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^{182}Hf-^{182}W chronometry and the early evolution history in the acapulcoite-lodranite parent body

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Abstract–An acapulcoite, Northwest Africa (NWA) 725, a transitional acapulcoite, Graves Nunataks (GRA) 95209, and a lodranite, NWA 2235, have been studied with the short-lived chronometer ^{182}Hf-^{182}W system in order to better constrain the early evolution history in the acapulcoite-lodranite parent body. Unlike the more evolved achondrites originating from differentiated asteroids—e.g., eucrites and angrites—bulk rock acapulcoites and lodranite are characterized by distinct ^{182}W deficits relative to the terrestrial W, as well as to the undifferentiated chondrites, ε_W varies from −2.7 to −2.4. This suggests that live-^{182}Hf was present during the formation of acapulcoites and lodranites, and their parent body probably had never experienced a global melting event. Due to the large uncertainties associated with the isochron for each sample, the bulk isochron that regressed through the mineral separates from all 3 samples has provided the best estimate to date for the timing of metamorphism in the acapulcoite-lodranite parent body, 5 (+6/−5) Myr after the onset of the solar system. It is thus inconclusive whether acapulcoites and lodranites have shared the same petrogenetic origin, based on the Hf-W data of this study. Nevertheless, the formation of acapulcoite-lodranite clan appears to have post-dated the metal-silicate segregation in differentiated asteroids. This can be explained by a slower accretion rate for the acapulcoite-lodranite parent body, or that it had never accreted to a critical mass that could allow the metal-silicate segregation to occur naturally.

INTRODUCTION

Acapulcoites and lodranites are 2 small groups of achondrites that share the same oxygen isotopic compositions (Clayton and Mayeda 1996) and therefore are regarded to have come from the same parent body. The acapulcoite-lodranite clan appears to be less evolved compared to the other groups of achondrites, such as the howardite-eucrite-diogenite-type achondrites, angrites, and ureilites (Mittlefehldt et al. 1998), suggesting that the acapulcoite-lodranite parent body had not experienced extensive thermal events as the differentiated asteroids. Acapulcoites and lodranites have different petrographic features, as well as mineral and bulk chemical compositions (McCoy et al. 1996, 1997a, 1997b; Mittlefehldt et al. 1998). However, some samples exhibit petrographic features and compositions that are transitional between the 2 endmembers, acapulcoite and lodranite, and thus several subtypes for the acapulcoite-lodranite clan have been proposed (Floss 2000; Patzer et al. 2004). Generally speaking, acapulcoites are fine-grained, with rare chondrule relicts and modal mineral and bulk compositions similar to that of ordinary chondrites (McCoy et al. 1996; Mittlefehldt et al. 1998). It has been suggested that most of the acapulcoites probably had not been heated to a temperature high enough to sustain partial melting of silicates, or removal of partial melt (McCoy et al. 1996, 2006). In contrast, lodranites are characterized by their coarse-grained texture and non-chondritic compositions, e.g., rich in Ca-pyroxene and deficient in plagioclase, troilite, and highly incompatible elements (Takeda et al. 1994; McCoy et al. 1997a; Mittlefehldt et al. 1998). It appears that some basaltic melt had been extracted during the formation of lodranites (McCoy et al. 2006), while the rest of the acapulcoite-lodranite clan samples show no evidence of melt moving (Mittlefehldt et al. 1998).

Although the acapulcoite-lodranite parent body did not experience a global melting event, some samples, e.g., Graves Nunataks (GRA) 95209 and Monument Draw, do preserve extensive metal-sulfide-phosphate veins that seem to reflect the initial stage of metal-silicate segregation in their parent body (McCoy et al. 1996, 2006). Numerous methods have been used to date the formation of acapulcoite-lodranite clan, however, most of the studies were focused on acapulcoites. While some results indicate an early formation or metamorphic age for acapulcoites (Göpel et al. 1992; Nichols et al. 1994; Brazzle et al. 1999), most of the ages are either imprecise or significantly younger than 4.55 Ga (Palme et al. 1981; Schultz et al. 1982; Kaneoka et al. 1992; Prinzhofer et al. 1992; Torigoye et al. 1993; McCoy et al. 1996; Mittlefehldt et al. 1996; Pellas et al. 1997; Renne 2000; Min et al. 2003). Furthermore, there is no indication of any systematic age difference between the acapulcoites and lodranites.

The short-lived chronometer ^{182}Hf-^{182}W, $t_{1/2}$ = 8.90 ± 0.09 million years (Vockenhuber et al. 2004), has been shown to be one of the best tools for studying the metal-silicate differentiation and thermal history of early planetary bodies (Harper et al. 1991; Harper and Jacobsen 1996; Lee and Halliday 1996, 1997; Horan et al. 1998; Schoenberg et al. 2002; Yin et al. 2002; Kleine et al. 2002, 2004, 2005a, 2005b; Quitté et al. 2000, 2005; Quitté and Birck 2004; Lee 2005; Markowski et al. 2006a, 2006b). This is due largely to the different chemical behavior between Hf and W, with Hf tending to concentrate in the silicate mantle, while W goes into the metal core during metal-silicate segregation (Lee and Halliday 1996; Kleine et al. 2005a, 2005b; Lee 2005; Quitté et al. 2005; Markowski et al. 2006a, 2006b). Consequently, compared to the undifferentiated chondrites (or CHUR), iron meteorites and metal grains in undifferentiated meteorites are characterized by ^{182}W deficits, and the scales of the deficits reflect the timing when metal-silicate segregation occurred in the respective parent body (Lee and Halliday 1996, 2000a, 2000b; Horan et al. 1998; Kleine et al. 2005a; Lee 2005; Quitté et al. 2005; Markowski et al. 2006a, 2006b; Schérsten et al. 2006). Furthermore, due to the differences in compatibility between Hf and W during partial melting, the Hf-W system is also very useful in deciphering the timing and the nature of the petrogenetic history of various meteorite parent bodies (Lee and Halliday 1997; Quitté et al. 2000; Kleine et al. 2002, 2004, 2005b; Yin et al. 2002; Quitté and Birck 2004). Therefore, the main focus for this study is to constrain the petrogenetic history in the acapulcoite-lodranite parent body using the short-lived ^{182}Hf-^{182}W isotope system, to compare it to the differentiated asteroids, e.g., HED and angrite parent bodies, and also to check if Hf-W data can help in deciphering the formation ages between the acapulcoites and lodranites.

METHOD

An acapulcoite Northwest Africa (NWA) 725 (~5 g), a transitional acapulcoite GRA 95209 (~5 g), and a lodranite NWA 2235 (~2 g) have been analyzed in this study. Detailed descriptions of the mineralogy and chemical compositions for these samples can be found elsewhere (Patzer et al. 2004; Takeda et al. 2005; McCoy et al. 2006; Yamaguchi et al. 2006). All 3 samples were cut into thin slices, so it was not possible to select pristine inner parts for this study. Consequently, a more rigorous cleaning with ~10 mL of 2N HCl in an ultrasonic bath for ~15 min was used to remove potential surface alterations, saw marks, and handling blanks before they were crushed using an aluminum oxide mortar inside a class 10,000 clean room at the Institute of Earth Sciences, Academia Sinica. Small amounts of metal phases and altered silicates on the surface might have been partially dissolved and attacked during the leaching, but the rest of the silicates should remain unaffected. A hand magnet was used to separate the high-magnetic (metal-rich) fractions out of the low-magnetic (silicate-rich) fractions for NWA 725 and NWA 2235. Consequently, 3 fractions, including the high-magnetic, the whole rock, and the low-magnetic were separated for NWA 725, and an extra medium-magnetic fraction was separated for NWA 2235. Due to the rarity and the first Hf-W study for these samples, the simple mineral separation employed in this study was aimed at getting some useful data first while minimizing the total experimental blanks. Therefore, each mineral fraction was not as clean and complete as possible, which, however, might affect the total spread of Hf/W ratios but not the slope of the isochron.

Because metal veins are inter-grown with silicates in GRA 95209, it is quite difficult to physically separate the silicates from the metal veins through crushing. Therefore, separation of the silicate fraction of GRA 95209 was achieved by preferentially dissolving the metal using 6N HCl plus a small amount of concentrated HNO_3 on a hot plate. Some silicates in GRA 95209 might have been attacked or partially dissolved by this process, however, the isochron are not affected. In addition to the lodranite and acapulcoite samples, the whole rock sample of an angrite Sahara 99555 (~1 g) was also analyzed in this study. With the exception of the metal (high-magnetic) fraction of GRA 95209, which was dissolved using 6N HCl + trace amount of HNO_3, all the fractions were dissolved sequentially with concentrated HF plus trace amount of HNO_3, 8N HNO_3, and 6N HCl plus trace amount of HF. Approximately 10% of the solution was split and spiked with a mixed ^{178}Hf-^{184}W spike for isotope dilution measurements. The mixed ^{178}Hf-^{184}W spike, originally set up at ETH, has been calibrated at ETH and at IES independently with mixed Hf-W standards, independently prepared from ~1 g of high-purity Hf and W metal. The results agreed to within 0.5%, and the offset was most likely due to evaporation lost over a period of ~6 yr. The remaining solution was then evaporated to dryness and re-dissolved with ~8 mL of 4N HF.

The column procedures used for W isotopic composition and Hf-W isotope dilution measurements have followed those described in Lee et al. (1997, 2002), except for the addition of a cleaning step for W isotopic measurement with a reduced column and slightly modified procedures. Approximately 3.5 mL of Bio-Rad AG-1 × 8, 200–400 mesh, anion resin was loaded into a Teflon column, ¼ inch in diameter, from Savillex. The resin was washed sequentially with ~30 mL of 5N HCl + 1N HF and deionized H_2O, and preconditioned with ~15 mL of

4N HF. All the sample solutions were centrifuged before they were loaded onto the columns. A column full, ~30 mL, of 4N HF was added to the column after the sample solutions had eluted through. An additional 8 mL of 5N HCl + 1N HF was eluted, aimed at taking out the bulk of Ti, Zr and Hf, before W was collected with 10 mL of 5N HCl + 1N HF. The W fraction collected from the first column was dried and re-dissolved with ~1 mL of 4N HF + trace amount of HNO_3, and loaded onto the clean up column, a Bio-Rad micro column filled with ~0.8 mL of Bio-Rad AG-1 × 8, 200–400 mesh, anion resins. After the sample solution has loaded and eluted, a column full (~6 mL) of 4N HF + trace HNO_3 was added subsequently before W was collected with a column full of 5N HCl + 1N HF. The same setup and procedure as the clean up column was used for the spiked samples, and Hf was collected together in the W fraction. Total procedural blank for W was ≤0.4 ng.

All the W isotope and Hf-W isotope dilution measurements were performed using the Nu Plasma, a multiple collector inductively coupled-plasma mass spectrometer, from Nu Instrument, at the Institute of Earth Sciences, Academia Sinica (Table 1). The NIST-3163 W standard was run in between every sample to monitor the performance of the Nu Plasma and to check for memory effects, which were negligible. All the W isotopic measurements were normalized to $^{186}W/^{184}W = 0.927633$ (Lee and Halliday 1995). The IES Nu Plasma gives a mean $^{182}W/^{184}W$ and $^{183}W/^{184}W$ of 0.864910 ± 18 and 0.467012 ± 15, respectively. The quoted 2σ standard errors all refer to the least significant figures. However, due to the lack of duplicate sample measurement, a minimum uncertainty of 0.4 epsilon unit, instead of the 2σ standard error from the measurement, for $^{182}W/^{184}W$ was used for all mineral fractions in isochron regression calculations. The Hf and W isotopic compositions of the spike sample were determined simultaneously, and approximately 10 ng of pure natural Re was admixed in the spiked sample to monitor the mass fractionation during the isotopic measurement. Although the uncertainties of the Hf and W isotope dilution measurements were typically 0.2% or better, an uncertainty of 0.5% was used in the isochron regression for each sample.

RESULTS

W Isotopic Compositions

All the data are shown in Table 1, and the W isotopic data are corrected for blank contributions, which vary from sub-ppm to ~3 ppm in the medium magnetic fraction of NWA 2235, significantly less than the analytical uncertainties. In contrast to the large and variable ^{182}W excesses observed in differentiated achondrites such as the eucrites and the angrites, bulk rock acapulcoite and lodranite are characterized with slightly unradiogenic W compared to that of the CHUR (Fig. 1), and are consistent with the results of Touboul et al. (2006). High-magnetic (metal-rich) fractions of all 3 samples exhibit consistently less radiogenic ε_W signatures, from −3.3 to −2.8, compared to the whole rock and the low-magnetic (silicate-rich) fractions within each sample (Fig. 1), and their W isotopic signatures are similar to the metal grains found in equilibrated, enstatite, and CH chondrites, and some iron and stony-iron meteorites (Lee and Halliday 1996, 2000a, 2000b; Horan et al. 1998; Kleine et al. 2005a; Lee 2005; Quitté et al. 2005; Markowski et al. 2006a, 2006b). Furthermore, the low-magnetic (silicate-rich) fractions also appear to be slightly unradiogenic to comparable W signatures relative to the CHUR (Fig. 1). Among the achondrites that have been studied with the ^{182}Hf-^{182}W system, only ureilites (Lee et al. 2005) show similar W isotopic signatures (Fig. 1), despite that ureilites are highly differentiated achondrites (Goodrich 1992; Mittlefehldt et al. 1998).

Internal Hf-W Isochron

It has been shown that bulk rock eucrites exhibit a general positive correlation in an isochron plot of Hf/W versus ε_W (Fig. 2) (Lee and Halliday 1997; Quitté et al. 2000; Kleine et al. 2004). The two angrites show similar Hf-W behavior to the eucrites in terms of the Hf-W systematic (Fig. 2), despite the fact that they do not exhibit a positive correlation between their Hf/W ratios and ε_W (Fig. 2). This can be explained if the Hf-W system has been disturbed by late thermal event in these two angrites, or if they did not share the same petrogenetic origin. The latter is consistent with the petrographic evidence (Mittlefehldt et al. 1998), and the results of Baker et al. (2005) and Markowski et al. (2007). Clearly, more data are needed for a better understanding of the differentiation history in the angrite parent body. Unlike the eucrites and the angrites, the mineral fractions of the 3 acapulcoite-lodranite samples, GRA 95209, NWA 2235, and NWA 725, exhibit very limited fractionation between Hf and W, the $^{180}Hf/^{184}W$ ratios varying from 0.007 to 1.5 (Table 1; Fig. 2). Generally speaking, such a limited variation of the Hf/W ratio is consistent with the petrographic evidence that the acapulcoite-lodranite parent body had never experienced extensive thermal history (Zipfel et al. 1995; McCoy et al. 1996, 1997a, 1997b, 2006; Mittlefehldt et al. 1996). The bulk rock fractions of NWA 725 and NWA 2235 were prepared using two smaller chips out of the total 5 g and 2 g samples, respectively. As a result, sample heterogeneities were probably responsible for the slight offsets of the bulk rock Hf/W ratios between the two acapulcoite-lodranite samples and the CHUR.

Mineral separates from each of the 3 acapulcoite-lodranite samples also define a straight line each with a positive slope (Figs. 3–5). Since only two fractions were analyzed for GRA 95209, the CHUR is also included in the regression of the isochron in order to better assess the

Table 1. Hf and W isotope data.

Sample	Hf (ppb)	W (ppb)	$^{180}Hf/^{184}W$ (atomic)	$^{182}W/^{184}W$ ± 2σ SE	ε_W ± 2σ SE
GRA 92029 (transition acapulcoite)					
High-magnetic	7.750	1244	0.007350	0.864626 ± 18	–3.28 ± 0.21
Low-magnetic	167.8	395.3	0.5007	0.864676 ± 16	–2.71 ± 0.19
NWA 2235 (lodranite)					
High-magnetic	25.63	756.7	0.03997	0.864639 ± 18	–3.13 ± 0.21
Medium-magnetic	54.87	198.2	0.3266	0.864660 ± 17	–2.89 ± 0.20
Whole rock	122.62	179.0	0.8085	0.864702 ± 17	–2.40 ± 0.20
Low-magnetic	77.48	60.18	1.519	0.864744 ± 24	–1.92 ± 0.28
NWA 725 (acapulcoite)					
High-magnetic	50.02	529.7	0.1114	0.864665 ± 20	–2.83 ± 0.23
Whole rock	123.7	248.1	0.5884	0.864687 ± 15	–2.58 ± 0.17
Low-magnetic	159.4	146.2	1.286	0.864728 ± 26	–2.10 ± 0.30
Sahara 99555 (angrite)					
Whole rock	1820	292.5	7.342	0.865153 ± 17	2.81 ± 0.20

All the data are single isotopic measurement, and the quoted 2σ SE (standard errors) are referred to the least significant figures.
The ε_W is defined as $[(^{182}W/^{184}W_{sample}/^{182}W/^{184}W_{standard})-1] \times 10{,}000$, where the standard is the NIST SRM-3163, which gives a mean $^{182}W/^{184}W$ of 0.864910 ± 18.

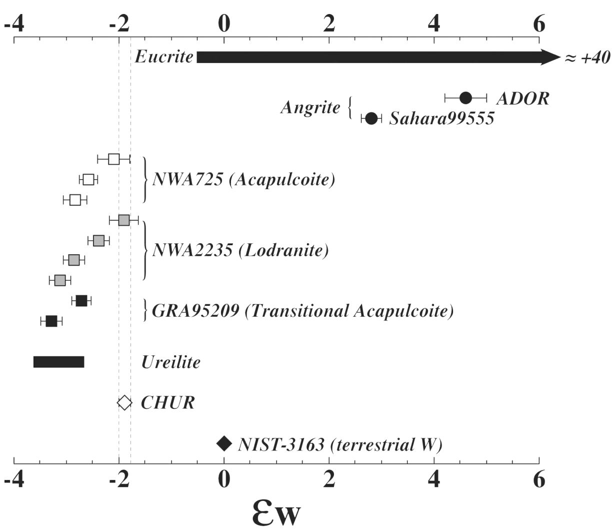

Fig. 1. ε_W of the 3 samples analyzed in this study. Also plotted are the ranges of ε_W for bulk rock eucrites (Lee and Halliday 1997; Quitté et al. 2000; Kleine et al. 2004, 2005b), the ureilites (Lee et al. 2005), the angrite (Quitté et al. 2000), and the CHUR (Yin et al. 2002; Kleine et al. 2004) for references. The ε_W is defined as $[(^{182}W/^{184}W_{sample}/^{182}W/^{184}W_{standard})-1] \times 10{,}000$, where the NIST SRM-3163 is used as the terrestrial standard.

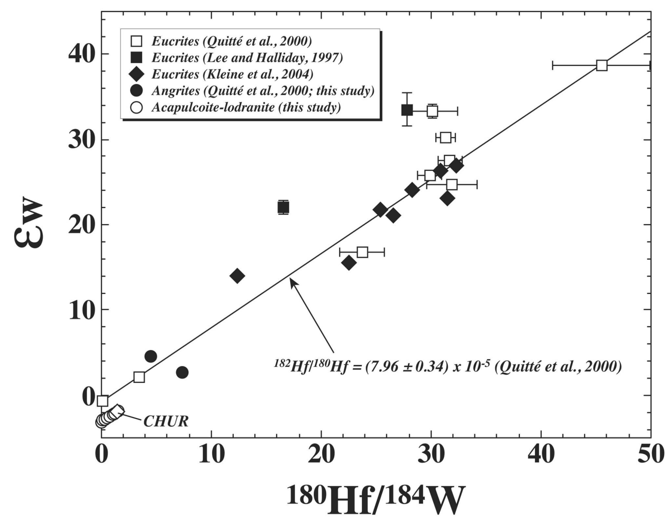

Fig. 2. $^{180}Hf/^{184}W$ versus ε_W for the mineral fractions of the acapulcoite, NWA 725, the transitional acapulcoite, GRA 95209, the lodranite NWA 2235, and the angrite Sahara 99555 from this study, along with the bulk eucrite isochron of Quitté et al. (2000), the eucrite data (Lee and Halliday 1997; Kleine et al. 2004;), the angrite ADOR (Quitté et al. 2000), and the CHUR (Yin et al. 2002; Kleine et al. 2004) for references.

uncertainty of the isochron, assuming the parent body of acapulcoite-lodranite was indeed chondritic in terms of the Hf-W system. The apparent isochron of GRA 95209 plus the CHUR gives a slope equivalent to an $^{182}Hf/^{180}Hf$ initial of $(9.9 \pm 2.7) \times 10^{-5}$, and an initial ε_W at -3.28 ± 0.29 (Fig. 3). In fact, the slope remains identical within errors regardless of whether CHUR is included, which justifies the addition of CHUR in the isochron regression for GRA 95209, and also that GRA 95209 was differentiated from a chondritic precursor. The slope of the apparent isochron of GRA 95209 is in fact overlapping within errors to the slope of the apparent isochron defined by the mineral fractions of NWA 2235 (Fig. 4), which gives an $^{182}Hf/^{180}Hf$ initial of $(7.1 \pm 3.0) \times 10^{-5}$, and an initial ε_W at -3.12 ± 0.26. The slope and the initial ε_W of NWA 2235 are also identical within errors regardless of whether the CHUR is included in the isochron calculation. As for the acapulcoite NWA 725, the mineral fractions also define an apparent isochron with a slope equivalent to an $^{182}Hf/^{180}Hf$ initial of $(5.4 \pm 4.0) \times 10^{-5}$, and an initial ε_W at -2.91 ± 0.33 (Fig. 5). Again, the apparent isochron for NWA 725 remains the same within errors if CHUR is included in the isochron regression. It appears that all 3 apparent isochrons go through CHUR, suggesting that

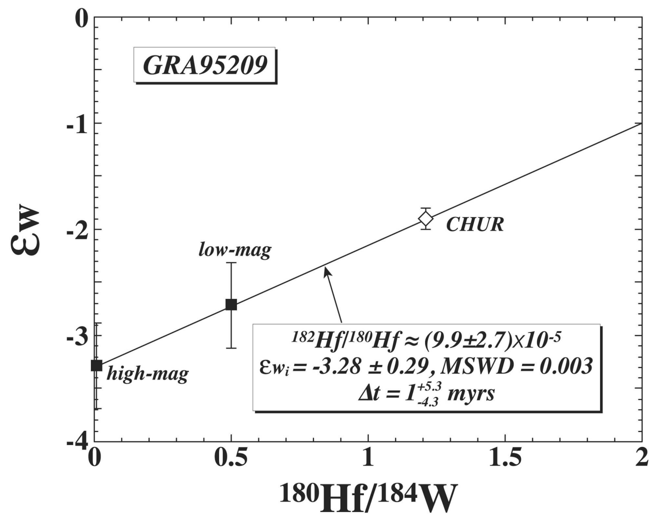

Fig. 3. $^{180}Hf/^{184}W$ versus ε_w for the mineral fractions of GRA 95209 from this study along with the data of CHUR (Kleine et al. 2004). Instead of the 2σ standard errors from the isotopic measurement, an uncertainty of 0.4ε was used for each of the mineral fractions in all of the isochron regressions (Figs. 3–6). The isochron regression was done using the Isoplot 3.0 of Kenneth R. Ludwig, and the 95% confidence limit was selected as the uncertainties of the isochron. The Δt was calculated using the relationship of $\Delta t = 1/\lambda \times \ln [(^{182}Hf/^{180}Hf)_{CHUR}/(^{182}Hf/^{180}Hf)_{GRA\,95209}]$, where $\lambda = 0.0779 \pm 0.0008$ Myr^{-1} (Vockenhuber et al. 2004). The upper limit of the Δt uncertainty was assessed using the upper limit of the $^{182}Hf/^{180}Hf_{CHUR}$ and the lower limit of the $^{182}Hf/^{180}Hf_{GRA\,95209}$ and λ, and vice versa for the lower limit. High-mag = high-magnetic; low-mag = low-magnetic.

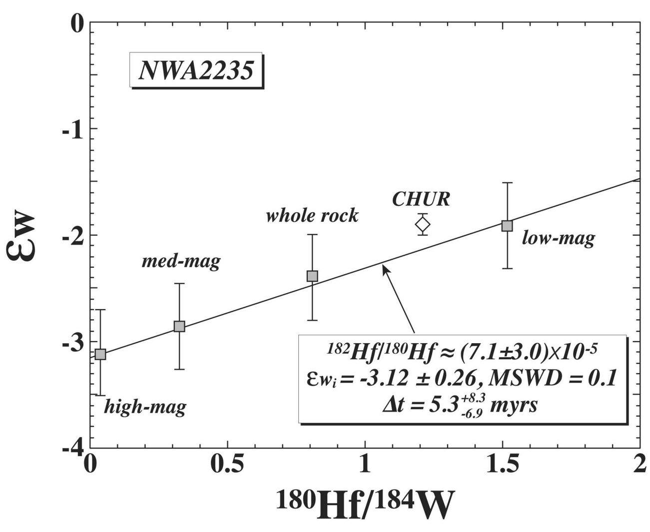

Fig. 4. Same isochron plot as Fig. 3, except for the mineral fractions of lodranite NWA 2235. High-mag = high-magnetic; med-mag = medium-magnetic; low-mag = low-magnetic.

both acapulcoites and lodranites were formed by direct heating of a chondritic precursor, consistent with the petrological and chemical evidence (McCoy et al. 1996, 1997a, 1997b; Mittlefehldt et al. 1998).

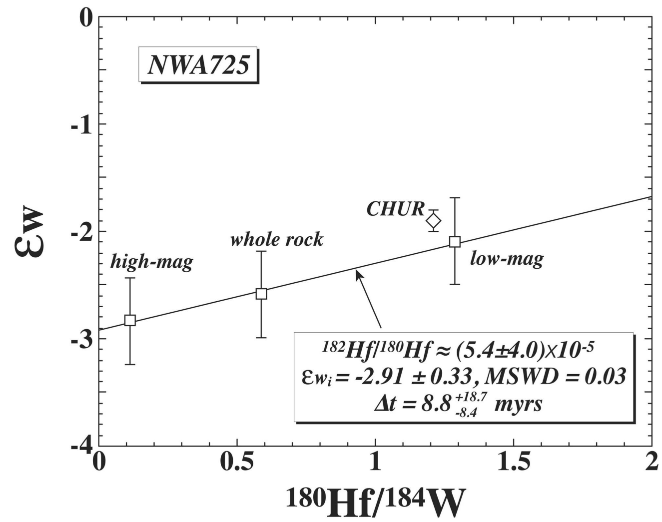

Fig. 5. Same isochron plot as Fig. 3 except for the mineral fractions of acapulcoite NWA 725. High-mag = high-magnetic; low-mag = low magnetic.

Hf-W Isochron Ages of Acapulcoites versus Lodranites

Similar to the equilibrated ordinary chondrites (Lee and Halliday 2000a; Kleine et al. 2002; Yin et al. 2002), enstatite chondrites (Lee and Halliday 2000b), and the primitive CH chondrites (Kleine et al. 2005a), the Hf-W isochron ages observed in these 3 samples, NWA 725, GRA 95209, and NWA 2235, must have recorded the timing of the metamorphic events in their parent body that resulted in the formation of the metal phases in acapulcoites and lodranites. The solar $^{182}Hf/^{180}Hf$ and ε_w initials are estimated at $(1.07 \pm 0.10) \times 10^{-4}$ and ~−3.5, respectively (Kleine et al. 2002, 2004; Yin et al. 2002). Using the initial $^{182}Hf/^{180}Hf$ of CHUR (Kleine et al. 2004), the Hf-W isochron age is estimated at 1 (+5.3/−4.3), 5.3 (+8.3/−6.9), and 8.8 (+18.7/−8.4) Myr after the start of the solar system for GRA 95209 + CHUR, NWA 2235, and NWA 725, respectively. Due to the small variations in Hf/W and W isotopic compositions observed in these samples, the Hf-W isochron ages are relatively imprecise and overlapping with each other, although the acapulcoite may have formed slightly later. If, however, the acapulcoites and lodranites formed around the same time, the timing of which could be better determined by the isochron of the combined Hf-W data (Fig. 6). However, the combined isochron age exhibits very modest improvement, and places the timing of thermal metamorphism in the acapulcoite-lodranite parent body at 4.9 (+6.1/−4.7) Myr since the start of the solar system. Despite being relatively imprecise, the Hf-W data suggest that the thermal metamorphism in the acapulcoite-lodranite parent body occurred within the first 10 Myr after the start of the solar system. Although acapulcoites and lodranites probably did not share the same petrogenetic origin, it is

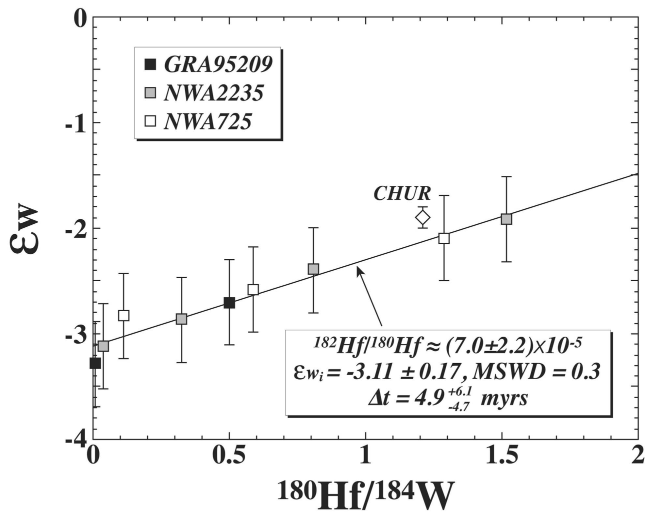

Fig. 6. Same isochron plot as Fig. 3, but was calculated using the combined mineral fractions of all 3 samples.

premature to conclude whether separate thermal events were responsible for the formations of lodranites and acapulcoites based on the Hf-W data of this study. Further studies with better precision are needed to confirm if the apparent isochron age differences among these 3 acapulcoite-lodranite samples are accurate.

DISCUSSION

Thermal History in Acapulcoite-Lodranite Parent Body

Lodranites and the transitional acapulcoite GRA 95209 have previously been dated by ^{40}Ar-^{39}Ar chronology (McCoy et al. 1997a, 2006), and the 4.52 Ga ^{40}Ar-^{39}Ar age is significantly younger than the Hf-W isochron age. This is to be expected, since the Ar-Ar age has been interpreted as the cooling age (McCoy et al. 2006). It has been suggested that lodranites experienced a relatively slow cooling from the peak metamorphic temperature to the closure temperature of Ar, followed by a rapid cooling (McCoy et al. 1997a). Because the Hf-W system is very sensitive to the formation of metal phases (Lee and Halliday 1996, 2000a, 2000b; Kleine et al. 2002, 2005a), the Hf-W age should have dated the formation of metal-sulfide veins in NWA 2235 and GRA 95209 (McCoy et al. 1997a, 2006). However, depending on the closure temperature of W in various mineral phases, the Hf-W age may also be the cooling age as the ^{40}Ar-^{39}Ar ages (McCoy et al. 1997a, 2006), albeit at a higher closure temperature. Although relatively imprecise, both samples are in isotopic equilibrium, and the Hf-W isochron ages are noticeably older than the 4.52 Ga Ar-Ar age, yet comparable to slightly younger than the metal-silicate segregation observed in differentiated asteroids (Lee and Halliday 1996, 2000a, 2000b; Horan et al. 1998; Kleine et al. 2005a; Lee 2005; Quitté et al. 2005; Markowski et al. 2006a, 2006b; Schérsten et al. 2006), as well as the CH and CB chondrites (Amelin and Krot 2005; Kleine et al. 2005a). This implies that either both samples experienced relatively fast cooling after the peak metamorphism and the cooling rate slowed down below the closure temperature of W, or the closure temperature of W is comparable to the peak metamorphic temperatures. Nevertheless, within the current analytical uncertainties, the Hf-W ages have dated the formation of metal and sulfide veins, and hence the formation of GRA 95209 and NWA 2235 (McCoy et al. 1997a, 2006). A more precise estimate of the cooling rate and dating of the peak metamorphism may provide more stringent constraints to the metamorphic history in the acapulcoite-lodranite parent body, however, at present, the bulk acapulcoite-lodranite isochron age of ~5 (+6/−5) Myr is the best estimate for the metamorphic event responsible of the formation of lodranites and transitional acapulcoites.

Unlike the lodranites, acapulcoites have been dated by various methods, and with the exception of the Pb-Pb and I-Xe ages (Göpel et al. 1992; Nichols et al. 1994; Brazzle et al. 1999), most of the ages are either relatively imprecise, or significantly younger than 4.55 Ga (Palme et al. 1981; Schultz et al. 1982; Kaneoka et al. 1992; Prinzhofer et al. 1992; Torigoye et al. 1993; McCoy et al. 1996; Pellas et al. 1997; Renne 2000; Min et al. 2003). Pellas et al. (1997) suggested that acapulcoites had quickly cooled to ~700 °C after the initial heating to account for the significant differences between the Pb-Pb and Ar-Ar ages. NWA 725 is also in isotopic equilibrium in terms of the Hf-W system, and which seems to be consistent with a fast initial cooling for acapulcoites. Consequently, the Hf-W age of NWA 725 should also mark the formation of metal-sulfide-phosphate blebs or veins observed in acapulcoites (McCoy et al. 1996; Mittlefehldt et al. 1998), hence the formation of NWA 725. Despite the large uncertainties, the Hf-W isochron age of NWA 725 is generally consistent with the Pb-Pb and I-Xe ages (~6 to 11 Myr after the start of the solar system) determined on the phosphates and feldspars extracted from Acapulco (Göpel et al. 1992; Nichols et al. 1994; Brazzle et al. 1999). Although the ages are self-consistent among the acapulcoites, they do overlap with the bulk Hf-W isochron age (Fig. 6), therefore, ~5 (+6/−5) Myr after the start of the solar system remains the best estimate for the formation of acapulcoites. Similar to the lodranites, the same ^{40}Ar-^{39}Ar cooling age of ~4.52 Ga is also found in acapulcoites (McCoy et al. 1996; Pellas et al. 1997). The same ^{40}Ar-^{39}Ar cooling age among the acapulcoites and lodranites is consistent with the Hf-W ages that they formed contemporaneously, or within a small time window. Alternatively, the same cooling ages among the acapulcoites and lodranites may reflect a subsequent thermal event, e.g., an impact-induced breakup and reassembly (McCoy et al. 1997a) that affected the entire parent body.

When considering the individual Hf-W age, the acapulcoite NWA 725 is significantly younger than most of the iron meteorites, while the lodranite NWA 2235 and the transitional acapulcoite GRA 95209 range from slightly younger to overlapping with the W model ages of iron meteorites (Kleine et al. 2005a; Lee 2005; Markowski et al. 2006a, 2006b; Schérsten et al. 2006). The Hf-W isochron ages show no relationship to the degree of metamorphism, suggesting that the metamorphism was localized. However, at present the Hf-W age of the bulk acapulcoite-lodranite (Fig. 6) reflects the best estimate for the earliest thermal event occurred in the acapulcoite-lodranite parent body, the Hf-W data suggest a slightly delayed and less intensive thermal events occurred in the parent body of acapulcoites and lodranites, in contrast to the differentiated asteroids. Such a delayed and reduced thermal history in the acapulcoite-lodranite parent body suggests that it probably had a slower accretion rate compared to the differentiated asteroids. This is because a slower accretion rate will result in a slower or insufficient time to build up enough heat from the decay of short-lived nuclides, e.g., ^{26}Al and ^{60}Fe, and the accretional energy to melt the entire asteroid. Alternatively, the accretion rate may have started the same for all the planetesimals, but the accretion for the acapulcoite-lodranite parent body may have seized prematurely.

Hf-W Systematic of Achondrites versus Ordinary, Enstatite, and CH Chondrites

Despite the different environment and peak metamorphic temperatures, ~900 to 1200 °C for the acapulcoite-lodranite clan (Zipfel et al. 1995; McCoy et al. 1996, 1997a, 1997b, 2006; Mittlefehldt et al. 1996) versus ~500–1000 °C for type 4–6 chondrites (Keil 2000), the thermal history in the parent body of acapulcoites and lodranites is actually more in line with that of equilibrated ordinary chondrites (Lee and Halliday 1996, 2000a; Kleine et al. 2002; Yin et al. 2002), enstatite chondrites (Lee and Halliday 2000b), and the primitive CH chondrites (Kleine et al. 2005a). The Hf-W ages of the metals in these 3 groups of chondrites are consistent, within errors, with the formation age of chondrules, 2–5 Myr post-CAI (Amelin et al. 2002; Amelin and Krot 2005), and they are noticeably younger than the metal-silicate segregation that occurred in differentiated asteroids (Kleine et al. 2005a; Lee 2005; Markowski et al. 2006a, 2006b). Acapulcoite-lodranite as a whole appears to have formed, or metamorphosed, around the same time as these 3 groups of chondrites, if Hf-W and chondrule formation ages are indeed marking the formation, or thermal metamorphism, of the above groups of chondrites. Apart from the Hf-W ages, the concentrations of Hf and W and the Hf/W ratios from various phases are all quite similar among these samples. As illustrated in Fig. 7, where ^{180}Hf/^{184}W is plotted versus W and Hf, for the samples in this study and the published results (Lee and Halliday 2000a, 2000b; Quitté et al. 2000; Kleine et al. 2002, 2004, 2005a, 2005b; Yin et al. 2002). The acapulcoite-lodranite data overlap with those of the ordinary, enstatite, and CH-CB chondrites, but are quite distinct from the bulk rock eucrites and the angrites (Fig. 7). It is evident that both eucrites and angrites are the products of silicate melting in two asteroids that had already experienced metal-silicate differentiation (Fig. 7), while the acapulcoite-lodranite parent body experienced no planetary-wise metal-silicate segregation, with only thermal metamorphism and/or localized partial melting and melt extraction (McCoy et al. 1996, 1997a, 2006).

The Hf-W data of the acapulcoite and lodranites studied here exhibit a better match to the ordinary and CH-CB chondrites than the enstatite chondrites (Fig. 7). This is not surprising given the similarities in mineralogy and chemical compositions between the acapulcoite-lodranite clan and the ordinary chondrites (McCoy et al. 1997a; Mittlefehldt et al. 1998). However, apart from the mineralogy and bulk compositions, the acapulcoite-lodranite clan is quite distinct from the ordinary chondrites in terms of oxygen isotopes (Clayton and Mayeda 1996), and mineral compositions (Mittlefehldt et al. 1998). In fact, the oxygen isotopes of the acapulcoite-lodranite clan are quite distinct from all the other groups of meteorites, but actually fall within the range of CR-CH chondrites (Clayton 2004). Although there is not yet evidence that can provide a genetic link between the acapulcoite-lodranite clan and the CR-CH chondrites, the consistency in the formation ages, the Hf-W data, and more importantly the oxygen isotopes (Clayton 2004) seem to support such a possibility. More detailed mineralogical, chemical, and isotopic studies are needed in order to provide more convincing proof whether the acapulcoite-lodranite clan can be genetically linked to the CR-CH chondrites.

Petrogenesis of Acapulcoites and Lodranites

Adapted from the H-chondrite parent body model of Trieloff et al. (2003), Eugster and Lorenzetti (2005) proposed a two-layered model for the parent body of acapulcoites and lodranites. They suggested that the faster cooled acapulcoites sit at the outer layer, while the slowly cooled lodranites are located in the inner layer of their parent body. However, the cooling history described in Eugster and Lorenzetti (2005) seems inconsistent with the same ^{40}Ar-^{39}Ar cooling ages observed in acapulcoites and lodranites, suggesting that they both had experienced the same fast cooling after the initial heating, then slowly cooled to below the closure temperature of Ar (McCoy et al. 2006). Due to the lack of proper age determination for lodranites, Eugster and Lorenzetti (2005) did not offer specific constraints about the relative timing for the formation of acapulcoites and lodranites. The same cooling ages between the acapulcoites and lodranites are conceivable if they were formed around the same time through different

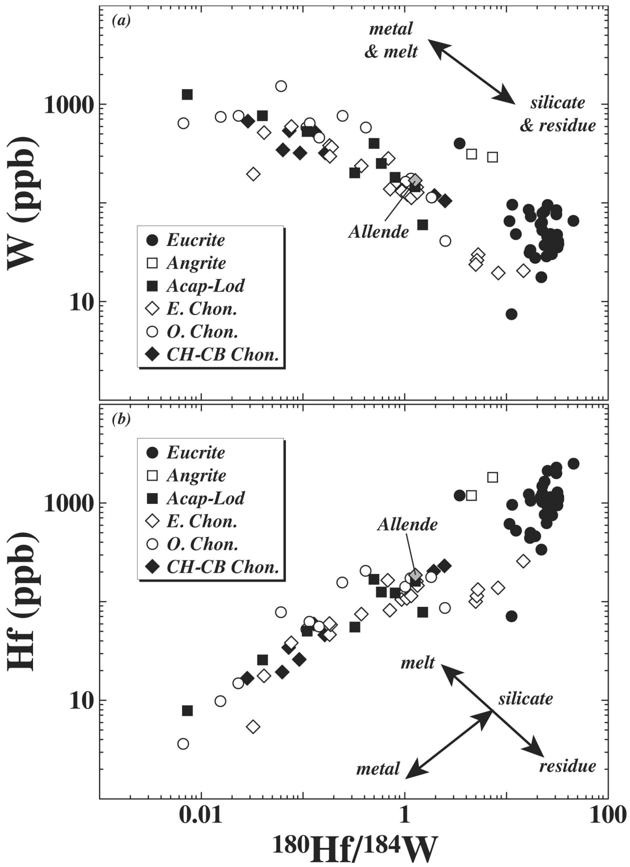

Fig. 7. Log-log plot of ^{180}Hf/^{184}W versus a) W (ppb) and b) Hf (ppb) for the samples analyzed in this study. Also plotted are the published results for the bulk rock eucrites (Lee and Halliday 1997; Quitté et al. 2000; Kleine et al. 2004, 2005b), the angrite (Quitté et al. 2000), the mean of Allende as CHUR (Kleine et al. 2004), the ordinary chondrites (Lee and Halliday 2000a), the enstatite chondrites (Lee and Halliday 2000b), and the CH-CB chondrites (Kleine et al. 2005a) for references. The arrows shown are general fractionation trends for the end products during metal-silicate segregation and partial melting of a chondritic precursor-CHUR.

localized thermal events, as suggested by the bulk acapulcoite-lodranite isochron. Alternatively, the same Ar cooling ages may reflect a separate thermal event that postdated the formation of the acapulcoite-lodranite clans (McCoy et al. 2006). Nevertheless, the formation of each subgroup of the acapulcoite-lodranite clan must have depended solely on the energy released for each localized thermal event.

Heating of an asteroid is generally accomplished by the radioactive decay of short-lived nuclides, such as ^{26}Al and ^{60}Fe, plus the energy released through impact, and in principle both can be responsible for the heating of the acapulcoite-lodranite parent body. Given the same ^{40}Ar-^{39}Ar cooling ages, acapulcoites and lodranites should have similar thermal histories and will most likely be located approximately at the same depth, even though they probably do not share the same petrogenetic origin. Heating by the decay of short-lived nuclides is entirely viable for the acapulcoite-lodranite parent body, however, depending on the depth where acapulcoites and lodranites are located, it requires additional mechanisms to either help dissipate the heat more efficiently in the beginning if they are deeply buried, or to slow down the cooling rate after the initial heating if they are sitting near the surface. Furthermore, constrained by the available ^{26}Al and ^{60}Fe remaining in the acapulcoite-lodranite parent body, radioactive heating is viable for acapulcoites and lodranites, if the thermal events occurred near the beginning of the time window (~1 to 5 Myr) (Fig. 6), but it is unlikely to work towards the end of the time window of ~9 Myr after the start of the solar system. Alternatively, heating by impact near the surface and subsequently being buried by the falling debris, or by other mechanisms, can satisfy a rapid cooling in the beginning, and followed by a slow cooling scenario observed in acapulcoites and lodranites. Unlike short-lived nuclides, impact heating was not confined by the timing, and also occurred frequently during the run-away growth stage of the planetary accretion. If this scenario is correct, it suggests that acapulcoites and lodranites were heated by different impact events while sitting near the surface, and subsequently got buried after they had cooled below ~700 °C (Pellas et al. 1997; McCoy et al. 2006). Furthermore, the localized impact origin is consistent with either a single or multiple thermal event(s) responsible for the formation of the acapulcoite-lodranite clan. Despite the simplicity of an impact origin, heating by the decay of ^{26}Al and ^{60}Fe may still be responsible for the early metamorphism that leads to the formation of GRA 95209, and it may require additional mechanisms to help bury acapulcoites and lodranites to a greater depth in order to explain the high abundance of trapped noble gases (Weigel et al. 1999). More data, such as petrographic evidence of impact induced melting and high precision Hf-W measurements for other samples from the acapulcoite-lodranite clan, are needed in order to better determine if the above scenario is correct.

CONCLUSION

Due to the large errors associated to the isochron ages of these 3 acapulcoite-lodranite samples, the Hf-W data obtained here cannot reliably distinguish if acapulcoites and lodranites shared the same petrogenetic origin. At present, the best estimate for the timing of thermal metamorphism in the parent body of acapulcoite-lodranite is ~5 (+6/−5) Myr after the start of the solar system, provided by the bulk acapulcoite-lodranite isochron (Fig. 6). The Hf-W data seem to indicate that localized thermal metamorphic events were responsible for the formation of the primitive acapulcoite-lodranite clan, in contrast to the partial melting of an already differentiated silicate mantle for more evolved achondrites (e.g., eucrites and angrites). Furthermore, the formation of the acapulcoite-lodranite clan seems to be comparable to the slightly post-dated metal-silicate segregation that occurred in differentiated asteroids. This can be explained if the accretion rate was low, or the accretion had seized prematurely for the acapulcoite-lodranite parent body due to an insufficient supply of building materials. This delayed and protracted thermal history in the acapulcoite-lodranite parent body is also in favor of an impact origin for the formation of the acapulcoite-lodranite clan. Although the initial results are very encouraging, more data are needed for multiple samples from all the subgroups of the acapulcoite-lodranite clan in order to have a thorough understanding about the petrogenetic history in the acapulcoite-lodranite parent body.

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