for bulk angrites, suggesting that it may reflect the timing of Fe/Ni fractionation in the sources of angrites during core formation and differentiation of the parent body.

Unequilibrated ordinary chondrites (UOC) experienced minimal thermal metamorphism on their parent bodies (Huss et al. 2006) and chondrules within them should therefore preserve their original ⁶⁰Fe-⁶⁰Ni isotope systematics. This is especially the case for Semarkona (LL3.00) and QUE 97008 (L3.05), which are among the least altered UOC (Grossman and Brearley 2005). Evidence for live ⁶⁰Fe has also been reported for chondrules from these two meteorites using *in situ* techniques (Tachibana et al. 2006; Mishra et al. 2010; Telus et al. 2012). The relatively high initial ⁶⁰Fe/⁵⁶Fe ratios reported in these studies for some UOC chondrules would be readily detectable using bulk chemistry techniques provided the chondrules had sufficiently high Fe/Ni ratios. Here we investigate the ⁶⁰Fe-⁶⁰Ni systematics of angrites and individual chondrules from UOC in order to better constrain the initial Solar System abundance of ⁶⁰Fe.

RESULTS

Here I report Ni isotope and Fe/Ni ratios (Table 2.1) measured using multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS). This study includes bulk samples and mineral separates (pyroxene and olivine) from the D'Orbigny angrite, bulk samples of three plutonic angrites (NWA 4801, NWA 4590 and NWA 6291) and several chondrules from three different UOC (Chainpur, Semarkona and QUE 97008).

The D'Orbigny samples span a wide range in ⁵⁶Fe/⁵⁸Ni ratios from ~4600 to ~10000 and all have excesses of ⁶⁰Ni (expressed as ε^{60} Ni*, the deviation from the terrestrial ⁶⁰Ni/⁵⁸Ni ratio in parts per 10⁴). The ⁶⁰Ni excesses (~0.2 ε to ~0.8 ε) in D'Orbigny bulk samples and mineral separates correlate with their Fe/Ni ratios (Fig. 2.1) indicating the former presence of extant ⁶⁰Fe when this meteorite formed. The internal ⁶⁰Fe-⁶⁰Ni isochron determined here for D'Orbigny (Fig. 2.1) has a slope corresponding to an initial ⁶⁰Fe/⁵⁶Fe ratio of (3.7 ± 1.0) × 10⁻⁹ and an ε^{60} Ni*₀ = -0.22 ± 0.19 at the time this meteorite formed. The initial ⁶⁰Fe/⁵⁶Fe ratio determined here for D'Orbigny also agrees well with the values of (4.1 ± 2.6) × 10⁻⁹ and (3.2 ± 0.5) × 10⁻⁹ reported recently by Quitté et al. (2010) and Tang and Dauphas (2012), respectively.

Table 2.1

Sample	⁵⁶ Fe/ ⁵⁸ Ni ^a	ε ⁶⁰ Ni*	$\pm 2SE^{b}$	ε ⁶¹ Ni	± 2SE ^b	n
Angrites						
D'Orbigny						
WR1	4631	0.20	0.04	0.24	0.15	9
WR2	9469	0.62	0.05	0.08	0.18	8
OL	5894	0.39	0.09	-0.42	0.43	4
PX	10312	0.80	0.06	0.60	0.20	5
NWA 6291	71	0.02	0.04	0.11	0.11	13
NWA 4801						
HCl washed (0.05 M)	1085	0.00	0.06	0.35	0.26	9
H ₂ O washed	985	0.06	0.05	0.37	0.26	9
NWA 4590						
HCl washed (0.05 M)	9646	0.04	0.04	-0.10	0.24	10
HCl washed (0.5 M)	9058	0.08	0.09	0.40	0.19	7
H ₂ O washed	4048	0.04	0.08	0.40	0.14	5
2						
UOC						
Semarkona (LL 3.00)						
Smk-1	190	-0.03	0.05	0.02	0.20	17
Smk-3	795	0.11	0.08	-0.03	0.22	6
Smk-4	150	-0.10	0.05	0.16	0.23	15
Smk-6	206	-0.02	0.06	0.51	0.45	9
Smk-7	93	0.01	0.04	0.33	0.27	5
QUE 97008 (L3.05)						
QUE-2	916	0.14	0.07	0.06	0.35	10
QUE-3	29	-0.09	0.09	0.22	0.67	5
QUE-6	92	-0.1	0.15	0.22	0.54	5
QUE-mix	844	0.1	0.08	0.90	0.52	7
Chainpur (LL 3.4)						
Chp-1	203	-0.06	0.05	0.56	0.35	9
Chp-3	578	0.06	0.05	0.92	0.22	4
Chp-5	142	0	0.08	0.23	0.36	5
Chp-6	100	-0.05	0.07	0.27	0.27	9
Chp-8	165	-0.11	0.04	0.05	0.25	16
Ni Standards						
DTS-2b		-0.01	0.02	0.03	0.08	103
AGV-2	2426	-0.05	0.08	0.39	0.39	8
Alfa Aesar Ni		-0.02	0.01	-0.06	0.06	157

⁶⁰Fe-⁶⁰Ni isotope systematics of angrites, chondrules, and terrestrial Ni standards

^aErrors on ⁵⁶Fe/⁵⁸Ni are $\pm 10\%$ ^bErrors on Ni isotope ratios are $\pm 2SD/\sqrt{n}$



Figure 2.1. ⁶⁰Fe-⁶⁰Ni internal mineral isochron for D'Orbigny. Errors are $\pm 10\%$ on ⁵⁶Fe/⁵⁸Ni and the larger of $\pm 2SE$ or the external reproducibility ($\pm 0.10\varepsilon$) on ε^{60} Ni*. The solid line corresponds to the least-squares regression of the data. WR = whole rock; OL = olivine; PX = pyroxene.

The three plutonic angrites included in this study are all finds from the deserts of Northwestern Africa where they were exposed to terrestrial surface conditions for an unknown time period. In order to investigate the potential effects of terrestrial contamination on the ⁶⁰Fe-⁶⁰Ni isotope systematics, multiple samples of NWA 4801 and 4590 were washed in different solvents of varying strength prior to dissolution (see section: Materials and Methods). Separate samples of NWA 4590 were washed with either ultrapure water, 0.05 M HCl, or 0.5 M HCl. One sample of NWA 4801 was washed in ultrapure water and another in 0.05 M HCl. Only one sample of NWA 6291 (paired with NWA 2999) that had been washed in 0.05 M HCl was measured. The amount of Ni leached from the

samples during washing varied from <0.5% for the water and 0.05 M HCl up to \sim 6% for the 0.5 M HCl of the total sample Ni. Bulk samples of three plutonic angrite span a wide range in 56 Fe/ 58 Ni ratios from ~80 to ~9000. The Fe/Ni ratios are identical within errors for both the HCl and water washed samples of NWA 4801. Both of the HCl washed samples of NWA 4590 also have identical Fe/Ni ratios within errors, while the water washed sample has a significantly lower Fe/Ni. All of the samples of the three plutonic angrites have ϵ^{60} Ni* values identical to terrestrial composition within errors (Fig. 2.2). While NWA 4801 and NWA 4590 formed at roughly the same time, NWA 6291 likely formed a few Ma earlier (Brennecka and Wadhwa 2012). A regression of the ⁶⁰Fe-⁶⁰Ni isotope data from NWA 4801 and NWA 4590 does not yield a slope that is resolved from zero within errors and can only be used to define an upper limit on the initial 60 Fe/ 56 Fe ratio of $\leq 5.4 \times 10^{-10}$. The NWA 6291 sample has near chondritic ⁶⁰Fe-⁶⁰Ni systematics (Fig. 2.2), consistent with data for the paired NWA 2999 (Quitté et al. 2010).



Figure 2.2. ⁶⁰Fe-⁶⁰Ni systematics of bulk angrites. Errors are $\pm 10\%$ on ⁵⁶Fe/⁵⁸Ni and the larger of $\pm 2SE$ or the external reproducibility ($\pm 0.10\epsilon$) on ϵ^{60} Ni*. For the plutonic angrites (blue data), filled squares are samples that were washed in HCl and open squares are samples that were washed in ultra-pure water. The solid blue line is the least squares regression of the bulk plutonic angrites (excludes NWA 6291, red square). The black squares are D'Orbigny bulk samples and the solid black line corresponds to the least squares regression of bulk D'Orbigny. The gray circles and dashed line represent the angrite whole-rock isochron from Quitté et al. 2010 for comparison.

The ⁶⁰Fe-⁶⁰Ni isotope systematics of chondrules separated from the Semarkona (LL3.00), Chainpur (LL3.4) and QUE97008 (L3.05) UOC are shown in Fig. 2.3. Five individual chondrules each from Semarkona and Chainpur, and three individual chondrules and one pooled sample of chondrule fragments from QUE 97008 were analyzed in this study. The chondrule samples have ⁵⁶Fe/⁵⁸Ni ratios ranging from ~30 to ~900 and all have ϵ^{60} Ni* values within errors (±2SD) of the terrestrial value (Table 2.1). The ϵ^{60} Ni* values of the chondrules correlate

with their Fe/Ni ratios and define a slope corresponding to an initial 60 Fe/ 56 Fe ratio of $(0.9 \pm 0.4) \times 10^{-8}$ and an ε^{60} Ni* $_0 = -0.08 \pm 0.05$, if the array is assumed to be an isochron. This regression includes only the chondrules from Semarkona and QUE 97008 because they are lower metamorphic grade than Chainpur and less likely to have disturbed isotope systematics. Nevertheless, the Chainpur data are consistent with that from other two UOC and lie on the isochron they define (Fig. 2.3). The initial 60 Fe/ 56 Fe ratio reported here for chondrules agrees well with other values recently reported by other groups for individual UOC chondrule isochrons, also using MC-ICPMS (Tang and Dauphas 2012; Wielandt et al. 2012), but does not confirm the higher 60 Fe/ 56 Fe ratios (~10⁻⁷) reported for some chondrules using *in situ* techniques (Tachibana et al. 2006; Mishra et al. 2010; Telus et al. 2012).



Figure 2.3. ⁶⁰Fe-⁶⁰Ni systematics of individual chondrules from UOC. Errors are $\pm 10\%$ on 56 Fe/ 58 Ni and the larger of ± 2 SE or the external reproducibility ($\pm 0.10\epsilon$) on ϵ^{60} Ni*. The solid line corresponds to the least-squares regression of the data for Semarkona and QUE 97008 only.

DISCUSSION

Initial Solar System abundance of ⁶⁰Fe

D'Orbigny and plutonic angrites

The ⁶⁰Fe/⁵⁶Fe ratio in D'Orbigny that reported here and the precisely

known age difference between the formation of this angrite and CAIs can be used to estimate the Solar System initial ⁶⁰Fe abundance. It was recently demonstrated that Solar System materials have variable ²³⁸U/²³⁵U ratios requiring adjustments of their Pb-Pb ages of up to a few Ma (Brennecka et al. 2010a,b; Brennecka and Wadhwa 2012). Adjusting the Pb-Pb age of D'Orbigny (Amelin 2008a) using its measured U isotope composition, yields the most precise and accurate age estimate for this meteorite of 4563.37 \pm 0.25 Ma (Brennecka and Wadhwa 2012). This age is either 4.8 \pm 0.3/-0.5 Ma or 3.8 \pm 0.6 Ma after the beginning of the Solar System depending on what Pb-Pb age is assumed for CAIs (4568.2 \pm 0.2/-0.4 Ma, Bouvier and Wadhwa 2010; 4567.2 \pm 0.5 Ma, Amelin et al. 2010). Using these age differences and the ⁶⁰Fe abundance determined here for D'Orbigny, implies a Solar System initial ⁶⁰Fe/⁵⁶Fe ratio of either (1.0 \pm 0.3) \times 10⁻⁸ or (1.3 \pm 0.4) \times 10⁻⁸.

Quitté et al. (2010) recently reported ϵ^{60} Ni* values correlated with Fe/Ni ratios in bulk samples of two quenched angrites (D'Orbigny and Sahara 99555) and the coarse-grained metal-rich angrite NWA 2999. The authors interpret these data as a ⁶⁰Fe-⁶⁰Ni whole-rock isochron that dates the timing of widespread Fe/Ni fractionation in the sources of the various angrites on the parent body during core formation and differentiation, as has been suggested for the ⁵³Mn-⁵³Cr systematics of bulk angrites (Shukolyukov and Lugmair 2007). However, this interpretation is ambiguous, requiring more data from plutonic angrites with higher Fe/Ni ratios. The quenched angrites D'Orbigny and Sahara 99555 are known to have crystallized contemporaneously (Markowski et al 2007; Amelin 2008a,b; Spivak-Birndorf et al. 2008; Kleine et al. 2012) and bulk samples of these meteorites with variable Fe/Ni ratios would be expected to lie on a common ⁶⁰Fe-⁶⁰Ni isochron, as has been reported (Quitté et al. 2010). The metal-rich angrite NWA 2999 has ⁶⁰Fe-⁶⁰Ni isotope systematics nearly identical to chondrites, differing slightly in their Fe/Ni ratio (Regelous et al. 2008; Ouitté et al. 2010). If the chondritic ε^{60} Ni* and Fe/Ni ratio is used instead of NWA 2999 in the regression of the bulk angrite data, it yields an indistinguishable ⁶⁰Fe-⁶⁰Ni isochron. It is therefore unclear if the bulk angrite data from Quitté et al. (2010) corresponds to the timing of Fe/Ni fractionation in the angrite source magmas or to the crystallization of the quenched angrites from an essentially chondritic Ni source. The two separate bulk samples of D'Orbigny (WR1 and WR2) analyzed in this study have different Fe/Ni ratios that span a similar range to the bulk samples of D'Orbigny and Sahara 99555 in the study by Quitté et al. (2010) (Fig. 2.2). The variable Fe/Ni ratios in bulk samples of D'Orbigny are consistent with previous studies of this meteorite and most likely reflect the heterogeneous distribution of Ni-rich minerals such as sulfides (Mittlefehldt et al. 2002). The two bulk D'Orbigny samples (WR1 and WR2) presented here define a ⁶⁰Fe-⁶⁰Ni isochron with slope corresponding to a ${}^{60}\text{Fe}/{}^{56}\text{Fe}$ ratio = $(3.3 \pm 1.3) \times 10^{-9}$, identical to that reported by Quitté et al. (2010) for bulk angrites (Fig. 2.2).

Magmatic activity on the angrite parent body likely lasted several Ma based on the younger Pb-Pb ages of plutonic angrites relative to quenched angrites (Amelin 2008a,b; Brennecka and Wadhwa 2012). If the ⁶⁰Fe-⁶⁰Ni chronometer closed at the same time as the Pb-Pb chronometer in plutonic angrites they would be expected to have smaller or no excesses of ⁶⁰Ni and lower initial ⁶⁰Fe/⁵⁶Fe ratios than are observed in quenched angrites. Alternatively, it is possible that the various angrite source magmas established their Fe/Ni ratios during differentiation. If this occurred when the ⁶⁰Fe/⁵⁶Fe ratio of the parent body
was at the level recorded by the quenched angrites and the source magmas remained as closed systems with respect to the ⁶⁰Fe-⁶⁰Ni systematics, then bulk samples of plutonic angrites would lie on the same isochron as bulk quenched angrites. The bulk samples of plutonic angrites measured in this study span a wide range in Fe/Ni ratios that is comparable to that of the quenched angrites (Fig. 2.2). These samples can therefore help determine whether or not the bulk angrite ⁶⁰Fe-⁶⁰Ni systematics reflect Fe/Ni fractionation in their sources during differentiation of the parent body. It can be seen in Fig. 2.2 that the two bulk samples of NWA 4801 and the three bulk samples of NWA 4590 measured here have terrestrial ϵ^{60} Ni* values and do not fall on the isochron defined by the quenched angrites. These data are consistent with formation of the plutonic angrites at a later time than the quenched angrites when ⁶⁰Fe had decayed significantly, or disturbance of their ⁶⁰Fe-⁶⁰Ni systematics after crystallization. The data do not support a bulk angrite ⁶⁰Fe-⁶⁰Ni isochron corresponding to the time of parent body differentiation (Quitté et al. 2010). When anchored to the 60 Fe/ 56 Fe ratio reported here for D'Orbigny, the upper limit on 60 Fe/ 56 Fe that can be calculated from the NWA 4801 and NWA 4590 bulk samples (Fig. 2.2) corresponds to an age of \leq 4556.1 Ma. This age is ~1-2 Ma younger than the U-corrected Pb-Pb ages for these meteorites (Brennecka and Wadhwa 2012) suggesting a possible later closure or disturbance in the Fe-Ni chronometer for these samples. The lack of a resolved ⁶⁰Fe-⁶⁰Ni isochron in the plutonic angrites measured here precludes the use of these samples to precisely constrain the Solar System initial ⁶⁰Fe/⁵⁶Fe ratio. However, if it is assumed that the ⁶⁰Fe-⁶⁰Ni chronometer closed in the plutonic

angrites at the same time as the Pb-Pb chronometer at ~10 Ma after CAI formation (Brennecka and Wadhwa 2012), an upper limit on the initial Solar System ⁶⁰Fe/⁵⁶Fe \leq ~0.7 × 10⁻⁸ can be inferred, which is still close to the estimate from D'Orbigny. In contrast to the data for NWA 4801 and NWA 4590 here, Tang and Dauphas (2012) report scattered ⁶⁰Ni excesses in bulk samples of these plutonic angrites. The reasons for these discrepancies are not known, but are unlikely to be due to terrestrial contamination since the ε^{60} Ni* values of the different NWA 4590 samples are identical within errors (Fig. 2.2) regardless of the amount of Ni removed by washing (<0.5% to ~6% of total). It is still possible that these coarse-grained samples are heterogeneous with respect to Ni, having some sections that experienced greater degrees of Ni isotope equilibration.

Chondrules from unequilibrated ordinary chondrites

The ⁶⁰Fe/⁵⁶Fe ratio defined by the ⁶⁰Fe-⁶⁰Ni systematics of individual chondrules from UOC (Fig. 2.3) can be used to estimate the initial Soar System abundance of ⁶⁰Fe. Though the precise ages of the chondrules in this study are unknown, most chondrules from UOC formed at around 2 ± 1 Ma after CAIs based on multiple isotope chronometers (e.g., Kita et al. 2005; Kita and Ushikubo 2012; Villeneuve et al. 2009). Assuming this time difference yields an estimate of the initial Solar System ⁶⁰Fe/⁵⁶Fe = $(1.5 \pm 0.8) \times 10^{-8}$ from the chondrule ⁶⁰Fe-⁶⁰Ni data. This estimate is in good agreement with that determined from the D'Orbigny internal ⁶⁰Fe-⁶⁰Ni data presented here.

The ⁶⁰Fe-⁶⁰Ni isotope systematics of chondrules from UOC presented here are consistent with previous investigations using bulk chemical analysis of individual chondrules (Tang and Dauphas 2012; Wielandt et al. 2012), but are inconsistent with results from *in situ* studies (Tachibana et al. 2006; Mishra et al. 2010; Telus et al. 2012). The reason for the discrepancy is not entirely clear but is unlikely to result from a sampling bias because chondrules from the same UOC were measured here and in the *in situ* studies (i.e., Semarkona; Tachibana et al. 2006; Mishra et al. 2010; Telus et al. 2012). It was recently shown that the data reported in studies of the ⁶⁰Fe-⁶⁰Ni systematics of chondrites using *in situ* measurement techniques might suffer from analytical artifacts involving both unresolved mass interferences and bias during data reduction (Huss et al. 2010, 2011). While accounting for these issues has lowered the estimates of the 60 Fe abundance in most of the chondrules from UOC, some of the chondrules measured recently by ion microprobe still have evidence for higher ⁶⁰Fe/⁵⁶Fe ratios of up to 3×10^{-7} (Telus et al. 2012). These *in situ* chondrule data correspond to higher estimates of the initial Solar System 60 Fe/ 56 Fe ratio of ~2-5 × 10^{-7} . However, the chondrules that do still show evidence for higher 60 Fe/ 56 Fe ratios based on *in situ* measurements also have clearly disturbed ⁶⁰Fe-⁶⁰Ni systematics (Telus et al. 2012). The chondrules presented in this study span a wide range in Fe/Ni ratios, with some as high as ~900. If these high Fe/Ni chondrules formed with the high ⁶⁰Fe/⁵⁶Fe ratios suggested by *in situ* investigations (~10⁻⁷) they would be expected to have excess ε^{60} Ni* of at least $\sim 2.5\varepsilon$ that would have been easily detectable with our analytical techniques.

Comparison with reported estimates of the initial Solar System ⁶⁰Fe abundance from other meteorite types

There are several previous estimates of the Solar System initial ⁶⁰Fe/⁵⁶Fe ratio based on the ⁶⁰Fe-⁶⁰Ni systematics of a variety of different meteorite types (Shukolyukov and Lugmair 1993a,b; Regelous et al. 2008; Chen et al. 2009; Moynier et al. 2011; Quitté et al. 2011). The estimates of the initial Solar System ⁶⁰Fe/⁵⁶Fe ratio determined here are in good agreement with those made from ⁶⁰Fe-⁶⁰Ni studies of howardite-eucrite-diogenite (HED) clan meteorites using bulk chemistry techniques (Shukolyukov and Lugmair 1993a,b; Quitté et al. 2011; Tang and Dauphas 2012). While the internal mineral ⁶⁰Fe-⁶⁰Ni systematics of eucrites are disturbed, clear evidence for live ⁶⁰Fe has been reported in bulk samples of a individual eucrites that have variable Fe/Ni ratios (Shukolyukov and Lugmair 1993a,b; Quitté et al. 2011) as well as for bulk samples of several eucrites and diogenites that define a ⁶⁰Fe-⁶⁰Ni whole-rock isochron (Tang and Dauphas 2012). However, absolute Pb-Pb ages have not been determined for the eucrites analyzed in those studies, so their time of formation after the beginning of the Solar System must be estimated indirectly from another chronometer. The relative ages of several individual eucrites and the formation time of the HED meteorite sources during differentiation of the parent body have been determined previously using the ⁵³Mn-⁵³Cr chronometer (Lugmair and Shukolyukov 1998; Trinquier et al. 2008). These Mn-Cr ages can be tied to an absolute timescale by anchoring them to an object that has been dated using both the relative Mn-Cr

chronometer and the absolute ²⁰⁷Pb-²⁰⁶Pb chronometer. D'Orbigny is a well-suited anchor for this purpose and all the Mn-Cr data discussed here are tied to its U isotope corrected Pb-Pb age (Amelin 2008a; Brennecka and Wadhwa 2012), assuming a 53 Mn/ 55 Mn ratio of (3.24 ± 0.04) × 10⁻⁶ at the time it formed (Glavin et al. 2004). As described above for D'Orbigny, the age difference between a meteorite and CAIs can be used to estimate the initial Solar System ⁶⁰Fe abundance if the 60 Fe/ 56 Fe ratio is known at the time that meteorite formed. Assuming a Mn-Cr age for the eucrite Chervony Kut (Lugmair and Shukolyukov 1998) of $+0.7 \pm 0.6$ Ma relative to D'Orbigny, the reported 60 Fe/ 56 Fe ratio (Shukolyukov and Lugmair 1993a) for this meteorite translates to a Solar System initial 60 Fe/ 56 Fe ratio of either (0.9 ± 0.2) × 10⁻⁸ or (1.2 ± 0.3) × 10⁻⁸ depending again on the age assumed for CAIs (Bouvier and Wadhwa 2010; Amelin et al. 2010). The ⁶⁰Fe-⁶⁰Ni isotope systematics have also been reported for the eucrite Juvinas (Shukolyukov and Lugmair 1993b; Quitté et al. 2011), and bulk samples from two studies define an apparent isochron that may correspond to the formation time of this eucrite (Shukolyukov and Lugmair 1993b; Quitté et al. 2011). Assuming a Mn-Cr age of -0.4 ± 0.9 Ma for Juvinas relative to D'Orbigny, an initial Solar System ${}^{60}\text{Fe}/{}^{56}\text{Fe}$ ratio of either $(0.7 \pm 0.3) \times 10^{-8}$ or $(0.9 \pm 0.3) \times 10^{-8}$ 10^{-8} can be estimated. The Mn-Cr age for the differentiation of the HED parent body (Trinquier et al. 2008) at $+1.4 \pm 0.6$ Ma, anchored to D'Orbigny, translates to an initial Solar System 60 Fe/ 56 Fe ratio of $(0.6 \pm 0.1) \times 10^{-8}$ or $(0.8 \pm 0.2) \times 10^{-8}$ using the recently reported ⁶⁰Fe-⁶⁰Ni systematics for bulk eucrites (Tang and Dauphas 2012). Despite disturbances in the internal ⁶⁰Fe-⁶⁰Ni systematics of most

HED meteorites (Shukolyukov and Lugmair 1993ab; Quitté et al. 2011), bulk samples appear to provide meaningful information about the ⁶⁰Fe abundance at the time these meteorites formed. The HED ⁶⁰Fe-⁶⁰Ni data from previous studies are generally in good agreement with the low initial Solar System ⁶⁰Fe/⁵⁶Fe ratio ($\sim 10^{-8}$) estimated here from D'Orbigny and UOC chondrules.

There have also been some recent studies of the ⁶⁰Fe-⁶⁰Ni systematics of components from chondrites and iron meteorites (Regelous et al. 2008; Chen et al. 2009; Moynier et al. 2012). None of these studies were able to precisely constrain the ⁶⁰Fe abundance at the time these meteorites formed. For samples with low Fe/Ni such as Chainpur chondrules (Chen et al. 2009), bulk chondrites and iron meteorites (Regelous et al 2008) they report upper limits on ⁶⁰Fe/⁵⁶Fe \leq ~3 × 10⁻⁷ that are marginally consistent with the higher initial Solar System ⁶⁰Fe/⁵⁶Fe ratio of ~2-5 × 10⁻⁷ implied by *in situ* chondrule data (Telus et al. 2012). However high Fe/Ni sulfides from chondrites and iron meteorites yield upper limits on the ⁶⁰Fe/⁵⁶Fe \leq ~10⁻⁸ (Chen et al. 2009; Moynier et al. 2012) that are more consistent with the lower estimates of the initial Solar System ⁶⁰Fe abundance reported here.

Origin of ⁶⁰Fe in the early Solar System

The abundance of 60 Fe that would be expected in the Solar nebula without a late-stage addition from a nearby stellar source can be estimated by models of galactic chemical evolution (GCE; Wasserburg et al. 1996; Huss et al 2009) and by direct measurements of galactic 60 Fe gamma-ray emissions (Wang et al. 2007). Using the recently determined 60 Fe half-life of 2.62 Ma (Rugel et al. 2009), GCE models (Wasserburg et al. 1996; Huss et al. 2009) predict an average 60 Fe/ 56 Fe \approx $3-5 \times 10^{-8}$ for the interstellar medium. Using gamma-ray flux measurements of ⁶⁰Fe and ²⁶Al (Diehl et al. 2006; Wang et al. 2007) yields an estimate of the for the galactic background ${}^{60}\text{Fe}/{}^{56}\text{Fe} \approx 10^{-7}$. Both estimates of the galactic background ⁶⁰Fe abundance are higher than the initial Solar System abundance reported here from D'Orbigny and UOC chondrules. The higher initial ⁶⁰Fe/⁵⁶ ratio $(\sim 10^{-7})$ implied by *in situ* measurements of some chondrules (Tachibana et al. 2006; Mishra et al. 2010; Telus et al. 2012) would require an additional input of ⁶⁰Fe to the early Solar System such as from a nearby supernova (e.g., Huss et al. 2009). In contrast, the lower initial 60 Fe/ 56 Fe ratio (~10⁻⁸) estimated in this study are consistent with the Solar System inheriting all of its ⁶⁰Fe from the galactic background abundance in the interstellar medium and does not necessitate a late-stage stellar input. Assuming that the ⁶⁰Fe in the Solar System was inherited from the galactic background implies a maximum free-decay interval (Δ) of ~10 Ma. This is significantly shorter than estimates for Δ of ~100 Ma based on abundances of ²⁴⁷Cm, ²⁴⁴Pu and ¹²⁹I (Nittler and Dauphas 2006; Brennecka et al. 2010a) and ~30 Ma for ¹⁸²Hf (Nittler and Dauphas 2006). This apparent discrepancy could be explained by a later stage addition of ⁶⁰Fe from a stellar source or a decoupling of the sources of r-process nuclides and ⁶⁰Fe (e.g. Wasserburg et al. 1996).

CONCLUSION

The ⁶⁰Fe-⁶⁰Ni isotope systematics of the D'Orbigny angrite and individual chondrules from low metamorphic-grade UOC (Semarkona and QUE 97008) both indicate an initial Solar System 60 Fe/ 56 Fe ratio of $\sim 1-2 \times 10^{-8}$. Bulk samples of plutonic angrites (NWA 4801 and NWA 4590) have ⁶⁰Fe-⁶⁰Ni systematics consistent with their formation ages at several Ma after quenched angrites (Brennecka and Wadhwa 2012), and provide an estimate on the upper limit of the initial Solar System ⁶⁰Fe/⁵⁶Fe ratio that is marginally consistent with the ⁶⁰Fe abundance determined from D'Orbigny and UOC chondrules. The rapid formation and excellent preservation of D'Orbigny (Mittlefehldt et al. 2002; Floss et al. 2003), as well as its accurate and precisely defined age difference relative to CAIs (Amelin 2008a; Bouvier and Wadhwa 2010; Amelin et al. 2010; Brennecka and Wadhwa 2012), makes it likely that the estimate reported here for the initial Solar System ⁶⁰Fe abundance using the internal mineral ⁶⁰Fe-⁶⁰Ni systematics of this angrite is among the most robust currently available. Furthermore, the initial Solar System ⁶⁰Fe abundance derived from D'Orbigny agrees well with the estimate reported here using the ⁶⁰Fe-⁶⁰Ni systematics of individual UOC chondrules, suggesting that ⁶⁰Fe was homogenously distributed in the Solar nebula. The UOC chondrules measured here show no evidence for higher initial Solar System 60 Fe/ 56 Fe ratios (~10⁻⁷) inferred from *in situ* studies of similar objects (Tachibana et al. 2006; Mishra et al. 2010; Telus et al. 2012). Investigations of the ⁶⁰Fe-⁶⁰Ni systematics of a variety of meteorite types (HED, iron meteorites, chondrites) using bulk chemistry techniques also suggest initial

Solar System ⁶⁰Fe/⁵⁶Fe ratios of ~10⁻⁸ or slightly lower (Shukolyukov and Lugmair 1993a,b; Regelous et al. 2008; Chen et al. 2009; Moynier et al. 2011; Quitté et al. 2011). There is mounting evidence that the ⁶⁰Fe abundances inferred from *in situ* measurements of chondrules are too high, possibly due to analytical artifacts (Huss et al. 2010, 2011), and that the initial Solar System ⁶⁰Fe/⁵⁶Fe ratio is about 10⁻⁸. The lower ⁶⁰Fe abundance reported here has important implications for the astrophysical setting the Sun formed in and possible sources of ⁶⁰Fe and other extinct-radionuclides in the early Solar System. Estimates of the galactic background ⁶⁰Fe abundance (Wasserburg et al. 1996; Huss et al. 2009; Diehl et al. 2006; Wang et al. 2007) are at or above values determined from meteorites, indicating that ⁶⁰Fe in the Solar nebula could have been inherited from the interstellar medium. This weakens the argument for the initial Solar System abundance of ⁶⁰Fe as unequivocal evidence for late-stage addition of material from a nearby stellar source (i.e., supernova).

MATERIALS AND METHODS

Samples

Angrites

Several of the angrite samples in this study were previously processed for a U isotope investigation using methods described therein (Brennecka and Wadhwa 2012). This includes the two bulk samples (WR) of D'Orbigny, weighing between ~600-700 mg, and the ~175 mg pyroxene (PX), as well as one bulk sample weighing ~600-700 mg each of the plutonic angrites NWA 4801, NWA 4590, and NWA 6291 (the 0.05 M HCl washed samples, see below). For

these samples, Ni for isotopic measurements was purified from the residual U-free solutions of aliquots that were already processed to separate U (Brennecka and Wadhwa 2012). The Fe/Ni ratios were measured on chemically unprocessed aliquots (2-5%) of the dissolved samples that were reserved for this purpose. The ~20 mg olivine (OL) mineral separate was hand picked out of the D'Orbigny sample from which the PX was picked (Brennecka and Wadhwa 2012), and then ultrasonicated for ~5 minutes in ultrapure Milli-Q water to remove possible surface contamination. Two additional bulk samples of NWA 4590 and one of NWA 4801 (weighing \sim 150-250 mg each) were also obtained from the collection in the Center for Meteorite Studies (CMS) at Arizona State University (ASU) for this study. These samples were gently crushed with a boron carbide mortar and pestle and ultrasonicated for ~5 minutes in either ultra-pure Milli-Q water (NWA 4801 and one sample of NWA 4590) or 0.5M HCl (the other sample of NWA 4590), in order to test the effects of possible terrestrial contamination on the ⁶⁰Fe-⁶⁰Ni isotope systematics. After washing, the D'Orbigny OL separate and the additional plutonic angrites (those not previously processed for U) were dissolved using a combination of concentrated HF, HNO₃, and HCl at ambient pressure. An aliquot of ~5-10% of each unprocessed sample solution was saved for Fe/Ni ratio measurements and the rest were processed for Ni isotope analyses.

Chondrules from unequilibrated ordinary chondrites

This study includes individual chondrules and chondrule fragments (weighing $\sim 0.35-12$ mg) separated from three unequilibrated ordinary chondrites (UOC): Chainpur (LL3.4; five chondrules), Semarkona (LL3.00; five chondrules) and QUE 97008 (L3.05; three chondrules, one pooled chondrule fragment sample). The Chainpur samples were obtained from the collection in the CMS, where whole chondrules were separated from the disintegrated friable matrix. Chips weighing ~500 mg each of Semarkona and QUE 97008 were obtained from the collection at the Smithsonian Institution and from the Meteorite Working Group, respectively. The Semarkona and QUE 97008 samples were gently crushed with a boron carbide mortar and pestle before chondrules and chondrule fragments were handpicked from the matrices. As much adhering matrix material as possible was removed from the chondrules with stainless steel dental tools and by abrading with alumina polishing paper. The matrices of UOC contain relatively abundant low Fe/Ni ratio materials (e.g., FeS, Fe-Ni metal) that could hinder the search for radiogenic ε^{60} Ni* anomalies by effectively lowering the Fe/Ni ratio of the chondrules. After removing the matrices, the chondrules were ultrasonicated for ~5 minutes in ultra-pure Milli-Q water to remove any possible surface contamination and then dissolved in acid as described above for angrites. A 10% aliquot of the unprocessed sample solutions were set aside for Fe/Ni ratio measurements and the remainder were used for Ni isotopes.

Analytical Techniques

Chemical separation of Ni

Nickel was purified from sample solutions with a combination of anion and cation exchange chromatography and a Ni-specific resin containing dimethylglyoxime (DMG), using methods modified from (Cook et al. 2006; Quitté and Oberli 2006; Yamakawa et al. 2009). The first two column procedures are very similar to those described by (Cook et al. 2006) and use anion exchange (AG1-X8 resin, cleaned with HCl and HNO₃) to remove Fe and Zn and Ti, respectively. The third column uses cation exchange (AG50-X8 resin, cleaned with HCl and HNO₃) to separate Ni from most of the remaining cations, with the exception of Mg, and some Ca and Al. Samples were loaded onto and eluted from the cation column in 1 M HNO₃ and for large samples (WRs and PX) were split into two aliquots that were then recombined after Ni purification. The chondrules were not processed through the Ti-removal column because this step was not necessary to reduce the residual Ti to an acceptable level in these samples. The final column uses Eichrom Ni-specific resin with DMG to separate Ni from the remaining matrix elements and is modified from methods described by (Quitté and Oberli 2006; Yamakawa et al. 2009). The resin is cleaned with Milli-Q water followed by 0.2 M ammonium citrate adjusted to a pH of 8-9 with NH₄OH. The samples are loaded on the columns in a combination of 1 M HCl and 1 M ammonium citrate that has been adjusted to a pH of 9-10 with concentrated NH₄OH. After removal of the matrix elements, Ni is eluted from the column in 3 M HNO₃ as Ni-DMG. The samples are then dried at ~165° C after a few drops of

concentrated HClO₄ are added to the sample to break up the Ni-DMG complex. After drying completely, the samples are redissolved in concentrated HNO₃ and an additional few drops of HClO₄ and dried again. Once the HClO₄ is completely evaporated, the purified Ni samples are redissolved and dried several times in concentrated HNO₃ and finally brought up in 3% HNO₃ to the appropriate concentration for isotopic analysis. Total procedural blanks for Ni were ~20 ng for samples that were previously processed for U separation (D'Orbigny WRs and PX, and 0.05 M HCl-washed NWA 4801, NWA 4590 and NWA 6291; Brennecka and Wadhwa 2102) and <5 ng for the bulk plutonic angrites, D'Orbigny OL separate and UOC chondrules that were not processed prior to this study. The blanks are insignificant relative to the total amount of Ni in each of the angrite and chondrule samples ranged from ~2-5 µg.

Mass spectrometry

The Ni isotope ratios were measured using the ThermoFinnigan Neptune MC-ICPMS housed in the Isotope Cosmochemistry and Geochronology Laboratory (ICGL) at ASU. The measurements were made in medium resolution mode to avoid interferences from ⁴⁰Ar¹⁷O on ⁵⁷Fe and ⁴⁰Ar¹⁸O on ⁵⁸Ni. Ion intensities from ⁵⁷Fe, ⁵⁸Ni, ⁶⁰Ni, ⁶¹Ni, ⁶²Ni, ⁶⁴Ni and ⁶⁶Zn were measured simultaneously on faraday cups L4, L2, L1, center, H1, H2 and H4, respectively. Pure Ni solutions were diluted to concentrations of ~250 ppb with 3% HNO₃ and introduced into the plasma using an ESI APEX desolvating nebulizer. Each sample or standard run consisted of either 25 eight-second integrations or 50 foursecond integrations, with no difference in the analytical uncertainties using either routine. The samples were measured by sample-standard bracketing with the Ni isotopic standard SRM 986 and the measured Ni isotope ratios are normalized to a 62 Ni/ 58 Ni ratio of 0.0533886 (Gramlich et al. 1989) using the exponential law. The ϵ^{60} Ni* values for each measurement of a sample are calculated as the part per 10⁴ difference between the normalized 60 Ni/ 58 Ni ratio in a sample and the average of the ratios in the two surrounding standard brackets. The external reproducibility on ϵ^{60} Ni* over the course of this investigation is $\pm 0.10\epsilon$, calculated as two times the standard deviation (2SD) of repeat measurements of the USGS standard DTS-2b, which was processed identically to the meteorites and run during the same analytical sessions as the angrite and chondrule samples (Table 2.1, Fig. 2.4). The external reproducibility on ϵ^{61} Ni calculated the same way as for ϵ^{60} Ni* is $\pm 0.36\epsilon$ (2SD).



Figure 2.4. Reproducibility of terrestrial USGS standards. The circles correspond to DTS-2b dunite and the squares are AGV-2 andesite. The filled symbols represent the mean ⁶⁰Ni* of all sample-standard brackets run on a single day when meteorite samples were also measured. The open symbols are the mean of all sample standard brackets of a particular rock standard run over the course of this study. All error bars are $\pm 2SE$. The solid black line corresponds to the mean of all the daily DTS-2b means (filled circles) and the black dashed lines are the external reproducibility for the method ($\pm 0.1\varepsilon$) calculated as the 2SD of the daily DTS-2b means.

Several experiments were conducted to ensure that the Ni isotopic measurements were accurate and did not suffer from analytical artifacts induced by our methods. In addition to DTS-2b, another USGS rock standard with a higher Fe/Ni ratio (AGV-2) was also processed through the same chemical separation and Ni isotopic measurement technique as the meteorite samples. Both rock standards had terrestrial Ni isotope composition (i.e., ε^{60} Ni* = 0) within analytical uncertainties (Table 2.1, Fig. 2.4), demonstrating that our Ni separation procedures do not induce any artifacts on the normalized ⁶⁰Ni/⁵⁸Ni ratios. A pure Ni ICPMS standard solution (Alfa Aesar Ni) was also run during each analytical session to monitor the instrument performance (Table 2.1)

Doping experiments were also performed where solutions of the SRM 986 Ni isotopic standard were spiked with variable amounts of other elements that could potentially introduce interferences or matrix effects that alter the measured Ni isotope compositions. For the elements Na, Mg, Al, Ca and Cr, SRM 986 solutions with [Elt]/[Ni] ratios ranging from 0.1 to 1 were measured (Fig 2.5a). Some of the Ni solutions doped with these elements had ϵ^{60} Ni* values that are resolved from zero within the estimated external reproducibility for the meteorite samples based on repeats of the DTS-2b standard ($\pm 0.1\varepsilon$; Fig2.4). However, there is no correlation between the amount of dopant in the Ni solution and the measured ε^{60} Ni* values, suggesting that these effects may not be solely due to the presence of matrix elements. Because only three repeats were run of each doped Ni solution (less than for a typical sample), the error estimate from the DTS-2b analyses may not be representative of these samples. The errors for these doped samples is more appropriately estimated as $\pm 0.20\epsilon$ (2SD) from repeats Alfa Aesar Ni standard solution that was run during the same sessions as the doped solutions (Fig. 2.5a). Within these errors, all of the Ni solutions doped with these elements had terrestrial ε^{60} Ni* values. This demonstrates that the presence of very high levels (i.e., up to [Elt]/[Ni] = 1) of residual Na, Mg, Al, Ca and Cr in Ni solutions does not introduce detectable analytical artifacts on the measured ϵ^{60} Ni* values. For Na, Mg, Al, Ca and Cr, all of the sample solutions measured in this study had

 $[Elt]/[Ni] < \sim 0.01$, and should therefore not affected by the presence of these residual matrix elements.

The elements Fe, Zn and Ti have isobaric interferences that could interfere with the measurement of Ni isotopes. The ⁵⁸Fe interference on ⁵⁸Ni is corrected by monitoring the ⁵⁷Fe signal during measurement. The ⁶⁴Zn isobaric interference should only affect the ⁶⁴Ni/⁵⁸Ni ratios, which are not reported here. For Ni solutions with [Fe]/[Ni] ≤ 0.01 and [Zn]/[Ni] ≤ 0.1 , there are no measureable effects on ε^{60} Ni* (Fig. 2.5b). Titanium is the most problematic interference for the accurate measurement of ε^{60} Ni*, due to the molecular interference on ⁶²Ni from ⁴⁶Ti¹⁶O generated in the plasma. Apparent excesses of ⁶²Ni caused by the Ti-oxide interference induces deficits in the measured ε^{60} Ni* values because the ⁶²Ni/⁵⁸Ni ratio is used to normalize the ⁶⁰Ni/⁵⁸Ni ratio. However, at [Ti]/[Ni] ≤ 0.001 there are no analytical artifacts on ε^{60} Ni* within uncertainties (Fig. 2.5b). All of the sample solutions analyzed for Ni isotopes in this study had [Ti]/[Ni] $\leq \sim 10^{-4}$ and [Fe]/[Ni] $\leq \sim 0.001$, and are therefore not affected by these isobaric interferences. These solutions also had [Zn]/[Ni] $\leq \sim 0.01$ with most having [Zn]/[Ni] $\leq \sim 0.001$.



Figure 2.5. a) ε^{60} Ni* vs. [Elt]/[Ni] ratio for Ni solutions doped with Mg, Na, Al, Ca and Cr. The data are the average of repeat measurements (n = 3) of aliquots of SRM 986 Ni standard doped with high purity elemental standard solutions of the various elements at the concentration ratios shown. Error bars on the data points are omitted for clarity. The dashed lines correspond to ±2SD of the pure Ni standard solution run during the doping experiments (see text for details). b) ε^{60} Ni* vs. [Elt]/[Ni] ratio for Ni solutions doped with Fe, Ti and Zn. The data are the average of repeat measurements (n = 4-6) of aliquots of SRM 986 Ni standard doped with pure ICPMS standard solutions of the various elements at the concentration ratios shown. The dashed lines are the same as in a).

It is also important to ensure that differences in Ni concentrations of sample and standard solutions do not induce any analytical artifacts on the measured ε^{60} Ni* values. To test this, solutions of SRM 986 that were diluted by up to 50% compared to the bracketing standard SRM 986 solution with 250 ppb Ni and run as if they were samples. Differences in the Ni concentrations of the sample and standard solutions do not introduce any measureable artifacts in the measured ε^{60} Ni* values (Fig. 2.6); all of the sample solutions measured in this study had Ni concentrations within 50% of the bracketing standard.



Figure 2.6. ϵ^{60} Ni* vs. sample/standard intensity ratio of diluted SRM 986 Ni solutions run against a solution with a Ni concentration normally used for analysis. Each data point is the mean of sample-standard brackets (n=4) and errors are ±2SE.

The Fe/Ni ratios were measured on the Neptune MC-ICPMS and/or the

ThermoFinnigan X-series quadroploe ICPMS at ASU using chemically

unprocessed aliquots that were reserved for that purpose. For the Neptune, the

instrument was calibrated using a set of gravimetrically prepared ICPMS standard solutions with a range of Fe/Ni ratios that included the unknown angrite samples. The X-series ICPMS was calibrated with serial dilutions of a multi-element standard solution. The errors on the Fe/Ni are estimated to be $\pm 10\%$ based on repeated measurements of the USGS standard AGV-2 during the same analytical sessions that the samples were measured. The Fe/Ni ratio measured in our lab for AGV-2 of 2426 \pm 243 agrees well with of the certified Fe/Ni ratio 2463 \pm 392 (Wilson).

Chapter 3

²⁶AL-²⁶MG CHRONOMETRY OF THE UNGROUPED ACHONDRITE GRAVES NUNATAK 06129 AND BRACHINA

The ²⁶Al-²⁶Mg data presented here for GRA 06129 in this chapter were collected as part of a consortium study on this recently recovered meteorite. The results for GRA 06129 only were included in two publications on which I am coauthor that are listed below. My contribution to this research was the ²⁶Al-²⁶Mg chronology, including all data collection and written portions of the paper that focus on the chronometer. I created the figure presenting the ²⁶Al-²⁶Mg data for GRA 06129 that was published in the paper in Geochimica et Cosmochimica Acta, and is duplicated here (Fig. 3.1). The additional data for Brachina are my original unpublished work, as is all of the writing in this chapter.

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INTRODUCTION

Graves Nunatak 06128 and 06129 (GRA 06128/9) are paired achondrites from Antarctica with distinct mineralogy dominated by Na-rich plagioclase (e.g., Shearer et al. 2008). These unusual meteorites differ from other more common types of achondrites, such as eucrites and angrites, that are the products of basaltic magmatism on asteroids (e.g., Mittlefehldt et al. 1998). GRA 06128/9 also have a complex petrogenetic history involving partial melting of a chondrite-like source followed by accumulation of plagioclase and crystallization from that melt, thermal metamorphism at subsolidus temperatures, shock metamorphism and episodes of aqueous alteration (Shearer et al. 2010). These meteorites therefore allow us to explore asteroidal magmatic processes that are previously unrepresented in the meteoritic record. Although GRA 06128/9 formed under magmatic conditions that are unrepresented by known meteorite groups, it is not clear that if they formed on a yet unsampled parent body or are derived from an unsampled part of a known parent body composed of various types of igneous rocks. Some geochemical and mineralogical characteristics provide evidence that the ultramafic brachinite meteorites may be from the same parent body as GRA 06128/9, representing residual material left in the mantle after the extraction of melt from which GRA 06128/9 crystallized (Shearer et al. 2008; Day et al. 2009). Establishing the chronology of these unique samples is a fundamental step toward understanding how they relate to other meteorites that record the various stages of planetesimal differentiation in the early Solar System.

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This study includes the ²⁶Al-²⁶Mg isotope systematics of GRA 06129 and Brachina to see if this extinct-radionuclide chronometer can provide useful information about the ages of these two types of meteorites. The Al-rich mineralogy of GRA 06129 makes it a suitable sample to date with the ²⁶Al-²⁶Mg chronometer, provided it formed early in the history of the Solar System. Brachina also has relatively abundant plagioclase (Nehru et al. 1983) and an ancient age determined from the presence of extant ⁵³Mn when it formed (Wadhwa et al. 1998), making it possible that it could also be dated with the Al-Mg chronometer. The high-precision ages that can potentially be determined for GRA 06129 and Brachina using the ²⁶Al-²⁶Mg chronometer could also provide important insights into the possible genetic link between these two types of meteorites.

SAMPLES AND ANALYTICAL TECHNIQUES

Samples of GRA 06129 used here were initially processed in a clean laboratory at Lawrence Livermore National Laboratory. Several interior fragments from GRA 06129 weighing a total of ~185 mg were lightly crushed and leached for ~1 hour in 1N HCl at room temperature. The sample was then rinsed in ultrapure water and dried on a hotplate. All subsequent processing for the ²⁶Al-²⁶Mg isotopic analyses of GRA 06129 conducted under clean laboratory conditions in the Isotope Cosmochemistry and Geochronology Laboratory (ICGL) in the School of Earth and Space Exploration at Arizona State University. A ~30 mg bulk "whole rock "sample (WR) fraction from the HCl leached GRA 06129

and two ~1-2 mg plagioclase mineral separates, handpicked from the remainder of the leached bulk sample, were included in this study. An interior fragment of Brachina initially weighing $\sim 300 \text{ mg}$ was used in this investigation. The Brachina fragment was gently crushed in a boron-carbide mortar and a chip weighing ~ 25 mg was sampled for the bulk rock (WR.) The remainder of the crushed sample was sieved into three size fractions ($<53 \mu m$, $53-74 \mu m$ and $74-105 \mu m$) from which small (<1 mg) plagioclase-enriched mineral separates and an olivine separate (from the 74-105 µm fraction) were obtained using density separation with heavy liquids (tribromoethane) and hand-picking. All of the samples were digested using a 3:1 mixture of HF:HNO₃, followed by dissolution in concentrated nitric acid and finally in 1N nitric acid. Aliquots of ~5-10% were reserved for Al/Mg ratio measurements from each solution. The remainder of the mineral separate sample solutions and a ~3-4 mg rock equivalent aliquot of bulk samples were processed using ion-exchange chromatography to separate Mg from the matrix for Mg isotope ratio measurements. Column chromatography procedures for Mg separation have been described in detail elsewhere (Spivak-Birndorf et al., 2009; Chapter 4). Mg isotope ratio analyses were conducted with a Thermo Neptune multicollector inductively coupled plasma mass spectrometer (MC-ICPMS) in the ICGL using analytical protocols similar to those described by Spivak-Birndorf et al. (2009) and below in chapter 4. Radiogenic excesses in ²⁶Mg from the decay of ²⁶Al (δ^{26} Mg*, permil deviation from a terrestrial standard) were calculated from the normalized ${}^{26}Mg/{}^{24}Mg$ ratios (using the exponential fractionation law and assuming a ${}^{25}Mg/{}^{24}Mg$ ratio of 0.12663, Catanzaro et al.

1966) of the samples and the mean of the normalized ${}^{26}Mg/{}^{24}Mg$ ratios of the bracketing standards.

RESULTS

The Al/Mg ratios and δ^{26} Mg* for mineral separates and bulk samples of GRA 06129 and Brachina are shown in Table 3.1. The GRA 06129 bulk rock and mineral separates span a range in ²⁷Al/²⁴Mg from ~5 to ~250 and all have uniform excesses of radiogenic ²⁶Mg (δ^{26} Mg* ≈ 0.08) regardless of their Al/Mg ratios. This indicates that Mg isotopes were equilibrated in this meteorite subsequent to the complete decay of ²⁶Al. The slope of the internal mineral ²⁶Al-²⁶Mg isochron for GRA 06129 (Fig. 3.1) is not resolved from zero and corresponds to an upper limit on the ²⁶Al/²⁷Al ratio of 2.08 × 10⁻⁸ at the time of last equilibration of Mg isotopes.

Table 3.1

Sample ^a	$^{27}\text{Al}/^{24}\text{Mg}^{b}$	$\delta^{26}Mg^{*}$ (‰)	±2SE ^c	n
Graves Nunatak (GRA) 06129				
WR	5.25	0.080	0.009	12
PL-1	256.10	0.088	0.029	3
PL-2	85.82	0.084	0.018	7
Brachina				
WR	0.05	-0.023	0.034	8
OL	0.01	-0.007	0.045	8
<53 μm	0.78	0.022	0.030	4
53-74 μm	7.7	-0.004	0.014	4
74-105 μm	1.68	-0.011	0.042	6

²⁶Al-²⁶Mg isotopes systematics of GRA 06129 and Brachina

^aWhole rock (WR), plagioclase (PL) and olivine (OL). Numbered Brachina samples correspond to grain size of density separates (see text for details) ^bErrors in the 27 Al/ 24 Mg ratios are $\pm 2\%$.

^cErrors in the Mg isotope ratios are twice the standard error.



Figure 3.1. ²⁶Al-²⁶Mg systematics for GRA 06129. Radiogenic excesses in the ${}^{26}Mg/{}^{24}Mg$ ratio are expressed as permil deviations from the terrestrial value ($\delta^{26}Mg^*$, see text for definition). The slope of the isochron (solid black line) is not resolved from zero and provides an upper limit on the timing of the last Mg isotope equilibration (\leq 4560.1 Ma) relative to the D'Orbigny angrite. WR = whole rock; PL = plagioclase.

However, the initial ²⁶Al/²⁷Al ratio at the time of the major fractionation event that established the Al/Mg ratio in the GRA 06129 whole rock (presumably plagioclase accumulation and crystallization) may be inferred from the Mg isotopic composition of the GRA 06129 whole rock which records a δ^{26} Mg* value of 0.080 ± 0.009 ‰. Assuming that GRA 06129 originated from a chondritic source reservoir, i.e., characterized by an initial Δ^{26} Mg of -0.001 ± 0.002 ‰ and ²⁷Al/²⁴Mg = 0.101 ± 0.004 (Thrane et al., 2006), a model initial ²⁶Al/²⁷Al ratio of (2.19 ± 0.25) × 10⁻⁶ is inferred at the time of its crystallization.

The Brachina bulk sample and mineral separates span a relatively narrow range of ²⁷Al/²⁴Mg ratios from 0.01 to ~8, most likely due to the presence of Mg rich olivine in the plagioclase enriched mineral separates. All of the Brachina samples had terrestrial Mg isotope compositions within analytical errors and do not yield a statistically significant ²⁶Al-²⁶Mg isochron, but give an upper limit on the ²⁶Al/²⁷Al $\leq 4.11 \times 10^{-7}$ (Fig. 3.2).



Figure 3.2. ²⁶Al-²⁶Mg systematics for Brachina. The samples define a best-fit line with a slope that is indistinguishable from zero, corresponding to an upper limit on the ²⁶Al/²⁷Al \leq 4.11 × 10⁻⁷ (solid line). Errors are ±2SE on δ^{26} Mg* and ±2% on ²⁷Al/²⁴Mg ratios. The shaded region corresponds to the possible expected δ^{26} Mg* values if the ²⁶Al-²⁶Mg age was concordant with that from the ⁵³Mn-⁵³Cr chronometer for this meteorite (Wadhwa et al. 1998). OL = Olivine; WR = Whole Rock; <53 µm, 53-74 µm, and 74-105 µm correspond to the grain size of the plagioclase enriched mineral separates.

DISCUSSION

The excess ²⁶Mg in the GRA 06129 bulk sample indicates that its source originally formed early in the Solar System when ²⁶Al was extant. The slope of the bulk rock two-stage model ²⁶Al-²⁶Mg isochron described above for GRA 06129 corresponds to an age of 4564.9 \pm 0.3 Ma relative to D'Orbigny (Amelin 2008a; Spivak-Birndorf et al. 2009; Brennecka and Wadhwa 2012). This is likely the time at which the source magma of GRA 06129 was generated and potentially the timing of plagioclase accumulation and crystallization of GRA 06129 from that magma. The flat slope of the internal mineral ²⁶Al-²⁶Mg systematics of GRA 06129 reflects the equilibration of Mg isotopes in the minerals of this meteorite after the decay of ²⁶Al, and yields an upper limit of \leq 4560.1 Ma for this event (Fig. 3.1).

The upper limit on the ²⁶Al/²⁷Al determined here for Brachina corresponds to an age of < 4563.2 Ma (Fig. 3.2) anchored to the 26 Al- 26 Mg systematics of D'Orbigny (Amelin 2008a; Spivak-Birndorf et al. 2009; Brennecka and Wadhwa 2012). The 53 Mn- 53 Cr age of Brachina is 4564.2 ± 0.6 Ma, also anchored to D'Orbigny (Amelin 2008a; Wadhwa et al. 1998; Glavin et al. 2004; Brennecka and Wadhwa 2012), ~1 Ma older than the upper limit inferred for the ²⁶Al-²⁶Mg. Taken at face value this would imply that the Al-Mg chronometer closed at least ~0.4 Ma after the Mn-Cr in Brachina, possibly during secondary thermal alteration that equilibrated this meteorite at temperatures $\sim 1000^{\circ}$ C (Nehru et al. 1983. This heating event would have to be relatively short in order to equilibrate the Mg isotopes but not the Cr isotopes, considering the diffusion rates of these elements in plagioclase and olivine, respectively (LaTourrette and Wasserburg 1998; Ito and Ganguly 2006). However, the Al-Mg and Mn-Cr (both anchored to D'Orbigny) are only marginally discordant, and this apparent discrepancy could also be due in part to limitations in the analytical methods. Because the Al/Mg ratios of the plagioclase-enriched density separates analyzed here are so low $({}^{27}\text{Al}{}^{/24}\text{Mg} < 8)$, the ${}^{26}\text{Mg}$ * excesses they are expected to have if the Al-Mg and Mn-Cr closed contemporaneously in Brachina might be too small

to resolve outside of the analytical reproducibility. The errors on both the Brachina Mn-Cr age (Wadhwa et al. 1998) and the Mg isotope composition of the bulk sample affect whether or not the predicted δ^{26} Mg* could possibly be resolved, and thus mineral separates with higher Al/Mg ratios would be useful to get a more meaningful comparison of the two chronometers in Brachina.

The ²⁶Al-²⁶Mg systematics of Brachina, GRA 06129 and the paired GRA 01628 were also recently reported (Wimpenney et al. 2011). The Mg isotope compositions of Brachina and GRA 06128/9 measured by Wimpenny et al. (2011) agree with those here within errors, although the δ^{26} Mg* value for GRA 06128/9 is slightly lower at ~ 0.06 ‰. However, the Al/Mg ratios for both of these meteorites differs from those reported here (by about a factor of 2 for the GRA samples). The ²⁶Al-²⁶Mg model isochron for GRA 06128/9 reported by these authors has a slope of $(3.9 \pm 0.7) \times 10^{-6}$, slightly higher than that determined here. Nevertheless, the model 26 Al- 26 Mg age of 4565.5 ± 0.4 Ma for GRA 06128/9 based on the data of Wimpenny et al. (2011) is concordant within uncertainties with that reported here. The reason for the difference in Al/Mg ratios between the studies is not known, but could possibly be due to heterogenous distribution of mafic phases in various samples of GRA 06128/9, since the meteorites have varible textures (Shearer et al. 2010; Day et al. 2009, 2012). Another possibility is that the different washing procedures used here and in the study by Wimpenney et al. 2011 affected the Al/Mg ratios of the samples differently. For example, GRA 06128/9 have relatively abundant low-temperature alteration minerals, some of which are likely terrestrial weathering (Shearer et al. 2010; Day et al. 2009,

2012). Wimpenny et al. 2011 cleaned their GRA 06128/9 samples with ultrapure water and acetone to remove possible terrestrial contamination, whereas our sample was treated with a more aggressive leach in 1N HCl. It is possible that our cleaning procedure removed more of the alteration materials resulting in a different bulk Al/Mg ratio for the sample. If the alteration material contains terrestrial Mg, the slightly lower δ^{26} Mg* (i.e., closer to terrestrial values) reported for these meteorites by Wimpenny et al. (2011) could possibly reflect a larger contribution of Mg from the alteration products in that study. Alternatively, the HCl wash in our study could have preferentially dissolved the olivine compared to plagioclase, thereby increasing the Al/Mg ratio of the bulk sample.

The ²⁶Al-²⁶Mg systematics of GRA 06129 indicate a very early crystallization or source melt extraction age within ~2-3 Ma of the formation of the Solar System, followed by heating that equilibrated the Mg isotopes a minimum of around 5 Ma later. The chronology of GRA 06128/9 has also been studied using several other radioisotope chronometers (see review in Day et al. 2012 and references therein). The various chronometers indicate a complex history for GRA 06128/9 involving early formation with later thermal and shock metamorphism that is essentially consistent with the basic thermal history that can be inferred from the ²⁶Al-²⁶Mg systematics. The Pb-Pb age of phosphate in GRA 06128/9 is fairly old at 4.52 ± 0.06 Ga suggesting that the meteorite had cooled to < 500° C within a maximum of the first ~100 Ma of the Solar System forming (Day et al. 2009). Excess ¹²⁹Xe in GRA 06128/9 provides evidence for live ¹²⁹I when it formed, indicating that this occurred early in Solar System history (Shearer et al. 2010). However, the ³⁹Ar-⁴⁰Ar chronometer indicates later disturbance in GRA 06128/9 at ~4.4 Ga, most likely related to impact shock metamorphism (Shearer et al. 2010). This shock metamorphism may have also affected the Rb-Sr and Sm-Nd chronometers in GRA 06128/9 (Nyquist et al. 2009b). While several chronometers provide evidence an early formation age for GRA 06128/9, the model ²⁶Al-²⁶Mg age for the bulk rock is the the most precise.

The felsic mineralogy of GRA 06128/9 is unique among asteroidal meteorites, raising the question of whether it originated on parent body that has not yet been sampled or represents an unknown lithology from the parent body of a know meteorite group. A possible genetic link between GRA 06128/9 and the brachinites has been inferred from some geochemical characteristics that are often considered diagnostic of origin on common parent body, such as O isotope composition (Δ^{17} O) and mafic mineral Fe/Mn ratios (Shearer et al. 2008). Brachinites and GRA 06128/9 also have complementary petrologic and geochemical characteristics that are consistent with them forming as the residue and melt, respectively, from low degrees of partial melting of a common, chondrite-like source (Shearer et al. 2008, 2010: Day et al. 2009, 2012). The chronology of GRA 06128/9 and the brachinites has implications for whether or not these meteorites could have originated on the same parent body. The chronology of brachinites is not well constrained but the limited age data suggest early formation and later metamorphism at times that are generally consistent with those inferred for GRA 06128/9 (Day et al. 2012). However, most of the chronometers that have been applied to these meteorites are relatively imprecise,

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limiting the utility of chronological data for establishing a genetic link between brachinites and GRA 06128/9. The only precise age estimate for a brachinite is a 53 Mn- 53 Cr age for Brachina (Wadhwa et al. 1998), which can be compared to the precise 26 Al- 26 Mg model age for GRA 06129 determined here. The Brachina Mn-Cr age of 4564.2 ± 0.6 Ma (Wadhwa et al. 1998) is concordant with the Al-Mg model age of 4564.9 ± 0.3 Ma for GRA 06129. The good agreement of the highresolution extinct radionuclide chronometers in Brachina and GRA 06129 is consistent with these meteorites forming by the same partial melting process on a common parent body.

Chapter 4

NEW CONSTRAINTS ON EARLY SOLAR SYSTEM CHRONOLOGY FROM AL-MG AND U-PB ISOTOPE SYSTEMATICS IN THE UNIQUE BASALTIC ACHONDRITE NORTHWEST AFRICA 2976

This chapter was originally published as the paper listed below on which I am second author. My contribution to this work included all Al-Mg isotope data collection excluding the doping experiments and the standard addition test. I wrote sections of the paper that focus on the ²⁶Al-²⁶Mg chronology of NWA 2976 and created the table and figure presenting this data. I also helped develop the chemical techniques for Mg separation for isotopic analyses used in the paper and contributed rock standard data for both Mg isotope and ²⁷Al ratios.

Bouvier, A., Spivak-Birndorf, L., Brennecka, G. A., Wadhwa, M. (2011). New constraints on early solar system chronology from Al-Mg and U-Pb isotope systematics in the unique basaltic achondrite Northwest Africa 2976. *Geochimica et Cosmochimica Acta*, 75, 5310-5323.

INTRODUCTION

High precision absolute and relative dates based on long- (e.g., ²⁰⁷Pb-²⁰⁶Pb) and short-lived (e.g., ²⁶Al-²⁶Mg, ¹⁸²Hf-¹⁸²W, ⁵³Mn-⁵³Cr) radiochronometers are essential for resolving the sub-Ma timescales of early Solar System events, such as asteroidal accretion and differentiation (e.g., Wadhwa et al. 2006; Nyquist et al. 2009a). Concordance of these chronometers can also provide insight into the spatial distribution of the parent radionuclides in the solar nebula, which has implications for the origin of these nuclides (Russell et al. 2001). Yet, relatively few meteoritic materials have been dated successfully with multiple long- and short-lived chronometers. In particular, the Pb-Pb and Al-Mg chronometers have been applied simultaneously to only four individual calcium aluminum-rich (CAI) inclusions from Efremovka (Amelin et al. 2002, 2009), Allende (Jacobsen et al. 2008; Bouvier et al. 2008) and NWA 2364 (Bouvier and Wadhwa 2010), and three differentiated meteorites, including the D'Orbigny and SAH 99555 angrites (Amelin 2008a,b; Connelly et al. 2008; Spivak-Birndorf et al. 2009), and the ungrouped basaltic achondrite Asuka 881394 (Nyquist et al. 2003; Wadhwa et al. 2009).

Extinct radionuclides provide the means for high-resolution dating of meteoritic objects, but the robustness of model ages based on these radionuclides relies on the assumptions that (1) they were homogeneously distributed in the early Solar System, (2) parent-daughter isotope systematics have remained undisturbed since the time of last equilibration and (3) the U-Pb age of the anchor, which must take into account possible ²³⁸U/²³⁵U variations (Weyer et al. 2008; Brennecka et al. 2010a,b), is accurately and precisely known. Isotopic disturbance due to secondary processes and possible variations in the U isotopic composition may be responsible for some or all of the apparent discrepancies between the absolute and relative ages of some CAIs, such as the E60 inclusion from Efremovka (Amelin et al. 2002, 2009) and achondrites such as D'Orbigny (Nyquist et al. 2009a) and Asuka 881394 (Nyquist et al. 2003, 2009; Wadhwa et al. 2009). Also, in the particular case of the Al-Mg chronometer, the question of

the initial distribution of ²⁶Al has been recently debated (e.g., Krot et al. 2010; Larsen et al. 2010; MacPherson et al. 2010), and some of the aforementioned age discrepancies may also result from variations in the initial Solar System ²⁶Al/²⁷Al ratio.

The goals of the present study were to assess the concordancy of Pb-Pb and Al-Mg ages and the homogeneity of ²⁶Al in the early Solar System through isotopic investigations of a recently recovered ungrouped basaltic achondrite, Northwest Africa (NWA) 2976. This meteorite likely originated on a parent body distinct from that of other achondrites such as eucrites or angrites, and thus sampled a distinct region of the protoplanetary disk. Based on its petrographic features, NWA 2976 is thought to be paired with two other ungrouped basaltic achondrites, NWA 011 and NWA 2400 (Connolly et al. 2007), although no oxygen isotopic data have yet been obtained for NWA 2976 to confirm this pairing. These ungrouped basaltic achondrites are texturally similar to eucritic meteorites, but show some distinctive isotopic characteristics. In particular, oxygen isotope systematics of NWA 011 suggest possible affinities to the CR chondrite parent body (Yamaguchi et al. 2002). Moreover, Ti and Cr isotope systematics of NWA 2976 also suggest affinities to the carbonaceous chondrites (Trinquier et al. 2009). Previous investigations have demonstrated the presence of live ²⁶Al and ⁵³Mn in NWA 011 at the time of its crystallization, indicating an ancient formation age (Sugiura and Yamaguchi 2007). If a precise absolute formation age for NWA 2976 can be determined, these paired achondrites have the potential to serve as time anchors for several short-lived chronometers. We
report here the results of a chemical and isotopic investigation of NWA 2976, including measurements of elemental abundances, and of U, Pb-Pb and Al-Mg isotope systematics in whole-rock fractions and mineral separates of this meteorite.

EXPERIMENTAL METHODS

Similar to the basaltic eucrites, the ungrouped basaltic achondrites NWA 011/2400/2976 are composed primarily of pyroxene, plagioclase, and chromite, with minor amounts of sulfides, silica and phosphates (Connolly et al. 2007). We performed analyses of major and trace element abundances in a whole-rock fraction and determined Al-Mg and U-Pb isotope systematics in whole-rock fractions as well as plagioclase and pyroxene mineral separates.

Sample processing and chemical procedures

All sample processing was performed under clean laboratory conditions in the Isotope Cosmochemistry and Geochronology Laboratory (ICGL) at Arizona State University (ASU). The two interior fragments of NWA 2976 (weighing ~640 mg and ~560 mg, respectively) were obtained from the collection at the Center for Meteorite Studies (CMS) at ASU. Fragment #1 (~640 mg) was split and processed for elemental and U isotopic analyses as well as for Pb-Pb isotopic work, while fragment #2 (~560 mg) was split and processed for Pb-Pb and Al-Mg isotopic work.

Sample processing and chemical procedures for elemental and U isotopic analyses

The ~640 mg interior fragment #1 of NWA 2976 was ultrasonicated in Milli-Q (18 M Ω /cm) water, then dried before being split for elemental and U isotopic analyses (540 mg) and for Pb-Pb isotopic work (100 mg). The 540 mg whole-rock fraction (WR1, for elemental and U isotopic analyses) was crushed in an agate mortar. The powder was washed for one minute in cold 0.05 M HNO₃ in a PFA beaker to remove surficial contamination or staining from residence of this meteorite in the Northwest African desert. The powder was dried and then digested in concentrated HF-HNO₃ (5:1) using a pressurized Parr bomb PTFE vessel held at 155°C in an oven for 5 days. The digested sample was dried and subsequently treated with perchloric acid at 200°C on a hot plate to break down fluorides, dried and then fully dissolved by treatment with 6M HCl at 155°C in an oven for 1 day. A ~5% aliquot of the solution was reserved for elemental analyses and the remainder of the solution was processed for U separation using a U-Teva column procedure, as described in Brennecka et al. (2010a).

Sample processing and chemical procedures for Pb-Pb isotopic analyses

A ~260 mg fraction from interior fragment #2 of NWA 2976 was processed for the analysis of Pb isotope systematics. From this fraction, two pieces, weighing ~70 mg (WR2) and ~50 mg (WR3), were removed and powdered. The remainder was subjected to mineral separation using heavy liquids, followed by hand picking, to obtain pyroxene-rich (PX1) and plagioclaserich (PL1) mineral separates.

The WR2 powder was leached using a 9-step leaching protocol similar to the protocol #2 described by (Amelin 2008a), but with two additional washes using 1M HF: the first leach step was at room temperature with ultrasonication for 1 hr, and was followed by a second leach step at 90°C for 12 hr. The final (hot 1M HF) leach step resulted in almost complete dissolution of the residue remaining after the first 8 leach steps; the resulting residue did not contain sufficient Pb for analysis, and therefore the last leachate for this sample (WR2-L₉) is considered as the final digestion step. The WR3 powder as well as the mineral separates were leached using an 8-step protocol similar to that for WR2, except that the cold 1M HF step was of longer duration (6 hr), and the final hot 1M HF step was omitted. All leachates were dried down prior to further processing. Residues (denoted as R) and the dried leachates (denoted as L_1 - L_9 for WR2 and L_1 - L_8 for WR3, PX1 and PL1) were fully dissolved in concentrated HF:HNO₃ (5:1), and converted to the chloride form before sample uptake in 1.5M HBr, loading on 50µl anionic columns, rinsing matrix with 1.5M HBr, and then Pb extraction in 0.5M HNO₃. This Pb extraction procedure was repeated to insure a clean Pb cut.

A ~250 mg fraction of interior fragment #2 of NWA 2976 was similarly subjected to mineral separation to obtain two additional pyroxene and plagioclaserich separates (PX2 and PL2), and these were processed through to the same chemical procedures as the mineral separates PX1 and PL1 (see above) to obtain residues and 8 leachates. The ~100 mg fraction obtained from interior fragment #1 was crushed and prepared as a whole-rock sample (WR4) that was subjected to the same chemical processing as the WR3. As such, a total of 7 samples of NWA 2976, including 3 whole-rock samples (WR2, WR3 and WR4) as well as 2 pyroxene (PX1 and PX2) and 2 plagioclase (PL1 and PL2) mineral separates, were processed for Pb isotope analyses. The total procedural blank was 1.2 ± 0.2 pg. We measured the isotopic composition of Pb separated from the final leachates (L₈ and L₉ for WR2; L₈ for WR3 and WR4; L₈ for the pyroxene and plagioclase separates) and the respective residues.

Sample processing and chemical procedures for Al-Mg isotopic analyses

Our chemical procedures for Al-Mg isotope analyses are similar to those described in detail by Spivak-Birndorf et al. (2009). For the whole-rock sample (WR5), a small fraction (~20 mg) of the interior fragment #2 of NWA 2976 was powdered. Another fraction (~30 mg) from fragment #2 was crushed and processed for mineral separation using heavy-liquid density separation, followed by hand-picking, to obtain one pyroxene (PX3) and four plagioclase feldspar (PL3-6) separates. The mineral separates and whole-rock sample were digested in concentrated HF:HNO₃ (3:1) at ambient pressure, and finally brought into solution in 1M HNO₃. A ~10% aliquot of each sample solution was set aside for Al/Mg ratio measurements while the rest was processed through column chemistry for Mg purification.

Magnesium was separated from the rest of the matrix elements using a cation exchange column chromatography procedure similar to that described by Spivak-Birndorf et al. (2009). The only modification that we made for this study was the collection of a slightly wider Mg elution interval to ensure quantitative recovery of close to ~100% Mg. The equivalent of ~0.1-3 μ g of Mg for plagioclase and up to 50 μ g of Mg for pyroxene and whole-rock samples were loaded onto the column. To reduce the proportions of matrix elements to levels where they did not affect the Mg isotopic analyses, the whole-rock and pyroxene samples were passed through the column twice, while the plagioclase separates were passed through three times. The Ti clean-up column used by Spivak-Birndorf et al. (2009) was not necessary in this study given the low abundances of Ti in the NWA 2976 whole-rock sample and mineral separates.

We tested the accuracy of our methods by passing pure DSM-3 Mg isotope standard, DSM-3 isotope standard doped with the matrix (excluding Mg) of an Allende whole-rock sample solution, and a homogenized powder of San Carlos Olivine prepared at Harvard University (SCOL) through the column. We additionally performed doping experiments to assess the effects of matrix elements on the Mg isotope ratio measurements. These tests and their results are discussed in further detail below in the section *Mg isotopes and Al/Mg ratios*.

Mass spectrometry

The measurements of the isotopic compositions of U, Pb and Mg as well as of Al/Mg ratios were made on a Thermo-Finnigan Neptune multicollector inductively coupled plasma mass spectrometer (MC-ICPMS) in the ICGL at ASU equipped with an ESI APEX[®] desolvating nebulizer system. The elemental analysis of a whole-rock sample (WR1) was carried out on a Thermo X7 Series quadrupole ICP-MS in the Keck Foundation Laboratory for Environmental Biogeochemistry at ASU.

Elemental abundances and U isotopes

Concentrations of a suite of major and trace elements in the NWA 2976 whole-rock sample were determined using a calibration obtained from a multielement ICP-MS standard mixture run at 12 different concentrations (between 1ppt and 1ppm), and using double internal standard normalization (In and Bi). The elemental abundances measured for NWA 2976 WR1 are given in Table 4.1.

Table 4.1

Element	(%)	Element	(ppm)	Element	(ppb)
Na	0.416	Со	37.5	La	1188
Mg	2.992	Ni	148	Ce	5429
AI	4.227	Cu	22.1	Pr	611
К	0.021	Zn	20.4	Nd	2379
Ca	6.174	Ga	5.96	Sm	780
Ti	0.233	As	1.07	Eu	681
V	0.006	Rb	357	Gd	919
Cr	0.142	Sr	104	Tb	183
Mn	0.248	Y	5.59	Dy	1222
Fe	16.8	Zr	8.81	Ho	275
		Nb	559	Er	867
		Мо	299	Tm	118
		Ag	25.7	Yb	884
		Cd	17.4	Lu	117
		Ва	90.0	Hf	479
				W	7.5
				TI	7.2
				Pb	147
				Th	86
				U	96

Major and trace element composition of the NWA 2976 whole-rock. *The uncertainties on these concentrations are* $\pm 10\%$ (2 σ)

For the U isotope measurements, the instrumental mass-bias was corrected using a U double spike and sample-standard bracketing technique using the SRM 950a isotope standard. The ²³³U-²³⁶U double spike used in this study was originally calibrated at ASU against the SRM 950a standard for which a $^{238}U/^{235}U$ ratio of 137.88 was assumed (Shields 1960; Chen and Wasserburg 1980), and this spike composition was reported by Brennecka et al. (2010a). However, the new gravimetrically calibrated IRMM-3636 double spike (Richter et al. 2008) was recently used to obtain a revised value for the SRM 960 standard (identical to

SRM 950a) of 137.840 \pm 0.008 (Condon et al. 2010; Richter et al. 2010). Using this revised value for the SRM 950a standard, the isotopic composition of the double spike used in this study is ²³⁶U/²³³U = 1.00496, ²³⁸U/²³³U = 0.000958, ²³⁵U/²³³U = 0.000108. Samples were spiked to achieve ²³⁶U and ²³³U signals of ~2.5 × the voltage on the least abundant isotope, ²³⁵U. All measured isotopes of U (²³³U, ²³⁵U, ²³⁶U and ²³⁸U) were collected simultaneously in a Faraday cup collector array, utilizing 10¹¹ ohm resistors for all masses. Samples dissolved in 2% HNO₃ were introduced into the mass spectrometer using an Apex-Q sample introduction system with a 60 µl/min nebulizer. The concentration of the standard was matched with that of the sample (~60 ppb) to within 10%.

Pb isotopic measurements

We used Faradays cups for measuring ²⁰⁰Hg, ²⁰²Hg, ²⁰³Tl, ²⁰⁵Tl, ²⁰⁶Pb, and ²⁰⁷Pb simultaneously ($10^{12} \Omega$ resistors for 202 Hg, $10^{11} \Omega$ resistors for the rest), and used a secondary electron multiplier (SEM) to monitor the ²⁰⁴Pb signal. The background on ²⁰⁴Pb was lower than 200 counts per second, indicating only minimal interference from ²⁰⁴Hg contained in the Ar carrier gas. Solutions were introduced into the mass spectrometer using a pre-cleaned ESI Apex desolvating nebulizer, for which all the glass parts were soaked overnight in hot 50% nitric acid before remounting. Analyses of two Pb isotope standards SRM-NIST-981 and SRM-NIST-983 doped with Tl (2 ppb Pb – 1 ppb Tl) over the course of this investigation yielded values for SRM-NIST-983 consistent with the recommended values by National Institute of Standards and Technology (NIST) (Catanzaro et al. 1968) and the values of SRM-NIST 981 measured using Pb triple spike and TIMS techniques (Abouchami et al. 2000) (Table 4.2). The Pb isotopic ratios for the two standards were corrected for instrumental mass bias using the Tl-doping or the 202 Pb- 205 Pb double spike method on our MC-ICPMS instrument at ASU. We have previously verified that both the Tl-doping and the 202 Pb- 205 Pb double spike methods yield similar corrected Pb isotopic compositions and precisions (Amelin et al. 2008a; Bouvier and Wadhwa 2010). The Pb separated from each of the samples was brought into solution in 200-300 µl of 3% HNO₃ and spiked with a Tl standard solution to obtain a final concentration of 1 ppb Tl for correction of the instrumental mass bias. Blanks were measured before and after each sample and standard measurement. Blank contribution during sample processing was corrected following the method described in Bouvier et al. (2007).

Table 4.2

Sample	Total Pb	Uncorr.	Corr.	% corr.	Corr.	Corr.	% corr.	Sample	e Sample/
Sample	analyzed (ng) ²⁰⁶ Pb ^{/204} Pb	²⁰⁶ Pb ^{/204} Pb	error	²⁰⁷ Pb ^{/204} Pb	²⁰⁷ Pb ^{/206} Pb	error	/blank ²⁰⁶ Pb	blank ²⁰⁴ Pb
WR 2-L8	0.01	29.152	30.132	2.22	23.141	0.767979	0.6234	14.6	8.4
WR 2-L9	0.35	1092.3	1180.3	2.20	740.29	0.627204	0.0209	713	6.8
WR 3-L8	0.03	39.417	40.827	1.61	29.680	0.726984	0.3368	28.5	12.3
WR 3-R	0.83	1269.2	1316.7	1.12	825.37	0.626839	0.0162	1713	14.0
WR 4-L8	0.71	122.74	123.89	0.275	81.730	0.659698	0.0231	548	62.8
WR 4-R	0.82	1676.0	2094.8	6.60	1310.6	0.625666	0.0336	411	2.5
PX 1-L8	1.5	1056.5	1081.3	0.778	678.69	0.627669	0.0112	2241	23.2
PX 1-R	0.88	975.45	1010.5	1.02	634.34	0.627770	0.0136	1366	14.5
PX 2-L8	0.65	545.12	571.20	1.29	360.74	0.631547	0.0241	570	11.4
PX 2-R	1.07	2066.0	2468.8	5.19	1544.0	0.625377	0.0232	622	3.1
PL 1-L8	0.16	71.215	72.300	0.595	49.436	0.683949	0.0683	172	34.3
PL 1-R	0.03	115.59	138.53	6.40	90.682	0.654580	0.4494	29.5	3.6
PL 2-L8	0.19	46.383	46.900	0.409	33.772	0.720240	0.0790	121	36.6
PL 2-R	0.08	146.09	182.50	7.13	118.23	0.647788	0.3667	32.2	3.1
NIST-SRM 981	Session 1		16.940	0.0298		0.914744	0.0186		n 8
2 ppb Pb – 1ppb Tl	Session 2		16.940	0.0276		0.914767	0.0152		11
Recommended values [1]			16.941	0.0089		0.91475	-		
NIST-SRM 983	Session 1		2750 3	1 16		0 07123	0 139		3
2 nnh Ph - 1nnh Tl	Session 2		2736.8	0.618		0.07122	0.056		6
	0000012		2,00.0	5.010		0.07400	0.000		U U
Recommended values [2]			2695	5.39		0.07120	0.056		

Pb-Pb isotope compositions of leachates and residues of whole-rock samples and mineral separates of NWA 2976.

[1] Abouchami et al., 2000. [2] Catanzaro et al., 1968. Shown here are the uncorrected ²⁰⁶Pb/²⁰⁴Pb ratios, the corrected Pb isotopic compositions (after correction of the blank contribution), along with their corresponding correlated errors (in %), and sample/blank ratios for the ²⁰⁶Pb and ²⁰⁴Pb. Total amount of Pb analyzed for each sample is also indicated. The measured compositions and associated uncertainties of the Pb isotopic standards NIST-SRM 981 and 983 analyzed during two analytical sessions are additionally shown.

Mg isotopes and Al/Mg ratios

Pure Mg solutions diluted in 3% HNO₃ were introduced into the mass

spectrometer with an Apex-Q sample introduction system using a 100 µl/min

nebulizer, typically at a concentration of 250 ppb Mg (125 ppb for the PL-3

plagioclase Mg solution). The concentration of the standard was matched to that

of the sample to within 20%. The mass spectrometer was operated in medium-

resolution mode in order to eliminate a small interference from ${}^{12}C^{14}N^+$ on the ${}^{26}Mg$ peak. The instrumental mass bias was corrected using the sample-standard bracketing technique using the DSM-3 Mg isotope standard. The radiogenic excesses in ${}^{26}Mg$ (i.e., $\delta^{26}Mg^*$) were determined by sample-standard bracketing and internal normalization of the ${}^{26}Mg/{}^{24}Mg$ ratio measured for the standard and the sample to a ${}^{25}Mg/{}^{24}Mg$ ratio of 0.12663 (Catanzaro et al. 1966) using the exponential law. Each measurement cycle consisted of 15 integrations of 16 seconds and the reported Mg isotope ratios are the average of 2 to 8 repeat measurements (n) of the sample bracketed with measurements of DSM-3 (Table 4.3). Long-term reproducibility (2σ , or twice the standard deviation) of our Mg isotope analyses is based on repeated measurements over the course of this study of a 250 ppm SPEX Mg solution made prior to analyzing the Mg isotope compositions of the unknown samples.

The accuracy of Mg isotope ratio measurements by MC-ICPMS can be hindered by matrix effects and interferences from other elements. Therefore, to assess these effects and to determine the level to which various elements can be present in our clean Mg solution without adversely affecting the accuracy of the measured Mg isotope composition, we performed element doping tests. Specifically, we measured the Mg isotopic compositions of the DSM-3 standard doped with different proportions of a single element (X) with X/Mg ratios of 0.001 for X=Al, and 0.05, 0.10, 0.25, 0.5 and 1.00 for X=Al, Ca, Na, Ti and Fe. The results from these element doping tests are shown in Fig. 4.1 (and are also reported in Table 4.S in the supplemental data section below). There are no resolvable deviations of the δ^{26} Mg and δ^{26} Mg* for X/Mg ratios <0.1 (Figs. 4.1a and 4.1b respectively); for comparison, the clean Mg sample solutions processed through our chemical procedures have typical measured Al/Mg ratios <0.005.

To test the efficacy of our chemical procedures for quantitative recovery of a sufficiently clean Mg solution, we doped the matrix of a solution of a 80 µg whole-rock sample of the Allende CV3 meteorite from which Mg has previously been removed (using procedures as described above) with 2 µg of DSM-3 Mg, and then processed this mixture through our column chemistry procedure (2) passes). The clean Mg separate was then analyzed and the results are shown in Table 4.3. Furthermore, to test the accuracy of our Mg isotope ratio measurements, we also analyzed Mg separated from an aliquot of a San Carlos olivine (SCOL) stock solution made by dissolution of \sim 50 mg of a homogenized powder of a San Carlos olivine sample prepared at Harvard University. The Mg isotopic composition of this same SCOL sample has been previously reported by Young et al. (2009a) and Chakrabarti and Jacobsen (2010). As shown in Table 3, we find an average δ^{26} Mg value for SCOL of -0.27 (±0.04) ‰ (2 σ_m , n=8) (where $2\sigma_m$ is twice the standard deviation of the mean or $2\sigma/\sqrt{n}$ where n is the number of repeated measurements of a sample). This value differs from the Mg isotopic composition reported by Chakrabarti and Jacobsen (2010) of δ^{26} Mg = -0.55 (± 0.06) ‰ $(2\sigma_m)$, but is similar to that reported for this same sample by Young et al. (2009a) of δ^{26} Mg = -0.193 (±0.013) ‰ (2 σ_m) (in particular, when the typical 2σ external reproducibility for Mg isotope analyses of ± 0.05 ‰ amu⁻¹ is

considered). The reason for the apparent discrepancy between the Mg isotope composition of SCOL reported by Chakrabarti and Jacobsen (2010) and that reported here as well as by Young et al. (2009a) remains unclear at this time. Importantly for this study, however, for each of these tests, the δ^{26} Mg* values are normal (or terrestrial, i.e., = 0) within the uncertainties.

The Al/Mg ratios were measured using techniques similar to those described by (Spivak-Birndorf et al. 2009), with Al and Mg isotopes being measured simultaneously on Faraday collectors. In order to assess the accuracy and precision of our Al/Mg ratio measurements, low-Al/Mg (BCR-2, Columbia River Basalt) and high-Al/Mg (JR-2, Japanese Rhyolite) rock standards were always run along with the unknown samples. The Al/Mg ratios of the unknown samples were determined during two analytical sessions, and during each session a calibration curve was first generated from gravimetrically prepared ICPMS standard solutions with a range of Al/Mg ratios (~0.5-100). This calibration vielded ${}^{27}\text{Al}/{}^{24}\text{Mg}$ ratios for the rock standards for BCR-2 of 3.75 ± 0.08 and JR-2 of 314 ± 16 (Table 3), in excellent agreement with the certified values of $3.77 \pm$ 0.08 (Wilson 1997) and 318 ± 80 (Imai et al. 1995), respectively. The uncertainties (2σ) in the measured Al/Mg ratios were estimated based on the accuracy and reproducibility of repeated measurements of these rock standards and the unknown solutions. The data for the NWA samples and rock standards that were measured in both analytical sessions were in good agreement and the Al/Mg ratios reported here are the averages of all measurements during both sessions. Based on the reproducibility and accuracy of repeat measurements of

these rock standards, we estimate the analytical uncertainties in the ${}^{27}\text{Al}/{}^{24}\text{Mg}$ ratios to be $\pm 2\%$ for samples with ${}^{27}\text{Al}/{}^{24}\text{Mg} \le 100$ and $\pm 5\%$ for samples with ${}^{27}\text{Al}/{}^{24}\text{Mg} > 100$ (see Table 4.3).

Table 4.3

²⁷*Al*/²⁴*Mg* ratios and *Mg* isotopic compositions of terrestrial mineral, rock and solution standards.

Sample	²⁷ Al/ ²⁴ Mg ^a	δ ²⁶ Mg*	$\pm 2\sigma_m^c$	δ ²⁵ Mg	±20m ^D	δ ²⁶ Mg	±20m ^D	n°
Mineral and rock standards for AI/Mg and Mg isotopes								
San Carlos olivine	-	-0.008	0.024	-0.13	0.03	-0.27	0.04	8
BCR-2 basalt	3.750							7
JR-2 rhyolite	313.7							7
Mg Solution standards								
SPEX Mg solution		0.016	0.020	-0.98	0.05	-1.91	0.09	16
DSM-3, no chemistry		0.00	0.01	0.00	0.01	-0.01	0.01	4
DSM-3 (2 mg), 1 column	pass	0.01	0.00	0.00	0.01	0.01	0.02	4
DSM-3 (2 mg) with Allend	e WR matrix, 2	0.02	0.01	0.01	0.02	0.00	0.07	4
column passes		-0.02	0.01	0.01	0.03	0.00	0.07	4

^aErrors (2 σ) in the ²⁷Al/²⁴Mg ratio are ±2% and ±5% for BCR-2 and JR-2 respectively.

^bErrors in the Mg isotope ratios are twice the standard deviation of the mean (i.e., standard error). ^cNumber of repeat measurements for Mg isotope compositions.



Figure 4.1. The Mg isotope compositions of DSM-3 Mg standard solutions doped with various proportions of Al, Ca, Fe, Na and Ti. (a) δ^{26} Mg (‰) relative to pure DSM-3 and (b) δ^{26} Mg* (‰) relative to pure DSM-3 for each doped solution (data point is the average of 4 repeats with the typical $2\sigma_m$ uncertainty shown on the lower right of the figure). The Mg sample cuts after column chromatography were always characterized by X/Mg < 0.001 (X= Al, Ca, Fe, Na or Ti) for each of these elements.

RESULTS

Major and trace element composition

The major and trace element composition of the NWA 2976 whole-rock

(WR1) is given in Table 4.1. This ungrouped basaltic meteorite is enriched in the

rare earth elements (REE) and high field strength elements (HFSE), depleted in volatiles and shows variable degrees of chemical fractionation for the transition metals relative to chondrites (Fig. 4.2).



Figure 4.2. The elemental composition of the NWA 2976 whole-rock shown relative to CI chondrites. For comparison, the whole-rock compositions of other basaltic achondrites such as the paired achondrite NWA 011 (Yamaguchi et al., 2002), the eucrite Juvinas (Kitts and Lodders, 1998; Yamaguchi et al., 2002), and the quenched angrite D'Orbigny (Mittlefehldt et al., 2002) are also shown here. The whole-rock patterns of the two ungrouped basaltic achondrites NWA 2976 and NWA 001 are clearly different from those of the eucrites and angrites. See text for further details.

The NWA 2976 whole-rock has a REE pattern is generally flat with

abundances at ~5 × CI and is characterized by positive anomalies in Ce (Ce/Ce*

~1.5, where Ce* is the value interpolated between CI-normalized values of La and

Pr) and Eu (Eu/Eu* ~2.5, where Eu* is the value interpolated between CI-

normalized values of Sm and Gd). A similar degree of enrichment as the REE

relative to CI chondrites is also found for the HFSE (Ti, Hf, and Zr \sim 3-5 × CI). The Th/U ratio of the whole-rock sample analyzed here is \sim 0.9. The abundances of volatile alkali metals such as K and Rb (\sim 0.24 and \sim 0.15 × CI, respectively) are depleted relative to chondrites, as is also the case for Ni (\sim 0.01 × CI). Finally, the NWA 2976 whole-rock sample is chondritic in V, but sub-chondritic in Cr abundances, and there are slight enrichments in Mn and Nb (1.2-1.9 × CI).

U-Pb systematics

The measured ²³⁸U/²³⁵U ratio in the NWA 2976 WR1 sample was 137.751 ± 0.018 (2 σ ; n=3). We note that the external reproducibility (2 σ) on our ²³⁸U/²³⁵U ratio measurements (based on 12 repeat analyses of the SRM 950a U isotope standard) is ± 0.016 . As such, we conservatively used the larger uncertainty associated with the repeat measurements of the NWA 2976 WR1 sample for the calculation of the Pb-Pb internal isochron age (discussed below).

We analyzed the last two leachates (L_8 and L_9) and the residue (R) for WR2 as well as the last leachates (L_8) and corresponding residues (R) for WR3-4, PX1-2, and PL1-2. The L8 leachates have variable compositions with ²⁰⁶Pb/²⁰⁴Pb ratios that range from relatively unradiogenic (e.g., 30.13 for WR2-L8) to quite radiogenic (e.g., 1,081 for PX1-L8). All of the respective residues are highly radiogenic, with ²⁰⁶Pb/²⁰⁴Pb ratios between 1,010 (PX1-R) and 2,469 (PX2-R), indicating efficient removal of common Pb during the preceding leaching steps.

Because the Pb isotopic compositions of these samples can be so radiogenic, we used the uncertainty associated with our measurements of the NBS 981 Pb standard as the uncertainty on our measured 207 Pb/ 206 Pb ratio (±0.020%, $2\sigma_m$), and of the NBS 983 Pb standard as the uncertainty on our measured 206 Pb/ 204 Pb ratios (±1.15%, $2\sigma_m$) (Table 4.2) when the internal correlated errors on the samples were lower, and we used a correlation coefficient of 0.16 between these two ratios (Albarède et al. 2004) and the model 1 solution for the isochron age calculations using Isoplot version 3.64 (Ludwig 2008).

The Pb-Pb model ages assuming a single stage evolution from the initial composition of the Solar System represented by the Canyon Diablo troilite (CDT) (Tatsumoto et al., 1973) range from 4544.0 ± 8.8 Ma (for WR2-L₈) to 4566.5 ± 1.8 Ma (for PL2-L₈) for the last leachates, and 4563.0 ± 6.5 Ma (for PL2-R) to 4563.88 ± 0.37 Ma (for PX2-R) for the residues, if the conventionally assumed value of 238 U/ 235 U = 137.88 is used. However, using the 238 U/ 235 U ratio of 137.751 ± 0.018 measured here for the NWA 2976 whole-rock sample, these model ages are ~1.4 ± 0.2 Ma younger.

In contrast to the CDT model ages (discussed above), the internal isochron method avoids any assumption of the initial isotopic composition of the Solar System and the NWA 2976 parent body. The 14 fractions with 206 Pb/ 204 Pb > 30 analyzed here yield an internal Pb-Pb isochron age of 4562.27 ± 0.37 (MSWD = 5.9) using the measured U isotopic composition of the NWA 2976 whole-rock (238 U/ 235 U = 137.751 ± 0.018) (Fig. 4.3a). However, the plagioclase residues had extremely small amounts of Pb and their measured Pb isotope compositions are relatively unradiogenic and imprecise (Table 4.2). If only the WR2 L9 leachate (WR2-L₉, considered as the final digestion step for the WR2 sample) and the four

whole-rock and pyroxene residues (WR3-R, WR4-R, PX1-R, and PX2-R), with corrected 206 Pb/ 204 Pb > 1010, are regressed together, we obtain an internal isochron age of 4562.89 ± 0.59 Ma (MSWD = 0.02) (Fig. 4.3b), again using 238 U/ 235 U = 137.751 ± 0.018.



Figure 4.3. a) ²⁰⁴Pb-²⁰⁶Pb versus ²⁰⁷Pb/²⁰⁶Pb isotope systematics of the 14 acid leachates and residues of whole-rocks and mineral separates of the NWA 2976 achondrite (see details in the text and the Pb isotopic data in Table 2). The ellipses represent the $2\sigma_m$ errors for the sample or for the standard, whichever is larger (as described in section 3.2), and include the errors from correction of the blank contribution. The most radiogenic fractions are contoured by a box that is shown in Fig. 3b. The internal isochron on the 13 fractions with ²⁰⁶Pb/²⁰⁴Pb>30 gives an age of 4562.30 ± 0.37 (MSWD = 5.9) using ²³⁸U/²³⁵U = 137.751 and model 1 solution in Isoplot) A blow up of the boxed area shown in Fig. 3a, showing the Pb isotope compositions of the most radiogenic samples with ²⁰⁶Pb/²⁰⁴Pb > 1,010 (the last leachate L9 of WR2 considered at its residue, the residues following the 8 leaching steps for WR3,4 and PX1,2, and PX-1 L8 which is not regressed in the isochron calculations; see text for further details). The internal isochron age of 4569.87 ± 0.59 Ma was obtained on the 5 residue samples using the U isotope composition measured here for the NWA 2976 whole-rock (i.e., ²³⁸U/²³⁵U = 137.751 ± 0.018).

²⁶Al-²⁶Mg systematics

The magnesium isotope compositions and ${}^{27}\text{Al}/{}^{24}\text{Mg}$ ratios measured in pyroxene (PX3) and plagioclase (PL3-6) separates and a whole-rock sample (WR5) of NWA 2976 are shown in Table 4.4. The samples span a wide range in 27 Al/ 24 Mg ratios (~0.7 to ~514). The WR5 and pyroxene separate PX3 have normal (terrestrial) Mg isotope compositions (i.e., δ^{26} Mg* ≈ 0) within the uncertainties. All four plagioclase separates (PL3-6) analyzed here have excesses in radiogenic ^{26}Mg with $\delta^{26}Mg^*$ values ranging from ~0.25‰ to ~1.45‰ that correlate with the corresponding ²⁷Al/²⁴Mg ratios. The mineral separates and whole-rock define an internal ²⁶Al-²⁶Mg isochron with a slope corresponding to an initial ${}^{26}\text{Al}/{}^{27}\text{Al}$ ratio of $(3.94 \pm 0.16) \times 10^{-7}$ (MSWD = 0.23) and an initial 26 Mg/ 24 Mg ratio (δ^{26} Mg*₀) of -0.005 ± 0.013‰ (Figs. 4.4a and 4.4b).

Table 4.4

Al-Mg isotope systematics of NWA 2976.

Sample ^a	²′Al/²⁴Mg⁵	δ²⁵Mg*	±2 $\sigma_{\rm m}$ c	δ ²⁵ Mg	±2 $\sigma_{\rm m}$ c	δ²⁵Mg	±20m ^c	nª
WR5	1.87	0.002	0.025	-0.12	0.03	-0.24	0.05	8
PX3	0.67	-0.004	0.017	-0.08	0.02	-0.16	0.03	7
PL3	513.6	1.452	0.022	-0.18	0.07	1.11	0.16	2
PL4	143.0	0.393	0.014	-0.26	0.03	-0.12	0.09	4
PL5	121.6	0.340	0.016	-0.27	0.02	-0.20	0.02	4
PL6	82.27	0.254	0.068	-0.26	0.03	-0.26	0.07	4

^aWhole rock (WR), pyroxene (PX), and plagioclase (PL). ^bErrors (2σ) in the ²⁷Al/²⁴Mg ratio are ±2% for samples with ²⁷Al/²⁴Mg ≤ 100 and $\pm 5\%$ for samples with ${}^{27}\text{Al}/{}^{24}\text{Mg} > 100$.

^cErrors in the Mg isotope ratios are twice the standard deviation of the mean (i.e., standard error).

^dNumber of repeat measurements for Mg isotope compositions.



Figure 4.4. a) ²⁶Al-²⁶Mg internal isochron for NWA 2976. The black squares are data from this study. The isochron determined from these data is depicted as a solid black line with the uncertainty shown by the dotted lines. This isochron has a slope corresponding to an initial ²⁶Al/²⁷Al = $(3.94 \pm 0.16) \times 10^{-7}$ (MSWD = 0.23). Shown for comparison is the Al-Mg isochron previously determined for NWA 2976 (Schiller et al., 2010; open grey squares and solid grey line). b) Blow-up of a portion of Fig. 4a showing the initial δ^{26} Mg* values determined in this study and by Schiller et al. (2010). In contrast to the study by Schiller et al. (2010), we find no evidence for an elevated initial δ^{26} Mg*. Furthermore, the chondritic data point (grey symbol; Thrane et al. 2006) lies on the isochron determined in this study (within uncertainties) suggesting that the NWA 2976 parent melt formed from a source reservoir that was chondritic with respect to Mg isotopes.

DISCUSSION

Bulk chemical characteristics of NWA 2976: Comparison with other basaltic achondrites and implications for its petrogenesis

Although the mineralogical characteristics of NWA 2976 are similar to those of the basaltic eucrites (Connolly et al. 2007), its bulk chemical composition is quite distinct from that of eucrites, but rather similar to that of another ungrouped achondrite, NWA 011. Specifically, the abundances of transition elements (such as V, Cr, Mn, and Ni) and alkali metals (such as K and Rb) in NWA 2976 are similar to those in NWA 011 (Yamaguchi et al. 2002) (Fig. 4.2). Of note, the higher abundances of Ni and other siderophiles in NWA 011 compared to eucrites were attributed to the assimilation of material from an iron meteorite impactor (Yamaguchi et al. 2002); a similar Ni concentration in the NWA 2976 achondrite implies an origin similar to NWA 011.

The REE patterns of NWA 2976 and NWA 011 are also relatively similar, i.e., with distinct positive anomalies in Ce (suggesting the effects of residence in the terrestrial desert environment; Crozaz et al. 2003) and in Eu (possibly related to plagioclase accumulation or melt extraction under highly reducing conditions on the parent body) (Fig. 4.2). These patterns (excluding Ce anomalies, which are the result of weathering in the terrestrial environment) are clearly distinct from those of the basaltic eucrites (e.g., Juvinas) and angrites (e.g., D'Orbigny), which are typically characterized by flat REE patterns with slight negative Eu anomalies (Kitts and Lodders 1998; Mittlefehldt et al. 2002; Yamaguchi et al. 2002). The higher absolute abundances of the REE as well as the higher Th and U

concentrations of NWA 2976 compared to NWA 011 are likely to be due to a relatively higher abundance of phosphates in the NWA 2976 whole-rock sample analyzed in this study. The Th/U ratio of NWA 2976 is ~0.9 in agreement (within errors) with the value reported for NWA 011 (Yamaguchi et al. 2002). Along with the similarity in their mineralogical and petrological features, the bulk chemical characteristics reported here indicate that NWA 2976 is likely to be paired with NWA 011 (and also NWA 2400, which is also suggested to be paired with the latter; Russell et al. 2005).

The Th/U ratio reported here for NWA 2976 WR1 has implications for the origin of the variations in the U isotope compositions of meteorites and their components. Brennecka et al. (2010a) demonstrated a correlation between the Th/U (or Nd/U) and 238 U/ 235 U ratios measured in CAIs. Since Th (or Nd) has geochemical behavior similar to Cm, this correlation was the first definitive evidence for the presence of 247 Cm (which decays to 235 U with a half-life ~15.6 Ma) in the early Solar System. With a measured Th/U ratio of ~0.9 and a 238 U/ 235 U ratio of -0.67‰ relative to the SRM 950a U isotope standard, the NWA 2976 whole-rock sample clearly does not lie on the correlation line defined by Allende CAIs (Brennecka et al. 2010a). The Th/U of ~0.9 for the NWA 2976 whole-rock is substantially lower than for other basaltic meteorites. The Th/U ratios for the Juvinas eucrite and the D'Orbigny angrite are ~ 3.1 and ~ 3.7 , respectively (Fig. 4.2), and the average terrestrial crustal rocks is \sim 3.8 (Taylor and McLennan 1985). This likely reflects a highly fractionated Th/U ratio in the source reservoir of the NWA 2976 parent melt.

The chronology of NWA 2976

The 5 whole-rock and pyroxene Pb samples obtained from the last dissolution step (WR2-L₉, PX1,2-R, and WR3,4-R; Table 2), with 206 Pb/ 204 Pb>1010, have model ages (calculated assuming 238 U/ 235 U = 137.88) that range from 4563.33 ± 0.24 Ma (PX1-R) to 4563.88 ± 0.37 Ma (PX-2-R), using the Canyon Diablo troilite as the initial Solar System Pb isotope composition (Tatsumoto et al. 1973); model ages range from 4563.30 ± 0.28 Ma (PX1-R) to 4563.86 ± 0.37 Ma (PX-2-R) if the Nantan troilite is assumed as the initial composition (Blichert-Toft et al. 2010). As such, it is evident that the model ages for the 5 most radiogenic samples are identical within errors, and the assumption of either the Canyon Diablo or the Nantan troilite as the initial Solar System Pb isotopic composition does not make a resolvable difference to these model ages.

Recent work has demonstrated that the U isotope ratio of terrestrial and meteoritic materials can vary significantly from the previously assumed "standard" value (238 U/ 235 U = 137.88) (Amelin et al. 2010; Brennecka et al. 2010a,b; Weyer et al. 2008). The origin of the U isotopic variations in meteorites may be from the decay of 247 Cm decay to 235 U (Brennecka et al. 2010a), the presence of nucleosynthetic anomalies or isotopic fractionation (Amelin et al. 2010), or a combination of the above. If the measured U isotope composition of NWA 2976 is now used, the calculated model ages are ~1.4 ± 0.2 Ma younger. As discussed previously, the Pb-Pb internal isochron age of NWA 2976 is 4562.89 ± 0.59 Ma (Fig. 4.3b) including all uncertainties related to the measurements of the

U and Pb isotope compositions. Within the uncertainties, this age agrees with the model ages based on the most radiogenic samples, calculated using the measured U isotope composition for NWA 2976 (discussed above). As such, we believe that this internal isochron age best represents the time of crystallization of this basaltic meteorite in the crust of its parent asteroid.

The ²⁶Al-²⁶Mg extinct radionuclide chronometer can only provide relative time differences and must be anchored to an absolute chronometer with comparable precision (i.e., ²⁰⁷Pb-²⁰⁶Pb dates) to obtain absolute ages. The Al-Mg model ages for the NWA 2976 basaltic achondrite can be obtained using the Al-Mg internal isochron obtained in this study and published chronological data from different meteoritic materials that may be utilized as appropriate time anchors. An important criterion for a meteoritic object to be used as a time anchor is that it must have cooled rapidly to ensure that all radiochronometers of interest were closed to isotopic diffusion within a time interval less than their time resolution. One such anchor is the D'Orbigny angrite, a basaltic meteorite in which the Al-Mg (Spivak-Birndorf et al. 2009) and Pb-Pb systematics (Amelin 2008a) were previously determined and the U isotope composition of pyroxene separates (Brennecka et al. 2010b) was also recently measured.

The initial ²⁶Al/²⁷Al ratio of NWA 2976 of $3.94 (\pm 0.16) \times 10^{-7}$ determined here (Figs. 4.4a and 4.4b) compared to the initial ²⁶Al/²⁷Al ratio of $(5.06 \pm 0.92) \times 10^{-7}$ for D'Orbigny (Spivak-Birndorf et al. 2009) corresponds to a time interval of -0.3 Ma for the formation of NWA 2976 relative to the D'Orbigny angrite. If the Pb-Pb age of 4564.42 ± 0.12 Ma reported for D'Orbigny by Amelin (2008) is

used as a absolute time anchor, we obtain a Al-Mg model age of 4564.2 ± 0.2 Ma for NWA 2976. However, Amelin (2008) had assumed a 238 U/ 235 U ratio of 137.88 for D'Orbigny. As noted earlier, recent work has demonstrated that the U isotope ratio of Solar System materials, including D'Orbigny pyroxenes, can vary significantly from this assumed value (Brennecka et al. 2010b). After making a correction for the ²³⁸U/²³⁵U ratio in the bracketing SRM 950a U isotope standard (137.84; Condon et al. 2010; Richter et al. 2010), the measured 238 U/ 235 U ratio of the D'Orbigny pyroxenes (Brennecka et al. 2010b) is 137.778 ± 0.028 . This translates to an age adjustment on the absolute Pb-Pb age of D'Orbigny reported by Amelin (2008) of -1.06 ± 0.34 Ma and yields a corrected Pb-Pb age of 4563.36 ± 0.34 Ma. Taking this corrected Pb-Pb age for the D'Orbigny age anchor into consideration, we deduce an Al-Mg age for NWA 2976 of $4563.10 \pm$ 0.40 (Fig. 4.5), which is in excellent agreement with the Pb-Pb internal isochron age reported here (Fig. 4.3b). Hereafter, for all Al-Mg ages anchored to D'Orbigny, we will use the corrected Pb-Pb age of 4563.36 ± 0.34 Ma discussed above.

Other meteoritic materials that have been used as time anchors for Al-Mg chronometry are the calcium aluminum-rich inclusions (CAIs). A Type B inclusion from the NWA 2364 CV3 chondrite recently analyzed by Bouvier and Wadhwa (2010) has a canonical initial 26 Al/ 27 Al ratio of ~5.03 × 10⁻⁵ and an absolute Pb-Pb age of 4568.2 ${}^{+0.2}_{-0.4}$ Ma. Using this CAI as a time anchor results in an Al-Mg age of 4563.16 ${}^{+0.21}_{-0.40}$ Ma for NWA 2976, in agreement with the Pb-Pb

internal isochron age reported here and its Al-Mg age calculated using the D'Orbigny angrite as an anchor (discussed above).



Figure 4.5. Absolute Pb-Pb age and model Al-Mg age (anchored to the D'Orbigny angrite) determined in this study for the basaltic achondrite NWA 2976 (black squares). Also shown here is the Pb-Pb internal isochron age for a CAI from the NWA 2364 CV3 chondrite (Bouvier and Wadhwa 2010), along with the Al-Mg model ages for CAIs assuming a canonical value for the initial 26 Al/²⁷Al of 5 × 10⁻⁵ (Jacobsen et al. 2008) and anchored to the Pb-Pb and Al-Mg systematics of NWA 2976 ((1); this study) and D'Orbigny ((2); Amelin, 2008; Spivak-Birndorf et al. 2009; Brennecka et al. 2010b; Condon et al. 2010; Richter et al. 2010). The grey bar shows the Pb-Pb age of the D'Orbigny angrite (Amelin 2008a) that has been corrected for its measured U isotope composition (Brennecka et al. 2010b; Condon et al. 2010; Richter et al. 2010). As seen in this figure, these Pb-Pb and Al-Mg ages for NWA 2976 and for CAIs are entirely consistent with each other.

The ²⁶Al-²⁶Mg and ⁵³Mn-⁵³Cr extinct chronometers were recently

investigated in NWA 2976 and the paired meteorite NWA 011 (Sugiura and

Yamaguchi 2007; Schiller et al. 2010). Sugiura and Yamaguchi (2007) reported

an internal Al-Mg isochron for NWA 011 corresponding to an initial ${}^{26}Al/{}^{27}Al =$

 $6.93 (\pm 2.12) \times 10^{-7}$, determined using an ion microprobe; this is slightly higher

than the value reported in this study for NWA 2976 ($3.94 (\pm 0.16) \times 10^{-7}$). It is possible that the difference between these two slopes could be a reflection of slightly different closure times for mineral domains analyzed at different spatial scales with two separate techniques. Nevertheless, the Al-Mg age for NWA 011 relative to D'Orbigny is 4563.7 ± 0.5 Ma (Sugiura and Yamaguchi 2007; Amelin 2008a; Brennecka et al. 2010b; Spivak-Birndorf et al. 2010); this is in agreement, within the errors, with the Al-Mg ages estimated here for NWA 2976 (see above). Sugiura and Yamaguchi (2007) also report a Mn-Cr isochron for NWA 011 that corresponds to an age of 4562.8 ± 2.5 Ma relative to D'Orbigny (Glavin et al. 2004; Amelin 2008a; Brennecka et al. 2010b; Condon et al. 2010; Richter et al. 2010). Although relatively imprecise, this age is nevertheless in agreement with the Al-Mg model ages for NWA 2976 determined here using different age anchors.

The ²⁶Al-²⁶Mg systematics of NWA 2976 were also recently investigated using MC-ICPMS techniques by Schiller et al. (2010). As in this study, these authors report an internal Al-Mg isochron for NWA 2976 using a whole-rock sample as well as pyroxene and plagioclase separates. They also report small excesses in ²⁶Mg in their whole-rock sample and pyroxene separates of ~20 ppm that are resolvable outside of their $2\sigma_m$ uncertainties (based on up to 47 repeat measurements of their samples) (Schiller et al. 2010). In this investigation, we do not find any resolvable ²⁶Mg excesses in either the whole-rock (WR5) or the pyroxene (PX3) samples (Table 4.4). When the whole-rock Mg isotope data from this study are compared with that of Schiller et al. (2010), the δ^{26} Mg* values are

actually indistinguishable within the $2\sigma_m$ uncertainties for both studies. It is also noted that the Al/Mg ratio reported here for WR5 is in agreement with that reported by Schiller et al. (2010) for their whole-rock sample, suggesting that representative samples of NWA 2976 whole-rocks were used in both studies. However, Mg isotope data reported by Schiller et al. (2010) for their two pyroxene separates show small excesses in δ^{26} Mg* that are just barely resolved, outside of $2\sigma_m$ uncertainties, from the value reported for the pyroxene separate in this study. Schiller et al. (2010) also report an internal Al-Mg isochron for NWA 2976 corresponding to an initial ${}^{26}\text{Al}/{}^{27}\text{Al} = 4.91 (\pm 0.46) \times 10^{-7} \text{ and } \delta^{26}\text{Mg*}_0 =$ 0.0175 ± 0.0034 ‰. The slope and initial δ^{26} Mg* reported by Schiller et al. (2010) are both slightly higher than those determined here (Fig. 4.4a). To calculate the slope of their Al-Mg isochron, Schiller at al. (2010) assumed uncertainties on their measured δ^{26} Mg* values of 1.5 times the $2\sigma_m$; at this level of precision, the Mg isotope data for the whole-rock and pyroxene samples from their study are indistinguishable from those reported here (Fig. 4.4b). The small but resolvable δ^{26} Mg* excess reported in the NWA 2976 whole-rock sample by Schiller et al. (2010) allows them to calculate a model Al-Mg age assuming that the parent melt of this basalt was derived from a chondritic source reservoir. This model Al-Mg age is older than their internal Al-Mg age by >1 Ma (Schiller et al. 2010), and is interpreted by these authors as representing the time at which the NWA 2976 source reservoir was formed on its parent body, rather than when this basaltic meteorite crystallized.

Despite these differences, the Al-Mg age for NWA 2976 calculated using the data of Schiller et al. (2010) and anchored to the Al-Mg and corrected Pb-Pb isotopic systematics of D'Orbigny (Amelin 2008a; Spivak-Birndorf et al. 2009; Brennecka et al. 2010b; Condon et al. 2010; Richter et al. 2010) is 4563.3 ± 0.5 Ma, which is indistinguishable from the Al-Mg ages reported here, within the uncertainties. However, whether or not there is a small but resolvable positive value for the δ^{26} Mg*₀ has important implications for the chronology of NWA 2976. The resolved positive δ^{26} Mg*₀ reported by Schiller et al. (2010) for NWA 2976 (+0.0175 \pm 0.0034‰; $\pm 2\sigma_m$) is interpreted by these authors as most likely indicating disturbance and partial resetting of the Al-Mg chronometer caused by diffusion of Mg during thermal metamorphism. In contrast, we find a δ^{26} Mg*₀ value for NWA 2976 to be zero (-0.005 \pm 0.013‰) within the 2 σ_m errors (Fig. 4.4b), and find no evidence for significant later disturbance of the Al-Mg systematics in this meteorite. The reason for this apparent discrepancy between the two studies is not clear at this time. However, the isochron reported in this study includes twice as many plagioclase mineral separates that span a larger range of Al/Mg ratios (by a factor of ~ 2) than that reported by Schiller et al. (2010). Also, the δ^{26} Mg* values reported here for plagioclase separates represent averages of 2-4 repeat measurements, while those reported by Schiller et al. (2010) are each based on a single analysis. The internal isochron reported here is therefore likely to provide the most robust Al-Mg systematics available for the NWA 2976 basalt. Furthermore, the chondritic data point $(^{27}Al)^{24}Mg = 0.1$ and δ^{26} Mg* = -0.0010 ± 0.0023‰; Thrane et al. 2006) lies (within error) on the AlMg isochron reported here (Fig. 4.4b), suggesting that this meteorite originated from a chondritic source reservoir with respect to Mg isotopes. Although it is likely that NWA 2976 has experienced some metamorphism similar to NWA 011 (Yamaguchi et al. 2002), the lack of a resolvable positive δ^{26} Mg*₀ suggests that the initial crystallization from a chondritic source and subsequent metamorphism all occurred within a short interval while ²⁶Al was still extant.

Was ²⁶Al homogenously distributed in the inner Solar System?

The apparent discrepancies of up to ~ 2 Ma between model Al-Mg ages and absolute Pb-Pb ages of various meteoritic objects (e.g., Amelin et al. 2009; Wadhwa et al. 2009) raise the question of whether or not 26 Al was homogeneously distributed in the inner Solar System, which in turn has implications for the origin of this short-lived radionuclide (SLR) in the solar protoplanetary disk (Wadhwa et al. 2007; 2009). If it can be demonstrated that ²⁶Al (and several other SLRs) were inhomogeneously distributed in the solar protoplanetary disk, this would lend credence to the hypothesis that these SLRs were predominantly produced by local irradiation processes (e.g., Gounelle 2006; Hsu et al. 2006). In contrast, if it is demonstrated that in fact ²⁶Al, along with some other key SLRs, were homogeneously distributed, it would support the origin of ²⁶Al in the early Solar System in a nearby stellar source and subsequent injection followed by mixing and homogenization of matter (gas and dust) in the presolar molecular cloud (e.g., Young et al. 2009b). Much of the meteoritic evidence thus far suggests that the latter possibility is the more likely. Some AlMg investigations of meteoritic materials indicate that injection of ²⁶Al from a nearby stellar source occurred as a single, discrete event. In particular, the socalled FUN (Fractionated and Unknown Nuclear) inclusions, record significant anomalies in the stable isotope compositions of a variety of elements such as O, Mg, and Ca, but show an absence (or significantly lower abundance than the "canonical" value) of live ²⁶Al at their time of formation compared to "normal" CAIs (e.g., Esat et al. 1978), possibly suggesting that they formed prior to the injection of ²⁶Al into the early Solar System (MacPherson et al. 1995). Furthermore, normal CAIs indicate a canonical initial abundance of ²⁶Al. suggesting rapid formation (within 30,000-300,000 years) and homogeneous distribution of ²⁶Al at least by the time of their formation (Jacobsen et al. 2008; MacPherson et al. 2010). The Mg isotope composition of chondrules also suggests a homogeneous distribution (within 10%) of ²⁶Al in the Solar System (Villeneuve et al. 2009). However, some recent Mg isotope data reported for corundum grains extracted from CAIs of CH meteorites indicate a bimodal distribution of the initial 26 Al/ 27 Al ratios in these objects, i.e., with ~40% having values of $(3.5-6.5) \times 10^{-5}$ and $\sim 55\%$ having values $< 3 \times 10^{-6}$, which may suggest injection of ²⁶Al in the solar nebula while these CAIs were forming, implying a period of heterogeneous distribution of ²⁶Al at least during the earliest stages of CAI formation (Krot et al. 2010).

In this study, we have demonstrated that the high-precision Pb-Pb internal isochron age for the ungrouped basaltic achondrites NWA 2976 (calculated using the measured U isotope composition) is concordant with its model Al-Mg ages,

estimated using such diverse meteoritic objects as the D'Orbigny angrite (Amelin 2008a; Spivak-Birndorf et al. 2009; Brennecka et al. 2010b; Condon et al. 2010; Richter et al. 2010) and a Type B CAI from the NWA 2364 CV3 chondrite (Bouvier and Wadhwa 2010) as age anchors (Fig. 5). However, we note that previously reported high precision Pb-Pb internal isochron ages of other CAIs from Allende and Efremovka are systematically younger (Amelin et al. 2002, 2009, 2010; Bouvier et al. 2008; Jacobsen et al. 2008). With the exception of one recent study (Amelin et al. 2010), all of these reported ages assumed a ²³⁸U/²³⁵U ratio of 137.88. As demonstrated by Brennecka et al. (2010a), this assumption is no longer valid and therefore most of these ages may be inaccurate by as much as a few Ma. Nevertheless, Amelin et al. (2010) have determined the U isotopic composition of the Allende inclusion for which they reported a Pb-Pb internal age that is still systematically younger than that of the Type B CAI from NWA 2364 (Bouvier and Wadhwa 2010). As discussed previously by Bouvier and Wadhwa (2010), the systematically younger ages of inclusions in Allende (and Efremovka) may be the result of secondary alteration.

Thus, the fact that the Pb-Pb and Al-Mg chronologies are concordant for such diverse meteoritic objects (specifically, the NWA 2976 ungrouped basaltic achondrite, the D'Orbigny angrite and the NWA 2364 CAI) that are likely to have formed in different spatial regions of the inner Solar System over a time interval spanning ~5-6 Ma, suggests that ²⁶Al was homogeneously distributed in the meteorite-forming region of the early Solar System at least by the time that the oldest of these objects was formed (i.e., the NWA 2364 CAI), and the likely

origin of this SLR is one or more nearby stellar sources that contaminated the presolar molecular cloud. This is supported by ¹⁶O isotopic anomalies in normal and FUN refractory inclusions that may have had the same stellar origin and carrier into the solar nebula (Krot et al. 2010). However, while dust grains are thought to be the most efficient carriers of supernova material into the presolar molecular cloud (Ellinger et al. 2010), their injection is unlikely to yield a homogeneous distribution of SLRs over a short time frame and a later dynamic process is required to produce efficient homogenization (Ouellette et al. 2007). The timing of such a process would be of the order of ~10,000-100,000 years (Vanhala and Boss 2002) which may possibly be resolved with future chronological investigations of high-precision Pb-Pb and Al-Mg systematics in meteoritic materials.

CONCLUSIONS

We have dated the ungrouped basaltic achondrite NWA 2976 using its U isotopic composition (238 U/ 235 U= 137.751 ± 0.018) and its Pb-Pb isotope systematics. Based on a Pb-Pb internal isochron of the most radiogenic samples (206 Pb/ 204 Pb >1010), we report here an absolute age of 4562.89 ± 0.59 Ma. This age is consistent with its Al-Mg model ages of 4563.10 ± 0.38 and 4563.16 $^{+0.21}_{-0.40}$, anchored to the D'Orbigny angrite and the NWA 2364 CAI, respectively. The concordance of the Al-Mg and Pb-Pb chronometers for distinct objects that are likely to have originated in different spatial regions of the protoplanetary disk over a time span of ~5-6 Ma suggests that by the time of formation of the normal

(i.e., non-FUN) CAIs (such as the Type B inclusion from NWA 2364; Bouvier and Wadhwa 2010), ²⁶Al was already homogeneously distributed in the inner Solar System.

SUPPLEMENTAL DATA

Table 4.S

Mg isotope composition (average and respective 2SE of 4 repeated measurements) of DSM-3 doped with different proportions of Ca, Ti, Al, Fe and Na SPEX standards.

Doping Experiments	Ratio	δ ²⁵ Ma	2SE	δ ²⁶ Ma	2SE	δ ²⁶ Ma*	2SE
4 repeats each							
mixture							
Ca/Mg	0.05	0.03	0.01	0.05	0.01	0.00	0.02
	0.1	0.01	0.02	0.01	0.05	-0.01	0.03
	0.25	-0.09	0.01	-0.16	0.03	0.02	0.03
	0.5	-0.02	0.07	-0.06	0.13	-0.01	0.02
	1	-0.04	0.04	-0.08	0.06	0.00	0.02
Ti/Mg	0.05	0.08	0.03	0.14	0.04	-0.02	0.02
	0.1	-0.01	0.01	-0.05	0.01	-0.02	0.02
	0.25	0.03	0.04	0.02	0.04	-0.03	0.04
	0.5	0.00	0.11	-0.07	0.24	-0.07	0.05
	1	-0.25	0.03	-0.63	0.05	-0.13	0.03
Al/Mg	0.001	0.00	0.02	0.00	0.04	-0.01	0.02
	0.005	0.01	0.03	0.04	0.06	0.01	0.03
	0.01	0.04	0.02	0.07	0.02	-0.01	0.05
	0.05	0.05	0.02	0.12	0.04	0.01	0.04
	0.1	-0.08	0.03	-0.14	0.06	0.01	0.02
	0.25	-0.08	0.04	-0.15	0.07	0.00	0.02
	0.5	-0.04	0.09	-0.08	0.14	-0.01	0.03
	1	-0.09	0.04	-0.17	0.07	0.01	0.04
Fe/Mg	0.05	0.00	0.01	-0.01	0.02	-0.01	0.01
	0.1	0.03	0.04	0.07	0.09	0.01	0.03
	0.25	0.03	0.08	0.04	0.11	-0.01	0.05
	0.5	0.10	0.02	0.19	0.03	-0.01	0.01
	1	0.10	0.02	0.21	0.01	0.01	0.04
Na/Mg	0.05	0.00	0.04	0.00	0.07	0.00	0.01
	0.1	-0.05	0.02	-0.10	0.04	0.00	0.01
	0.25	-0.08	0.01	-0.16	0.01	0.00	0.03
	0.5	-0.17	0.02	-0.33	0.06	0.01	0.03
	1	-0.14	0.02	-0.29	0.06	-0.01	0.05
Chapter 5

TRACE ELEMENT GEOCHEMISTRY AND CHRONOLOGY OF THE UNGROUPED BASALTIC ACHONDRITE BUNBURRA ROCKHOLE

This data presented in this chapter are part of a collaborative research effort with Phil Bland, who supplied samples of Bunburra Rockhole. The chapter was originally written as a paper on which I am first author that is intended for publication in a scientific journal. My contribution to this research was the collection of all of the data except for the Pb-Pb isotopic chronology, which was collected by Audrey Bouvier, the second author of the manuscript. I wrote all sections of the paper and made all tables and figures, with the exception of those that focus on the Pb-Pb system and the associated table (5.3) and Fig (5.11)

INTRODUCTION

Bunburra Rockhole (BR) is the first meteorite recovered following observation of its atmospheric entry by the Desert Fireball Network in the Nullarbor Desert, Australia (Bland et al., 2009). While initial petrographic observations suggested that BR is a basaltic eucrite, subsequent oxygen isotopic measurements revealed that its composition did not lie on the mass-fractionation line defined by the howardite-eucrite-diogenite (HED) group, and thus that it likely formed on a parent body distinct from that of the HED meteorites (Bland et al. 2009). The orbital trajectory inferred from the BR fall additionally suggests that it most likely did not come from asteroid 4 Vesta, the commonly assumed parent body of the HED meteorites (Bland et al. 2009). Variations in the O isotope compositions of a small number of other "eucrites" have recently been interpreted as indicating that eucrite-like basaltic meteorites originated from a number of distinct asteroidal parent bodies (Scott et al. 2009).

Like many of the non-cumulate eucrites, BR is considered a monomict breccia, in that it is composed of basaltic clasts that all have very similar mineral abundances and chemistries (Bland et al. 2009; Benedix et al. 2010). As with some eucrites (e.g., Takeda and Graham 1991; Yamaguchi et al. 1994; Metzler et al. 1995; Gardner-Vandy et al. 2011) the clasts in BR have variable grain size, and they can be broadly separated into three groups on this basis: coarse-grained (CG), medium-grained (MG) and fine-grained (FG) (Bland et al. 2009). While the CG and MG fractions seem to mostly preserve their original igneous textures, the FG fraction of BR appears to have a metamorphic texture (Benedix et al. 2010). While these different grain size lithologies all have very similar modal mineralogies and mineral chemistries (Benedix et al. 2010), their O isotope compositions exhibit a relatively high degree of variability from one another (Bland et al. 2009). This scatter in the O isotope data among BR clasts is not typical of eucrites and could potentially be interpreted as resulting from a lower degree of melting and equilibration on the BR parent body as compared to the eucrite parent body (assumed to be the asteroid 4 Vesta) (Bland et al. 2009).

Here we present a study of the trace element geochemistry and chronology of the unique achondrite BR. This includes an investigation of the microdistributions of rare earth elements (REE) and other trace elements in minerals of the different grain size fractions of BR, as well as the relative ²⁶Al-²⁶Mg and absolute ²⁰⁷Pb-²⁰⁶Pb chronologies of this meteorite. We also report the major element chemistry of pyroxenes in which trace elements were measured. The goals of this study are to better understand the origin and evolution of this unique meteorite and to determine if it is anomalous compared to eucrites in terms of geochemical characteristics other than its O isotope composition. The study also aims to provide insight into the potential heterogeneity in the mineral chemistry of the various lithologies in BR characterized by different grain sizes, as may be suggested by their O isotope compositions (Bland et al. 2009), by comparing the trace element compositions of minerals in these lithologies. Preliminary results of this investigation were reported by Spivak-Birndorf et al. (2010).

SAMPLES AND ANALYTICAL METHODS

Major and Trace Elements

The analyses were performed on a polished thin section of BR containing all three of the grain size lithologies. This sample was initially characterized using a JEOL 845 scanning electron microscope at ASU. The textures vary within and between the three different lithologies of BR that are broadly defined by grain size. The CG lithology of BR has essentially uniform coarse-grained subophitic texture consisting of predominately pyroxene and plagioclase, with opaque phases occurring as interstitial grains and small inclusions within the pyroxene (Fig. 5.1).



Figure 5.1. Representative backscattered electron image of the coarse-grained lithology in Bunburra Rockhole.

The MG and FG lithologies both have phenocrysts embedded in a relatively finergrained pyroxene-plagioclase groundmass. The groundmass in portions of the MG lithology has a subophitic texture that is partially recrystallized in some areas and the phenocrysts are pyroxenes that are comparable in size to those in the CG lithology (Fig. 5.2). Other MG areas of BR have subophitic texture with more uniform grain sizes that are intermediate to the MG groundmass and CG minerals (Fig. 5.3).



Figure 5.2. Backscattered electron image of a pyroxene phenocryst embedded in a medium-grained groundmass in Bunburra Rockhole.



Figure 5.3. Representative backscattered electron image of the medium-grained lithology in Bunburra Rockhole.

Trace elements were measured in pyroxene phenocrysts, as well pyroxene and plagioclase from the intermediate grain size portions of the MG lithology with subophitic texture. The FG lithology consists of pyroxene and plagioclase phenocrysts in a fine-grained granular groundmass (Fig. 6.4). The spatial resolution of the ion microprobe limited the analyses in the FG lithology to the phenocrysts. The major element chemistry of pyroxenes analyzed for trace elements were determined using a JEOL 8800 electron microprobe at ASU calibrated with a set of reference mineral standards.



Figure 5.4. Representative backscattered electron image of the fine-grained lithology in Bunburra Rockhole.

The concentrations of rare earth elements (REE) and other trace elements in BR minerals were measured *in situ* by secondary ion mass spectrometry (SIMS) using the Cameca IMS-6f ion microprobe at Arizona State University (ASU). In order to avoid interferences from molecular ions, the analyses were made using an energy filtering technique previously described by Zinner and Crozaz (1986). The sample surface was sputtered using an O⁻ primary beam accelerated at -12.5 KeV with currents ranging from ~3-5 nA, resulting in analysis pits that are typically \sim 25-35 µm in diameter. The secondary ion beam was accelerated with a voltage of +10 KeV with a -75 eV offset. Secondary ions of selected trace elements and a reference element, either Si for silicates or Ca for phosphate, were detected using an electron multiplier in peak jumping mode. The abundances of the trace elements were determined from the measured ion intensities using published sensitivity factors (Zinner and Crozaz 1986; Hsu 1995). In order to verify the validity of this method, the NIST SRM 610 and SRM 612 glasses were measured at the beginning of, and periodically throughout, the analytical sessions. During the session in which phosphate was measured, the well-characterized Durango apatite was also analyzed. For the REE analyses, it is also necessary to correct for the effects of isobaric interferences from monoxides, which are not removed by energy filtering. In particular, Ba and some of the light rare earth elements (LREE) form oxides that are isobaric interferences on some of the heavy rare earth elements (HREE). We correct for the effects of these isobaric interferences using the measured ion intensities of the interfering elements and previously published monoxide to element ratios that are applicable to our energy filtering conditions (Zinner and Crozaz 1986; Hinton 1990).

Al-Mg Isotope Systematics

The analytical procedures used in this study for measuring Mg isotopes and Al/Mg ratios were recently described in detail by Spivak-Birndorf et al. (2009) and Bouvier et al. (2011), and we therefore only provide a brief description here. Samples of both the FG and the CG lithologies were separated from an interior fragment of the meteorite. Bulk "whole-rock" (WR) samples of ~ 20 mg were taken from each of these two grain size lithologies. To obtain mineral separates, the samples were crushed and sieved, followed by a density separation with heavy liquids (tribromoethane). The plagioclase separates (PL, typically weighing ~0.5-1 mg) from the CG lithology were hand-picked from the 53-74 μ m and 74-105 μ m fractions, while that from the FG lithology (with a weight of less than 0.1 mg) was generated from the $<53 \mu m$ fraction. Pyroxene separates (PX, \sim 1-2 mg) were hand-picked from the heavy fraction following heavy liquid separation. All of the samples were digested and processed to separate Mg from the matrix using cation exchange chromatography (Spivak-Birndorf et al. 2009; Bouvier et al. 2011). Pyroxene and WR samples were passed through the cation exchange column twice, while plagioclase separates were passed through three times, and total recovery of Mg was >99%. Prior to chemical separation of Mg, a ~10% aliquot from the unprocessed dissolved fraction of each mineral separate was reserved for Al/Mg ratio analysis, while the rest was used for Mg isotope measurements. For the WR samples, a ~10% aliquot from the unprocessed dissolved fraction was reserved for Al/Mg ratio analysis, and an equivalent of 1-2 mg was used for Mg isotope measurements following the same

procedures as those used for the mineral separates. All Al/Mg and Mg isotope ratios were measured using the Neptune MC-ICPMS in the Isotope Cosmochemistry and Geochronology Laboratory (ICGL) at ASU.

Pb-Pb Isotope Systematics

Sample Preparation

A ~250 mg interior fragment of BR, from the same piece of the FG lithology used for Al-Mg isotopic analyses (see above), was processed for the analysis of Pb isotope systematics. From this fragment, a piece of ~180 mg was powdered and split to obtain two bulk samples (WR1 and WR2). The remainder was crushed below 100 μ m grain size and sieved. The 30-100 μ m fraction was subjected to density separation using methylene iodide (d~3.25) heavy liquid, followed by hand picking, to obtain ~6 mg pyroxene-rich (PX) and ~46 mg plagioclase-rich (PL) separates.

The mineral separates and whole-rock powders were leached using a 8step leaching protocol similar to the protocol #2 described by (Amelin 2008a), but with an additional final wash using 1M HF at room temperature with ultrasonication for \sim 3h. Residues (denoted as R) and the dried last leachates (denoted as L₈) were fully dissolved in concentrated HF-HNO₃, and converted to the chloride form before Pb extraction following the methods detailed in Bouvier and Wadhwa (2010).

Pb-Pb Isotope Measurements

The Pb isotopic compositions of the samples were obtained using the Neptune MC-ICPMS at ASU using procedures similar to those described in Bouvier and Wadhwa (2010). The Pb sample cuts were brought into solution in 200-800 μ l of 3% HNO₃ and spiked with a Tl standard solution to obtain a final concentration of 1 ppb Tl for correction of the instrumental mass bias. The total procedural blanks (chemistry and mass spectrometry) were 0.8 and 1.4 pg for leachates and residues, respectively, and their contribution to the sample isotopic compositions was corrected following the method described in Bouvier et al. (2007). The amount of Pb in the residue of the pyroxene separate (PX-R) was too small for high-precision isotopic analysis and only the last leachate L₈ is reported for this sample.

RESULTS

Major and Trace Element Microdistributions

The concentrations of the REE were measured in pyroxene and plagioclase grains in the FG, MG and CG lithologies in BR, and the concentrations of selected major elements were also determined in pyroxene grains that were analyzed for trace elements. The REE concentration of a small (~50 µm diameter) Ca-phosphate grain in the MG lithology was also measured. The trace elements Ti, Zr and Y were additionally measured in the pyroxenes. These results are shown in Table 1 and Figs. 5.5-5.9.

Pyroxene

Pyroxenes in BR are Fe-rich, similar to those in normal non-cumulate eucrites (Fig. 5.5; Takeda and Graham 1991; Yamaguchi et al. 1994; Metzler et al. 1995; Gardner-Vandy et al. 2011). In the CG and MG lithologies, low-Ca pyroxene contains exsolution lamellae of high-Ca pyroxene (augite) with variable thickness (Figs. 5.1-5.3). All of these pyroxenes fall on a single tie-line in the pyroxene quadrilateral between low- and high-Ca pyroxene with intermediate compositions resulting as an artifact of incomplete resolution of the exsolution lamellae by the electron microprobe beam (Fig. 5.5). In contrast to the CG and MG lithologies, the pyroxene phenocrysts from the FG lithology that were measured in this study did not have exsolution lamellae (Fig. 5.4) and have a uniform low-Ca composition (Fig. 5.5). The pyroxenes in BR do not show igneous zoning trends and are comparable to the type 5 and 6 equilibrated eucrites defined by Takeda and Graham (1991).



Figure 5.5. Pyroxene quadrilateral for Bunburra Rockhole. White circles = CG lithology, gray squares = MG lithology and black triangles are FG lithology.

Although individual pyroxene grains in each lithology of BR have fairly uniform trace element microdistributions and do not display igneous zoning trends, the elemental abundances do vary between different grains within the same lithology. The ranges of REE abundances in BR pyroxenes from each of the three lithologies are shown in Fig. 5.6. It is also possible that some of the variability of REE abundances in pyroxenes from the CG and MG lithologies of BR is an artifact of the ion microprobe predominately sampling either the low- or high-Ca composition. However, the diameter of the ion microprobe beam exceeds the width of typical lamellae suggesting that analyses should be a representative sample of the original pyroxene composition before exsolution occurred. All of the BR pyroxenes have HREE-enriched patterns with negative Eu anomalies (i.e., Eu/Eu* <1, where Eu* is the interpolated value between the CI-normalized Sm and Gd abundances). The ranges of REE concentrations measured in pyroxenes in the CG and MG lithologies are nearly identical. The lowest and highest REE abundances in the MG lithology were measured in a phenocryst and a groundmass pyroxene, respectively. However, the low end of the REE concentration range measured in the MG groundmass pyroxenes is similar to the concentrations typically observed in the phenocrysts in this lithology. It is possible that the MG groundmass pyroxenes and pyroxene phenocrysts have similar ranges in REE concentrations and that a phenocryst on the high end of the range was not sampled in this investigation. Compared to the MG and CG lithologies, pyroxene phenocrysts in the FG lithology have slightly lower REE concentrations and span a narrower range in REE abundances (Fig. 5.6). This is consistent with the

uniformly low Ca concentrations and lack of exsolved augite in the FG pyroxenes. Also, the pyroxenes in the CG and MG lithologies have larger negative Eu anomalies (Eu/Eu* \approx 0.1-0.2) compared to pyroxenes in the FG lithology (Eu/Eu* \approx 0.4-0.5).



Figure 5.6. Range of REE abundances in BR pyroxenes normalized to CI chondrite abundances of Palme and Beer (1993). Triangles = FG lithology, squares = MG lithology, circles = CG lithology; solid and open symbols represent analyses with the lowest and highest REE concentrations, respectively. The shaded grey area shows the range of REE concentrations in pyroxenes from some non-cumulate eucrites (Hsu and Crozaz, 1996).

The concentration ranges of Ti, Zr and Y in BR pyroxenes are shown in Fig. 5.7. The concentration of Ti measured in most of the BR pyroxenes was ~1000-2000 ppm. While some pyroxene analyses show higher Ti concentrations, it is possible that overlap of the ion microprobe beam with included or adjacent Ti-bearing oxide phases (Figs. 5.1-5.4) could have artificially increased the apparent Ti contents. The Zr concentrations range from \sim 0.5 to 6 ppm and the Y concentrations range from \sim 2 to 14 ppm in BR pyroxenes. Pyroxenes from the different grain size lithologies all have similar ranges in Ti, Zr and Y concentrations, with the possible exception of systematically lower Y and Zr contents in the FG phenocrysts compared to other pyroxenes.



Figure 5.7. A) Ti vs. Y abundances and B) Ti vs. Zr abundances in BR pyroxenes. Triangles = FG lithology, squares = MG lithology, circles = CG lithology. The ellipses correspond to the compositional ranges reported for pyroxenes in non-cumulate eucrites (Hsu and Crozaz, 1996).

Plagioclase

The CI-normalized abundances of REE in BR plagioclase grains are shown in Fig. 5.8. Plagioclase from the three lithologies of BR all has similar REE abundances. The REE patterns of BR plagioclase are LREE-enriched with positive Eu anomalies (Eu/Eu* \approx 50-70). It should be noted that for the plagioclase, the Eu* value was obtained by assuming a CI-normalized value for Gd from interpolation between CI-normalized abundances of Sm and Tb. This is because the abundance of Gd is very low in BR plagioclase and could not be reliably determined by our analytical technique due to the large correction required for the contribution from LREE-oxides on the small Gd signal.



Figure 5.8. Representative CI-normalized REE abundances in BR plagioclase. Triangles = FG lithology, squares = MG lithology, circles = CG lithology. The shaded grey area shows the range of REE concentrations reported for plagioclase in non-cumulate eucrites (Hsu and Crozaz, 1996).

Ca-Phosphate

One Ca-phosphate grain large enough to measure with the ion microprobe was identified in the MG lithology of BR. It is highly enriched in REE compared to other phases in BR, with abundances ranging from ~7,000-17,000 × CI. The CI-normalized REE pattern for this mineral is LREE-enriched with a negative Eu anomaly (Fig. 5.9).



Figure 5.9. CI-normalized REE abundances of Ca-phosphate in the MG lithology of BR (black squares). The shaded grey area shows the range of REE abundances reported for merrillite in non-cumulate eucrites (Hsu and Crozaz, 1996). The CI-normalized abundance patterns of merrillite from some other asteroidal basalts are also shown for comparison; dotted line = Ibitira (a unique non-cumulate eucrite; Hsu and Crozaz, 1996), dashed line = NWA 011 (an ungrouped basaltic achondrite; Floss et al., 2005), solid line = Sahara 99555 (a fine-grained angrite; Floss et al., 2003).

Table 5.1 Trace element microdistributions in Bunburra Rockhole minerals

Fine-grained Lithology												
	Pyroxene							Plagiocla	se	_		
		Low*			High*							
Ti	989	±	2	1764	±	2		n.d.				
Y	1.36	±	0.02	3.79	±	0.03		n.d.				
Zr	0.54	±	0.02	1.18	±	0.02		n.d.				
La	0.082	±	0.007	0.132	±	0.007	0.376	±	0.011			
Ce	0.132	±	0.009	0.217	±	0.010	0.532	±	0.014			
Pr	0.020	±	0.003	0.033	±	0.004	0.073	±	0.005			
Nd	0.191	±	0.019	0.198	±	0.017	0.288	±	0.018			
Sm	0.044	±	0.012	0.071	±	0.013	0.061	±	0.011			
Eu	0.008	±	0.003	0.015	±	0.003	1.168	±	0.027			
Gd	0.093	±	0.012	0.150	±	0.013		n.d.	0.004			
	0.039	±	0.004	0.056	±	0.005	0.004	±	0.001			
Dy	0.395	±	0.029	0.487	±	0.028	0.037	±	0.005			
Ho	0.119	±	0.008	0.174	±	0.009	0.006	±	0.001			
Er	0.640	±	0.033	0.720	±	0.031	0.039	±	0.006			
1 m	0.141	±	0.009	0.159	±	0.009	0.004	±	0.000			
YD	1.274	±	0.050	1.554	±	0.049	0.017	±	0.005			
LU	0.236	±	0.013	0.288	±	0.013	0.0004	±	0.0003			
				Modiu	m araiı	and Litholog	N.					
			Pyroxene			y I	Plagioclase			snhat	P	
-		Low		exerie -	High			lagioola				
					•							
Ti	3120	±	2	10444	±	5		n.d		n.c	1.	
Y	4.73	±	0.03	12.83	±	0.06		n.d		n.c	1.	
Zr	2.05	±	0.03	10.01	±	0.08		n.d		n.c	1.	
La	0.175	±	0.008	0.545	±	0.017	0.519	±	0.019	3869.7	±	1.9
Ce	0.370	±	0.012	1.514	±	0.031	0.871	±	0.026	8716.8	±	3.2
Pr	0.056	±	0.004	0.301	±	0.012	0.107	±	0.008	1322.1	±	1.1
Nd	0.314	±	0.020	1.772	±	0.057	0.395	±	0.030	6112.2	±	4.5
Sm	0.123	±	0.016	0.870	±	0.053	0.094	±	0.020	2195.1	±	3.5
Eu	0.008	±	0.002	0.062	±	0.008	1.491	±	0.043	23.7	±	0.2
Gd	0.177	±	0.012	1.428	±	0.048		n.d.		3464.7	±	2.7
Tb	0.068	±	0.005	0.335	±	0.013	0.014	±	0.003	506.9	±	0.6
Dy	0.667	±	0.031	2.723	±	0.076	0.114	±	0.015	3248.8	±	3.2
Ho	0.212	±	0.009	0.611	±	0.019	0.032	±	0.005	551.6	±	0.8
Er	0.798	±	0.030	1.938	±	0.058	0.086	±	0.013	1607.4	±	2.1
Tm	0.177	±	0.008	0.323	±	0.014	0.015	±	0.002	182.2	±	0.4
Yb	1.745	±	0.048	2.539	±	0.070	0.126	±	0.018	1232.1	±	1.9
Lu	0.310	±	0.013	0.401	±	0.017	0.010	±	0.003	174.1	±	0.4
				Coarse	e-graine	ed Lithology						
_		Pyroxene			P	Plagioclase						
		Low			High							
ті	1774	+	2	1100	-	2		nd				
v	4.05	+	0.03	13 36	+	2 0.06		n.u.				
7r	1.56	±	0.00	3.64	±	0.00		n.u.				
21	0 142	+	0.03	0.404	+	0.05	0.520	+	0.017			
Ce	0.283	+	0.007	1 481	÷ +	0.014	0.920	+	0.026			
Pr	0.050	+	0.004	0.337	+	0.012	0.106	+	0.008			
Nd	0.282	+	0.019	2,110	÷	0.058	0.353	÷ +	0.027			
Sm	0,129	÷	0.017	1,225	- +	0.058	0.113	- ±	0.020			
Eu	0.006	- +	0.002	0.039	±	0.006	1.917	- +	0.045			
Gd	0.257	÷	0.017	1.829	- ±	0.052		n.d.	0.010			
Tb	0.077	±	0.005	0.417	±	0.014	0.011	±	0.002			
Dv	0.733	÷	0.033	3,119	+	0.075	0.113	±	0.014			
Ho	0.225	±	0.010	0.688	±	0.019	0.025	±	0.004			
Er	0.815	±	0.031	1.928	±	0.053	0.072	±	0.011			
Tm	0.181	±	0.009	0.329	±	0.013		n.d.				
Yb	1.788	±	0.049	2.689	±	0.066	0.064	±	0.012			
Lu	0.316	±	0.013	0.416	±	0.016	0.007	±	0.002			

*The low and high values for pyroxenes correspond to the analyses with the lowest and highest REE contents, respectively. The errors are $\pm 1\sigma$ standard deviation from counting statistics only; n.d. = not detected

²⁶Al-²⁶Mg Isotope Systematics

The results of the Mg isotope and Al/Mg ratio measurements of wholerock samples and mineral separates from the CG and FG lithologies of BR are shown in Table 5.2 and in Fig. 5.10. Although somewhat limited, the range of ²⁷Al/²⁴Mg ratios measured in mineral separates from the CG lithology (~0.3-27) exceeds that from the FG lithology (~2-16) due to the difficulty of separating the minerals in the FG lithology. A greater number of mineral separates, each consisting of more material (thus allowing for more repeat measurements), were also generated from the CG lithology. Due to these circumstances, the ²⁶Al-²⁶Mg isotope systematics for the CG lithology are considered more robust than the FG lithology. Nevertheless, the results of the ²⁶Al-²⁶Mg isotope investigation of the FG lithology are consistent with those of the CG lithology.

The whole-rock sample and mineral separates from the CG lithology of BR all have small excesses in radiogenic ²⁶Mg (δ^{26} Mg*) relative to the terrestrial Mg isotope composition. The excesses are identical in all the CG samples within analytical errors, and therefore do not vary with the sample Al/Mg ratio. It is important to note that the small ²⁶Mg excesses (~15-30 ppm) in the CG lithology of BR are only resolvable from terrestrial Mg isotope composition outside of ± 2SE uncertainty, but not outside of the more conservative ± 2SD errors. The Al-Mg isochron regressions reported here were calculated using the ± 2SE uncertainty. The slope of the internal ²⁶Al-²⁶Mg isochron for the CG lithology is not resolved from zero, and therefore only an upper limit on the ²⁶Al/²⁷Al ratio of $\leq 8.8 \times 10^{-8}$ (Fig. 5.10) at the time of last equilibration of Mg isotopes can be obtained.

Although the internal ²⁶Al-²⁶Mg isochron for the CG lithology yields only limited chronological information (i.e., an upper limit on its crystallization age), the slight excess of radiogenic ²⁶Mg in the whole-rock sample allows a model ²⁶Al-²⁶Mg age to be determined assuming that BR evolved from a silicate mantle reservoir on its parent planetesimal with bulk chondritic composition (i.e., δ^{26} Mg* ≈ 0 and ²⁷Al/²⁴Mg ≈ 0.1 ; Thrane et al., 2006). The slope of this model ²⁶Al-²⁶Mg isochron for the CG lithology of BR corresponds to a ²⁶Al/²⁷Al = (2.35 ± 1.30) × 10⁻⁶ (Fig. 5.10) at the time when the Al/Mg ratio of the BR source was established.

A whole-rock sample, a plagioclase mineral separate and a sample of the heavy (pyroxene-rich) fraction from density separation were analyzed for the ²⁶Al-²⁶Mg investigation of the FG lithology. The ²⁷Al/²⁴Mg ratios of the wholerock sample and the heavy density separate were both ~2, suggesting that the separation procedure was rather inefficient for this sample due its fine-grain size. Despite having different Al/Mg ratios, the plagioclase separate and the heavy density separate both have small radiogenic ²⁶Mg excesses of ~45 ppm that are resolvable outside of ± 2SE uncertainty. Although systematically slightly higher, these excesses agree with those measured in the CG samples within the analytical errors. The whole-rock sample of the FG lithology of BR does not show a resolvable excess of radiogenic ²⁶Mg. This result is inconsistent with the δ^{26} Mg* values obtained for the heavy density separate (having the same Al/Mg ratio) if the ± 2SE uncertainties are considered. Nevertheless, the δ^{26} Mg* value measured in the FG lithology whole-rock sample is consistent with that of the CG lithology whole-rock sample. The lack of a resolvable radiogenic δ^{26} Mg excess in the whole-rock sample of the FG lithology precludes the determination of a model ²⁶Al-²⁶Mg isochron. As with the CG lithology, the slope of the internal ²⁶Al-²⁶Mg isochron for the FG lithology of BR is not resolved from zero and provides only an upper limit on the ²⁶Al/²⁷Al ratio of ≤ 5.06 × 10⁻⁶.



Figure 5.10. ²⁶Al-²⁶Mg isochron diagram for BR CG and FG lithologies. Circles = CG lithology and triangles = FG lithology. The solid line corresponds to the CG lithology isochron and the dotted line corresponds to the FG lithology isochron. The slopes of the internal mineral isochrons for the two different BR lithologies are not resolved from zero and provide only upper limits on the initial ²⁶Al/²⁷Al ratio at the time of last equilibration of Mg isotopes. The dashed line corresponds to the model ²⁶Al-²⁶Mg isochron fro the BR CG lithology assuming a two-stage evolution from a chondritic source reservoir. Errors are ± 2SE for δ^{26} Mg* and ± 2% on ²⁷Al/²⁴Mg ratios.

Table 5.2

Sample ^a	²⁷ Al/ ²⁴ Mg ^b	δ ²⁶ Mg*	± 2SE ^c	n ^d
Fine-Grained (FG) Lithology				
WR	2.01	0.004	0.020	8
dense fraction	2.00	0.045	0.014	9
PL	15.88	0.047	0.020	7
Coarse-Grained (CG) Lithology				
WR	1.94	0.030	0.018	12
PX	0.34	0.016	0.014	12
PL1	26.94	0.030	0.019	12
PL2	25.03	0.019	0.011	8

²⁶Al-²⁶Mg isotope systematics in Bunburra Rockhole

^aWR = whole-rock, PL = plagioclase, PX = pyroxene, dense fraction = density separate with d>2.85

^bThe errors in the 27 Al/ 24 Mg ratios are ± 2%.

^cThe errors in the Mg isotope ratios are twice the standard error.

^dn corresponds to the number of repeats for Mg isotope ratio measurements;

²⁷Al/²⁴Mg ratios are average of 5-6 repeats

²⁰⁷Pb-²⁰⁶Pb Isotope Systematics

We report the Pb isotopic compositions of the final leachate L_8 for the pyroxene separate (PX) and the final leachates (L_8) and corresponding residues (R) for the plagioclase separate (PL) and two whole-rock samples (WR1 and WR2). These samples have raw ²⁰⁶Pb/²⁰⁴Pb ratios ranging from 2,709 (for WR1- L_8) to 4,694 (for PX- L_8) (Table 5.3 and Fig. 5.11), indicating efficient removal of common Pb during the preceding leaching steps.

Because these samples have such radiogenic compositions, we used the uncertainties on the 207 Pb/ 206 Pb ratio measured in NBS 981 (0.91475 ± 0.030%, 2SD; n=14), and on the 206 Pb/ 204 Pb ratio measured in NBS 983 (2,766 ± 1.60%, 2SD; n=4) during the course of this study when internal correlated errors on the samples were lower. The Pb-Pb age calculations were made using a correlation coefficient of 0.16 between these two ratios and assuming 238 U/ 235 U = 137.84

(i.e., the value for SRM 960 and SRM 950a U standards; Richter et al., 2010) using Isoplot version 3.72 by Ludwig (2009).

The Pb-Pb model ages, assuming a single stage evolution from the initial Solar System Pb isotopic composition represented by the Canyon Diablo troilite (CDT) (Tatsumoto et al. 1973), are 4271.3 Ma for PX-L₈, 4325.7 Ma for PL-R, 4311.5 for WR1-R, and 4308.4 For WR2-R (\pm 0.3 Ma) (Table 5.3).

There is no significant internal Pb-Pb isochron obtained from the last leachates and residues of the whole-rock samples and mineral separates (Fig. 5.11). When all 7 fractions shown in Fig. 6 are regressed together, an errorchron age of 4211 ± 88 (MSWD = 264) is obtained. However, if only the 4 whole-rock samples are considered (WR1-L₈, WR2-L₈, WR1-R and WR2-R), these yield a Pb-Pb whole-rock age of 4102 ± 24 Ma (MSWD=1.2) (Fig. 5.11).



Figure 5.11. Plot of 204 Pb/ 206 Pb vs. 207 Pb/ 206 Pb showing the last leachates (L₈) and corresponding residues (R) of the pyroxene (PX) (L₈ only) and plagioclase (PL) mineral separates and two whole-rock samples (WR1 and WR2). The solid line is the isochron regressed through just the WR1-L₈, WR2-L₈, WR1-R and WR2-R samples and yields a whole-rock reequilibration age of 4102 ± 24 Ma (MSWD=1.2).

Table 5.3

Samples ^a	total Pb analyzed (ng)	²⁰⁶ Pb/ ²⁰⁴ Pb	²⁰⁴ Pb/ ²⁰⁶ Pb	corr. error % ^c	²⁰⁷ Pb/ ²⁰⁶ Pb	corr. error %°	sample/ blk ²⁰⁶ Pb	sample /blk ²⁰⁴ Pb	CDT model age (±0.3 Ma) ^d
		raw	corr. ^b		corr. ^b				·
PX-L ₈	0.73	4694.4	0.000186	3.70	0.511506	0.012	1811	5	4271.3
PL-L ₈	4.43	3038.4	0.000324	0.429	0.516295	0.007	9368	51	4282.9
PL-R	0.72	2402.9	0.000367	3.34	0.531700	0.018	1006	6	4325.7
WR1-L ₈	4.70	2709.8	0.000364	0.398	0.516790	0.005	9865	60	4283.7
WR1-R	1.15	2184.0	0.000428	1.82	0.526933	0.012	1607	10	4311.5
WR2-L ₈	5.89	2729.4	0.000363	0.399	0.516770	0.006	12353	75	4283.7
WR2-R	1.33	2274.3	0.000413	1.65	0.525763	0.011	1824	11	4308.4

Pb–Pb isotope data and Canyon Diablo Troilite (CDT) model ages.

^aData are shown for the last leachates (L_8) and corresponding residues (R) of the pyroxene (PX) (L_8 only) and plagioclase (PL) mineral separates and two whole-rock samples (WR1 and WR2) of Bunburra Rockhole.

^bPb isotopic compositions are corrected for instrumental mass fractionation using the Tl doping method, and for a blank contribution (details are provided in Bouvier and Wadhwa, 2010). ^cCorrelated errors on corrected Pb isotopic ratios from errors related to isotopic measurements and correction of blank contribution (details on these calculations are given in Bouvier et al., 2007). ^dCanyon Diablo Troilite (CDT) model ages (one stage evolution) calculated using external reproducibilities measured on NBS 981 and NBS 983 standards during the course of this study (see details in text) and ²³⁸U/²³⁵U = 137.84 (Richter et al., 2010).

DISCUSSION

Textures

The variety of textures found among lithic clasts in BR includes primarily igneous subophitic textures with a range of grain size as well as fine-grained granular textures with abundant 120⁰ triple junctions that are characteristic of metamorphosed rocks (Figs. 5.1-5.4). Similar variations in texture are reported in the monomict eucrite breccias, where the subophitic clasts are commonly thought to represent the original igneous texture of the basalts, while the fine grained material represents comminuted breccia matrix that was recrystallized during thermal metamorphism (Takeda and Graham 1991; Yamaguchi et al. 1994; Metzler et al. 1995; Gardner-Vandy et al. 2011).

Major and Trace Element Mineral Chemistry

Pyroxenes in the Three Lithologies

Analogous to many non-cumulate eucrites, the equilibrated major element chemistry and presence of high-Ca pyroxene exsolution lamellae in the low-Ca pyroxenes in BR (Fig. 5.5) are consistent with it having experienced extensive thermal metamorphism and long periods of slow subsolidus cooling or reheating (e.g., Takeda and Graham 1991; Yamaguchi et al. 1994; Metzler et al. 1995; Gardner-Vandy et al. 2011). The major element compositions of BR pyroxenes measured in the variably textured clasts of are also consistent with all of the lithologies originating from a common or very similar parent melt. However, the lack of exsolution lamellae and uniformly low-Ca composition of pyroxene phenocrysts in the FG lithology suggests that it may have been affected differently than the other two lithologies during the post-crystallization thermal history of BR. Similar to what is observed for BR here, the presence of pyroxene with exsolution lamellae in clasts with subophitic texture as well as pyroxene of either high- or low-Ca composition with no exsolution fabric occurring in recrystallized clastic matrix has been documented in non-cumulate eucrite breccias (Metzler et al. 1995). Only low-Ca pyroxene phenocrysts were observed in the FG recrystallized portions of BR in this investigation, which could be a natural feature of the meteorite or possibly an artifact of a lack of augite phenocrysts in the thin section examined here.

The ranges of REE abundances in BR pyroxenes from each of the three lithologies are shown in Fig. 5.6. The similarity of the CI-normalized REE patterns (including the Eu/Eu* values) as well as the ranges of REE abundances in pyroxenes from the CG and MG lithologies further suggests that these two lithologies were derived from the same parent melt. This is in contrast to REE abundances in pyroxenes of the FG lithology, which differ from those of the other two lithologies in these characteristics. The lower REE abundances in FG pyroxene phenocrysts, as compared to the other lithologies, is consistent with their uniformly low-Ca composition and suggests the FG material experienced a different post-crystallization history of thermal metamorphism and equilibration. This is also supported by the differences in textures between the CG and MG (igneous) lithologies and the FG (metamorphic) lithology (Figs. 5.1-5.4).

There is considerable overlap in the compositional ranges of other trace elements such as Ti, Y and Zr in pyroxenes of the CG and MG lithologies (Fig. 5.2), which is also consistent with them originating from a common parent melt. The range of Ti concentrations in pyroxenes of the FG lithology also largely overlaps with those of the CG and MG lithologies. However, Y and Zr abundances in FG pyroxenes appear to be slightly lower than those in the other two lithologies, which is consistent with the generally lower abundances of other incompatible trace elements such as the REE in these pyroxenes. The textural evidence, along with the major element, REE, and other trace element abundances reported here for pyroxenes in the three BR lithologies suggest that the FG lithology most likely experienced a different post-crystallization thermal history than the other two lithologies. As with some eucrites, the variability of textures and the mineral chemistry of BR reflect a complex geologic history that likely includes initial rapid cooling from a melt, slow cooling and/or reheating during burial under secondary lava flows and impact related brecciation and heating (e.g., Metzler et al. 1995).

Comparison To Non-Cumulate Eucrites

We can compare the geochemistry of BR to that of typical non-cumulate eucrites to investigate whether other characteristics besides its unique O isotope composition also distinguish this meteorite from the eucrites. The range of pyroxene major element compositions overlaps with that reported for many equilibrated non-cumulate eucrites (Fig. 5.5; Takeda and Graham 1991; Metzler et al. 1995, Gardner-Vandy et al. 2011). The ranges of REE abundances in BR pyroxene, plagioclase and Ca-phosphate (Figs. 5.6, 5.8 and 5.9) are similar to those reported for these minerals in non-cumulate eucrites (Hsu and Crozaz 1996). As can be seen in Fig. 5.7, the ranges of Ti, Y and Zr concentrations in BR pyroxenes are also generally similar to the ranges reported for pyroxenes in non-cumulate eucrites (Hsu and Crozaz 1996).

Therefore, on the basis of the major and trace element (including REE) microdistributions, BR appears to be similar to a typical non-cumulate eucrite. The O isotope composition of BR is thus the only geochemical characteristic yet observed that suggests its formation on a different parent body than the eucrites. The striking similarities in the textures and major and trace element geochemistry of BR and that of typical non-cumulate eucrites indicate that these meteorites experienced comparable petrogenetic and post-crystallization thermal histories. This further suggests that there may have been many differentiated asteroids of essentially the same composition forming in different parts of the solar protoplanetary disk characterized by different O isotope compositions, but otherwise similar conditions. Given that there may be as many as ~ 50 differentiated parent asteroids represented by the iron meteorites (Wasson 1990), it is perhaps not surprising that there could be many complimentary samples of crustal material from these asteroids. Alternatively, the numerous petrologic and geochemical similarities of BR to the non-cumulate eucrites could be interpreted as evidence that BR is a true eucrite and that the HED parent body maintained some degree of heterogeneity with respect to O isotopes during differentiation and crust formation (Weichert et al. 2004), despite the fairly homogeneous O isotope compositions of most HED samples (Scott et al. 2009).

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Chronology

²⁶Al-²⁶Mg Extinct Chronometer

The ²⁶Al-²⁶Mg chronometer is useful for high-precision relative age dating of ancient meteorites and their components (e.g., Spivak-Birndorf et al. 2009; Wadhwa et al. 2009; Bouvier and Wadhwa 2010). The upper limit on the ²⁶Al/²⁷Al ratio and the model ²⁶Al-²⁶Mg isochron for the CG lithology of BR can be mapped on to an absolute timescale using the D'Orbigny angrite as a time anchor. D'Orbigny has initial ${}^{26}\text{Al}/{}^{27}\text{Al} = (5.06 \pm 0.92) \times 10^{-7}$ (Spivak-Birndorf et al. 2009) at an absolute Pb-Pb age of 4563.37 ± 0.25 Ma (corrected for its measured U-isotope composition; Amelin, 2008; Brennecka and Wadhwa 2012). The internal ²⁶Al-²⁶Mg isotope systematics for the CG lithology of BR indicate that the last equilibration of Mg isotopes occurred in this sample after the complete decay of ²⁶Al (Fig. 5.10). Relative to D'Orbigny, the timing of this equilibration event is ≤ 4561.5 Ma, based on the upper limit of the 26 Al/ 27 Al ratio inferred for the CG lithology. The slope of the model ²⁶Al-²⁶Mg isochron for the CG lithology of BR corresponds an age of 4565.0 ± 0.7 Ma. This age most likely corresponds to the timing of the Al/Mg fractionation event that resulted of the formation of the BR parent melt from a chondritic source. The ²⁶Al-²⁶Mg systematics are also reset after the decay of ²⁶Al in the FG lithology of BR and provide an upper limit on the timing of the equilibration event of \leq 4565.8 Ma.

Although BR most likely formed on a different parent body than the HED meteorites, it is nevertheless useful to compare its chronology to that of the eucrites to better understand the timing and duration of basaltic volcanism in the

early Solar System. The model ²⁶Al-²⁶Mg age for BR is identical, within errors, to the timing of the global Mn/Cr fractionation event on the eucrite parent body as determined from the "whole-rock" ⁵³Mn-⁵³Cr isochron for the HED parent body (Lugmair and Shukolyukov 1998; Trinquier et al. 2008) and anchored to D'Orbigny (Glavin et al. 2004; Amelin 2008a; Brennecka and Wadhwa 2012). Recent data on the ²⁶Al-²⁶Mg isotope systematics of bulk eucrites (Schiller et al., 2010) also yield similar model ages for the timing of Al/Mg fractionation event (i.e., most likely the formation of their parent melts from their source reservoirs on the HED parent body). Therefore, the extinct radionuclide chronometers in both BR and the eucrites record evidence of large-scale planetesimal differentiation within the first ~3 Ma after Solar System formation. Thus this process may have been ubiquitous and widespread in the early Solar System and probably occurred contemporaneously on many asteroidal bodies.

Pb-Pb Chronology

As discussed in the previous section, the Al-Mg chronometer shows evidence of resetting in BR. It is inferred that a late thermal event reset and equilibrated the Mg isotopic composition between the mineral phases subsequent to the decay of ²⁶Al. This event is also likely to have caused the disturbance of the Pb-Pb isotope systematics of the BR whole-rock samples and mineral separates (as evidenced in Fig. 5.11). There is substantial scatter in the Pb isotopic data for these BR samples, but they all yield CDT model ages close to ~4.3 Ga (assuming a single stage model). Furthermore, the last leachates and residues of the two whole-rock samples yield a statistically good Pb-Pb whole-rock isochron with an even younger age of ~4.1 Ga. The fact that the CDT model ages are discordant by ~200 Ma with the WR internal isochron age is suggestive of a major late U/Pb fractionation event in BR. Relatively young Pb-Pb resetting ages of ~4.1 Ga (compared to crystallization ages that are typically close to ~4.5 Ga) have also been found for other achondrites such as eucrites (e.g., Tera et al. 1997), most likely attesting to late thermal events associated with a period of intense bombardment in the asteroid belt.

It has recently been shown that the ²³⁸U/²³⁵U ratio of terrestrial and meteoritic materials cannot be assumed to be 137.88 (Weyer et al. 2008; Brennecka et al. 2010a,b; Brennecka and Wadhwa 2012). As such, the precise and accurate determination of the Pb-Pb age of a sample requires the measurement of its U isotope composition. Given the scatter in the Pb isotopic data for BR and the relatively young Pb-Pb model ages and whole-rock internal isochron age, we did not measure the U isotope composition of this sample. However, we can assess the degree of uncertainty in the calculated Pb-Pb ages based on the range of U isotope compositions measured thus far in all meteoritic and terrestrial samples.

The largest variations in the ²³⁸U/²³⁵U ratios observed so far in any natural samples have been measured in refractory inclusions from the Allende meteorite and these are attributed to the decay of ²⁴⁷Cm (Brennecka et al. 2010a). Although deviations of the U isotope composition relative to the terrestrial standard value have been measured in other terrestrial and meteoritic samples (and are likely attributable to other processes; Weyer et al., 2008), these are nevertheless smaller

than those measured in the refractory inclusions and imply a maximum uncertainty in the calculated Pb-Pb ages of <5 Ma. This level of uncertainty does not affect the interpretation (discussed earlier in this section) of the disturbed Pb-Pb isotope systematics of BR reported here.

CONCLUSIONS

Bunburra Rockhole is eucrite-like basaltic achondrite believed to have originated on a unique parent body. It is similar to typical non-cumulate eucrites in terms of mineralogy and petrology, but is inferred to be from an asteroid other than 4 Vesta (the inferred HED parent body) and unrelated to the eucrites on the basis of orbital and oxygen isotope data (Bland et al. 2009; Benedix et al. 2010). The major element compositions of pyroxenes and trace element abundances (REE, Ti, Y and Zr) of individual mineral grains (pyroxene and plagioclase) in BR determined in this investigation are also very similar to those of typical noncumulate eucrites and do not distinguish BR from this group of related meteorites. The geochemical and textural resemblance of BR to typical non-cumulate eucrites suggests that BR experienced a similar petrogenesis and post-crystallization thermal history this group of meteorites, and thus represents a sample of a unique parent body that formed with essentially the same initial composition and under conditions very similar to the HED parent body.

The texture of BR is heterogeneous, with three distinct lithologies that are defined by their average grain size as either fine-, medium- or coarse-grained (FG, MG and CG lithologies, respectively; Bland et al. 2009). Comparison of the major and trace element microdistributions in minerals from these three lithologies provides some insight into the relationship of these lithologies to one another. Minerals in the MG and CG lithologies appear identical in terms of their major and trace element compositions, indicating that these materials were derived from the same parent melt and experienced similar post-crystallization thermal histories. The major and trace element abundances, particularly the REE, in pyroxenes the FG lithology of BR differ from those in the other two lithologies. This may be due to differences in the parent melt compositions, but is perhaps more likely related to the different metamorphic histories of these lithologies, which is also reflected in their textures.

The chronology of BR reflects initial formation of its parent melt on its parent planetesimal early in Solar System history, followed by a late metamorphic equilibration event. The ²⁶Al-²⁶Mg chronometer provides a model age for the timing of the Al/Mg fractionation event (most likely formation of its parent melt from its source reservoir) that is within the first ~3 Ma of the beginning of the Solar System. The internal ²⁶Al-²⁶Mg isotope systematics were reset in BR after the complete decay of ²⁶Al and can thus only provide an upper limit on the timing of this equilibration event. This upper limit on the age when this chronometer was reset is within a few Ma of the ²⁶Al-²⁶Mg model age for the Al/Mg fractionation event, leaving open the possibility that Mg isotopes in BR were equilibrated during slow cooling after its initial crystallization. However it is also possible that the ²⁶Al-²⁶Mg chronometer was reset during a much later thermal event, such as impact heating. The Pb-Pb age of ~4.1 Ga for the BR whole-rock samples

reflects reequilibration of the Pb isotopes during an episode of thermal metamorphism that post-dates the initial formation of the meteorite. Taken together, the relative and absolute chronologies suggest a petrogenetic history for BR that includes early melting and differentiation of its source reservoir to form its parent melt (at ~4565 Ma), perhaps followed by slow cooling after the meteorite crystallized, and finally a thermal metamorphic event at a much later time (at ~4.1 Ga). Investigations of these chronometers in some eucrites provide similar results to those reported for BR here (Tera et al. 1997; Schiller et al. 2010).

The resemblance of BR to the non-cumulate eucrites in terms of its textures, major and trace element microdistributions and chronology suggests that this ungrouped basaltic meteorite formed from an analogous source reservoir and evolved under very similar conditions to the eucrite basalts. However, the distinct O isotope systematics in BR compared to the eucrites provide evidence that formation of eucrite-like basalts in the early Solar System occurred on several differentiated asteroids that formed in isotopically (and therefore also spatially) distinct regions of the protoplanetary disk.

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APPENDIX A

⁶⁰FE-⁶⁰NI SYSTEMATICS OF BULK UREILITES

INTRODUCTION

The ureilites are a group of C-rich ultramafic achondrites that most likely formed as the residual products of partial melting in the mantle of their parent body (Mittlefehldt et al. 1998; Goodrich et al. 2004). Despite the role of asteroidal differentiation processes in forming these meteorites, they have some characteristics in common with primitive chondrites that could reflect nebular processing of the ureilite parent material (Goodrich 1992). These include highly heterogeneous oxygen isotope compositions like carbonaceous chondrites, which do not form a single mass-dependent array (Clayton and Mayeda 1988), and the presence of phases with noble gas compositions similar to those seen in primitive chondrites (Rai et al. 2003). These primitive characteristics may in part reflect a very early formation time in the Solar System for the ureilites. The ultramafic composition of ureilites makes them difficult to date with many of the radionuclide chronometers that are useful for materials formed in the early Solar System. Volcanic activity on the ureilite parent body likely occurred ~5 Ma after Solar System formation, as inferred from the ²⁶Al-²⁶Mg and ⁵³Mn-⁵³Cr ages of rare feldspathic igneous clasts found in polymict ureilites (Goodrich et al. 2010). It has been suggested that the ureilites record the early stages of S-rich metallic melt migration and core formation on their parent asteroid (Warren et al. 2006). The ¹⁸²Hf-¹⁸²W chronometer, which can be used to date the timing of metalsilicate fractionation in early Solar System materials, was recently investigated in ureilites (Lee et al. 2009). In that study, bulk ureilites were found to have W isotope compositions indicating that metal segregation and core formation were

taking place on the parent body within the first ~1-2 Ma of the start of the Solar System (Lee et al. 2009). Core formation also fractionates Fe from Ni and bulk ureilites span a relatively wide range of 56 Fe/ 58 Ni ratios from ~50-600 (Rankenburg et al. 2008). If the Fe/Ni ratios of bulk ureilites were established at the same time as the Hf/W ratios, they could potentially record evidence for the former presence of live 60 Fe, and could thus be used to estimate the initial Solar System abundance.

MATERIALS AND METHODS

The ⁶⁰Fe-⁶⁰Ni isotope systematics of bulk samples of four ureilites: Kenna, Haverö, Dhofar 1519 and a coarse-grained ureilite lithology of the Almahata Sitta meteorite were also measured in this study. Kenna, Dhofar 1519 and Haverö are monomict ureilites, while Almahata Sitta is an anomalous polymict sample that was part of the small asteroid 2008 TC₃ that recently fell in Sudan. Interior fragments (weighing ~50 mg) from each ureilite were obtained from the collection at the CMS at ASU. A detailed description of our procedures for the measurement of ⁶⁰Fe-⁶⁰Ni systematics is given in the Materials and Methods section of chapter 2 of this thesis. There are a few notable differences in the way the ureilite samples were processed as compared to the methods described previously for angrites and UOC. The ureilite samples were gently crushed in a boron-carbide mortar and were not washed with any solvent prior to dissolution in concentrated HF, HNO₃ and HCl. Chemical separation of Ni from the ureilite samples was achieved using only the first (Fe + Zn removal) and last (DMG based Ni-specific resin) column chromatography procedures described in the main chapter, which was adequate to remove the matrix elements from the ureilites. Also, the ⁴⁰Ar¹⁸O interference was not resolved from ⁵⁸Ni, which could have affected the measured Ni isotope compositions of the ureilites.

RESULTS

The Ni isotope Fe/Ni ratios of bulk ureilites are shown in Table A.1 and Fig. A.1. The ⁵⁶Fe/⁵⁸Ni ratios of ureilites ranged from ~60-250 and all the samples had terrestrial ε^{60} Ni* values within the analytical errors. If these meteorites are assumed to have formed contemporaneously, the data correspond to an upper limit on the ⁶⁰Fe/⁵⁶Fe $\leq 6.7 \times 10^{-9}$ at this time. Several groups have recently investigated the ⁶⁰Fe-⁶⁰Ni systematics of bulk ureilites. The results here are in agreement with the absence of ε^{60} Ni* anomalies reported for bulk ureilites by Quitté et al. (2010) and Tang and Dauphas (2012), but do not support the claims of uniform ε^{60} Ni* deficits of about -0.3 ε in these meteorites by Bizzarro et al. (2007).

Table A.1. ⁶⁰Fe-⁶⁰Ni isotope systematics of bulk ureilites.

Sample	⁵⁶ Fe/ ⁵⁸ Ni ^a	ε ⁶⁰ Ni*	± 2SE ^b	$\epsilon^{^{61}}Ni$	$\pm 2SE^{b}$	n
Dhofar 1519	119	-0.06	0.06	0.1	0.35	10
Kenna	125	-0.02	0.05	0.18	0.35	10
Almahata Sitta	64	0.02	0.06	-0.14	0.44	5
Haverö	254	-0.14	0.17	0.25	0.62	4

^aErrors on 56 Fe/ 58 Ni are $\pm 10\%$

^bErrors on Ni isotope ratios are ± 2 SD/ \sqrt{n}



Figure A.1. ⁶⁰Fe-⁶⁰Ni isotope systematics of bulk ureilites. Errors are ±10% on ${}^{56}\text{Fe}/{}^{58}\text{Ni}$ and the larger of ±2SE or the external reproducibility (±0.10 ϵ) on $\epsilon^{60}\text{Ni}*$. The solid line corresponds to the least-squares regression of the data, which is not resolved from zero and corresponds to an upper-limit on ${}^{60}\text{Fe}/{}^{56}\text{Fe} \le 6.7 \times 10^{-9}$.

DISCUSSION AND CONCLUSIONS

There are currently only a few chronological data available for the ureilites. Feldspathic clasts in polymict ureilites have Al-Mg and Mn-Cr ages of \sim 4-5 Ma after the beginning of the Solar System (Goodrich et al. 2010), however it is not entirely clear if these ages also correspond to the formation of typical monomict ureilite materials. Older ages of \sim 1-2 Ma after CAIs are inferred from W isotope compositions of monomict ureilites, and these may correspond to the timing of incipient core formation on the parent asteroid (Lee et al. 2009). Baker et al. (2012) report sub-chondritic Al/Mg ratios and very small deficits in ²⁶Mg for

bulk monomict ureilites that are used to infer model ²⁶Al-²⁶Mg ages for silicate differentiation in the ureilite parent body mantle of ~1-4 Ma after Solar System formation. In contrast, the ⁵³Mn-⁵³Cr systematics of bulk samples, acid leaches and the complementary residues of two monomict ureilites indicate either later formation of or Cr isotopic equilibration in these meteorites, after the decay of ⁵³Mn (Shukolyukov and Lugmair 2006).

If the range of ureilite ages is then considered to be from 1-5 Ma after CAIs, the upper limit on the 60 Fe/ 56 Fe ratio reported here for these meteorites corresponds to an initial Solar System 60 Fe/ 56 Fe = ~0.9-2.5 × 10⁻⁸. These values are in reasonably good agreement with the estimates of initial Solar System 60 Fe/ 56 Fe based on D'Orbigny and chondrules from UOC (see Section 3. Discussion). The ureilite 60 Fe- 60 Ni systematics are unable to provide strong constraints on the initial Solar System 60 Fe abundance. However, it should be noted that the data also do not provide any clear evidence for the high initial Solar System 60 Fe/ 56 Fe ratios (~10⁻⁷) inferred from *in situ* studies of chondrules (Tachibana et al. 2006; Mishra et al. 2010; Telus et al. 2012).

APPENDIX B

BORON ISOTOPE COMPOSITION OF PRIMARY MAGMATIC AND SECONDARY ALTERATION PHASES IN THE NAKHLITES: IMPLICATIONS FOR ALTERATION ON MARS

INTRODUCTION

The surface of Mars is currently unlikely to support life due to the instability of liquid water under present conditions. However, the geomorphlogy of the martian surface is considered evidence that liquid water may have been present in the past (Carr 1996), possibly creating habitable environments. Understanding the conditions that are necessary for development of life in the universe is the fundamental question in the field of astrobiology. Whether or not Mars ever could have or did sustain a biosphere can provide important insights into the origins of life in our Solar System and the extent to which life would be expected to develop throughout the universe. The recent detection of large deposits of aqueously deposited minerals (i.e., phyllosilicates) on the surface of Mars (Bibring et al. 2006; Poulet et al. 2005) represents important additional evidence for the presence of liquid water on the surface of Mars in the past. However, there are still many open questions about the origin of such deposits and the exact processes that characterize the martian hydrological cycle. Whether martian phyllosilicate deposits formed at the surface or at depth in the crust is a critical question for assessing the possible types of habitable environments that may have been present on early Mars (e.g., Bibring et al. 2006). The formation of extensive clay deposits on the martian surface in situ would have required warmer, wetter conditions and thus a more dense atmosphere on early Mars (Bibring et al. 2006; Poulet et al. 2005). On the other hand, if martian phyllosilicates were formed predominately by subsurface hydrothermal fluids liberated from permafrost during transient volcanic or impact heating events

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(Abramov and Kring 2005; Schwenzer and Kring 2000), then warmer, wetter climatic conditions on Mars are not required to explain the presence of these deposits (Bibring et al. 2006; Poulet et al. 2005). The former scenario implies the possibility of long-lived water sources on the surface of Mars that could have potentially sustained a biosphere, while the latter scenario would result in more limited deep aqueous environments on Mars that could also potentially host life, such as thermophillic microorganisms (Abramov and Kring 2006; Schwenzer and Kring 2009). Knowing the physical and chemical properties of the fluids that altered the martian crust could help to better constrain the characteristics of the hydrological cycle on Mars and determine if there were ever abundant water reservoirs on the surface, or if hydrothermal systems from melted subsurface ice are the primary aqueous environment on Mars. However, details on the composition of fluids that altered the martian curst are currently limited.

A small number of martian meteorites are the only samples of the crust of Mars that are available for detailed laboratory investigations. As such they can provide valuable information about the geologic evolution of Mars that cannot be acquired through remote sensing observations. Some martian meteorites show evidence of having interacted with water while still emplaced in the crust of Mars (e.g., Leshin and Vincenzi 2006 and references therein). One type of martian meteorite in particular, the nakhlites, have relatively abundant assemblages of hydrous minerals indicating that they have been altered by crustal fluids on Mars (Gooding et al. 1991; Treiman et al. 1993; Leshin et al. 1996; Bridges and Grady 2000; Bridges et al. 2001; Gillet et al. 2002; Changela and Bridges 2011). These

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assemblages of alteration products include Fe-rich clay minerals, salts and Feoxyhydroxides that are collectively known as "iddingsite" (Gooding et al. 1991; Treiman et al. 1993; Bridges et al. 2001). Valuable information about the hydrologic cycle and composition of aqueous fluids on Mars can potentially be obtained from investigations of the secondary alteration phases in the nakhlites.

Boron is relatively soluble and can be readily mobilized in aqueous fluids during rock alteration and weathering (Leeman and Sisson, 1996). The fractionation of B isotopes during aqueous alteration processes can also be used to better understand and trace fluid-rock interactions (e.g., Palmer and Swihart 1996; Williams et al., 2001 a,b; Williams and Hervig 2002; Hervig et al., 2002). Boron has no natural redox chemistry and the fractionation of its isotopes is attributed entirely to the preference of each isotope for a different coordination state (Palmer and Swihart, 1996). The heavier isotope (^{11}B) is concentrated in trigonally coordinated species (e.g., $B(OH)_3$), while the lighter isotope (¹⁰B) is concentrated in tetrahedrally coordinated species (e.g., $B(OH)_4$) (Palmer and Swihart, 1996). Fractionation of B isotopes then occurs when phases having different B coordination states, such as natural waters (predominately trigonal B at pH < 7)) and clay minerals (tetrahedral B in framework crystallographic sites), react and equilibrate. When the coordination state of B is nearly the same in two phases that are equilibrating, there is little to no isotope fractionation (e.g., Hervig et al., 2002).

The aqueous alteration minerals found in martian meteorites can readily incorporate B during their formation and subsequent interaction with fluids.

Boron isotopes can be measured in geologic materials *in situ* using secondary ion mass spectrometry (SIMS), which is ideal for the analysis of small phases that cannot be easily extracted for bulk measurement such as the nakhlite alteration assemblages. The thesis appendix describes an investigation of the B isotope systematics of primary magmatic and hydrous alteration minerals with the objective of providing new constraints on the origins and characteristics of fluids that interact with the martian crust and the martian hydrologic cycle.

MATERIALS AND METHODS

Sample Preparation

This study includes three nakhlites: Nakhla, Lafayette and Miller Range (MIL) 03346. One-inch round thin or thick sections of these nakhlite were obtained from the collection in the Center for Meteorite Studies at ASU (Nakhla and Lafayette) and from the meteorite working group (MIL 03346). The samples were first carbon-coated and then mapped using a JEOL 845 scanning electron microscope (SEM) at ASU to identify alteration phases that could be targeted for B isotope measurements. The carbon coating was removed from the sections with 1-µm diamond paste followed by several rinses with "B-free" water (prepared by passing ultrapure Milli-Q water through a column packed with B-specific ion-exchange resin; Amberlite IRA 743) in clean Teflon beakers sitting in an ultrasonic bath. All reagents used in this study were prepared with this B-free water. Boron is ubiquitous in the environment and can be readily adsorbed to the surfaces of clays and Fe-oxides such as those in the nakhlites. Removal of any B

from terrestrial contamination is therefore essential to the accurate measurement of B isotopes in martian meteorites. In order to do this, the nakhlite sections were ultrasonicated in solution of 1.82 wt% mannitol, which scavenges easily leachable surface B (Leeman et al. 1991; Williams et al. 2001a), followed by several rinses in B-free water. After a round of B isotopic measurements on the SIMS, the samples were soaked in 1 M ammonium chloride to expand and exchange with the clay interlayers in order to release any B that may have been trapped when the clay minerals contracted. Such B could have a different isotopic composition from B that is bound in the phyllosilicate structures (Williams and Hervig 2002), which can obscure interpretations of the fluid-rock interactions based on B isotopes. The samples were analyzed before and after cation exchange.

Boron Isotope Measurements

The boron isotopic analyses were made using the Cameca 6f ion microprobe at ASU. Detailed description of the analytical procedures for B isotope analyses in clay minerals by SIMS were described previously (Hervig, 1996; Chaussidon et al., 1997; Williams et al., 2012). The instrument was calibrated with the Silver Hills illite standard, IMT-1 (a reference material from the Clay Minerals Repository, Purdue University, IN). Small (~5µl) drops of suspended solution of the < 2µm size fraction (which had also been treated with mannitol and ion-exchanged to remove trapped interlayer B) were dropped onto the edge of the meteorite slides (made with B-free glass) where they would not contaminate the meteorites. The sample was then gold coated to prevent charging during analysis. The samples were sputtered with an O⁻ primary beam and introduced into the mass spectrometer with a ~10 kV accelerating voltage. Instrumental mass fraction used to correct the measured isotope ratios varied from about -40‰ to -60‰ over the course of this study but did not vary during the course of an analytical session. Sample runs consisted of 100 ratios, calculated from four- and one- second integration times for ¹⁰B and ¹¹B, respectively, on single electron-multiplier using magnet jumping. Boron concentrations were calculated from the ¹¹B/³⁰Si ratio measured in or near the analysis crater of an isotopic measurement. The typical primary beam intensity used for analysis was 10-15 nA with a spot size of ~25-50 µm

RESULTS

The B concentrations and isotope compositions of magmatic phases and alteration assemblages (iddingsite) in martian meteorites are shown in Fig. B.1. The pyroxene had very low B concentrations of <0.5 ppm and thus the B isotope compositions were calculated as the ratio of the mean ¹¹B and ¹⁰B counts, as opposed to the mean of the ¹¹B/¹⁰B ratios, to avoid bias (Ogliore et al. 2011). This results in very large errors ~30‰ for individual measurements, so only the average and standard deviation of all the pyroxenes analyses are considered here (Nakhla -10.2 ± 8.0‰; Lafayette -16.6 ± 8.2‰; MIL 03346 -10.1 ± 12‰).



Figure B.1. Boron isotope compositions (‰) of magmatic minerals and hydrous alteration minerals in Nakhla (Nak; red symbols), Lafayette (Laf; blue symbols), and MIL 03346 (MIL, green symbols) vs. Boron concentrations (ppm). Idd = iddingsite; Meso = mesostasis; PX = pyroxene; OPQ = opaque. For Lafayette there are two different types of alteration products that were analyzed type-A is a mix of phyllosilicates and Fe-oxyhydroxides replacing mesostasis and type-B is mildly altered mesostasis that has not been full replaced by hydrous minerals. Alteration products growing on three different mineral sites were analyzed in MIL 03346, Idd-MS = mesostasis-hosted; Idd-OL = olivine-hosted; and Idd-OPQ = opaque phase in mesostasis. XC is for samples that were cation exchanged with 1 M NH₄Cl to remove any trapped interlayer B that is not bound in the structure of alteration minerals. The ovals show possible mixing trends among minerals within Lafayette and MIL 03346. The isotopic compositions of most terrestrial, and possibly martian surface waters are shown as possible sources of contaminant B to the samples. Errors are ±1SE on the individual runs.

All of the iddingsite and mesostasis analyses had enough B counts such that the data would not be biased by the reduction process and the values are the mean of the ¹¹B/¹⁰B ratios \pm 1 SE for the run. Nakhla iddingsite and mesostasis data overlap and show considerable scatter in δ^{11} B from about -20‰ to +5‰ and

[B] of ~1-30 ppm. After treatment with NH₄Cl, the iddingsite (Nak idd-XC) appeared to have lower B contents, but a similar range in δ^{11} B, suggesting that any trapped interlayer B had the same isotope composition as that fixed in the structure of the alteration products. It should be noted that the B concentrations were only measured in a few of the Nakhla iddingsite analyses and the values for most of the data are estimated from the B counts alone based on the values determined in spots where [B] had been measured, and thus should be taken as approximate.

Iddingsite from Lafayette has variable δ^{11} B from around 0‰ to -25‰ and [B] from ~5-30 ppm. Two types of alteration were observed in Lafayette based on petrographic evidence (Fig. B.2) and they have different B isotope systematics. Iddingsite "type-A" consists of intergrown clays and Fe-rich minerals (Feoxyhydroxides and siderite, Fig. B.2). Lafayette iddingsite "type-B" appears rust colored in plane-polarized light (Fig. B.2.d), but does not show extensive alteration in SEM chemical maps where it can be seen to consist of plagioclase and other Si-rich phases (Fig. B.2.b), indicating that the alteration consists of a very thin layer. It is likely that iddingsite type-B is essentially Lafayette mesostasis with incipient alteration. Treiman et al. (1993) also note the presence of visible alteration along some of cracks and grain boundaries in Lafayette that are not detected by SEM back-scattered electron images. Lafayette iddingsite type-A and -B/mesostasis can be grouped on the basis of their B isotope systematics. Type-B/mesostasis has fairly restricted $\delta^{11}B \sim 0\%$ and B concentrations of ~5-15 ppm, but with most analyses having ~10 ppm. Type-A

shows a much wider range of δ^{11} B from around -10% to -25% and [B] from ~5-30 ppm, with an apparent trend toward lower δ^{11} B with increasing B content. However, the B concentration data for Lafayette iddingsite type A should be considered somewhat approximate due to a potential analytical artifact caused by the variable mineralogy in these alteration products. The B concentration measurements are determined from the measured B/Si ratios, assuming an SiO₂ abundance (0.5 in this study). This is problematic for Lafayette iddingsite A because the material clearly consists of two phases, one with abundant Si (clay) and one with essentially no Si (Fe-rich phase), both of which are sampled to some degree during each SIMS analysis because the spot size is too large to fit exclusively on one phase. As a result, if an analysis overlaps substantial portions of the Fe-rich phase that could contain B but not Si, the apparent [B] will be artificially elevated. It is therefore possible that the Lafayette iddingsite A has a large range of B isotope compositions, but more homogenous B content than appears from the presentation of this data in Fig. B.1. For both types of iddingsite in Lafayette, the B isotope systematics are similar before and after the NH₄Cl interlayer exchange process, again suggesting similar B was trapped and fixed in clays.



Figure B.2. Representative areas of the two types of iddingsite alteration assemblages in Lafayette. a) False-colored x-ray chemical map of type-A, green minerals are Fe-rich (Fe-oxyhydroxides and/or siderite) hydrous phases intergrown with orange colored phyllosilicates. The assemblage is filling the void between purple colored pyroxene crystals where mesostasis used to be. b) False-colored x-ray map of type-B iddingsite. The brighter orange colored minerals are plagioclase laths intergrown with a reddish Si-rich phase. The rusty colored alteration products seen in plane-polarized light (d) is not prominent in the x-ray maps, indicating that it is a relatively thin surface layer. c) and d) plane-polarized light images of the same areas of alteration in a) and b) respectively. The rectangles indicate the same area in the corresponding images.

Mesostasis from MIL 03346 had a fairly narrow range in δ^{11} B from about -5‰ to 0‰ and B contents of ~10 ppm. Iddingsite in MIL 03346 had a similar though slightly wider range δ^{11} B from about 0% to -10% compared to mesostasis. It also has much wider range of B concentrations from $\sim 15-100$ ppm (the highest B content measured in nakhlite alteration products), with a slight trend toward lower δ^{11} B values at higher [B]. There are some differences in the B isotope systematics of olivine-hosted and mesostasis hosted iddingsite in MIL 03346 that will be described in more detail in the following section. A single grain of altered opaque material in the mesostasis, similar to the "spongy" Fe-Tioxides described by Day et al. (2006) was also measured and had the lowest $\delta^{11}B$ value of -14‰ observed in MIL 03346 (Fig. B. 1). As with the Lafayette iddingsite, the mixed mineralogy (including non-silicates) of this inclusion may have made the [B] artificially high due to the incorrect estimate of silica abundance in this phase. While the use of a silicate calibration curve to quantify the B abundance in a non-silicate phase may be problematic, this has not yet been investigated. If the SiO₂ abundance of the sampled area is estimated from the Si signal of the standard, the [B] calculated for this phase is ~ 15 ppm.

DISCUSSION

Petrogenesis of Nakhlites

The nakhlites are often considered to all be samples of the same igneous body on Mars (e.g. Treiman 2005 and references therein). This is based on a variety of evidence including their petrology, mineralogy, common formation age, common ejection age, and aqueous alteration histories (Treiman 2005). They are cumulate pyroxenites that are believed to have formed in a thick basaltic lava flow near the surface of Mars, largely based on similarities with an analog site in Canada (Lentz et al. 1999). It is also suggested that the differences between individual nakhlites such as, modal abundance of crystals and mesostasis, degree of crystallinity and textures of the mesostais, and chemical zonation of cumulus minerals and growth rims formed during interaction with the magma are essentially consistent with closed system crystallization in a single lava flow (e.g., Treiman 2005; Mikouchi et al. 2006; Day et al. 2006). Furthermore, these differences are largely due to variable cooling rates of the interstitial melt and crystal settling effects and are therefore to thought to correlate with the emplacement depth of each nakhlite within the flow (e.g., Mikouchi et al. 2006; Day et al. 2006). The relative burial depths, from shallowest to deepest of nakhlites analyzed in this study are: MIL 03346 > Nakhla > Lafayette (e.g., Mikouchi et al. 2006; Day et al. 2006). Lafayette is the most equilibrated nakhlite and formed near the bottom of the flow, while Nakhla likely experienced the slowest cooling rate in the middle of the pile based on its equilibrated mineralogy and highly crystallized mesostasis (Day et al. 2006). In contrast, MIL 03346 is thought to have formed near the top of the flow based on its higher proportion of mesostasis, which is also glassy and has quench textures indicative of rapid cooling (Day et al. 2006). This model of nakhlite petrogenesis and geologic setting is also a useful framework for understanding the context of aqueous alteration of these meteorites while they were emplaced on Mars.

The iddingsite alteration products in nakhlites record valuable information about the characteristics of fluid-rock interactions and have been extensively studied (e.g., Gooding et al. 1991; Treiman et al. 1993; Leshin et al. 1996; Bridges and Grady 2000; Bridges et al. 2001; Gillet et al. 2002; Changela and Bridges 2011) Recent detailed analyses of the structures and compositions of aqueous alteration products in nakhlites (i.e., iddingsite) suggests that variations in the characteristics of these assemblages among the different meteorites are also likely correlated with their emplacement depth in a thick lava flow (Changela and Bridges 2011). Based on the overall extent of alteration and the specific mineralogy of aqueous assemblages in different meteorites, it is suggested that the nakhlite igneous body was altered from the bottom up (Changela and Bridges 2011), as opposed to by infiltration of surface waters into the crust (Bridges and Grady 2000). The source of this fluid was most likely melting of ice trapped in the martian crust possibly by impact heating (Schwenzer and Kring 2009; Changela and Bridges 2011). The bottom to top alteration scenario is supported by the presence of relatively abundant alteration phases in Lafayette compared to other nakhlites, as it had the most prolonged fluid exposure at the bottom of the lava flow closer to the fluid source (Changela and Bridges 2011). Lafayette iddingsite includes siderite, Fe-oxyhydroxides and crystalline phyllosilicates, whereas most other nakhlites contain only traces of some of these phases with less developed alteration products including poorly-crystallized amorphous silicates with Fe-rich clay compositions (e.g., saponite, serpentine, nontronite; Changela and Bridges 2011).

Boron Isotope Systematics of Nakhlites

As B is a highly fluid-mobile element, the B systematics and particularly the B isotope compositions of the nakhlite iddingsite can reveal insights into the martian hydrologic cycles. As described in the previous section, the probable geologic setting of the nakhlites at various depths in a cumulate igneous formation on Mars (e.g. Day et al. 2006) provides important geologic constraints that must be considered when trying to understand the aqueous alteration of these meteorites.

Lafayette and MIL 03346 are samples from near the bottom and top of the nakhlite formation, respectively, and therefore also near the beginning and end of the alteration fluid flow path. A comparison of the B isotope systematics in these two samples could yield new information about the evolution of fluids during the lifetime of the hydrothermal event that altered the nakhlites. The average B isotope composition of pyroxene (Fig. B.1) from MIL 03346 ($-10 \pm 12\%$) and Lafayette $(-16.5 \pm 8\%)$ are similar to each other and to mantle-derived rocks on Earth (Palmer and Swihart 1996), though the analytical errors are large due to the low B abundance (<0.5 ppm) in these phases, a result of the incompatible behavior of B in igneous minerals. Glassy mesostasis from MIL 03346 that does not appear to be severely altered, has higher [B] and slightly higher δ^{11} B from around -7% to +1% overlap with the average value for pyroxene in this sample (Fig. B.1). Lafayette iddingsite type-B, which appears to be mesostasis with only a thin rusty oxide alteration layer (Fig. B.2), also has B concentrations and δ^{11} B values that overlap those measured for the MIL 03346 mesostasis (Fig. B.1) The
slight offset between these phases could possibly be caused by fractionation during magmatic crystallization, but this is only likely if magmatic fluids are involved (Hervig et al. 2002) and this is not thought to be the case for nakhlites (e.g., Lentz et al. 2001). It is also possible that this is an analytical artifact during analysis, though B is not thought suffer significant matrix effects in SIMS (Chaussidon et al. 1997). A perhaps more likely reason for this difference is discussed below.



Figure B.3. δ^{11} B vs. 1/[B] for Lafayette iddingsite. The symbols are the same as in Fig B.1. The arrow shows a possible mixing line between Fe- and Si rich phases in type-A due to overlap of the microprobe beam onto multiple phases for each analysis.

As described previously, Lafayette iddingsite type-A is a complex intergrowth of Si rich phases (phyllosilicate) and Fe-rich phases (siderite and Fe-oxyhydroxides) (Fig. B. 2.). The analyses define a mixing trend in a plot of $\delta^{11}B$

vs. 1/[B], suggesting that each analysis is sampling a composite of variable proportions of these two phases (Fig. B.3.) However, it was also noted before that the assumption of a clay-like Si concentration for these samples is likely to bias the [B] toward higher values because the actual Si abundance of the mixture of clay and Fe-oxides and carbonates will be lower than that assumed for just clays. The spread in [B] in these samples should therefore be considered a maximum. Nevertheless, the large variation in δ^{11} B between these two phases in these meteorites is likely the result of mass fractionation during formation and equilibration of phyllosilicates and Fe rich phases (Fe-oxyhydroxides and siderite) in the presence of fluids. Phyllosilicates and Fe-oxyhydroxides both adsorb substantial B from solutions at circumneutral pH and relatively low temperatures (i.e., where B in solution is predominately trigonal $B(OH)_3$), with a preference for 10 B enriched B(OH)₄⁻ (e.g., You et al. 1995; Lemarchand et al. 2007) though there is evidence that adsorption to Fe-oxyhydroxides (i.e., goethite) results in larger B isotope fractionations than for clays under the same conditions (Lemarchand et al. 2007). Though siderite has not been studied, carbonates also take up isotopically light B, but their low B concentrations (Palmer and Swihart 1996) makes them an unlikely contributor to the B budget in Lafayette iddingsite. This could in part explain the variability of δ^{11} B measured in the Lafavette iddingsite type-A. This type of alteration formed as a replacement of mesostasis in Lafayette (Fig. B. 2.) and it is likely that the fluids from which they are deposited would become isotopically heavier as ¹⁰B is preferentially partitioned into the solids. The relatively ¹¹B rich fluids formed by this process could be the source of heavier B

in the slightly altered Lafayette mesostasis/iddingsite type-B. As this material is less altered than the fully replaced mesostasis (iddingsite type-A), it is likely that it was exposed to less water, or did not get exposed to water until later in the alteration process at which point significant ¹⁰B could have been adsorbed or bound into hydrous minerals. Being less reactive, the pyroxene would probably be mostly unaffected by this process despite it having lower B contents than the mesostasis. The original source of B in the fluids that altered the nakhlites was likely B leached from similar rocks in the area that were closer to the original hydrothermal source, as B is quantitatively leached from basalts by fluids at temperatures >150° C (Seyfried et al. 1984). The original fluid most likely also had a δ^{11} B similar to that of pyroxene or mesostasis, which has higher [B]. The slightly higher B concentrations in Lafayette iddingsite type-A (although these data might be biased toward higher [B]) as compared to the mesostasis could require that the fluids that altered the nakhlites brought in B from an additional source as the mafic phases alone cannot account for the B abundances in the alteration phases. This could involve the interaction of hot nakhlite hydrothermal fluids with sediments that had been previously enriched in B during diagenesis and low temperature alteration. This source of B would also be isotopically light and could perhaps account for the trend toward lower $\delta^{11}B$ at higher [B] in the iddingsite type-A alteration products. Alternatively, the original fluid may have been rather salty with high Cl⁻ concentrations, as has been suggested for martian fluids (Burt and Knauth 2003), and may also have brought in some additional B that did not originate from the dissolution of mafic minerals from nakhlite

lithologies. Boron and chloride are both fluid mobile elements and can be concentrated in brines (Vengosh et al. 1995). It has been suggested that the fluids that altered nakhlites brought in additional Cl⁻ (Treiman et al 1993) and it is therefore likely that some additional B was also introduced. If the source of the B in saline waters on Mars was also dissolution of evaporite deposits with borate minerals in them, then it would also probably be isotopically light relative to the igneous Mars, as these salts preferentially uptake tetrahedral B (Vengosh et al. 1995; Palmer and Swihart 1996).

Iddingsite in MIL 03346 generally has much higher [B] than in Nakhla and Lafayette (up to ~100 ppm, Fig. B.1). This may be due to an increase in the B concentration of the nakhlite alteration fluids caused by the evaporation of water as it approached the surface of the lava flow, where MIL 03346 was emplaced. Even though the fluid alteration of the nakhlite cumulate pile can be considered essentially a closed system, removal of water to the atmosphere near the surface of the flow is very likely. Traces of this process have been left in the nakhlites in the form of evaporite minerals such as sulfates and halides (Bridges and Grady 2000). Boron can concentrate in progressively evaporated brines (Vengosh et al. 1995) as it preferentially remains in solution. Nakhla in particular has the most evidence for the presence of evaporites (Changela and Bridges 2011) and its location beneath MIL 03346 in the nakhlite sequence is compatible with the evaporative concentration of fluids prior to their depositing iddingsite in MIL 03346.

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The position of MIL 03346 at the top of the nakhlite flow where fluids might ultimately migrate is favorable for investigating the overall evolution of the B isotope systematics in the fluid that altered the nakhlites. Additionally, the relatively low degree of alteration of MIL 03346 allows the effects of the early stages of this process to be evaluated. Day et al. (2006) reported the presence of "spongy" opaque assemblages that include pyrrhotite and hematite, associated with alteration areas in the mesostasis of MIL 03346. They also report some of the effects of this alteration on the local geochemistry of the surrounding phases (Day et al. 2006). An altered opaque inclusion from the mesostasis measured in this study (Fig. B.4) had the lowest δ^{11} B (-14‰) of all the MIL 03346 iddingsite analyzed in this study and falls within the range of mixed phyllosilicate and Ferich alteration phases found in Lafayette iddingsite type A (Fig. B.1. green X). Additionally, there is a correlation of the δ^{11} B of mesostasis-hosted iddingsite and its proximity to the opaque inclusion. The spots closest to the inclusion generally have the lowest [B] and the highest δ^{11} B (~0 to + 3‰). Analyses of other altered spots in the same mesostasis region generally have increasing [B] and lighter δ^{11} B values, trending toward the compositions of the olivine-hosted iddingsite (Fig. B.1. green open diamonds). This could possibly be explained by localized reactions induced by the oxidation of FeS. The fluids that altered the nakhlites likely became more oxidized as they evolved toward the surface (Changela and Bridges 2011), and oxidation of FeS could lead to the production of sulfuric acid (e.g. Belzile et al. 2004) and local reduction of pH near the altered sulfide inclusion. This could cause B to be released from the mesostasis, with high B

concentrations, and into the fluid phase. Some of the B could then be adsorbed into the Fe-oxide that is produced, with a preference for ¹⁰B adsorption (Lemarchand et al. 2007). The B left in solution would become isotopically heavier and would produce isotopically heavier clays upon precipitation. The B isotope systematics of mesostasis-hosted iddingsite could therefore be explained as variable amounts of ¹⁰B incorporation into the oxide alteration phases from B that was originally in the B-rich poorly crystallized clay material and mesostasis. This process could possibly have affected many of the iddingsite analyses in MIL 03346 as they show higher δ^{11} B values in the samples with lower [B] (Fig. B.1.).



Figure B.4. a) Photomicrograph of mesostasis-hosted alteration including large altered opaque assemblage in the center; plane-polarized light. The green ovals correspond to the analytical craters. b) Reflected light image near the same area showing the opaque assemblage. The scale is the same in both images.

Nakhla B isotope systematics are considerably more scattered than the

other two nakhlites measured here and it is unclear why this is the case. Some of

the scatter is almost certainly an analytical artifact of the approximate [B]

concentrations estimated for most of the analyses of Nakhla iddingsite, as

opposed to direct calibrated measurement of the B contents in the SIMS craters.

The pyroxene compositions are low in B, similar those in the other nakhlites and have identical δ^{11} B (within error) to the pyroxene in MIL 03346. The mesostasis data are broadly consistent with those of the other two meteorites, though showing much more scatter. The Nakhla iddingsite has some of the highest δ^{11} B values measured in these meteorites and a general trend toward higher [B] and δ^{11} B and may indicate terrestrial contamination issues. Though most of the Nakhla data cluster near the iddingsite data from other nakhlites. No clear conclusions about the B isotope evolution in nakhlites can be drawn from the Nakhla data yet.

The overall higher δ^{11} B values in MIL 03346 could be explained by the progressive evolution of the nakhlite alteration fluids to heavier isotope compositions due to 10 B being preferentially sequestered into hydrous phases as the brine migrated. The fluids would then precipitate iddingsite with relatively large isotope fractionations possible during B uptake into the solid phase. A similar conclusion was drawn from the Li isotope systematics of bulk nakhlites (Bridges et al. 2005). However, the δ^{11} B of MIL 03346 alteration products are very similar to nakhlite pyroxenes. Similar lithologies to the nakhlites may have been the source of many solutes in the alteration products, suggesting that B isotopes did not fractionate or were only slightly fractionated during the deposition of the MIL 03346 iddingsite. Changing conditions in the physical and chemical properties of the fluid as they reacted with the nakhlites could also affect the fractionation of B isotopes in MIL 03446 as compared to Lafayette. Lowering temperatures as fluids approached the surface would allow for larger isotope

fractionation (assuming low pH), but an increase in tetrahedral B with higher solution pH that results from reactions with the ultramafic rocks (e.g. Gysi and Stefánsson 2008) could diminish B isotope fractionation as the liquid and solid phases would have similar B coordination.

CONCLUSION

The B isotope systematics of alteration products in the nakhlite martian meteorites are complex and suggest local effects due to the mineralogy of individual samples, as well as possible broad scale trends as fluids evolved through the various lithologies represented by the meteorites. The generally heavier δ^{11} B values measured in MIL 03346, sampling the top of the nakhlite lava flow, as compared to Lafayette, which was at the bottom and experienced the most aqueous alteration, are consistent with essentially closed system evolution of a fluid during ascent through the crust where ¹⁰B is preferentially deposited in alteration phases, leaving the fluid progressively ¹¹B enriched toward the surface. It is also notable that the δ^{11} B of almost all of the alteration products are close to or lower than composition of igneous phases in the nakhlites. On Earth, most surface waters develop relatively high δ^{11} B from mineral precipitation reactions (Palmer and Swihart 1996). In particular the oceans are highly enriched in ¹¹B, largely due to extensive exchange reactions between hydrothermal fluids and the ocean crust at mid-ocean ridge spreading centers (Spivack and Edmond 1987). If there had been substantial surface waters present on Mars at some point, presumably undergoing similar fluid -rock reactions as on Earth, it is likely that

there would be a reservoir of isotopically heavy B on Mars. The lack of any evidence for high δ^{11} B in the nakhlites as they were altered on Mars provides evidence that the martian hydrological cycle consists mostly of small scale hydrothermal alteration in the crust, probably related to transient heating events such as impacts and volcanism. The few other B isotope data available for martian meteorites (Chaussidon and Robert 1999) might also support this idea. Chaussidon and Robert (1999) measured the B and Li isotopes in shergottites and found a general trend among samples toward lighter values in both isotope systems, the opposite direction of terrestrial seawater values and most assimilated crust signatures. The shergottites are believed to have formed with varying degrees of assimilation of older, oxidized crust (Wadhwa 2001). Chaussidon and Robert (1999) suggest that the observed variations in B and Li isotopes among these meteorites are due to assimilation processes but hypothesize that these processes are reverse in terms of direction of isotopic fractionation compared to those on Earth. Instead, it is possible that assimilation processes on Mars reflect incorporation of crust that has only minimally altered, such as is observed for nakhlites, perhaps during ascent of magmas through the crust. These types of rocks would most likely have acquired ¹⁰B enriched signatures from the deposition of alteration minerals in them as is observed for nakhlites. There is essentially no evidence for a large scale isotopically heavy B reservoir on Mars, such as with Earth's oceans, or the subduction processes that could help deliver isotopically heavy B to magma sources. As a result, subsurface hydrothermal

environments are probably the most likely setting to host or have hosted life on Mars in the last several Ga

APPENDIX C

STATEMENT OF PERMISSION FROM COAUTHORS

I have been granted permission by coauthors of the previously published article "New constraints on early solar system chronology from Al-Mg and U-Pb isotope systematics in the unique basaltic achondrite Northwest Africa 2976" to include this article as a chapter in this dissertation. The coauthors are: A. Bouvier, G. A. Brennecka, and M. Wadhwa