



PII S0016-7037(00)00482-8

## Re-Os isotopic evidence for early differentiation of the Martian mantle

A. D. BRANDON,<sup>\*,1,2</sup> R. J. WALKER,<sup>2</sup> J. W. MORGAN<sup>2,3</sup> and G. G. GOLES<sup>4</sup><sup>1</sup> Department of Geological Sciences, Northwestern University, Evanston, IL 60208 USA<sup>2</sup> Isotope Geochemistry Laboratory, Department of Geology, University of Maryland, College Park, MD 20910 USA<sup>3</sup> Colorado State University, College of Natural Resources, Department of Earth Resources, Fort Collins, CO 80523 USA<sup>4</sup> Department of Geological Sciences, 1272 University of Oregon, Eugene, OR 97402 USA

(Received February 8, 2000; accepted in revised form June 12, 2000)

**Abstract**—Variations in the short-lived systems of  $^{182}\text{Hf}$ - $^{182}\text{W}$  and  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  in the SNC meteorites indicate an early isolation of, and subsequent inefficient mixing between, mantle reservoirs in Mars. Correlations of  $\epsilon_{\text{W}}$  and  $\epsilon_{^{142}\text{Nd}}$  with initial  $\gamma_{\text{Os}}$  are consistent with the Re-Os isotopic systematics of these meteorites being set during the earliest differentiation history of Mars. Contamination by a juvenile Martian crust may have affected Zagami Os isotopic systematics but successful contamination models combining Nd and Os systematics, are inconsistent with such a process affecting the isotopic compositions of the shergottite lherzolites (EETA 77005, LEW 88516, Y 793605). At least two long-lived mantle reservoirs, and possibly three, are required to explain the observed systematics. One mantle reservoir (NC Group), represented by Nakhla and Chassigny, has a projected present day  $\gamma_{\text{Os}}$  of  $-5.4 \pm 2.6$ . Another mantle reservoir represented by the shergottite lherzolites and possibly Zagami, has a present day  $\gamma_{\text{Os}}$  of about +4. This represents a 2 to 3% enrichment in Re/Os relative to the primitive mantle estimated for the Earth (+1.6). A third mantle reservoir may be represented by DaG 476, having a nearly chondritic  $\gamma_{\text{Os}}$  coupled with very high  $\epsilon_{^{143}\text{Nd}}$  of around +40. The isotopic systematics of these reservoirs may be linked to development of cumulate crystal piles in a Martian magma ocean and variable amounts of late stage intercumulus melt (following Borg et al., 1997). In this model, fractional crystallization of olivine and possibly other phases with slightly subchondritic Re/Os, from a solidifying magma ocean, resulted in a lower Re/Os ratio in the NC Group source cumulates, and a resultant low  $\gamma_{\text{Os}}$ . Later cumulates or evolved melts crystallized with higher Re/Os ratios to produce the shergottite mantle reservoir(s), and hence, consequent higher  $\gamma_{\text{Os}}$ . Crystallization of the Martian magma ocean followed earliest core formation, as indicated by the correlation of  $\epsilon_{\text{W}}$  with  $\epsilon_{^{142}\text{Nd}}$  and initial  $\gamma_{\text{Os}}$ . Copyright © 2000 Elsevier Science Ltd

### 1. INTRODUCTION

Attempts to understand the earliest history of Earth have been clouded by approximately 4.5 billion years of planetary evolution. Hence, many of the chemical signatures imparted by accretion and early differentiation have been overprinted by later dynamic processes. In contrast to Earth, Mars displays no surface features indicative of a large-scale, long-lived plate tectonic history. Large scale convective mixing of the Martian mantle either may never have occurred, or was very short lived. Lack of efficient mixing is indicated by heterogeneities in the isotopic systematics of the short-lived  $^{182}\text{Hf}$ - $^{182}\text{W}$  and  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  systems of meteorites, presumed to have been derived from Mars (Harper et al., 1995; Lee and Halliday, 1997).

Given the apparent very early isolation of mantle reservoirs within Mars, a record of the earliest differentiation history may be retained in other isotopic systems in the Martian meteorites. For example, the Re-Os isotope system has the potential to provide constraints on mechanisms of core formation, early differentiation processes, and the late accretionary histories of the terrestrial planets (Shirey and Walker, 1998; Righter et al., 2000). Core formation early in the history of the terrestrial planets likely sequestered more than 99% of the Re, Os and other highly siderophile elements (HSE), leaving the silicate portions of these planets strongly depleted in HSE (Morgan,

1986; O'Neill, 1991, and references therein). Consequently, the approximately factor of 200 lower abundances of HSE in the Earth's upper mantle relative to chondrites, in part, must result from core formation. Most core formation models, however, predict even lower concentrations of HSE than are actually present in samples of the upper mantle. To account for the higher than expected concentrations of HSE, models invoking the post-core-formation addition of 0.3 to 1% of planetary mass in the form of a late veneer of chondritic material have been proposed for the Earth (Chou, 1978; Morgan et al., 1981; Morgan, 1986; O'Neill et al., 1995; Warren et al., 1999). Other models may account for the higher concentrations of HSE by metal-silicate equilibrium at high pressures, perhaps during metal-silicate segregation at the base of a deep magma ocean (Murthy, 1991; Righter and Drake, 1997). This latter possibility may be an option because some moderately siderophile elements, and at least one HSE (Re), have distinctly lower metal-silicate distribution coefficients at high pressures than low (e.g., Righter and Drake, 1997).

The fact that the present day Os isotopic composition of the Earth's upper mantle is similar to chondrites requires that the Re/Os of the mantle has been chondritic subsequent to core formation. Any model that purports to explain HSE abundances in the upper mantle must, therefore, account for this observation. Given the possibility that unique conditions during early Earth history, such as metal-silicate partitioning at the base of a deep magma ocean, could have resulted in the HSE signature of the upper mantle, it is critical to compare the HSE concentrations and

\*Author to whom correspondence should be addressed (albrand@earth.nwu.edu).

Os isotopic composition of the Earth's upper mantle with those of another terrestrial planet. Similarities or differences between two planets could help to discern among the existing models, or may require new models. As a first step toward more complex comparisons, the Re-Os isotope systematics of meteorites of presumed Martian provenance are examined here.

## 2. ANALYTICAL TECHNIQUES

Samples were processed into a fine powder with a ceramic alumina mortar and pestle. Rhenium and Os concentration data were obtained by isotope dilution (Table 1). The powders were spiked and dissolved in aqua regia at 250°C in glass Carius tubes to obtain sample-spike equilibration (Shirey and Walker, 1995). Osmium was purified using carbon tetrachloride solvent extraction (Cohen and Waters, 1996), followed by microdistillation (Birek et al., 1997). Rhenium was purified by anion exchange chromatography. With one exception, the Re and Os isotopic ratios for the concentration analyses were measured as oxides on a single collector mass spectrometer at the University of Maryland Isotope Geochemistry Laboratory (IGL) in the negative ion mode (Creaser et al., 1991). For one fraction of DaG 476 (fraction 2, Table 1), and a blank processed through the same chemical procedures, the Re isotopic ratios were measured by inductively coupled plasma mass spectrometry (ICPMS) at the University of Chicago using a Finnigan Element<sup>TM</sup>. The instrument was rapidly scanned using the electric scan mode for masses 185, 187 and 188. The <sup>188</sup>Os count rates were less than 4 counts per sec., which was indistinguishable from instrumental background noise determined on a 2% nitric acid blank solution. Background count rates for Re isotopes were 200–600 counts per sec., as a result of instrument memory from running standards. The blank corrections to the isotopic ratios of measured Re sample (DAG 476) and blank were 0.3% and 1.6%, respectively, which were negligible.

The measured <sup>187</sup>Os/<sup>188</sup>Os in Table 1 are relative to 0.11376 for the IGL in house standard. During each stage of the analysis campaign extending over two years, multiple procedural blanks were processed. These blanks substantially improved over the course of the study from 24.8 ± 6 pg for Re and 21.7 ± 3.5 pg for Os (n = 6, 1/28/97–2/26/97, 2σ), to 2.0 pg for Re and 0.80 pg for Os (n = 1, 8/2/99). The <sup>187</sup>Os/<sup>188</sup>Os of the blank remained constant over this time interval at 0.173 ± 0.008. The amount of blank correction for Re and Os for each sample analysis is listed in Table 1. Multiple blanks obtained at the IGL indicate reproducibility to better than ±25% (2σ of the mean) for Re and to better than ±15% (2σ of the mean) for Os for the blanks over each time interval while the same batches of reagents, Pt filaments, etc., were used. These uncertainties in the blanks were used to propagate the uncertainties in <sup>187</sup>Re/<sup>188</sup>Os and <sup>187</sup>Os/<sup>188</sup>Os, and also used to calculate initial <sup>187</sup>Os/<sup>188</sup>Os. In the case for Zagami and Nakhla, larger blank corrections resulting from their lower Os contents generated substantially larger uncertainties in the corrected concentrations. Despite the fact that the blank corrections resulted in larger uncertainties, the calculated initial <sup>187</sup>Os/<sup>188</sup>Os for both of these meteorites are similar within uncertainty to those for the other Martian meteorites that are petrogenetically related (Table 1).

## 3. RESULTS AND DISCUSSION

### 3.1. Re and Os Concentrations in SNC Meteorites

The SNC meteorites (short for Shergottite, Nakhlite, Chassignite) are most likely derived from Mars because of chemical characteristics and crystallization ages consistent with derivation from a single large parent body (McSween, 1994). In addition, trapped gases within some SNC's are in the same molecular proportions as the modern Martian atmosphere measured by the Viking landers (Bogard and Johnson, 1983; Becker and Pepin, 1984; Pepin, 1991). They are subdivided into the Shergottite (S) and the Nakhlite-Chassigny (NC) Groups on the basis of compositional relationships (the related meteorite, ALHA-84001 fits into neither group). In this study, 6 meteor-

ites of the S Group (ALHA 77005, LEW 88516, Y793605, Zagami, EETA 79001, DaG 476) and 2 meteorites from the NC Group (Chassigny, Nakhla) were analyzed for Re and Os concentrations and Os isotopic composition (Table 1). Two of the S Group meteorites, Zagami, and EETA 79001 (A and B lithologies) are basaltic, while the other 3 are lherzolites. The meteorite DaG 476 is also classified as a basaltic shergottite (Zipfel et al., 1999). However, some studies concluded that this meteorite is petrogenetically related to the clinopyroxenite Nakhla and the dunite Chassigny (Jagoutz et al., 1999). None of these rocks are direct samples of the Martian mantle. Instead, they represent magmatic cumulates and liquids (McSween, 1994).

Concentrations of Re and Os range from 22 to 633 pg/g and 9.1 to 3405 pg/g, respectively (Table 1). These concentrations are generally similar to the concentrations that have been reported for mafic and ultramafic terrestrial rocks (Shirey and Walker, 1998). The concentrations determined by isotope dilution here are similar to concentrations determined by neutron activation analysis by Warren and Kallemeyn (1996) and Warren et al. (1999), and by inductively coupled plasma mass spectrometry (Neal et al., 2000) for the same meteorites. In contrast, the concentrations reported in Table 1 are lower by approximately a factor of 2 relative to concentrations determined by Kong et al. (1999), who also utilized neutron activation analysis. Replicates for Chassigny and DaG 476 (Table 1), show that a wide range in Re and Os concentrations are present in these meteorites even when the same technique is used, in part likely attributable to the nugget effect (Shirey and Walker, 1998, and references therein).

The meteorites show a broad negative correlation between Os concentration and Re/Os (Fig. 1), where the cumulate rocks with relatively high Os contents can be modeled as crystallization products of primitive Martian magmas that ultimately evolved to liquids represented by the basaltic shergottites (Warren et al., 1999). Rhenium and Os concentrations also correlate with differentiation indices such as MgO, Ni, and Cr (Warren et al., 1999), as is common at least for Os in terrestrial mafic-ultramafic systems.

### 3.2. Calculation of Initial <sup>187</sup>Os/<sup>188</sup>Os: Assumptions, Alteration, and Age Dependence

#### 3.2.1. Shergottites

Initial <sup>187</sup>Os/<sup>188</sup>Os ratios for the S Group rocks were calculated on the basis of the best estimates for the crystallization ages, which range from ~150 to 183 Ma (Shih et al., 1982; Wooden et al., 1982; Chen and Wasserburg, 1986; Jagoutz, 1989; Nyquist et al., 1995; Misawa et al., 1997; Borg et al., 1998a; Borg et al., 1998b; Table 1). These initial values are presented in the  $\gamma_{Os}$  notation, where  $\gamma_{Os}$  is the percent deviation from average chondrites at a specified time (present day <sup>187</sup>Os/<sup>188</sup>Os = 0.1270, corrected to time in the past using <sup>187</sup>Re/<sup>188</sup>Os = 0.40186;  $\lambda = 1.666 \times 10^{-11} \text{y}^{-1}$ ). The initial  $\gamma_{Os}$  values calculated for the approximate ages of the three lherzolites and Zagami range from +3.0 to +4.4. The large uncertainty in  $\gamma_{Os}$  for Zagami (± 2.2 units) reflects the large <sup>187</sup>Re/<sup>188</sup>Os of 40.57 and the propagation of error as a result of uncertainty in the blank correction. Lithologies A and B of

Table 1. Re-Os isotopic data for SNC meteorites. The  $\epsilon_w$  data are from Lee and Halliday (1997), and the  $\epsilon_{142Nd}$  data are from Harper et al. (1995), except DaG 476 from Jagoutz (unpublished data used with permission).

Sample	Sample weight	Re (pg/g)	% Re blank	Os (pg/g)	% Os blank	$^{187}Os/^{188}Os$	$^{187}Re/^{188}Os$	$\gamma_{Os-R}$	$\epsilon_w$	$\epsilon_{142Nd}$
ALH 77005 <sup>a</sup> (hercynite)	202.9	256 ± 25	28	3405 ± 16	3.1	0.13242 ± 0.00030	0.363 ± 0.037	+4.38 ± 0.32	+0.34 ± 1.2	-0.17 ± 0.32
LEW 88516 <sup>d</sup> (hercynite)	103.8	22.2 ± 23	93	905 ± 1	0.9	0.13156 ± 0.00017	0.12 ± 0.39	+4.28 ± 0.96		
Y793605 <sup>f</sup> (hercynite)	58.9	277 ± 8	11	1019 ± 20	1.3	0.13358 ± 0.00035	1.31 ± 0.04	+3.05 ± 0.36		
Zagami <sup>f</sup> (basalt shergottite)	2052.7	75.5 ± 0.3	1.3	9.11 ± 0.11	7.7	0.2538 ± 0.0008	40.57 ± 0.63	+3.29 ± 2.16	+0.50 ± 0.34	-0.09 ± 0.18
DaG 476 b2 (basalt shergottite)	135.7	505 ± 3.5	2.8	1546 ± 9	0.4	0.13715 ± 0.00022	1.577 ± 0.030	-3.06 ± 0.47*	+2.14 ± 0.62	0.75 ± 0.29
1 <sup>f</sup>	41.6 <sup>1</sup>	633 ± 61	26	2008 ± 3	1.0	0.13710 ± 0.00013	1.521 ± 0.147	+0.66 ± 0.35 <sup>^</sup>		
2 <sup>g</sup>								-2.57 ± 1.50*		
								+0.97 ± 1.04 <sup>^</sup>		
EETA 79001 (basalt shergottite)	194.1	98.9 ± 4.3	15	481.1 ± 0.8	1.0	0.12768 ± 0.00018	0.991 ± 0.045	-0.88 ± 0.25	+2.14 ± 0.62	0.26 ± 0.23
Lithology A <sup>e</sup>	202.0	65.8 ± 4.2	20	159.7 ± 0.7	3.0	0.13087 ± 0.00019	1.987 ± 0.135	-0.72 ± 0.47		0.30 ± 0.10
Lithology B <sup>e</sup>										
Chassigny (dunite)										
1 <sup>a</sup> (Paris)	419.5	328 ± 12	13	861 ± 8	5.8	0.12206 ± 0.00018	1.835 ± 0.084	—		
2 <sup>b</sup> (Paris)	664.2	459 ± 9	7.7	1193 ± 13	0.7	0.11987 ± 0.00019	1.853 ± 0.041	—		
3 <sup>c</sup> (Paris via Oregon)	410.7	316 ± 11	12	1542 ± 10	0.4	0.12220 ± 0.00015	0.986 ± 0.035	—		
4 <sup>d</sup> (Paris via Oregon)	526.7	127 ± 14	31	1178 ± 3	0.1	0.12340 ± 0.00009	0.519 ± 0.058	-5.46 ± 1.25	+2.14 ± 0.36	0.63 ± 0.16
5 <sup>f</sup> (Paris via Oregon)	302.4	264 ± 1.5	2.5	702 ± 8	0.7	0.12615 ± 0.00025	1.814 ± 0.013	—		
Nakhlaf (clinopyroxenite)	2009.9	52.0 ± 0.3	1.9	13.68 ± 0.12	5.4	0.5725 ± 0.00018	19.32 ± 0.24	-5.5 ± 6.4	+3.13 ± 0.30	0.59 ± 0.13

Sample weights are in milligrams. Re and Os abundances in picograms per gram (pg/g). Errors are  $\pm 2\sigma$ . The  $\gamma_{Os-R}$  calculated are at 180 Ma for 77005, 88516, Y793605, and EETA 79001; 183 Ma for Zagami; 705 Ma <sup>a</sup>, and 474 Ma <sup>^</sup>, for DaG; and 1,417 Ga for Chassigny and Nakhlaf. The latter age is based on a two point isochron of 1,417 ± 0.015 Ga for Nakhlaf and the Chassigny aliquot with the lowest Re/Os (fraction 4). 1 – Re was obtained by ICPMS by Munir Humayun at the University of Chicago. The dates for obtaining the measurements are: a – 2/26/97, b – 5/4/97, c – 9/18/97, d – 1/5/98, e – 2/18/98, f – 8/2/99, g – 10/29/99. Two fractions of Chassigny came directly from the Paris Museum National D'Histoire Naturelle to RJ Walker (Paris), while the other three came from the Museum to GG Golez at Oregon, which were subsequently measured at University of Maryland (Paris via Oregon).

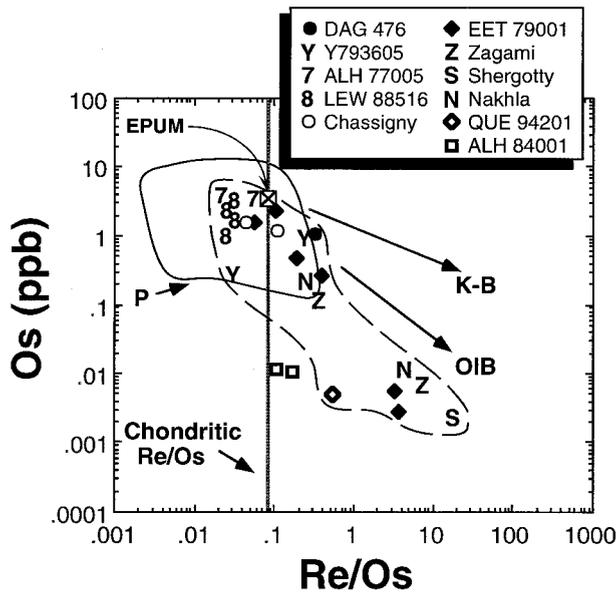


Fig. 1. Os versus Re/Os for SNC meteorites. Os in parts per billion (ppb). Data from Birck and Allegre (1994), Warren and Kallemeyn (1996), Warren et al. (1999) and this study. Samples for Chassigny considered to have had recent Re contamination or mobility (see text) are not plotted. The Earth's hypothetical primitive upper mantle (EPUM), the field for terrestrial peridotites, terrestrial komatiite and basalt (K-B), and ocean island basalt (OIB) trends, are shown for comparison (from Shirey and Walker, 1998, and references therein).

EETA 79001 have initial  $\gamma_{Os}$  values of  $-0.7$  and  $-0.9$  that overlap with each other within uncertainties. In all cases except for Zagami, the calculated initial  $\gamma_{Os}$  is not sensitive to age because the Re/Os ratios for these meteorites are similar to chondritic. For example, the reported crystallization ages for EETA 79001A range from  $150 \pm 15$  Ma (U-Pb),  $170 \pm 36$  Ma (Th-Pb), to  $173 \pm 25$  Ma (Rb-Sr), and for EETA 79001B, a Rb-Sr isochron gives  $185 \pm 25$  Ma (Wooden et al., 1982; Chen and Wasserburg, 1986). Taking a  $\pm 50$  Ma uncertainty in the crystallization age that spans the reported ages, plus their uncertainties, results in an uncertainty in  $\gamma_{Os}$  of  $\pm 0.4$  units for lithology A and of  $\pm 1.1$  units for lithology B. The uncertainties resulting from crystallization age for the three lherzolites are similar or less.

In contrast, the calculated initial  $\gamma_{Os}$  for Zagami is very sensitive to the crystallization age because of its high  $^{187}Re/^{188}Os$  of 40.57. The age used to calculate the initial  $\gamma_{Os}$  for Zagami is 183 Ma, based on Rb-Sr isochrons of  $180 \pm 4$  Ma (Shih et al., 1982), and  $186 \pm 5$  Ma and  $183 \pm 6$  for the fine and coarse grained lithologies, respectively (Nyquist et al., 1995). However, if the true age is as old as 190 Ma, the calculated initial  $\gamma_{Os}$  is as low as  $-0.5 \pm 2.2$ , or if it is as young as 176 Ma, the calculated initial  $\gamma_{Os}$  is  $+7.0 \pm 2.1$ . Both are significantly different from the calculated  $\gamma_{Os}$  at 183 Ma of  $+3.3 \pm 2.2$ . Of note, the well-constrained initial  $\gamma_{Os}$  values for the three lherzolites are similar and average at approximately  $+4$ . The basaltic shergottite EETA 79001 (both A and B lithologies) is then, significantly less radiogenic. A difference between EETA and the other S Group meteorites has also been noted for other isotope systems and will be discussed below (Harper et al., 1995; Lee and Halliday, 1997).

The true crystallization age for DaG 476 is presently under debate (Jagoutz et al., 1999; Jagoutz and Jotter, 2000; Borg et al., 2000b). It is not the purpose of this paper to define the crystallization age of DaG 476. Rather, existing age data are used to evaluate Os isotopic composition of the source for this meteorite and use such data in exploring the evolution of the Martian mantle. Borg et al. (2000b) obtained a Sm-Nd mineral isochron of  $474 \pm 11$  Ma, with an initial  $\epsilon_{143Nd}$  of  $+36.6 \pm 0.8$ , and a whole rock-plagioclase isochron of  $726 \pm 27$  with an initial  $\epsilon_{143Nd}$  of  $+14.2 \pm 1.8$  (using additional data from Jagoutz et al., 1999). Jagoutz and Jotter (2000) noted that combined leaches of Nakhla, the basaltic shergottite QUE 94201 (Borg et al., 1997), and DaG 476 together form an isochron at 1.2 Ga with an initial  $\epsilon_{143Nd}$  of  $+14.9$ . A leached mineral isochron for olivine and pyroxene from these meteorites gives an age of 705 Ma with an initial  $\epsilon_{143Nd}$  of  $+15.07$ . Therefore, the true crystallization age of this meteorite has not been conclusively determined.

In addition, this meteorite has undergone terrestrial alteration, including up to 2% addition of calcite and clay (Zipfel et al., 1999; Mikouchi, 1999). To test the effect of potential terrestrial alteration on the Re and Os isotopic systematics, two fractions of DaG 476 were measured (Table 1). Both fractions have Re/Os and  $^{187}Os/^{188}Os$  that are the same within uncertainty, despite having different Re and Os concentrations by 20% and 23%, respectively. The calculated initial  $\gamma_{Os}$  at the proposed crystallization ages of 474 Ma and 705 Ma are the same within uncertainty (Table 1). Terrestrial crustal materials typically have  $^{187}Os/^{188}Os$  of  $\geq 1$ , and widely varying, very high Re/Os (e.g., Esser and Turekian, 1993; Peucker-Ehrenbrink and Blum, 1998). Small but variable amounts of these materials could result in different  $^{187}Os/^{188}Os$  and Re/Os in the different bulk fractions if the Re and Os concentrations of the terrestrial alteration products are sufficiently large. Because the  $^{187}Os/^{188}Os$  and Re/Os for the two different bulk fractions of DaG are reproducible within analytical uncertainties, it is concluded that terrestrial alteration had no discernable effect on the Re and Os isotopic systematics of this meteorite. This is not unexpected, because of the relatively high concentrations of Re and Os in this sample of 0.5–0.6 ppb and 1.5–2 ppb, respectively (Table 1), combined with the low concentrations of Os in crustal rocks and minerals ( $<0.05$  ppb, Esser and Turekian, 1993; Peucker-Ehrenbrink and Blum, 1998; Shirey and Walker, 1998). Because of the better precision of the calculated initial  $\gamma_{Os}$  for fraction 1 (Table 1), it will be quoted in the rest of this paper. The calculated initial  $\gamma_{Os}$  for DaG 476 is strongly different for each possible crystallization age because of the suprachondritic Re/Os: at 474 Ma =  $+0.66 \pm 0.37$ , at 705 Ma =  $-3.06 \pm 0.47$ , and at 1.2 Ga =  $-11.43 \pm 0.69$ .

### 3.2.2. NC Group

The two meteorites from the NC Group have distinctly different age and Os isotopic characteristics from the S Group. Radiometric dates, ranging from approximately 1.3 to 1.4 Ga for both Nakhla and Chassigny, appear to be the best estimates of their crystallization ages (e.g., Lancet and Lancet, 1971; Gale et al., 1975; Nakamura et al., 1982; Jagoutz, 1996). The calculated initial  $\gamma_{Os}$  value for Nakhla is  $-5.5$ , much lower than the younger S Group meteorites, although the uncertainty for Na-

khla is quite large because of the high Re/Os (Table 1). This calculated value for  $\gamma_{\text{Os}}$  is at 1.417 Ga and is based on the observation that the Nakhla sample in this study forms a two-point isochron of this age with the Chassigny fraction measured with the lowest Re/Os ratio (Table 1), assumed to reflect uncontaminated material (see below). A similar crystallization age for these two meteorites is supported by Nd isotopic systematics (Jagoutz and Jotter, 2000).

Five different fractions of Chassigny were measured for Re and Os systematics (Table 1). The multiple fractions show that Re and Os concentrations are moderately heterogeneous on the scale of the size of the sample aliquots (~300–660 mg). This likely in part reflects the nugget effect for Re and Os as suggested above (e.g., Shirey and Walker, 1998; and references therein). This is exemplified by the measurement of two different parts EETA 79001 (A and B) which have varying Re, Os, and Re/Os, but have the same initial  $\gamma_{\text{Os}}$ , and for two different fractions of DaG 476, that have varying Re and Os, but similar Re/Os and initial  $\gamma_{\text{Os}}$  (Table 1).

More importantly, the Re/Os ratios do not correlate with the measured and variable  $^{187}\text{Os}/^{188}\text{Os}$ , and the calculated initial  $\gamma_{\text{Os}}$  for all five fractions of Chassigny are variable. These results indicate that the fractions experienced some type of post-crystallization disruption of Re-Os systematics (Table 1). The most likely scenario is terrestrial Re contamination, or Re mobility during impact on Mars or Earth. Of note, fraction 4 has a Re/Os that is only 1.29 times that of average chondritic. Thus, the calculated initial  $\gamma_{\text{Os}}$  for fraction 4 does not vary significantly owing to uncertainties in crystallization age. For example, the initial  $\gamma_{\text{Os}}$  for a 1.3 Ga crystallization age for Chassigny is  $-5.2 \pm 1.2$ , and for 1.5 Ga is  $-5.6 \pm 1.3$ . Unfortunately, it is unknown whether this Re/Os is representative of the pristine sample or still reflects some Re contamination or mobility. Consequently, a  $\gamma_{\text{Os}}$  of  $-5.5 \pm 1.3$  must be considered a minimum value. Similarly, if fraction 2 evolved until recently with no Re, the composition would equate to an initial  $\gamma_{\text{Os}}$  of +2.

Two previous studies have reported Re and Os data for Chassigny (Treiman et al., 1986; Birck and Allegre, 1994). Data from both studies have large uncertainties in Re concentration, but both report Re/Os of approximately 0.52 times chondritic. If the undisturbed Re/Os for Chassigny is similar those reported by these studies, and taking the lowest  $^{187}\text{Os}/^{188}\text{Os}$  measured of 0.11987 (fraction 2), a  $\gamma_{\text{Os}}$  of  $-2.34$  is calculated for 1.4 billion years ago. Given the various constraints, the best estimate of the true initial  $\gamma_{\text{Os}}$  for Chassigny appears to lie between  $-5.5$  and  $-2.3$ . This initial Os isotopic composition is significantly lower than those for the S Group meteorites (Table 1).

### 3.2.3. Os isotopic composition of Martian mantle reservoirs at 180 Ma

Assuming an isolation age for the NC Group mantle reservoir of ~4.54 Ga (Harper et al., 1995), the Sm/Nd and the Re/Os for such a reservoir can be obtained from the calculated initial  $^{143}\text{Nd}/^{144}\text{Nd}$  and  $\gamma_{\text{Os}}$  for each NC Group meteorite. Once the Sm/Nd and Re/Os ratios are obtained, then a comparison between meteorites derived from the same mantle reservoir at different times can be made by evolving the mantle reservoir Os and Nd systematics of each meteorite to a single age. Such

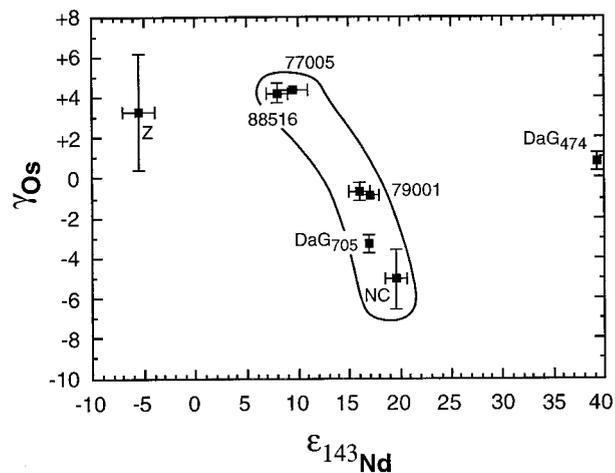


Fig. 2.  $\gamma_{\text{Os}}-\epsilon_{143\text{Nd}}$  systematics for SNC meteorites. Os data are from this study, Nd data are from Harper et al. (1995, and references therein) except DaG (Jagoutz and Jotter, 2000; Borg et al., 2000b), and LEW 88516 (Borg et al., 1998b). The data for the NC Group (Nakhla, Chassigny) and DaG are projected to 180 Ma for comparison with the other SNC data. See text for details on the projection assumptions.

an approach is illustrated in Figure 2 for  $\epsilon_{143\text{Nd}}$  versus  $\gamma_{\text{Os}}$  for the SNC data.

The data for DaG 476, Nakhla, and Chassigny are evolved to 180 Ma for comparison between them and with the S Group meteorites. If DaG 476 crystallized at 705 Ma, its mantle reservoir had similar Nd and Os isotope systematics to the NC Group mantle reservoir and falls on a trend in Os-Nd isotope space for all of the SNC meteorites except Zagami (Fig. 2). If the crystallization age for DaG is 1.2 Ga, its mantle reservoir would still have a similar  $\epsilon_{143\text{Nd}}$  to the NC Group at 180 Ma (+18.8), but have a vastly different  $\gamma_{\text{Os}}$  of  $-14$ . Such a mantle reservoir would still lie on a trend for the SNC meteorites in Figure 2, but would represent an end member on the low  $\gamma_{\text{Os}}$  side. Alternatively, if the crystallization age for DaG was as young as 474 Ma, its mantle reservoir would have an  $\epsilon_{143\text{Nd}}$  of +39 (using the data of Borg et al., 2000b, and following their arguments for DaG mantle reservoir evolution), and a  $\gamma_{\text{Os}}$  of +0.8 at 180 Ma. A high initial  $\epsilon_{143\text{Nd}}$  of +48 at 374 Ma has been obtained for the shergottite QUE 94201, leading to the suggestion that DaG and QUE are from a common mantle reservoir (Borg et al., 2000b). With respect to Os-Nd isotopic systematics, such a composition lies well to the right of the SNC trend in Figure 2. Jagoutz and Jotter (2000), suggested that the combined leached isochron age of 1.2 Ga may reflect terrestrial contamination presumably by an ancient crustal component. This contaminant likely did not affect the Os isotopic systematics as it would result in a very positive  $\gamma_{\text{Os}}$  given the extremely high Re/Os of ancient terrestrial crust and given the arguments presented above. The 474 Ma mineral isochron reported by Borg et al. (2000b) could reflect disturbance of late crystallizing phases that, in part, lie on this isochron (Jagoutz and Jotter, 2000). Nevertheless, the 705 Ma and 474 Ma ages for DaG are both plausible, and each will result in different combined Os-Nd systematics for potential Martian mantle reservoirs. Therefore, consideration will be given below to the Os isotopic systematics of DaG using both crystallization ages.

Further investigations of this meteorite are required in order to better resolve the crystallization age.

### 3.3. Crustal Contamination

The Re and Os concentrations in the SNC meteorites are similar to those for peridotites and mantle-derived lavas on Earth, especially when considered with respect to factors that reflect the state of magmatic evolution, such as Mg# and Ni content (Fig. 1; Treiman et al., 1986; Birck and Allegre, 1994; Warren and Kallemeyn, 1996; Warren et al., 1999). This has led to the conclusion that the inferred HSE concentrations in the Martian mantle are generally similar to those for the Earth's mantle (Warren and Kallemeyn, 1996; Warren et al., 1999). Hence, it is possible that similar processes controlled the HSE budgets for the mantles of both of these planets during their earliest differentiation histories (Warren et al., 1999).

The negative initial  $\gamma_{Os}$  for Chassigny, and possibly Nakhla, indicate that the NC Group meteorites were derived from a long-term subchondritic Re/Os mantle reservoir, relative to average chondrites. This is also the case for DaG if it crystallized at 705 Ma. In contrast, the Os isotopic compositions of the S Group Iherzolites require derivation from a mantle reservoir that evolved with a long term Re/Os that was slightly greater than average chondritic. How did such compositions develop on Mars? Possibilities include early planetary differentiation processes, such as core segregation, early melt depletion, or melt enrichment of mantle domains. These processes could be coupled with continued late accretion of chondritic materials. Processes occurring much later in planetary evolution could also plausibly have created the subchondritic and suprachondritic Os isotopic signatures in mantle-derived rocks. For comparison, although the bulk upper mantle of the Earth likely has a chondritic  $^{187}Os/^{188}Os$  composition (Meisel et al., 1996), it has developed domains with much larger positive and negative deviations from chondritic evolution than are observed in the SNC meteorites. Such deviations from chondritic are believed to result from processes occurring long after primary planetary differentiation. For example, periodic mantle melting throughout Earth history is likely responsible for the variably depleted Os isotopic compositions of samples of subcontinental lithospheric mantle (Walker et al., 1989; Pearson et al., 1995). These mantle materials evidently evolved to subchondritic compositions because mantle melting and subsequent melt removal depleted Re and enriched Os in the residue, stemming from the moderately incompatible nature of Re and compatible nature of Os (Walker et al., 1989). In contrast, positive  $\gamma_{Os}$  values in certain mantle-derived terrestrial lavas can reflect long-term recycling of crust characterized by relatively high Re and Re/Os. (Walker et al., 1991; Hauri and Hart, 1993), or shallow level crustal contamination of low Os abundance melts (Reisberg et al., 1993; Hart et al., 1997; Borg et al., 2000a). In some instances,  $^{187}Os$  enrichments may also reflect the recent addition of evolved outer core to the sources of some plumes at the core-mantle interface (Walker et al., 1995; Walker et al., 1997a; Brandon et al., 1998; Brandon et al., 1999).

Recent studies have suggested that the Hf-Nd-Sr isotopic systematics of the shergottites may be the result of isotopically primitive magmas (represented by DaG 476 and QUE 94201) being contaminated by a 4.5 Ga juvenile crust (Borg et al.,

1997; Blichert-Toft et al., 1999; Borg et al., 2000b), consistent with petrologic observations (Jones, 1989; Longhi, 1991). The case is particularly compelling for Zagami and Shergotty, which both have  $\epsilon_{143Nd}$  of  $-5$  to  $-8$  (Fig. 2, and Harper et al., 1995). Blichert-Toft et al. (1999), have also suggested that the 4.5 Ga juvenile crust on Mars, has chondritic  $\epsilon_w$ , and crustal contamination is the mechanism by which they explain the W systematics of Zagami. In such a case, the positive  $\gamma_{Os}$  in the Iherzolites and Zagami could also reflect crustal contamination.

In order to test whether crustal contamination can produce the Os isotopic systematics of the Iherzolites and Zagami, the following approach is taken. The Nd concentration of the Martian juvenile crust has been estimated to be  $\sim 10$ – $40$  ppm Nd, with a  $^{147}Sm/^{144}Nd$  of 0.15 to 0.17 (Norman, 1999), and considered to have been produced by 2 to 8% partial melting of the Martian mantle. This results in the development of a  $\sim 20$ – $60$  km thick crust, consistent with geophysical observations (Zuber et al., 2000). Evolution of 4.5 Ga crust to 180 Ma with such Sm/Nd systematics would result in an  $\epsilon_{143Nd}$  of approximately  $-20$ , assuming extraction from a chondritic reservoir at 4.5 Ga. This crust is considered to be the contaminant. The Re/Os and Os systematics of the ancient Martian crust are considered to be similar to the evolved SNC meteorites (Fig. 1). Permissible Re/Os ratios would be  $\sim 2$  to 20 ( $^{187}Re/^{188}Os \sim 9.6$  to 96). In the first set of calculations, the Os concentration is set at 10 ppt, at the upper end of the evolved shergottites (Fig. 1) in order to maximize the effect of crustal contamination. The primitive mantle melt is considered to have the Nd systematics of EETA 79001A (Norman, 1999). In order for the Os systematics to be consistent with those for Nd for the mixing calculation, the concentration for EETA 79001A measured in this study is used (Table 1). The concentration of Os in EETA 79001A (481 ppt) is similar to some primitive basalts from Earth (up to several 100 ppt, Shirey and Walker, 1998; Brandon et al., 1999). Melts with EETA 79001A Nd and Os concentrations, and Nd-Os isotopic compositions representing three potential mantle reservoirs at 180 Ma (NC, EETA 79001A, and DaG with a 474 Ma age), when mixed with juvenile crust, all result in concave up mixing curves (Fig. 3, curves 1, 3, 5). These curves all pass through the isotopic composition of Zagami, with 20% or less of the juvenile crustal component added (Table 2), consistent with previous models (Jones, 1989; Borg et al., 1997; Norman, 1999). Therefore, these models indicate that the Os isotopic composition of Zagami could result from crustal contamination of a juvenile Martian crust.

In order for the Os-Nd isotopic systematics of Zagami and the Iherzolites all to be explained by a single, juvenile crustal contaminant, concave down mixing curves must be generated (Fig. 3, curves 2, 4, 6). To generate such curves, two parameters must be shifted. First, the Os isotopic composition of the crustal component must be similar to or only slightly larger than, Zagami and the Iherzolites (Tables 1 and 2). A 4.5 Ga juvenile Martian crust with such a low  $\gamma_{Os}$  requires a  $^{187}Re/^{188}Os$  close to chondritic (i.e., 0.48 to 0.53). Second, assuming that the concentration of Nd in the crust is 10 to 40 ppm (Norman, 1999), then the concentration of Os must be on the order of  $\sim 30$  ppb. This gives a low Nd/Os of 667 for the crustal end-member, which in turn results in a strongly concave down curve (Fig. 3). A low Nd/Os is required to generate such a

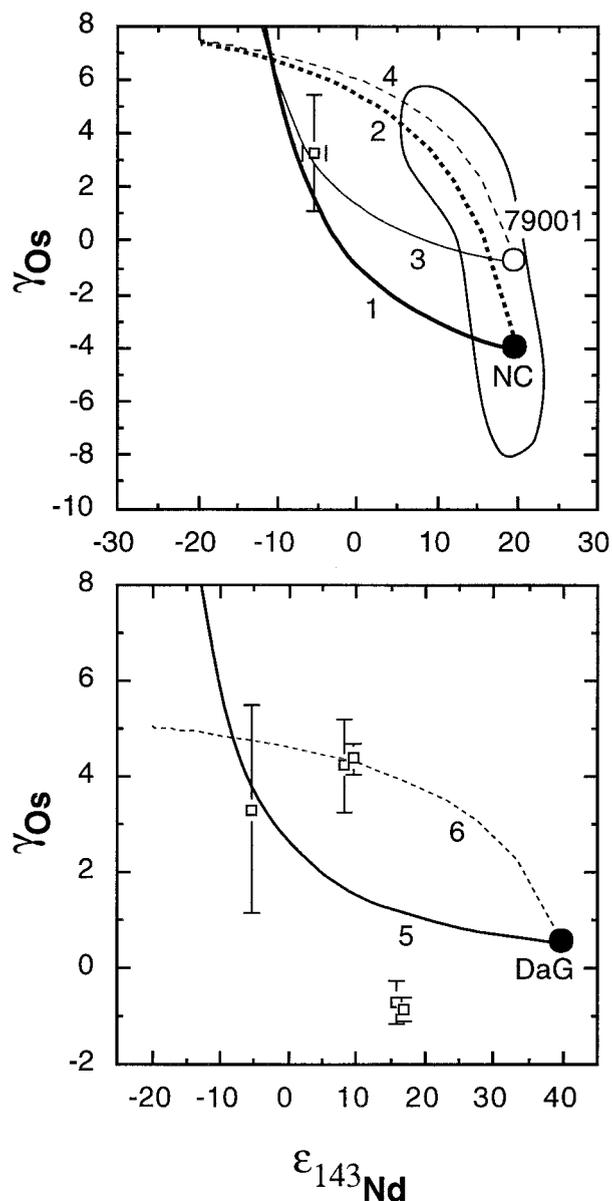


Fig. 3. Crustal contamination models for SNC meteorites. The numbers for the mixing curves correspond to the mixing parameters listed in the 6 columns of Table 2.

curve irrespective of the concentration of Nd in the crust. If the Nd concentration in the crust is 1 ppm, an order of magnitude lower than required by the Norman (1999) model, the concentration of Os must be 3 ppb, etc. However, a juvenile crust having only 1 ppm Nd would be 300 km thick (Norman, 1999), much thicker than most models used to explain geophysical measurements (Zuber et al., 2000).

Ancient crust having characteristics needed to generate curves 2, 4, and 6 (Fig. 3) is likely to be similar to primitive basalts or picrites on Earth. Such terrestrial rocks, having slightly suprachondritic Re/Os, would have approximately 400 ppt to 2 ppb Os, much too low for the mixing models to be successful (Fig. 1, Fig. 3, Table 2). Primitive terrestrial lavas with concentrations of 10's of ppm Nd, high Os concentrations,

and low Re/Os, typically have Nd/Os at least 3 orders of magnitude higher than the Nd/Os needed for the crustal end member to generate curves 2, 4, and 6 (Table 2, e.g., Hawaiian picrites, Bennett et al., 1996; Brandon et al., 1999; Norman and Garcia, 1999:  $\text{Nd/Os}_{\text{average}} = 190121$ ,  $n = 11$ ; Siberian flood basalts, Horan et al., 1995:  $\text{Nd/Os}_{\text{average}} = 77859$ ,  $n = 10$ ).

The concentration of Os in the Martian mantle is likely similar to or less than the concentration of Os in the Earth's mantle (Fig. 1 and Warren et al., 1999). Creating an ancient crust with 30 ppb Os, by 2 to 8% partial melting, and using a  $D_{\text{Os}}$  of 10 to 100 (Walker et al., 1999), requires the concentration of Os in the Martian mantle be 294 to 2940 ppb Os, which is approaching or exceeding the concentrations of Os in primitive chondrites (Jochum, 1996). These concentration levels of Os in a model Martian crust are much too large given the efficient removal of highly siderophile elements from the silicate portions of terrestrial planets by early core formation (Morgan, 1986).

Based on the above requirements, it appears highly unlikely that crustal contamination is a viable process for generating the concave downward mixing trends in Figure 3. Instead, two scenarios can be invoked to explain the Nd-Os isotopic systematics. In one scenario, Zagami Nd and Os isotopic systematics are generated by crustal contamination. In a second scenario, crustal contamination affects the Nd isotopic systematics of Zagami, but has little effect on Os (i.e., Os is decoupled from Nd during this process). This scenario requires that the crust has a similar concentration of Os to crust generated on Earth (i.e., strongly depleted, Fig. 1, Table 1), and that Re is more compatible during Martian differentiation processes (see below). Hence, the juvenile crust on Mars may have lower Re/Os than calculated here (Table 1), and mantle derived melts would be resistant to the effects of crustal contamination with respect to Os. In either scenario, the Os isotopic systematics of the lherzolites are not the result of crustal contamination. Instead, their parental magmas were derived from a Martian mantle reservoir that is isotopically distinct from those that generated NC Group meteorites, which has  $\gamma_{\text{Os}} \approx -5$ , or DaG (assuming a crystallization age of 474 Ma), and which has  $\gamma_{\text{Os}} \approx +1$ . These systematics demonstrate, that 2 or 3 isotopically distinct reservoirs exist within the Martian mantle.

### 3.4. Early Differentiation Processes

Calculated initial  $\gamma_{\text{Os}}$  values correlate well with the long-lived  $^{147}\text{Sm}$ - $^{143}\text{Nd}$  system (Fig. 2), and also with the short-lived  $^{146}\text{Sm}$ - $^{142}\text{Nd}$  and  $^{182}\text{Hf}$ - $^{182}\text{W}$  systems (Fig. 4). The correlation with  $\epsilon_{^{142}\text{Nd}}$  and  $\gamma_{\text{Os}}$  remains valid even in the case for a crystallization age of 474 Ma for DaG, which will not affect  $\epsilon_{^{142}\text{Nd}}$ , but result in  $\sim 4\%$  upward shift in  $\gamma_{\text{Os}}$ . The short half-lives of  $^{146}\text{Sm}$  and  $^{182}\text{Hf}$  ( $103 \times 10^6\text{a}$  and  $9 \times 10^6\text{a}$ , respectively) require the fractionations that produced heterogeneities in  $^{142}\text{Nd}$  and  $^{182}\text{W}$  among the SNC meteorites to have occurred within about 500 million years (for  $^{142}\text{Nd}$ ) and 45 million years (for  $^{182}\text{W}$ ), respectively, of the nucleosynthetic event that produced their parent isotopes. Lee and Halliday (1997) concluded that the  $^{142}\text{Nd}$  and  $^{182}\text{W}$  isotopic covariations are likely the result of the same planetary differentiation processes and that these processes must then have occurred within the first 50 million years of solar system history. If the Os

Table 2. End member parameters for mixtures of 3 mantle reservoirs represented by EETA 79001, DaG 476, and Nakhla-Chassigny, with a 4.5 Ga crust. Mixing results for 10% and 20% are also listed.

Mixing parameters	1	2	3	4	5	6
<b>4.5Ga Crust</b>						
Os (ppb)	0.01	30	0.01	30	0.01	30
$^{187}\text{Re}/^{188}\text{Os}$	49.26	0.525	49.26	0.525	12.08	0.485
$\gamma_{\text{Os}}$ @ 180 Ma	+2910	+7.4	+2910	+7.4	+696	+5.0
Nd (ppm)	20	20	30	20	20	20
$\epsilon_{^{143}\text{Nd}}$ @ 180 Ma	-20	-20	-20	-20	-20	-20
Nd/Os	$2 \times 10^6$	667	$3 \times 10^6$	667	$2 \times 10^6$	667
<b>Mantle melt characteristics</b>						
Os (ppb)	NC	NC	79001A	79001A	DaG, 474 Ma	DaG, 474 Ma
$\gamma_{\text{Os}}$ @ 180 Ma	0.481	0.481	0.481	0.481	0.481	0.481
$\gamma_{\text{Os}}$ @ 180 Ma	-4.2	-4.2	-0.88	-0.88	+0.66	+0.66
Nd (ppm)	1.6	1.6	1.6	1.6	1.6	1.6
$\epsilon_{^{143}\text{Nd}}$ @ 180 Ma						
<b>Mixtures</b>						
10% crust $\gamma_{\text{Os}}$	+0.4	+5.9	+3.7	+6.4	+1.9	+4.4
$\epsilon_{^{143}\text{Nd}}$	-3.3	-3.3	-7.0	-3.3	+5.1	+5.1
20% crust $\gamma_{\text{Os}}$	+6.1	+6.7	+9.3	+6.9	+3.7	+4.7
$\epsilon_{^{143}\text{Nd}}$	-10.3	-10.3	-13.0	-10.3	-5.5	-5.5

isotope correlations with the two short lived system are not coincidental, and this seems unlikely given the similar variations among the four different isotope systems, then the factors controlling their Re/Os must also have occurred early in planetary history. These processes are, therefore, likely reflections of the early differentiation history of Mars.

To preserve these systematics, a two stage melting history, one around 4.55 Ga, and one at the time of SNC melt generation, is required. Strong evidence from Nd isotopic systematics, young magmatic features on the surface of Mars, and from the young crystallization ages of SNC meteorites, indicates that

the Martian mantle has undergone melting long after early differentiation. However, multistage melting (i.e., no melting between the early event and melting at the time of formation of each SNC magma) of individual columns of Martian mantle may not have taken place. Jagoutz (1991) and Jagoutz (1998), have argued that the Rb-Sr isotopic system of the SNC meteorites lie on a  $\sim 4.55$  Ga isochron. This was interpreted to reflect a two step evolution—early mantle differentiation and another at the time of NC Group crystallization at  $\sim 1.3$  Ga. The U-Pb isotopic data for some SNCs (Shergotty, Zagami, EETA 79001) plot along lines which intersect concordia at

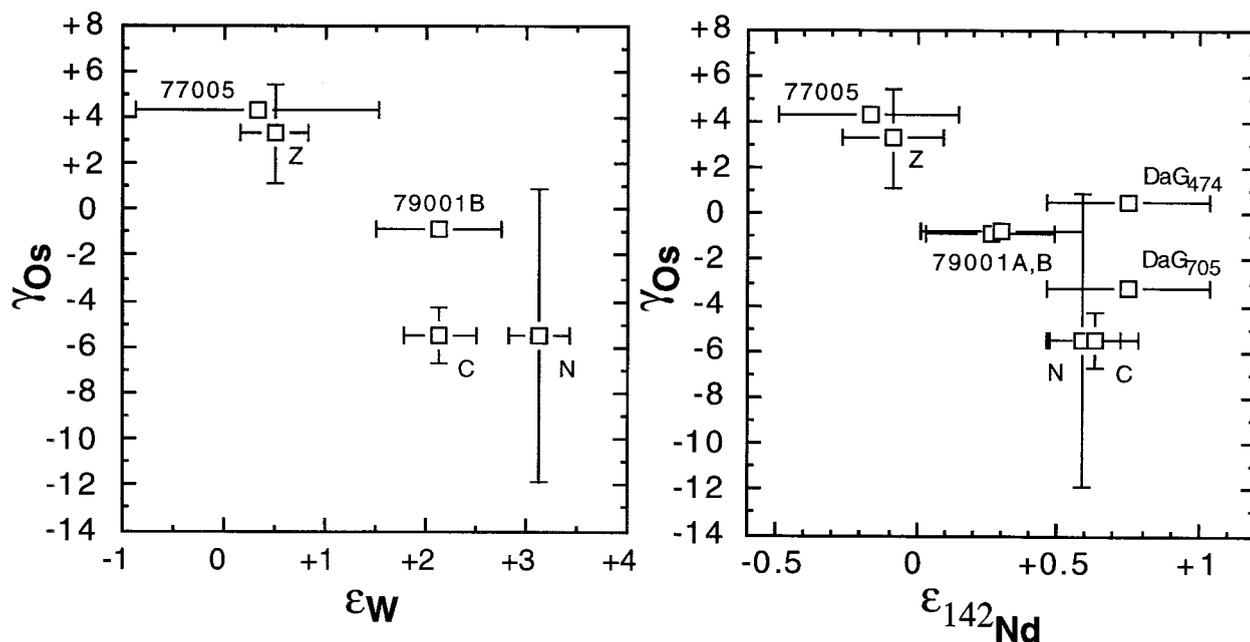


Fig. 4.  $\gamma_{\text{Os}}-\epsilon_{\text{W}}$  and  $\gamma_{\text{Os}}-\epsilon_{^{142}\text{Nd}}$  systematics for the SNC meteorites. The Os isotopic data are from this study, the W isotopic data are from Lee and Halliday (1997), and Nd isotopic data are from Harper et al. (1995) except DaG, which are unpublished data for E. Jagoutz (personal communication, 2000).

~4.5–4.6 Ga (Chen and Wasserburg, 1986). These data also imply only two stage melting histories for the mantle reservoirs of SNC meteorites (Jones, 1989).

Assuming that the bulk Re/Os of Mars is within the range of chondritic meteorites, the most straightforward explanation of the Os isotopic systematics of the SNC meteorites is that they reflect the compositions of their mantle reservoirs and that the Re/Os of these secondary reservoirs were established via early Martian differentiation and accretionary processes. At least three major processes can initially control the Re/Os ratio of planetary mantle materials, and the relative abundances of other HSE: core formation, late accretion, and crystallization-accumulation within a magma ocean. Core formation and late accretion likely work in opposition. Core formation greatly depletes the silicate portion of a planet in HSE and could have created a mantle that had either a suprachondritic or subchondritic Re/Os. At present, the partitioning of HSE between metal and silicate at various pressures is still poorly constrained, so the effects of core segregation on Mars are beyond conjecture. However, the fact that the Os isotopic compositions of SNC meteorites do not deviate more than a maximum of 5% from the average composition of chondrites suggests that the Re/Os was probably not established via metal-silicate equilibration. This is because published liquid metal/liquid silicate partition coefficients are orders of magnitude different between individual HSE (e.g., O'Neill et al., 1995; and references therein). Hence, core formation should result in much greater fractionation than 5% from chondritic for the Re/Os ratio of a planetary mantle after core separation (Walker et al., 1997b). If future experiments demonstrate similar (within  $\pm 20\%$ ) metal-silicate bulk distribution coefficient ( $D$ 's) for Re and Os under appropriate conditions for the Martian mantle, then further examination of this possibility will be warranted.

Alternatively, the roughly chondritic Re/Os of the Martian mantle coupled with HSE concentrations similar to those for the Earth's mantle (Fig. 1, Warren et al., 1999) are most consistent with late accretion of chondritic material after core formation. However, the present-day  $\gamma_{Os}$  of at least two of the Martian mantle reservoirs (Fig. 2) are too high (+4), and too low (-5), to be accounted for solely by late veneer addition of chondritic material (e.g., -1.2 to +2.7, Meisel et al., 1996). This range in  $\gamma_{Os}$  shows that fractionation of Re/Os within the Martian mantle must have occurred either during or following the time of late accretion.

The mantle reservoir that had a long-term subchondritic Re/Os relative to average chondrites, represented by the NC Group meteorites and possibly DaG (for a 705 Ma crystallization age), had a  $\gamma_{Os}$  value between 1.4 Ga and 700 Ma of approximately -4. If the primitive Martian mantle initially had a  $^{187}Re/^{188}Os$  of 0.402 (chondritic average) and an average chondritic initial  $^{187}Os/^{188}Os$  ratio, then the  $^{187}Re/^{188}Os$  of the NC Group mantle component, after a hypothetical fractionation event at 4.54 Ga, would have to have been  $0.316 \pm 0.043$  to generate a  $\gamma_{Os}$  of  $-4 \pm 2$  at 1.4 Ga. This mantle reservoir would extrapolate to a present day  $\gamma_{Os}$  of  $-5.4 \pm 2.6$  (Fig. 5). A change of this order in Re/Os in terrestrial mantle residues can be achieved via relatively low percentages of partial melting. The  $D$ 's for Re during terrestrial mantle melting have been estimated to be similar to those for Yb, and probably range from about 0.5 to  $\leq 0.1$  (Walker et al., 1989; Hauri and Hart,

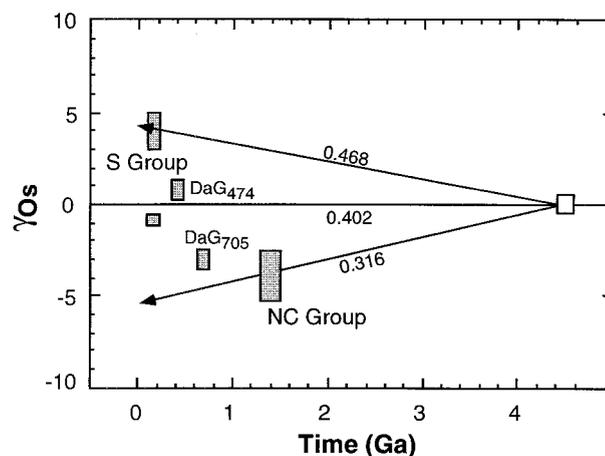


Fig. 5. Os isotopic evolution diagram for SNC meteorites. The evolution vectors with different  $^{187}Re/^{188}Os$  ratios are shown. A mantle reservoir with a chondritic  $^{187}Re/^{188}Os$  of 0.402 will evolve with a  $\gamma_{Os} = 0$ . The evolution vectors of the S Group mantle reservoir and the NC Group mantle reservoir are calculated for a change in Re/Os from chondritic at 4.54 Ga (following Harper et al., 1995).

1997; Walker et al., 1999). If Re partitioning is similar on Mars, partial melting and melt removal of less than 5% (Norman, 1999) could reduce the Re/Os to the level required. It should be noted, however, that the incompatibility of Re was evidently considerably diminished on the Moon, the eucrite parent body, and possibly on Mars, relative to the Earth (Birck and Allegre, 1994). This is exemplified in the SNC suite by the very low concentrations of Re in the basaltic SNC samples, much lower than comparable terrestrial basalts, and the fact that the Re/Yb ratio of the suite decreases with increasing Yb (Fig. 6).

If, in contrast to terrestrial mantle melting systems, Re had a solid/liquid  $D$  near 1 during melting of the Martian mantle, then little change would have occurred in the Re concentration of the Martian mantle over time. A corollary to this assumption is that Re-rich basaltic crust was probably not generated on Mars. In order to generate the approximately 30% change in the Re/Os required for the NC Group mantle reservoir, the highly compatible nature of Os, coupled with melt removal, must be appealed to. The change in Re/Os can occur simply by volume reduction. For example, for 25 to 30% melting, where  $D_{Re}$  is 1,  $D_{Os}$  must be about 10 to 20 in order to produce a residue with  $^{187}Re/^{188}Os$  of 0.31 (similar to that inferred for the NC Group mantle reservoir) from a chondritic mantle. This  $D_{Os}$  is within the range of approximately 10–100 predicted for melting of peridotite in Earth (Walker et al., 1999). Provided  $D_{Re}$  remains close to 1, increasing  $D_{Os}$  to 100, to reflect the maximum expected for Earth, would not result in reducing the amount of partial melting required to produce the NC Group below approximately 25%. These relationships suggest that if early melting generated the Os isotopic compositions of the NC Group meteorites, it was substantial. The proposed maximum of 8% partial melting to produce the Martian crust (Norman, 1999), cannot result in a residue with  $^{187}Re/^{188}Os$  0.31, unless  $D_{Re}$  is  $< 0.3$ , similar to the compatibility of Re during partial melting in Earth. Therefore, it appears that the negative  $\gamma_{Os}$  of the NC Group meteorites was not produced by early melting of

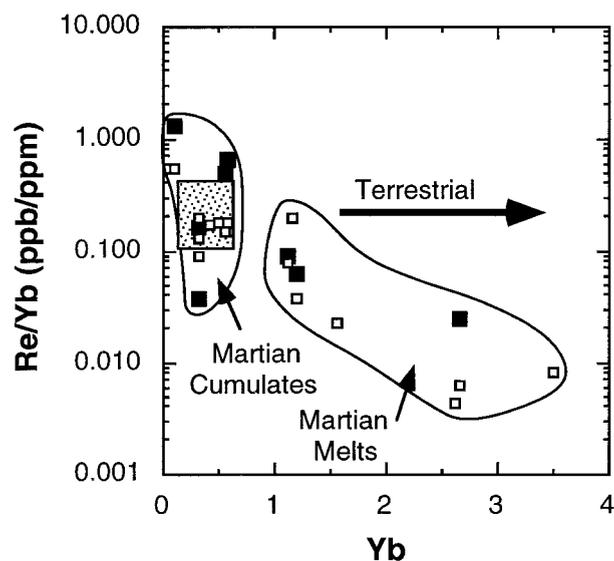


Fig. 6. Re/Yb-Yb systematics for Martian Cumulates (Iherzolites, DaG, Nakhilites) and Martian Melts (Shergottite basalts, 79001, EETA 79001). The large square represents terrestrial peridotites, and the terrestrial melts (mid-ocean ridge basalts and oceanic island basalts) vector is shown for comparison (from Righter and Hauri, 1998). Re values in this study are shown in large filled squares while previous work shown as small squares (Warren and Kallemeyn, 1996; Warren et al., 1999).

the Martian mantle unless this melting event is *unrelated* to generation of juvenile crust.

The mantle reservoir from which the S Group Iherzolites were derived had suprachondritic Re/Os relative to average chondrites. The enrichment need not have been as great as the depletion in Re/Os for the NC Group. These meteorites have an average  $\gamma_{Os}$  value of approximately +4 at 160 to 180 million years ago. As with the NC Group meteorites, if linear growth is assumed from a primitive composition early in Martian history, and extrapolated through the calculated initial ratios of these samples to 0 Ma (Fig. 5), this mantle reservoir yields a modern composition with a  $\gamma_{Os}$  averaging approximately  $+4 \pm 1$  ( $^{187}Os/^{188}Os$  of  $0.132 \pm 1$ ). Data for variably melt-depleted terrestrial peridotites suggest that the Earth's primitive upper mantle (PUM, Meisel et al., 1996) has a present day  $\gamma_{Os}$  of  $+1.6$  ( $^{187}Os/^{188}Os$  of  $0.129 \pm 1$ ), similar to that of ordinary and enstatite chondrites but not carbonaceous chondrites. Thus, the  $^{187}Os/^{188}Os$  of the mantle reservoir represented by the S Group Iherzolites may only be enriched 2 to 3% relative to the bulk Martian mantle, if the bulk Martian mantle has a similar Os isotopic composition to the PUM of the Earth. This is in contrast to the mantle reservoir of the NC Group meteorites, which is depleted by about 6 to 8% relative to the PUM (Fig. 5).

Some studies have suggested that during early differentiation of Mars, a magma ocean formed and included approximately 30 to 50% the mass of the silicate portion of the planet (Treiman et al., 1986; Treiman et al., 1987; Wanke and Dreibus, 1988; Gaetani and Grove, 1997; Righter and Drake, 1996; Righter and Drake, 1997; Righter et al., 1998). The positive  $\epsilon_{142Nd}$  in the NC Group meteorites, DaG, and QUE 94201, was likely inherited during crystallization of the Martian magma

ocean (Borg et al., 1997). The first cumulates to crystallize from a Martian magma ocean with chondritic proportions of rare earth elements, Rb, and Sr, would be strongly depleted, with elevated Sm/Nd and low Rb/Sr (Borg et al., 1997). Late stage, evolved liquids, resulting from 99% or greater crystallization of the magma ocean, would have lower Sm/Nd and high Rb/Sr. The calculated  $\epsilon_{142Nd}$  for the last liquids would be  $-0.47$  (Borg et al., 1997). Variable mixtures between cumulates and evolved liquids, the latter of which have been trapped intercumulus melt in the mantle, may explain the  $\epsilon_{143Nd}$ ,  $\epsilon_{142Nd}$ , and Sr isotopic systematics of SNC's (Borg et al., 1997).

In such a scenario, it is unclear how Re and Os will behave, because partitioning data for different potential crystallizing minerals is limited. In the Earth's mantle, Re and Os primarily reside in sulfide (Shirey and Walker, 1998, and references therein). Roy-Barman and Allegre (1995) used sulfide/silicate melt partition coefficients for  $D_{Re}$  of 4000, and for  $D_{Os}$  of 40000, to successfully model the terrestrial partial melting trend for Re and Os displayed by komatiites and basalts. These  $D$ 's are based on compilations from experimental and empirical data, which suggest that at least under the conditions of melting and crystallization in the terrestrial mantle, sulfide will partition Os more strongly than Re (Morgan, 1986; Jones and Drake, 1986; Walker et al., 1988; Peach et al., 1990; Fleet et al., 1991; Walker et al., 1991; Hart and Ravizza, 1996; Roy-Barman et al., 1998; Shirey and Walker, 1998; Rehkamper et al., 1999). If similar behavior of Re and Os occurred in a Martian magma ocean, then sulfide fractionation could conceivably have resulted in Re/Os variation in the cumulate piles. However, sulfur saturation would only occur when the magma ocean was approximately 80% crystallized (K. Righter, personal communication, 2000). Sulfide crystallization from late stage melts would result in stripping the remaining melt of both Re and Os, resulting in the formation of cumulates with very high concentrations of these elements. The residual melt and phases crystallizing after sulfide removal would have much lower concentrations of Re and Os. Strongly variable HSE concentrations in the different mantle reservoirs for the NC Group and the S Group meteorites is inconsistent with the similar HSE concentrations in these rocks and their inferred mantle reservoirs (Fig. 1, Fig. 6; Warren et al., 1999).

In order for differentiation within a magma ocean to explain the Re-Os isotopic systematics of the SNC's, the following conditions must apply. A fractionating phase or set of phases, must result in a modest change in the Re/Os ratio in the cumulate piles, coupled with little effect on the bulk concentrations of HSE between the cumulates and the residual melt. Such a phase(s) would therefore need to have  $D$ 's for Re and Os close to 1, but  $D_{Re} < D_{Os}$ . The crystallization of the phase or phases must also be able to replicate the Hf-W and Sm-Nd systematics observed in the  $\epsilon_W$  and  $\epsilon_{142Nd}$  variation in the SNC's. One mineral that would likely have crystallized from a Martian magma ocean that may meet these requirements, is olivine. The Martian upper mantle consists of  $\geq 50\%$  olivine (Longhi et al., 1992; Bertka and Fei, 1997). Olivine was likely to be precipitating from the Martian magma ocean throughout its crystallization history (Borg et al., 1997). Mineral/melt partition coefficients for olivine in terrestrial systems indicate that  $D_{Re}$  is  $< 0.01$ , and  $D_{Os}$  is  $> 1$  (Righter et al., 2000, and references therein). As suggested earlier in this paper,  $D_{Re}$  in Mar-

tian petrogenetic processes may be close to 1. Hence, crystallization of olivine throughout the evolution of the magma ocean could slightly fractionate Re from Os with little effect on the concentrations in the evolved magma. For example, if olivine represents 50% of the fractionating assemblage (e.g., Borg et al., 1997) and is the only phase controlling Re and Os partitioning where  $D_{\text{Re}} = 1$ , and  $D_{\text{Os}} = 1.5$ , a cumulate pile crystallizing after 50% solidification of the magma ocean would have a  $^{187}\text{Re}/^{188}\text{Os}$  of 0.318, or similar to the calculated NC Group mantle reservoir. A cumulate pile crystallizing after 90% solidification of the magma ocean would have a  $^{187}\text{Re}/^{188}\text{Os}$  of 0.477, or similar to the calculated S Group mantle reservoir. Cumulate piles developed earlier and later than these two examples would have lower and higher  $^{187}\text{Re}/^{188}\text{Os}$ , respectively. The absolute  $^{187}\text{Re}/^{188}\text{Os}$  at each stage of solidification would vary depending on the true bulk D of the cumulate phases.

Small fractionations between Re and Os in the crystallizing magma ocean may also be linked to other crystallizing phases, such as garnet, gamma spinel, clinopyroxene, etc. (Longhi et al., 1992; Bertka and Fei, 1997). Whether any of these minerals can be suitable hosts for Re and Os in the Martian mantle awaits additional experimental work. If olivine does turn out to be the phase that has moderately fractionated Re from Os, it cannot be the phase that controlled lithophile element fractionation in a Martian magma ocean. This is because little Hf, W, Sm, Nd, Rb, or Sr partitions into olivine (Borg et al., 1997, and references therein). Therefore, the correlations observed in  $\gamma_{\text{Os}}$  and the lithophile element isotopic systems may be controlled by different phases in the cumulate piles, but are related by the timing and location of crystallization within the magma ocean.

#### 4. CONCLUSIONS AND IMPLICATIONS

The bulk Martian mantle has a generally chondritic isotopic composition. This characteristic is best explained via the addition of a later veneer of chondritic material during or following core formation. Small heterogeneities are observed in the initial Os isotopic compositions of SNC meteorites and are consistent with at least two mantle reservoirs in the Martian mantle. A third possible reservoir is reflected by the DaG sample, assuming a 474 Ma crystallization age. A model where variable amounts of crystal cumulates and late stage evolved liquids from a magma ocean developed contemporaneous, or nearly so, to core formation and the generation of a light rare earth element enriched domain (crust?), may explain the combined Os-Nd-Sr-W systematics of the SNC meteorites. This resulted in production of a mantle reservoir with lower Re/Os, and evolution to the present day to a  $\gamma_{\text{Os}}$  of approximately  $-5.4 \pm 2$ , from which the NC Group parental magmas were derived from. The second mantle component, with present day positive  $\gamma_{\text{Os}}$  of approximately +4, represented by the shergottite lherzolites, may be an upper mantle reservoir, potentially formed from late stage crystallization of an early magma ocean resulting in evolved liquids with elevated Re/Os.

The Re-Os systematics support earlier arguments that chemical compositional variability resulting from early differentiation has been preserved in the SNC meteorites. This observation is consistent with the supposition that convective mixing of the Martian mantle has been limited (Lee and Halliday, 1997).

*Acknowledgments*—This work was supported by NASA grant NAG57634 (to RJW). Samples were provided by the Department of Antarctic Meteorites of the National Institute of Polar Research (Japan), the Johnson Space Center, Museum National d'Histoire Naturelle in Paris, and the Max Planck Institut für Chemie in Mainz. Munir Humayun is thanked for analyzing Re by ICPMS for a DaG fraction. Emil Jagoutz is thanked for providing his unpublished Nd data for DaG 476. Lars Borg, Clive Neal, Kevin Righter, Mini Wadhwa, and an anonymous reviewer are thanked for their comments.

*Special handling:* C. Koeberl

#### REFERENCES

- Becker R. H. and Pepin R. O. (1984) The case for a Martian origin of the shergottites: Nitrogen and noble gases in EETA 79001. *Earth Planet. Sci. Lett.* **69**, 225–242.
- Bennett V. C., Esat T. M., and Norman M. D. (1996) Two mantle plume components in Hawaiian picrites inferred from correlated Os-Pb isotopes. *Nature* **381**, 221–224.
- Bertka C. M. and Fei Y. (1997) Mineralogy of the Martian interior up to core-mantle boundary pressures. *J. Geophys. Res.* **102**, 5251–5264.
- Birck J. L. and Allegre C. L. (1994) Contrasting Re/Os magmatic fractionation in planetary basalts. *Earth Planet. Sci. Lett.* **124**, 139–148.
- Birck J. L., Roy-Barman M., and Capmas F. (1997), Re-Os isotopic measurements at the femtomole level in natural samples. *Geostand. Newslett.* **21**, 19–27.
- Blichert-Toft J., Gleason J. D., Telouk P., and Albarede F. (1999) The Lu-Hf isotope geochemistry of shergottites and the evolution of the Martian mantle-crust system. *Earth Planet. Sci. Lett.* **173**, 25–39.
- Bogard D. D. and Johnson, P. (1983) Martian gases in an Antarctic meteorite. *Science* **221**, 651–654.
- Borg L. E., Nyquist L. E., Taylor L. A., Wiesmann H. and Shih C.-Y. (1997) Constraints on Martian differentiation processes from Rb-Sr and Sm-Nd isotopic analyses of the basaltic shergottite QUE94201. *Geochim. Cosmochim. Acta* **61**, 4915–4931.
- Borg L. E., Nyquist L. E., and Wiesmann H. (1998a) Rb-Sr isotopic systematics of the lherzolitic shergottite LEW88516. *Lunar Planet. Sci.* **XXIX**, #1233.
- Borg L. E., Nyquist L. E., Wiesmann H., and Reese Y. (1998b) Samarium-neodymium isotopic systematics of the lherzolitic shergottite Lewis Cliff 88516. (*abs*) *Meteoritical Society, Dublin*.
- Borg L. E., Brandon A. D., Clynne M. A., and Walker R. J. (2000a) Re-Os isotopic systematics of primitive lavas from the Lassen region of the Cascade arc, California. *Earth Planet. Sci. Lett.* **177**, 301–317.
- Borg L. E., Nyquist L. E., Wiesmann H., Reese Y., and Papike J. J. (2000b) Sr-Nd isotopic systematics of Martian meteorite DaG 476. *Lunar Planet. Sci.* **XXXI**, #1036.
- Brandon A. D., Walker R. J., Morgan J. W., Norman M. D., and Prichard H. M., (1998) Coupled  $^{186}\text{Os}$  and  $^{187}\text{Os}$  evidence for core-mantle interaction. *Science* **280**, 1570–1573.
- Brandon A. D., Norman M. D., Walker R. J., and Morgan J. W. (1999)  $^{186}\text{Os}$ - $^{187}\text{Os}$  systematics of Hawaiian picrites. *Earth Planet. Sci. Lett.* **174**, 25–42.
- Chen J. H. and Wasserburg G. J. (1986) Formation ages and evolution of Shergotty and its parent planet from U-Th-Pb systematics. *Geochim. Cosmochim. Acta* **50**, 955–968.
- Chou C.-L. (1978) Fractionation of siderophile elements in the Earth's upper mantle. *Proc. Lunar Planet. Sci. Conf.* **9th**, 219–230.
- Cohen A. S. and Waters F. G. (1996) Separation of osmium from geological materials by solvent extraction for analysis by TIMS. *Anal. Chim. Acta* **332**, 269–275.
- Creaser R. A., Papanastassiou D. A., and Wasserburg G. J. (1991). Negative thermal ion mass spectrometry of osmium, rhenium, and iridium. *Geochim. Cosmochim. Acta* **55**, 397–401.
- Esser B. K. and Turekian K. K. (1993) The osmium isotopic composition of the continental crust. *Geochim. Cosmochim. Acta* **57**, 3093–3104.
- Fleet M. E., Stone W. E., and Crocket J. H. (1991). Partitioning of palladium, iridium, and platinum between sulfide liquid and basalt

- melt: Effects of melt composition, concentration, and oxygen fugacity. *Geochim. Cosmochim. Acta* **55**, 2545–2554.
- Gaetani G. A. and Grove T. L. (1997) Partitioning of moderately siderophile elements among olivine, silicate melt, and sulfide melt: Constraints on core formation in the Earth and Mars. *Geochim. Cosmochim. Acta* **61**, 1829–1846.
- Gale N. H., Arden J. W., and Hutchison R. (1975) The chronology of the Nakhla achondritic meteorite. *Earth Planet. Sci. Lett.* **26**, 195–206.
- Harper C. L., Nyquist L. E., Bansal B., Weismann H., and Shih C.-Y. (1995) Rapid accretion and early differentiation of Mars indicated by  $^{142}\text{Nd}/^{144}\text{Nd}$  in SNC meteorites. *Science* **267**, 213–217.
- Hart S. R. and Ravizza G. E. (1996) Os partitioning between phases in ilherzolite and basalt. In *Earth Processes: Reading the Isotopic Code* (A. Basu and S. R. Hart, eds.), *Geophys. Monogr.* **95**, 123–134.
- Hart W. K., Carlson R. W., and Shirey S. B. (1997) Radiogenic Os in primitive basalts from the northwestern USA: Implications for petrogenesis. *Earth Planet. Sci. Lett.* **150**, 103–116.
- Hauri E. H. and Hart S. R. (1993) Re-Os isotope systematics of EMII and HIMU oceanic island basalts from the south Pacific Ocean. *Earth Planet. Sci. Lett.* **114**, 353–371.
- Hauri E. H. and Hart S. R. (1997) Rhenium abundances and systematics in oceanic basalts. *Chem. Geol.* **139**, 185–205.
- Horan M. F., Walker R. J., Federenko V. A., and Czamanske G. K. (1995) Os and Nd isotopic constraints on the temporal and spatial evolution of the Siberian flood basalt sources. *Geochim. Cosmochim. Acta* **53**, 5159–5168.
- Jagoutz E. (1989) Sr and Nd isotopic systematics in ALHA77005: Age of shock metamorphism in shergottites and magmatic differentiation on Mars. *Geochim. Cosmochim. Acta* **59**, 2429–2441.
- Jagoutz E. (1991) Chronology of SNC meteorites. *Space Sci. Rev.* **56**, 13–22.
- Jagoutz E. (1996) Nd isotopic systematics of Chassigny. *Lunar Planet. Sci.* **XXVII**, 597–598.
- Jagoutz E. (1998) Isotopic constraints on differentiation and evolution of SNC meteorites. *Lunar Planet. Sci.* **XXIX**, #1453.
- Jagoutz E., Bogdanovski O., Krestina N., and Jotter R. (1999) DAG: A new age in the SNC family, or the first gathering of relatives. *Lunar Planet. Sci.* **XXX**, #1808.
- Jagoutz E. and Jotter R. (2000) New Sm-Nd isotope data on Nakhla minerals. *Lunar Planet. Sci.* **XXXI**, #1609.
- Jochum K. P. (1996) Rhodium and other platinum-group elements in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **60**, 3353–3357.
- Jones J. H. (1989) Isotopic relationships among the shergottites, nakh-lites, and Chassigny. *Lunar Planet. Sci.* **XIX**, 465–474.
- Jones J. H. and Drake M. J. (1986) Geochemical constraints on core formation in the Earth. *Nature* **322**, 221–228.
- Kong P., Ebihara M., and Palme H. (1999) Siderophile elements in Martian meteorites and implications for core formation in Mars. *Geochim. Cosmochim. Acta* **63**, 1865–1875.
- Lancet M. S. and Lancet K. (1971) Cosmic-ray and gas-retention ages of Chassigny meteorite. *Meteoritics* **6**, 81–86.
- Lee D.-C. and Halliday A. N. (1997) Core formation on Mars and differentiated asteroids. *Nature* **388**, 854–857.
- Longhi J. (1991). Complex magmatic processes on Mars: Inferences from SNC meteorites. *Lunar Planet. Sci.* **XXI**, 695–709.
- Longhi J., Knittle E., Holloway J. R., and Wanke H. (1992) The bulk composition, mineralogy, and internal structure of Mars. In *Mars* (H. Kieffer et al., eds.), pp. 184–208. Univ. Ariz. Press.
- McSween H. Y., Jr. (1994) What we have learned about Mars from SNC meteorites. *Meteoritics* **29**, 757–779.
- Meisel T., Walker R. J., and Morgan J. W. (1996) The osmium isotopic composition of the Earth's primitive upper mantle. *Nature* **383**, 517–520.
- Mikouchi T. (1999) Preliminary examination of Dar Al Gani 476: A new basaltic Martian meteorite similar to lithology A of EETA 79001. *Lunar Planet. Sci.* **XXX**, #1557.
- Misawa K., Nakamura N., Premo W. R., and Tatsumoto M. (1997) U-Th-Pb isotopic systematics of ilherzolititic shergottite Yamato 793605. *Ant. Met. Res.* **10**, 95–108.
- Morgan J. W., Wandless G. A., Petrie R. K., and Irving A. J. (1981) Composition of the Earth's upper mantle. 1. Siderophile trace elements in ultramafic nodules. *Tectonophysics* **75**, 47–67.
- Morgan J. W. (1986) Ultramafic xenoliths: Clues to Earth's late accretionary history. *J. Geophys. Res.* **91**, 12375–12387.
- Murthy V. R. (1991) Early differentiation of the Earth and the problem of mantle siderophile elements: A new approach. *Science* **253**, 303–306.
- Nakamura N., Unruh D. M., Tatsumoto M., and Hutchison R. (1982) Origin and evolution of the Nakhla meteorite inferred from the Sm-Nd and U-Pb systematics and REE, Ba, Sr, Rb abundances. *Geochim. Cosmochim. Acta* **46**, 1555–1573.
- Neal C. R., Ely J. D., and Jain J. C. (2000) PGE abundances in Martian meteorites: No need for a late veneer. *Lunar Planet. Sci.* **XXXI**, #1975.
- Norman M. D. (1999) The composition and thickness of the crust of Mars estimated from rare earth elements and neodymium-isotopic compositions of Martian meteorites. *Met. Planet. Sci.* **34**, 439–449.
- Norman M. D. and Garcia M. O. (1999) Primitive magmas and source characteristics of the Hawaiian plume: Petrology and geochemistry of shield picrites. *Earth Planet. Sci. Lett.* **168**, 27–44.
- Nyquist L. E., Bansal B., Wiesmann H., and C.-Y. Shih (1995) "Martians" young and old: Zagami and ALH84001. *Lunar Planet. Sci.* **XXVI**, 1065–1066.
- O'Neill H. St. C. (1991) The origin of the Moon and the early history of the Earth—A chemical model. Part 2: Earth. *Geochim. Cosmochim. Acta* **55**, 1159–1172.
- O'Neill H. St. C., Dingwell D. B., Borisov A., Spettel B., and Palme H. (1995) Experimental petrochemistry of some highly siderophile elements at high temperatures, and some implications for core formation at the mantle's early history. *Chem. Geol.* **120**, 255–273.
- Peach C. L., Mathez E. A., and Keays R. R. (1990) Sulfide melt-silicate distribution coefficients for noble metals and other chalcophile elements as deduced from MORB: Implications for partial melting. *Geochim. Cosmochim. Acta* **54**, 3379–3389.
- Pearson D. G., Carlson R. W., Shirey S. B., Boyd F. R., and Nixon P. H. (1995) Stabilization of Archean lithospheric mantle: A Re-Os isotope study of peridotite xenoliths from the Kaapval craton. *Earth Planet. Sci. Lett.* **134**, 341–357.
- Peucker-Ehrenbrink B. and Blum J. D. (1998) Re-Os isotopic systematics of Precambrian crustal rocks: Implications for the marine osmium isotope record. *Geochim. Cosmochim. Acta* **62**, 3193–3203.
- Pepin R. O. (1991) On the origin and early evolution of terrestrial planet atmospheres and meteoritic volatiles. *Icarus* **92**, 2–79.
- Rehkamper M., Halliday A. N., Fitton J. G., Lee D. C., Wieneke M., and Arndt N. T. (1999) Ir, Ru, Pt, and Pd in basalts and komatiites: New constraints for the geochemical behavior of the platinum-group elements in the mantle. *Geochim. Cosmochim. Acta* **63**, 3915–3934.
- Reisberg L., Zindler A., Marcantonio F., White W., Wyman D., and Weaver B. (1993) Os isotope systematics in ocean island basalts. *Earth Planet. Sci. Lett.* **120**, 149–167.
- Righter K. and Drake M. J. (1996) Core formation in Earth's Moon, Mars, and Vesta. *Icarus* **124**, 513–529.
- Righter K. and Drake M. J. (1997) Metal-silicate equilibrium in a homogeneously accreting earth: new results for Re. *Earth Planet. Sci. Lett.* **146**, 541–553.
- Righter K. and Hauri E. H. (1998) Compatibility of rhenium in garnet during mantle melting and magma genesis. *Science* **280**, 1737–1741.
- Righter K., Hervig R. L., and Kring D. A. (1998) Accretion and core formation on Mars: Molybdenum contents of melt inclusion glasses in three SNC meteorites. *Geochim. Cosmochim. Acta* **62**, 2167–2177.
- Righter K., Walker R. J., and Warren P. H. (2000) Significance of highly siderophile elements and osmium isotopes in the lunar and terrestrial mantles. *Origin of the Earth and Moon* (R. M. Canup and K. Righter, eds.) in press. Univ. Arizona Press.
- Roy-Barman M. and Allegre C. J. (1995)  $^{187}\text{Os}/^{186}\text{Os}$  in oceanic island basalts: Tracing oceanic crust recycling in the mantle. *Earth Planet. Sci. Lett.* **129**, 145–161.
- Roy-Barman M., Wasserburg G. J., Papanastassiou D. A., and Chaussidon M. (1998) Osmium isotopic compositions and Re-Os concentrations in sulfide globules from basaltic glasses. *Earth Planet. Sci. Lett.* **154**, 331–347.
- Shih C.-Y., Nyquist L. E., Bogard D. D., McKay G. A., Wooden J. L., Bansal B. M., and Wiesmann H. (1982) Chronology and petrogenesis of young achondrites, Shergotty, Zagami, and ALHA77005:

- Late magmatism on a geologically active planet. *Geochim. Cosmochim. Acta* **46**, 2323–2344.
- Shirey S. B. and Walker R. J. (1995) Carius tube digestion for low-blank rhenium-osmium analysis. *Anal. Chem.* **34**, 2136–2141.
- Shirey S. B. and Walker R. J. (1998) The Re-Os isotope system in cosmochemistry and high-temperature geochemistry. *Ann. Rev. Earth Planet. Sci.* **26**, 423–500.
- Treiman A. H., Drake M. J., Janssens M. J., Wolf R., and Ebihara M. (1986) Core formation in the Earth, Shergottite Parent Body (SPB): Chemical evidence from basalts. *Geochim. Cosmochim. Acta* **50**, 1071–1091.
- Treiman A. H., Jones J. H., and Drake M. J. (1987) Core formation in the shergottite parent body and comparison with the Earth. *Proc. Lunar Sci. Conf.* **17**, E627–E632.
- Walker R. J., Shirey S. B., and Stecher O. (1988) Comparative Re-Os, Sm-Nd, and Rb-Sr isotope and trace element systematics for Archean komatiite flows from Munro Township, Abitibi Belt, Ontario. *Earth Planet. Sci. Lett.* **87**, 1–12.
- Walker R. J., Carlson R. W., Shirey S. B., and Boyd F. R. (1989) Os, Sr, Nd, and Pb isotope systematics of Southern African peridotite xenoliths; implications for the chemical evolution of subcontinental mantle. *Geochim. Cosmochim. Acta* **53**, 1583–1595.
- Walker R. J., Echeverria L. M., Shirey S. B., and Horan M. F. (1991) Re-Os isotopic constraints on the origin of volcanic rocks, Gorgona Island, Colombia: Os isotopic evidence for ancient heterogeneities in the mantle. *Contrib. Mineral. Petrol.* **107**, 150–162.
- Walker R. J., Morgan J. W., and Horan M. F. (1995)  $^{187}\text{Os}$  enrichment in some mantle plume sources: Evidence for core-mantle interaction? *Science* **269**, 819–822.
- Walker R. J., Morgan J. W., Beary E., Smoliar M. I., Czamanske G. K., and Horan M. F. (1997a) Applications of the  $^{190}\text{Pt}$ - $^{186}\text{Os}$  isotope system to geochemistry and cosmochemistry. *Geochim. Cosmochim. Acta* **61**, 4799–4808.
- Walker R. J., Morgan J. W., Hanski E. J., and Smolkin V. (1997b) Re-Os systematics of Early Proterozoic ferropicrites, Pechenga Complex, NW Russia: Evidence for ancient  $^{187}\text{Os}$  enriched plumes. *Geochim. Cosmochim. Acta* **61**, 3145–3160.
- Walker R. J., Storey M., Kerr A. C., Tarney J., and Arndt, N. T. (1999) Implications of  $^{187}\text{Os}$  isotope heterogeneities in a mantle plume: Evidence from Gorgona Island and Curacao. *Geochim. Cosmochim. Acta* **63**, 713–728.
- Wanke H. and Dreibus G. (1988) Chemical composition and accretion history of terrestrial planets. *Phil. Trans. Roy. Soc. London* **A325**, 545–557.
- Warren P. H. and Kallemeyn G. W. (1996) Siderophile trace elements in ALH84001, other SNC meteorites and eucrites: Evidence of heterogeneity, possibly, time-linked, in the mantle of Mars. *Meteoritics & Planet. Sci.* **31**, 97–105.
- Warren P. H., Kallemeyn G. W., and KYTE F. T. (1999). Origin of planetary cores: Evidence from highly siderophile elements in Martian meteorites. *Geochim. Cosmochim. Acta* **63**, 2105–2122.
- Wooden J. L., Shih C.-Y., Nyquist L. E., Bansal B. M., Wiesmann H., and McKay G. A. (1982) Rb-Sr and Sm-Nd isotopic constraints on the origin of EETA79001: A second Antarctic shergottite. *Proc. Lunar Planet. Sci.* **XIII**, 879–880.
- Zipfel J., Spettel B., Palme H., and Dreibus G. (1999) Petrology of and chemistry of Dar Al Gani 476, a new basaltic shergottite. *Lunar Planet. Sci.* **XXX** #1206.
- Zuber M. T., Solomon S. C., and 13 others (2000) Internal structure and early thermal evolution of Mars from Mars Global Surveyor topography and gravity. *Science* **287**, 1788–1793.