



Precursors of Mars: Constraints from nitrogen and oxygen isotopic compositions of martian meteorites

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Abstract—We present an approach to assess the nature of materials involved in the accretion of Mars by the planet's nitrogen ($\delta^{15}\text{N}$) and oxygen ($\Delta^{17}\text{O}$) isotopic compositions as derived from data on martian meteorites. $\delta^{15}\text{N}$ for Mars has been derived from nitrogen and xenon systematics, while $\Delta^{17}\text{O}$ has been taken from the literature data. These signatures indicate that Mars has most probably accreted from enstatite and ordinary chondritic materials in a ratio of 74:26 and may not have a significant contribution from the carbonaceous (CI, CM, or CV) chondrites. This is consistent with the chromium isotopic ($\epsilon^{53}\text{Cr}$) signatures of martian meteorites and the bulk planet Fe/Si ratio for Mars as suggested by the moment of inertia factor (I/MR^2) obtained from the Mars Pathfinder data. Further, a simple homogeneous accretion from the above two types of materials is found to be consistent with the planet's moment of inertia factor and the bulk composition of the mantle. But, it requires a core with 6.7 wt% Si, which is consistent with the new results from the high pressure and temperature melting experiments and chemical data on the opaque minerals in enstatite chondrites.

INTRODUCTION

Terrestrial planets are believed (Taylor 1994) to have formed by the accretion of early solar system objects that are represented by primitive meteorites (such as chondrites). The bulk chemical, isotopic, and geophysical properties of a planet, to a large extent, depend on the nature of materials involved in its accretion. Thus, attempts have been made by various researchers to evaluate the nature of precursor materials for the accretion of Mars based on the above parameters, as reviewed in a number of recent articles (Longhi et al. 1992; Lodders and Fegley 1997; Sanloup, Jambon, and Gillet 1999; Lodders 2000). Two important developments have affected the course of such studies. Although the geophysical parameters (such as mass, radius, and moment of inertia factor) of Mars were the basis for most of the earlier models, the discovery of martian meteorites (or SNC meteorites, McSween 1994) has provided a new set of constraints that helped to refine our understanding of planet Mars. Similarly, the uncertainties associated with the moment of inertia factor used in the earlier models (0.345 to 0.377, see Longhi et al. 1992 for a review) could be minimized (e.g., 0.366 ± 0.002 , Folkner et al. 1997) by data from the recent Mars Pathfinder mission.

The chemical and isotopic compositions of the martian meteorites, obtained over the years, have been helpful in deriving a reasonable working model of the martian mantle (Wänke and Dreibus 1988). By using this and various geophysical constraints, a number of models have been proposed in recent years for the accretion of Mars. Thus, Wänke and Dreibus (1988, WD henceforth), have proposed in a number of papers (Dreibus and Wänke 1984, 1985, and 1987; Wänke and Dreibus 1994) that Mars probably accreted from two types (A and B) of materials in a ratio of 60:40. These two precursors were presumed to be similar to CI chondrites in their major (nonvolatile) element compositions. Component 'A' was considered to be reduced and volatile-free, while component 'B' was considered to be oxidized and volatile-rich. Although a number of drawbacks of the WD model have been pointed out (e.g., Bertka and Fei 1998a; Sanloup, Jambon, and Gillet 1999), this model of the martian mantle is still favored by many workers.

A somewhat different approach using martian meteorites is based on their oxygen isotopic compositions. Oxygen forms the bulk of Mars (~40% by weight, Wänke and Dreibus 1988). It serves as a means for classifying different types of objects in the solar system (Clayton, Onuma, and Mayeda 1976), and thus is a potential tracer in the search for the

planet's precursors. Oxygen isotopic data for martian meteorites (Clayton and Mayeda 1983, 1996; Franchi et al. 1999), on a three-isotope ($\delta^{17}\text{O}$ versus $\delta^{18}\text{O}$) plot, define a line parallel to the Terrestrial Fractionation Line (TFL), which in turn, is a trend defined by high precision measurements on a wide range of samples from Earth (see Clayton 1993 for a review). The martian (meteorite) fractionation line, as it is interpreted, is defined by an offset ($\Delta^{17}\text{O} = \delta^{17}\text{O} - 0.52 \times \delta^{18}\text{O}$) of 0.321 ± 0.013 (Franchi et al. 1999) from the TFL, and points to an oxygen reservoir different from those in other meteorite classes (Fig. 1). But the oxygen isotopic signature of Mars derived from such data has been shown to be consistent with mixtures of various types of chondritic signatures. Delaney (1994) has invoked a precursor for Mars that is a mixture of 90% H and 10% bulk Murchison (CM)

chondrites. Using the mean oxygen isotopic compositions ($\delta^{17}\text{O} = 2.51 \pm 0.21$ and $\delta^{18}\text{O} = 4.31 \pm 0.31$) of SNC meteorites, Lodders and Fegley (1997, henceforth LF) have proposed a mixture of three precursors comprising H, CV, and CI chondrites in a ratio of 85:11:4 for Mars. On the other hand, a similar approach by Sanloup, Jambon, and Gillet (1999), based on the mean $\delta^{18}\text{O}$ of 4.4 ± 0.3 , has proposed a mixture (45:55) of EH and H chondrites for Mars. An interesting point arises here: although these three models are apparently based on a similar database of martian meteorites (Clayton and Mayeda 1983, 1996) and on similar (within uncertainties) $\Delta^{17}\text{O}$ and mean oxygen isotopic ratios for Mars, their results on the nature of precursors for Mars are different. Although each of them requires a variable contribution from H chondrites, the derivation of the other component(s) is

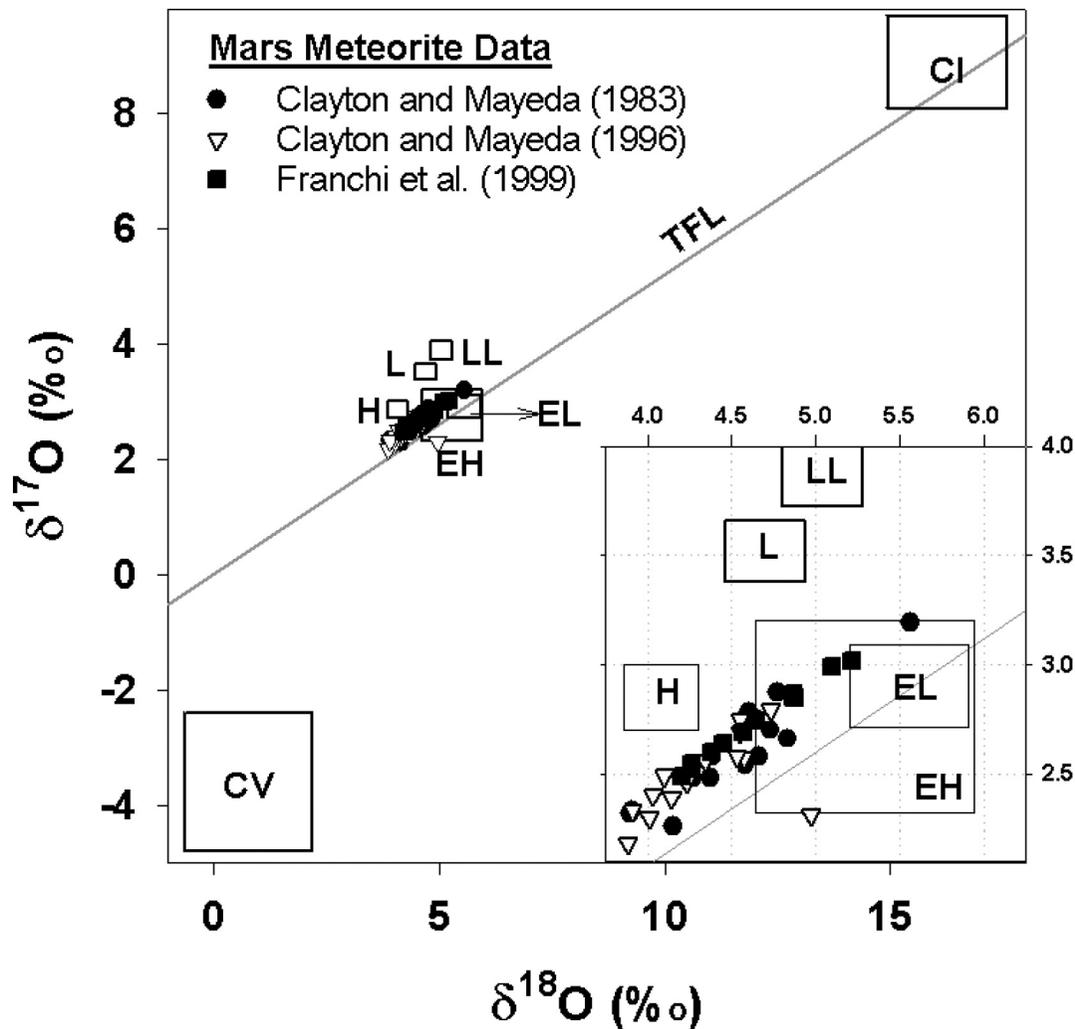


Fig. 1. Oxygen three-isotope plot showing the fields of carbonaceous (CI and CV; Clayton and Mayeda 1999), enstatite (Newton, Franchi, and Pillinger 2000), and ordinary (Clayton et al. 1991) chondrites. Also shown are the Terrestrial Fractionation Line (TFL, e.g., Clayton and Mayeda 1996) and the data for Mars (Clayton and Mayeda 1983, 1996; Franchi et al. 1999). The field of the CM chondrites, which exhibits a large scatter in the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ but is consistent with a $\Delta^{17}\text{O}$ of -4.28 (Clayton and Mayeda 1999), has not been included to avoid clutter.

somewhat ambiguous. The inconsistencies between the models of Delaney (1994) and Sanloup, Jambon, and Gillet (1999) can be explained by the fact that the oxygen isotopic signatures of Mars ($\Delta^{17}\text{O}$, $\delta^{17}\text{O}$, and $\delta^{18}\text{O}$) do not have a unique solution in terms of possible two-component mixing relations (as can be realized in Fig. 1). However, it is not clear why contributions from CM and EH chondrites are essential (respectively) in the models of Delaney (1994) and Sanloup, Jambon, and Gillet (1999), and why these have been discarded in the Lodders and Fegley (1997) model. It should be noted here that the solar type xenon isotopic signatures of the martian mantle, as inferred from the martian meteorite Chassigny (e.g., Ott 1988; Mathew and Marti 2001), are not consistent with the omission of a contribution from enstatite chondrites (which have solar-like noble gas isotopic compositions, Crabb and Anders 1981) to Mars. Further, xenon in the carbonaceous chondrites (which commonly have been invoked as a dominant precursor for Mars) is clearly different from solar in its isotopic compositions (e.g., Ozima and Podosek 1983). Similarly, the recent, more precise laser fluorination oxygen isotopic data on martian meteorites (Franchi et al. 1999) and enstatite chondrites (Newton, Franchi, and Pillinger 2000) also appear inconsistent with the omission of an enstatite chondritic component in Mars. This can be easily realized from Fig. 1, where about 30% of the martian meteorite data actually plot inside the compositional field of enstatite chondrites. We have calculated the $\Delta^{17}\text{O}$ for Mars expected for each of the models presented in Table 1. Within the uncertainties, all of these models can reproduce the $\Delta^{17}\text{O}$ of Mars (Table 1). It must however be noted that for the WD model, if we consider the mixture 60% EC + 40% CI as the source of oxygen, it would produce a low $\Delta^{17}\text{O}$.

A closer look at Fig. 1 suggests that it is very difficult to unambiguously assess the nature of precursor materials for Mars based only on the oxygen isotopic signatures of martian meteorites. Clearly, a number of mixing relations involving two or more chondritic end-members can be invoked, as can be realized from the above short review of the literature. Therefore, the results suggested by oxygen isotopic modeling have further been evaluated for each of the models by including other bulk features of Mars (see Delaney 1994; Lodders and Fegley 1997; Sanloup, Jambon, and Gillet 1999). As shown in Table 1, the density and moment of inertia of Mars, which are based on geophysical observations and are perhaps more rigid constraints than martian meteorites, also do not help us in minimizing the ambiguity presented by the earlier models. Therefore, the nature of precursor materials for Mars is far from being resolved. Clearly, other sources of constraints or information should be involved in this study.

In this paper, we present one such possible approach using the isotopic composition of nitrogen ($\delta^{15}\text{N}$) in Mars, which is based on a preliminary study presented as an abstract earlier (Mohapatra and Murty 2001). Nitrogen (like oxygen) has also been recognized as a tracer for distinguishing the different types of meteorites in the solar system (e.g., Kerridge 1993). Although it occurs in trace quantities, the isotopic composition of nitrogen in terrestrial planets has been shown to be a useful parameter that can be exploited in the search of precursor materials for a planet's accretion (e.g., Javoy 1995). But, its potential has so far not been exploited in earlier models of Mars, probably because of the lack of relevant data. We have organized the presentation in the following way: First, we derive the primordial nitrogen isotopic composition of Mars (retained in its interior-mantle,

Table 1. Models for accretion of Mars.

	Precursors	$\Delta^{17}\text{O}$ (‰)	Density (g/cc)			Moment of inertia factor
			Core	Mantle	Bulk	
Mars (observed/inferred)	?	0.321 ^a	–	–	3.935 ^b	0.3662 ^c
Models^d						
Wänke and Dreibus (1988)	(60% reduced + 40% oxidized) ^e	0.42 ^e 0.17 ^f	7.04 ^g	3.52 ^g	3.95 ^g	0.367 ^g
Delaney (1994)	90% H + 10% Murchison	0.23	7.38 ^g	3.46 ^g	3.94 ^g	0.363 ^g
Lodders and Fegley (1997)	85% H + 11% CV + 4% CI	0.20	7.27 ^g	3.5 ^g	3.92 ^g	0.367 ^g
Sanloup et al. (1999)	45% EH + 55% H	0.41	6.89 ^h	3.445 ⁱ	constraint	0.361 ^j
Present Study	74% EC + 26% OC	constraint	6.48 ^k	3.55 ^k	constraint	0.368 ^k

^aFranchi et al. (1999). The error in this estimate as quoted is 0.013.

^bTaken from a compilation by Kieffer, Jakosky, and Snyder (1992). The error in this estimate as quoted is 0.004.

^cFolkner et al. (1997). The error in this estimate as quoted is 0.0017.

^dNote that although the $\Delta^{17}\text{O}$ values for Mars obtained from the earlier models are different from that (tabulated) inferred from the recent data for martian meteorites obtained from the laser fluorination experiment of Franchi et al. (1999), they are consistent with the $\Delta^{17}\text{O}$ value of Mars (e.g., 0.3 ± 0.1 , Karlsson et al. 1992 or 0.28 ± 0.07 , Clayton and Mayeda 1996) known earlier.

^eAssuming CI as the source of oxygen.

^fBased on EC as the reduced and CI as the oxidized end-members.

^gTaken from the compilation by Lodders (2000).

^hThe error in this estimate as quoted is 0.01.

ⁱThe error in this estimate as quoted is 0.005.

^jThe error in this estimate as quoted is 0.002.

^kPlease, refer to Table 6. 'Constraint' means the (respective) value for Mars has been considered as a constraint in the models.

e.g., Mathew and Marti 2001) from the literature data on martian meteorites. Then, we try to minimize the ambiguity presented by the earlier oxygen isotopic models by considering simultaneously the isotopic composition of nitrogen ($\delta^{15}\text{N}$), as derived in the present study, and that of oxygen ($\Delta^{17}\text{O}$) for Mars as suggested by the recent laser fluorination data (Franchi et al. 1999). The results are then evaluated by using the chromium isotopic ($\epsilon^{53}\text{Cr}$) systematics of martian meteorites (e.g., Lugmair and Shukolyukov 1998), and further by the bulk planet Fe/Si ratio of Mars as predicted from its moment of inertia factor (e.g., Bertka and Fei 1998a). Finally, we present results from a preliminary geochemical modeling to derive the bulk planet chemical and geophysical properties that provide additional tests for the results obtained from the N-O isotopic systematics.

NITROGEN ISOTOPIC COMPOSITION OF MARS

Our knowledge of nitrogen in Mars is mostly based on the in situ measurements by the Viking missions and on data from laboratory study of martian meteorites. Although nitrogen in the atmosphere of Mars is isotopically distinctly heavy ($\delta^{15}\text{N} \sim +620\%$, e.g., Owen 1992), apparently because of the non-thermal loss (e.g., Fox and Dalgarno 1983) from the atmosphere, nitrogen in the interior (mantle) has been indicated to have much lighter isotopic composition ($\sim -30\%$) by data from martian meteorites (e.g., Mohapatra, Mahajan, and Murty 1998; Mathew, Kim, and Marti 1998; Marti and Mathew 2000; Mathew and Marti 2001). Nitrogen isotopic data on martian meteorites from a wide range of crystallization ages are consistent with this inference and further suggest that nitrogen in the planet's interior probably represents its primordial signatures (Pepin 1994; Mathew and Marti 2001).

Nitrogen isotopic signatures of martian meteorites are, in general, a mixture of components either trapped during their formation on Mars (indigenous component, from its mantle and atmosphere) or in situ produced during their exposure to

cosmic rays (cosmogenic component). Moreover, contamination from Earth's atmospheric nitrogen during their terrestrial residence (e.g., in the hot desert) can often be significant enough to mask the indigenous martian signatures (Murty and Mohapatra 1999; Mohapatra et al. 2001). It is not possible to resolve these components by using the isotopic composition of nitrogen alone, as it has only two isotopes. On the other hand, the measured nitrogen can be corrected for contributions from the components superimposed on the indigenous (martian) ones by using simultaneously measured nitrogen and noble gas data (Becker and Pepin 1984; Marti et al. 1995; Murty and Mohapatra 1997; Mathew, Kim, and Marti 1998; Marti and Mathew 2000; Miura and Sugiura 2000; Mathew and Marti 2001). The stepped temperature extraction commonly used in these experiments further helps in resolving the different components. The terrestrial (contamination) component in martian meteorites, as indicated by the (Earth's) air-like noble gas signatures (e.g., of $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{129}\text{Xe}/^{132}\text{Xe}$), is usually released in low temperature extractions and can be subtracted from the total gas when estimating the contributions from cosmogenic and trapped martian components.

We have derived the nitrogen isotopic composition of the martian interior (mantle) by using simultaneously measured nitrogen and xenon isotopic data on martian meteorites taken from the literature, as compiled in Table 2. It must be pointed out here that such data are available only on a few martian meteorites. In recent years, a considerable fraction of martian meteorites has been recovered from the hot deserts (see Grossman and Zipfel 2001 for a review). We have excluded data from these meteorites (Murty and Mohapatra 1999; Mohapatra et al. 2001) because of the considerable terrestrial contamination that leaves large uncertainties as to the indigenous martian signatures. Similarly, the data compiled in Table 2 have been corrected for the low temperature extractions where atmospheric contamination is indicated by the accompanying noble gas signatures, as discussed above and also by the respective sources from which the data have

Table 2. Simultaneously measured nitrogen and xenon data^a of martian meteorites used in the present study.

Sample	N (ppm)	$\delta^{15}\text{N}$ (‰)	^{132}Xe (10^{-12}ccSTP/g)	$^{129}\text{Xe}/^{132}\text{Xe}$	Meteorite
ALH 84001, B	0.75	84.9 (.6)	28.17	2.173 (.007)	ALH 84001 ^{b, c}
ALH 84001, G	0.87	55.3 (1.2)	28.92	2.04 (.010)	^c
ALH 84001, E	4.58	-17.6 (1.0)	48.07	1.63 (.02)	^c
ALH 84001, L	3.24	13.7 (.7)	43.70	2.16 (.09)	^c
AL84, 1	0.25	186 (7)	21.5	2.16 (.02)	^d
EET 79001, C2	0.264	180 (7)	28.3	2.07 (.03)	EET 79001 ^e
NK-30	0.62	32.5 (.5)	6.65	2.10 (.03)	Nakhla ^f
NK-34	0.40	32.5 (.5)	6.84	1.92 (.01)	Nakhla ^f

^aThe errors as quoted by the authors represent a 95% confidence level.

^bB, G, E, and L refer to the bulk, the >3 g/cc, ~ 3 g/cc, and <3 g/cc density separates of Murty and Mohapatra (1997).

^cMurty and Mohapatra (1997).

^dMathew, Kim, and Marti (1998).

^eBecker and Pepin (1984).

^fMurty et al. (1999).

been taken. The cosmogenic contributions for nitrogen are estimated either by using the accompanying cosmogenic ^{21}Ne and the theoretically calculated $(^{15}\text{N}/^{21}\text{Ne})_{\text{cosmogenic}}$ ratio (e.g., Mathew and Murty 1993) or by using the average $^{15}\text{N}_{\text{cosmogenic}}$ production rate of 11.6 pg/g/Ma (Kim, Kim, and Marti 1994) and the cosmic ray exposure age known from other means. The xenon data have been corrected for the cosmogenic contributions using the cosmogenic Xe spectrum suggested by Ott (1988) and Hohenberg et al. (1981). Table 3 presents the cosmogenic corrected nitrogen and xenon data in the form of $\delta^{15}\text{N}$ and $^{129}\text{Xe}^*/^{14}\text{N}$ (atomic ratio), where $^{129}\text{Xe}^*$ (radiogenic daughter produced by the decay of extinct ^{129}I , $t_{1/2} = 15.7$ Ma) is defined as:

$$^{129}\text{Xe}^* = ([^{129}\text{Xe}/^{132}\text{Xe}]_{\text{cor.}} - [^{129}\text{Xe}/^{132}\text{Xe}]_{\text{Chassigny}}) \times ^{132}\text{Xe}_{\text{cor.}} \quad (1)$$

In the above equation, the subscript cor. indicates corrected for cosmogenic contributions. The radiogenic $^{129}\text{Xe}^*$ calculated above represents an excess over the planet's initial signature for following reason: $^{129}\text{Xe}/^{132}\text{Xe}$ (of ~ 1.03) measured in Chassigny (e.g., Ott 1988; Mathew and Marti 2001) is similar (within uncertainties) to the solar signature (e.g., 1.05, Ozima and Podosek 1983), which is commonly believed to represent the initial $^{129}\text{Xe}/^{132}\text{Xe}$ signature for Mars (see Swindle 1995 for a review). At this point, it would be useful to explain the relevance of $^{129}\text{Xe}^*$ to the $\delta^{15}\text{N}$ of Mars (its mantle) that we need for the present study. As far as the noble gases are concerned, Chassigny is believed to represent the martian mantle (Swindle 1995), which is consistent with the meteorite's petrological features

(McSween 1994). The $^{129}\text{Xe}/^{132}\text{Xe}$ ratio (2.4 to 2.6; see Bogard and Garrison 1998 for a review) of the martian atmosphere is quite different from that of Chassigny. Therefore, by Equation 1, the mantle will have a $^{129}\text{Xe}^*$ value of zero, while the atmosphere will have a much higher $^{129}\text{Xe}^*$.

Also given in Table 3 are the N and Xe signatures of the martian atmosphere (MA) and mantle taken from the literature. The signatures of MA are those inferred from the Viking in situ measurements (Nier and McElroy 1977; Owen et al. 1977) and from the laboratory analyses (Becker and Pepin 1984; Marti et al. 1995) of glasses in the martian meteorites EET 79001 and Zagami (Z), while those for the mantle are based on the laboratory data on the martian meteorites only. The $^{129}\text{Xe}^*/^{14}\text{N}$ signature of the martian mantle, from the previous discussion, should be 0. Mathew and Marti (2001) have pointed out that the stepped heating data on ALH 84001 and Chassigny show the presence of a component with light $\delta^{15}\text{N}$ and solar-like $^{129}\text{Xe}/^{132}\text{Xe}$ (~ 1.03). Nitrogen isotopic composition of -30% , inferred for this component that has mantle-like xenon isotopic signatures, has been suggested by those authors to represent the ($\delta^{15}\text{N}$) of mantle nitrogen. Below, we present a different approach to derive the nitrogen isotopic composition of the martian mantle based on the radiogenic $^{129}\text{Xe}^*$.

The martian mantle is well resolved from the other known martian volatile reservoirs in terms of its $^{129}\text{Xe}^*$ (= 0) signature. In Fig. 2, a plot between $\delta^{15}\text{N}$ and $^{129}\text{Xe}^*/^{14}\text{N}$, we have shown the simultaneously acquired nitrogen and xenon isotopic data given in Table 3. A fairly good correlation

Table 3. Nitrogen and xenon data^a used in Fig. 2.

Sample	$\delta^{15}\text{N}_{\text{corr}}$ (‰)	$(^{129}\text{Xe}^*/^{14}\text{N})_{\text{atom}} (\times 10^8)$	Type of correction used
Martian meteorite data			
ALH 84001 B	46 ± 5	2.68 ± 0.38	Based on $^{21}\text{Ne}_{\text{cosm.}}$ ^b
ALH 84001 G	21 ± 5	2.11 ± 0.29	b
ALH 84001 E	-23.2 ± 1.2	0.39 ± 0.06	b
ALH 84001 L	8.8 ± 1.0	0.95 ± 0.13	b
AL84,1	85 ± 11	6.0 ± 0.6	Based on $^{15}\text{N}_{\text{cosmogenic}}$ production rate ^c
EET 79001,C2	175 ± 8	6.96 ± 0.98	b
NK-30	7.2 ± 3.8	1.21 ± 0.17	b
NK-34	4.6 ± 4.2	1.32 ± 0.18	b
Reference points ^d (based on independent other measurements)			
MM	-30	0	e
MA	620 ± 160	30 ± 6	f
Z	244 ± 25	11.9 ± 2	g

^a $\delta^{15}\text{N}$ has been corrected for cosmogenic contributions based on the procedures given by Mathew and Murty (1993) and Kim, Kim, and Marti (1994). $^{129}\text{Xe}^*$ has been estimated from the cosmogenic corrected data (based on Ott [1988] and Hohenberg et al. [1981]) by using Equation 1. Errors quoted represent 95% confidence limits.

^bMathew and Murty (1993).

^cKim, Kim, and Marti (1994).

^dRefers to the reference points in Fig. 2.

^eThe signatures of the martian mantle (MM) as inferred by Mathew and Marti (2001) from the gases released in certain temperature steps of ALH84001-b and Chassigny.

^fThe signatures of martian atmosphere (MA) inferred from the Viking in situ measurements (Nier and McElroy 1977; Owen 1992).

^gMartian atmospheric signature inferred from the stepped temperature data on Zagami (Marti et al. 1995); Z refers to the mean of ZA and ZB signatures.

between $\delta^{15}\text{N}$ and $^{129}\text{Xe}^*/^{14}\text{N}$ is observed for the martian meteorite data. The computed linear correlation with a consideration (using the algorithm suggested by Williamson 1968) of the uncertainties on both the variables yielded an intercept of $-30 \pm 9\%$ and slope of $(30 \pm 9) \times 10^8$. The regression in Fig. 2 (which only includes the martian meteorite data and not the reference points, see Table 3), passes on the lower end through Chassigny (martian mantle) and in the upper end (see inset) slightly above the Viking derived martian atmosphere. If we consider the uncertainties involved in the regression parameters, MA touches the regression line (wedge to be precise). It must be realized here that although the Viking data have provided us a base for defining MA, they have large uncertainties. More precise signatures of MA have been inferred however from the laboratory measurements of martian meteorites (e.g., Becker and Pepin 1984; Marti et al. 1995). In Fig. 2, we have shown the inferred signatures for MA based on the (mean) data from the Zagami glasses (Z) from Marti et al. (1995). The signature thus derived also falls (within uncertainties) in the regression

zone although it has also not been considered in the regression analysis. As mentioned above in estimating the regression in Fig. 2, we have excluded the Chassigny (MM), MA, and Zagami glass (ZA) points for the following reason: The datum for Chassigny is not included because we want to independently arrive at the $\delta^{15}\text{N}$ of Mars mantle. Similarly, the datum ZA (1200°C data from Zagami, Marti et al. 1995) could be affected by the possible elemental fractionation as a result of differential release patterns of N and Xe which can produce a further source of uncertainties (which also cannot be assessed) in the cosmogenic corrections involved and hence in the $\delta^{15}\text{N}$ and $^{129}\text{Xe}^*/^{14}\text{N}$ signatures of the point ZA. It should also be mentioned here that the points ZA and MA, with their larger uncertainties, do not significantly affect the regression in Fig. 2. On the contrary, we have computed the regression independent of these data points (which happened to be dominated by particular Mars components: Chassigny = mantle, MA and Zagami = atmosphere), which we use as reference points (in Table 3) to evaluate the regression.

The correlation in Fig. 2 is somewhat similar to that

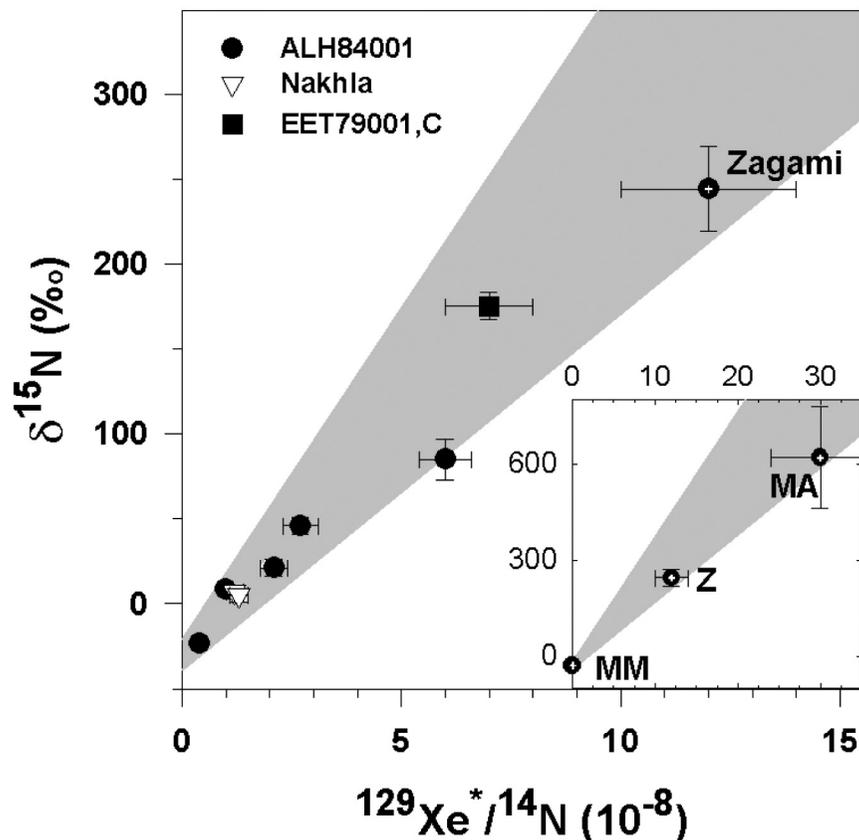


Fig. 2. Plot of $\delta^{15}\text{N}$ versus $(^{129}\text{Xe}^*/^{14}\text{N})_{\text{atom}}$ for the martian meteorite data in Table 3, (also in a compressed scale in the inset). Also shown are the data for three reference points: martian mantle (MM), martian atmosphere (MA), and martian atmosphere as derived from the data on Zagami. The linear correlation (intercept = $-30 \pm 9\%$, slope = $[30 \pm 9] \times 10^8$) between $\delta^{15}\text{N}$ and $(^{129}\text{Xe}^*/^{14}\text{N})_{\text{atom}}$, estimated by considering the uncertainties in both the variables (following Williamson 1968), has been shown along with the uncertainties in the regression parameters (as shown by the shaded region). It must be noted that the regression does not include the above reference points (MM, MA, and Z).

observed by Becker and Pepin (1984) for $\delta^{15}\text{N}$ and $^{40}\text{Ar}/^{14}\text{N}$. But as mentioned earlier, their observation is based on the data of EET 79001 only, while in Fig. 2, we have used several martian meteorites that differ widely in their ages. The correlation line (which is also a wedge) defined by their $\delta^{15}\text{N}$ and $^{40}\text{Ar}/^{14}\text{N}$ data also passes (within uncertainties) through the martian atmospheric point. In fact, this was one of the key arguments that established the genetic relationship between the SNC meteorites and Mars. The intercept (varying from ~ -50 to 0% , as read from their Fig. 2) of the line does not actually resolve the 'indigenous' martian component (as they refer to) from the terrestrial atmosphere. Becker and Pepin (1984) have interpreted the observed correlation (line) in their EET 79001 data as a two component mixing between the martian interior and atmosphere, as it passes through these two points. This is consistent with the geological evolution known for these meteorites. They trapped the mantle gases during crystallization from the mantle-derived magmas and the atmospheric gases later, either because of secondary processes (such as weathering, e.g., Drake et al. 1994) or impact implantation (e.g., Wiens and Pepin 1988). As one would expect the trapped gases in these meteorites to be a two-component mixture of the martian mantle and atmospheric gases, it is tempting to interpret the correlation in Fig. 2 as a mixing line.

However, the evolution of the atmospheric nitrogen and noble gases in Mars appears inconsistent to the above interpretation. Nitrogen in the martian atmosphere has been shown to be continuously being lost due to photo ionization by the solar ultraviolet rays (e.g., Fox and Dalgarno 1983; Pepin 1994). The experimental evidence for this loss process has been provided by nitrogen and noble gas data from ALH 84001 (Murty and Mohapatra 1997; Mathew and Marti 2001). As the atmospheric loss process more preferentially removes the light isotope of nitrogen (^{14}N), $\delta^{15}\text{N}$ (which is a function of the $^{15}\text{N}/^{14}\text{N}$ signature) of MA has been increasing in geological time. Thus, the MA trapped in ALH 84001, which formed ~ 4 Ga ago, appears to have a lower ($\sim +46\%$, Murty and Mohapatra 1997) $\delta^{15}\text{N}$ as compared to that ($\sim +620\%$, e.g., Owen 1992) of the contemporary MA. Therefore, in Fig. 2, it appears surprising to find the MA trapped in ALH 84001 (formed ~ 4 Ga ago) and in the younger martian meteorites (≤ 180 Ma) to fall along the same correlation line. The regressions computed separately for ALH 84001 (intercept = $-30 \pm 12\%$, slope = $[30 \pm 11] \times 10^8$) and the rest (intercept = $-31 \pm 9\%$, slope = $[29 \pm 5] \times 10^8$) in Fig. 2, within the uncertainties, are indistinguishable. Below, we present an explanation for this seemingly paradoxical situation.

In Fig. 2, the correlation line can be described by the following equation.

$$\delta^{15}\text{N} = (\text{slope} \times [^{129}\text{Xe}^*/^{14}\text{N}]) + \text{intercept} \quad (2)$$

In principle, such a line can be derived by varying the elemental ratio ($^{129}\text{Xe}^*/^{14}\text{N}$) plotted along the horizontal axis, which in turn must vary $\delta^{15}\text{N}$ (plotted along the vertical axis)

with the constraints from the slope and intercept of the line. A variation in the elemental ratio can be achieved in two ways: 1) by varying either of the two ($^{129}\text{Xe}^*$ or ^{14}N) elements, and 2) by mixing two reservoirs which have different $^{129}\text{Xe}^*/^{14}\text{N}$ signatures.

The concentrations of $^{129}\text{Xe}^*$ of MA can be considered constant in the time period during which ALH 84001 and the other martian meteorites formed. Because, ^{129}I (the parent nuclide) would only be active in the early history of Mars (the first ~ 100 Ma of the solar system) even before ALH 84001 formed. On the other hand, the atmospheric loss process discussed above, which decreases the amount of ^{14}N in MA with time, provides a mechanism to vary $^{129}\text{Xe}^*/^{14}\text{N}$ in Fig. 2. As the amount of $^{129}\text{Xe}^*$ in MA is constant, this (loss) would increase this elemental ratio with time. As shown earlier, a decrease in ^{14}N is also reflected in a corresponding increase in $\delta^{15}\text{N}$, as the loss is inefficient for the heavier isotope. The correlation line in Fig. 2 would therefore represent the evolution of martian atmospheric nitrogen. At the point (in time) when it formed, MA had signatures similar to that of the mantle (the intercept). Subsequent evolution by loss of atmospheric nitrogen moves it (MA) along the line. This might be an explanation for the reason why atmospheres trapped in ALH 84001 and the younger martian meteorites all fall along the same line. As per Equation 2, the slope of the line in Fig. 2 is a constant.

Samples which are the result of mixing of two reservoirs that have different $\delta^{15}\text{N}$ and $^{129}\text{Xe}^*/^{14}\text{N}$ signatures, will fall along (ideally on) a line joining these two end-members (e.g., Faure 1986). Therefore, a line through MM and MA, as observed in Fig. 2, can also be explained by a mixing line between these two end-members. A sample derived from the mantle (MM) at any point in time traps gases from the mantle (represented by the intercept) and acquires the ambient atmospheric gases (that fall along the line depending on the age) during its later evolution.

In either of these two cases, the intercept of the correlation line would give us the $\delta^{15}\text{N}$ of the martian mantle. We take the value of $-30 \pm 9\%$ (obtained from the regression of all the data) for the present purpose because it has the least error and is also similar to the signature that has been inferred from other independent means (e.g., Mathew and Marti 2001). In Fig. 2, the deviations of some of the data from the regression line could be a reflection of the possible presence of additional mantle components such as Chassigny-E (with slightly different $^{129}\text{Xe}^*$, Mathew and Marti 2001) and elemental fractionation during the trapping of martian atmospheric gases (as in Nakhilites and ALH 84001, Drake et al. 1994; Murty and Mohapatra 1997). An important corollary to the correlation in Fig. 2 is that the nitrogen isotopic compositions of the martian mantle trapped in the ancient (ALH 84001) as well as the younger martian meteorites are similar. (This feature is also pointed out by the earlier studies, as mentioned in the beginning of this section.) This, in turn, would mean that the mantle nitrogen isotopic composition has

been the same at least during the last 4 Ga, and probably represents the planet's primordial $\delta^{15}\text{N}$ signature, as pointed out by Mathew and Marti (2001).

The $\delta^{15}\text{N}$ for the martian mantle can also be obtained from the correlation of nitrogen and argon. The $^{40}\text{Ar}/^{36}\text{Ar}$ of the martian atmosphere has been measured by the Viking missions to be 3000 ± 500 (Owen et al. 1977; Owen 1992), while signatures like 2400 have been suggested from the study of martian meteorites (Wiens, Becker, and Pepin 1986). The $^{40}\text{Ar}/^{36}\text{Ar}$ signature of the martian mantle is not well constrained due to large and uncertain corrections involved for the in situ radiogenic growth of ^{40}Ar , and the cosmogenic contributions to ^{36}Ar , although martian meteorite data suggest values <900 (Bogard 1997; Mohapatra, Mahajan, and Murty 1998; Terribilini et al. 1998). Nevertheless, one observes a rough correlation between the trapped $\delta^{15}\text{N}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ signatures of martian meteorites. While heavy (trapped) $\delta^{15}\text{N}$ signatures (up to $\sim +280\%$) in martian meteorites (e.g., Becker and Pepin 1984; Marti et al. 1995) are accompanied by (trapped) $^{40}\text{Ar}/^{36}\text{Ar}$ values comparable to that of the martian atmosphere, light signatures ($\delta^{15}\text{N} \sim -30\%$, Mohapatra, Mahajan, and Murty 1998; Mathew and Marti 2001) are accompanied by lower $^{40}\text{Ar}/^{36}\text{Ar}$ values suggestive of mantle argon.

As compared to the $\delta^{15}\text{N}$ signature of $-30 (\pm 9)\%$ derived above for Mars, those predicted by the models compiled in Table 1 are: $1.6 (\pm 7.7)\%$ for Delaney (1994), $-2.4 (\pm 8.7)\%$ for LF, and $-13.8 (\pm 9.0)\%$ for Sanloup, Jambon, and Gillet (1999). The WD model would predict a $\delta^{15}\text{N}$ of $43 (\pm 15)\%$ if one assumes CI as the source of the nitrogen, and $0.4 (\pm 12)\%$ if one uses a mixture of 90% EC and 10% OC. It must be noted here that the Mars model proposed by Anderson (1972), which invokes a mixture of 75% C3 and 25% OC, would, however, produce a $\delta^{15}\text{N}$ of $-17 (\pm 11)\%$, similar (considering the uncertainties) to the value for Mars derived in the present study. But the $\Delta^{17}\text{O}$ signature of -2.75% predicted by this model is quite different from the signature for Mars as derived from the martian meteorite data (Table 1).

OXYGEN ISOTOPIC COMPOSITIONS OF MARTIAN METEORITES

Oxygen isotopic data for bulk samples of martian meteorites, in terms of $\delta^{18}\text{O}$, vary from 3.9 to 5.6‰ (Clayton and Mayeda 1983, 1996), while the extracted water (Karlsson et al. 1992) and the low temperature phases (e.g., Romanek et al. 1998; Treiman and Romanek 1998; Farquhar and Thiemens 2000) show a variation over a few tens of ‰ in $\delta^{18}\text{O}$. A variation like this is a feature common to differentiated solar system objects (such as achondrites and planets, Clayton and Mayeda 1996) and, in most cases, can be explained by mass dependent fractionation. Indeed, the martian meteorite data fall along a line parallel to the terrestrial fractionation line (TFL, Fig. 1), supporting the

view of mass dependent isotopic fractionation. As mentioned earlier, the offset ($\Delta^{17}\text{O} \sim 0.3$) of the martian fractionation line from the TFL on the $\delta^{17}\text{O}$ axis is characteristic of Mars and distinguishes it from other solar system objects. Unlike the earlier oxygen-isotope models (discussed above), which (probably except Delaney 1994) are based on the mean $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of Mars derived from the martian meteorite data, we have used the $\Delta^{17}\text{O}$ of Mars for the present study because of the following reasons. $\Delta^{17}\text{O}$ is a characteristic property of differentiated bodies like Mars (Clayton and Mayeda 1996) and (as the authors argue) preserves the signatures of the precursors better than the $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of such bodies. $\Delta^{17}\text{O}$ also provides a way to look at the nitrogen and oxygen isotopic systematics simultaneously (in a single plot), which we would use for evaluating the different precursors for Mars (in the next section). Moreover, by using $\Delta^{17}\text{O}$, the uncertainties associated with deriving the mean values, and with the assumptions regarding the effect of planetary differentiation on the samples chosen, are also minimized. The value of $\Delta^{17}\text{O}$ as derived by high precision data from recent laser fluorination experiments of Franchi et al. (1999) is 0.321 ± 0.016 (compared to the earlier values of 0.3 ± 0.1 , Karlsson et al. 1992; 0.28 ± 0.07 , Clayton and Mayeda 1996), which we use for the present study.

NITROGEN AND OXYGEN ISOTOPIC SYSTEMATICS OF MARS

The $\delta^{15}\text{N}$ and $\Delta^{17}\text{O}$ signatures from the above discussion provide the first-hand constraints on the nature of precursor materials for Mars. $\delta^{15}\text{N}$ of -30% narrows the precursors to enstatite (EC, $\delta^{15}\text{N} = -28 \pm 10\%$, Table 1A) and CV ($\delta^{15}\text{N} = -22 \pm 12\%$) chondrites. The $\Delta^{17}\text{O}$ of Mars does not match with any of the chondrites (or any single known solar system reservoir). One can, in principle, reproduce the martian signature by mixing an end-member having $\Delta^{17}\text{O} > 0.321$ with another having $\Delta^{17}\text{O} < 0.321$. As obvious from Fig. 1 and the earlier discussion, this leaves us with a number of possibilities. If we use the constraints imposed by $\delta^{15}\text{N}$, two (in addition to those inferred from $\delta^{15}\text{N}$) other end-members can be considered: the ordinary chondrites ($\Delta^{17}\text{O} = 0.73$ to 1.26) and CI chondrites ($\Delta^{17}\text{O} = 0.43$).

In Fig. 3 (in the inset), a plot between $\delta^{15}\text{N}$ and $\Delta^{17}\text{O}$, we have shown data for the four potential end-members (CI, CV, EC, and OC) short-listed above, the binary mixing lines between them, and the data for CM (as required by the Delaney 1994 model) and Mars. The end-member parameters used in the calculation of the mixing curves have been given in Table 1A. The datum for Mars falls in the mixing zone of EC and OC, indicating possible contributions (at least for its nitrogen and oxygen) from these two precursors. A blown up view of the EC-OC mixing zone has been given in the main figure, where the tick marks represent different contributions of OC. It requires a mixture of EC and OC in a ratio $\sim 74:26$

(±4) to explain the nitrogen and oxygen isotopic compositions of Mars. A significant contribution from the carbonaceous (CI, CM, or CV) chondrites can be ruled out, as in such cases, one would expect the Mars datum to fall in the mixing regimes involving those end-members. For example, the datum for Mars falls (in terms of $\delta^{15}\text{N}$) below the lower limit of the OC-CV mixing line. Possible mixing of three and four components was also examined, which resulted in negative contributions for one or two of the end-members considered. In Fig. 3, it is not possible to resolve the particular type of EC or OC that contributed to the accretion of Mars, as the mixing regimes between them overlap. Nevertheless, we examined the mixing between the

different types of the EC (EH, EL) and OC (H, L, LL) by considering any two at a time, the results of which have been presented in Table 4. As can be seen, the $\delta^{15}\text{N}$ and $\Delta^{17}\text{O}$ of Mars are consistent with a number of combinations, in which the EC (or its sub-class) contributions vary from 62 to 80%. Below, we try to resolve these mixing relations by the chromium-oxygen isotopic systematics and the bulk planet Fe/Si ratio of Mars.

$\varepsilon^{53}\text{Cr}$ VERSUS $\Delta^{17}\text{O}$

^{53}Cr is a decay product of the now extinct nuclide ^{53}Mn ($T_{1/2} = 3.7$ Ma). Different types of chondrites show a variation

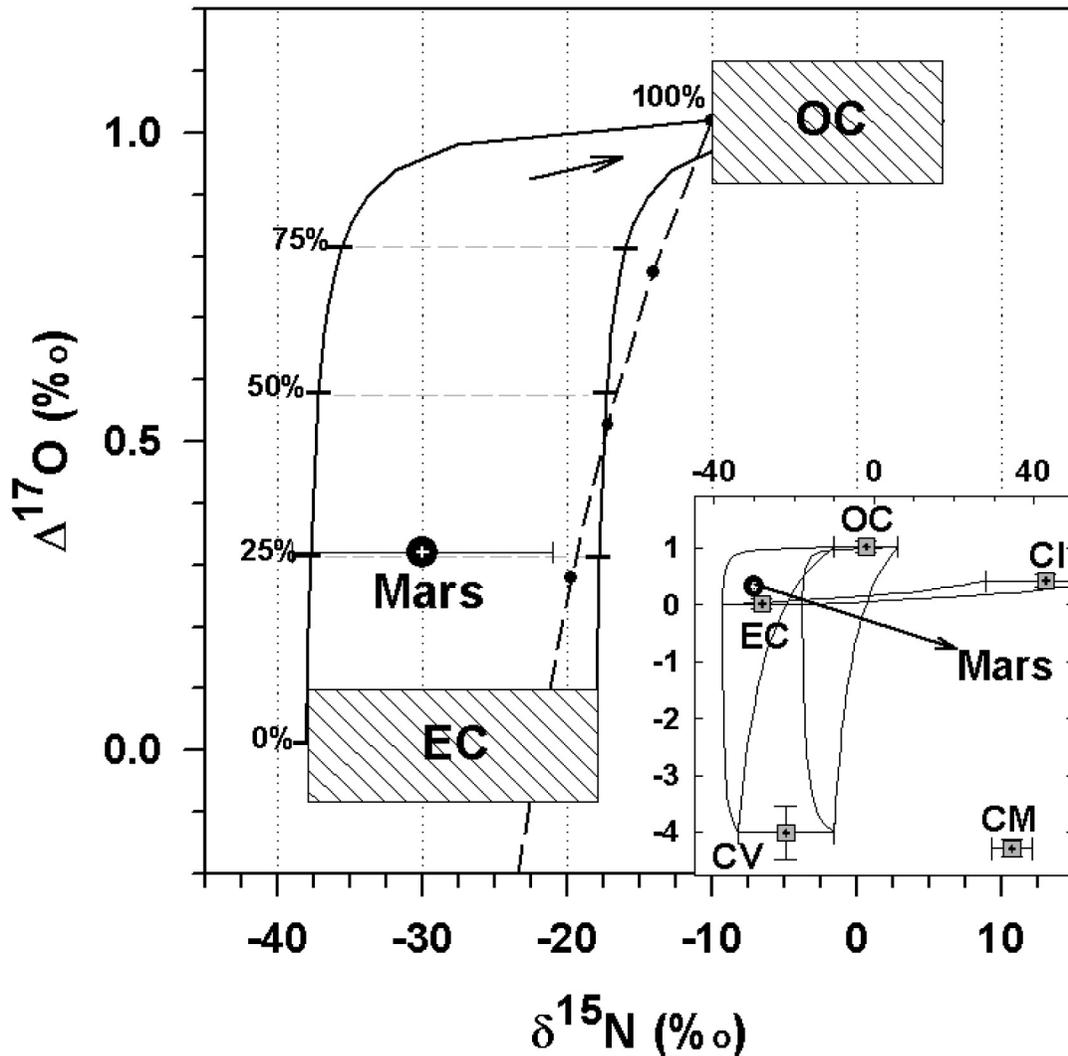


Fig 3. Binary mixings for four plausible (see text for discussion) precursor chondrites (inset) are shown in a plot between $\delta^{15}\text{N}$ and $\Delta^{17}\text{O}$. The datum for Mars falls in the mixing region between OC and EC (shown in the extended scale). Tick marks (of 25%) on the EC-OC mixing curves represent different contributions from OC, while the different contributions (in increments of 5%) from CV to a mixing between CV and OC can be read from the dots on the OC-CV mixing curve (which represents the lower limit). CI stands for carbonaceous Ivuna, CM for carbonaceous Murray, CV for carbonaceous Vigarano, EC for enstatite chondrites, and OC for ordinary chondrites.

in the concentration of the radiogenic daughter ^{53}Cr represented by $\epsilon^{53}\text{Cr}$, which is defined as the deviation (multiplied by 10,000) of the $^{53}\text{Cr}/^{52}\text{Cr}$ ratio of a sample from the corresponding normal terrestrial ratio (e.g., Lugmair and Shukolyukov 1998). $\epsilon^{53}\text{Cr}$ of martian meteorites vary from 0.21 to 0.27 (Lugmair and Shukolyukov 1998), from which a mean signature of 0.23 ± 0.05 can be derived for Mars. The ^{53}Cr excess for Mars is one of the parameters that distinguishes Mars from other objects in solar system. In Fig. 4, a plot between $\Delta^{17}\text{O}$ and $\epsilon^{53}\text{Cr}$, we show the end-members EC, OC, CI, and the binary mixing lines between them (and with CV), estimated based on the end-member parameters given in Table 1A. The datum for Mars lies on the mixing line between EC and OC and is consistent with the mixing relation (74% EC + 26% OC) suggested by the nitrogen and oxygen isotopic systematics (Fig. 3). It must be noted here that in Fig. 4, the $\epsilon^{53}\text{Cr}$ values of the carbonaceous chondrites (CI and CV, which falls beyond the scale) actually represent the lower limits, the upper limits of which are uncertain because of the second order correction (e.g., Shukolyukov et al. 2000) involved in their estimation. Still, possible contributions from the carbonaceous chondrites do not appear promising even if one considers the uncertainties (e.g., lower limits) in the $\epsilon^{53}\text{Cr}$ values of CI and CV as shown in the figure.

The $\epsilon^{53}\text{Cr}$ of Mars, falling between those for the Earth-Moon system and the ‘asteroidal belt’ (meteorites), is consistent with a radial gradient of ^{53}Mn distribution in the late solar nebula (Lugmair and Shukolyukov 1998; Shukolyukov and Lugmair 1999, 2000a). The $\epsilon^{53}\text{Cr}$ of Mars also falls in between enstatite chondrites ($\epsilon^{53}\text{Cr} = 0.16$, Shukolyukov and Lugmair 1999) and ordinary chondrites ($\epsilon^{53}\text{Cr} = 0.48$, Lugmair and Shukolyukov 1998). Shukolyukov and Lugmair (1999), from the correlation of $\epsilon^{53}\text{Cr}$ for solar system objects with the heliocentric distance, have suggested that enstatite chondritic materials (EC) probably formed near 1.4 AU in the solar nebula. If ordinary chondritic materials (OC) formed in the asteroidal belt (~2.6 AU), then the $\epsilon^{53}\text{Cr}$ of Mars at 1.524 AU would be consistent with an accretion from EC and OC type materials.

BULK PLANET Fe/Si RATIO

The bulk planet Fe/Si ratio is an important chemical parameter that has been used in evaluating the nature of materials that accreted to form terrestrial planets (e.g., Ohtani and Kamaya 1992; Sohl and Sphon 1997; Bertka and Fei 1998a and b). Bertka and Fei (1998a) have shown that the moment of inertia factor of Mars, derived from the Mars Pathfinder data, together with the model of the martian mantle (WD) inferred from the martian meteorites and possible core compositions, predicts a range of 1.319 to 1.509 for the bulk planet Fe/Si. The WD mantle (as it is commonly called) is based on the bulk chemical compositions of martian meteorites. Bulk features of the martian mantle obtained from

Table 4. Possible mixing combinations between the subclasses of EC and OC that can explain the $\delta^{15}\text{N}$, $\Delta^{17}\text{O}$, $\epsilon^{53}\text{Cr}$, and the predicted Fe/Si values for Mars.

	Mixing relations	EC	OC	Fe/Si ^a
		(Fractions)		
1.	EH – H	0.62	0.38	1.695
2.	EH – L	0.76	0.24	1.585
3.	EH – LL	0.80	0.20	1.565
4.	EH – Mean OC	0.74	0.26	1.603
5.	EL – H	0.62	0.38	1.340
6.	EL – L	0.76	0.24	1.178
7.	EL – LL	0.80	0.20	1.141
8.	EL – Mean OC	0.74	0.26	1.198
9.	Mean EC – H	0.62	0.38	1.511
10.	Mean EC – L	0.74	0.26	1.373
11.	Mean EC – LL	0.80	0.20	1.346
12.	Mean EC – Mean OC	0.74	0.26	1.392

^aValues that fall in the range 1.319–1.509, suggested by Bertka and Fei (1998a), are indicated in bold (also see Fig. 5).

the other models (e.g., Delaney 1994; Lodders and Fegley 1997; Sanloup, Jambon, and Gillet 1999) do not significantly differ from those predicted by the WD model.

We have calculated the expected Fe/Si for Mars for each of the mixing relations in Table 4, the results of which have been plotted in Fig. 5 in the form of a bar diagram. The numbers on the bars refer to corresponding mixing relations in Table 4. The mixing of (mean) EC and (mean) OC in a ratio 74:26 (derived in Fig. 3 and 4) gives a bulk planet Fe/Si ratio of 1.392, which (12) falls well within the range of the Fe/Si of Mars suggested by Bertka and Fei (1998a). As can be seen, three more cases (5, 10, and 11) also fall in the range of the Fe/Si for Mars. But these possibilities cannot be resolved from the mixing between mean EC and OC by the $\delta^{15}\text{N}$, $\Delta^{17}\text{O}$, and $\epsilon^{53}\text{Cr}$ systematics (in Figures 3 and 4). In Fig. 5 we also show the expected Fe/Si for some of the earlier models (Anderson 1972; WD; Delaney 1994; LF; Sanloup, Jambon, and Gillet 1999), all of which, except for Anderson (1972), result in Fe/Si ratios that are greater than the upper limit for Mars. The Fe/Si ratio for the Anderson (1972) model, if we use mean C3 (CV and CO, Heide and Wlotzka 1994) and mean OC values, would result in a Fe/Si (=1.464) ratio that is consistent with the Bertka and Fei (1998a) range. But this model, as mentioned earlier, is not consistent with the $\Delta^{17}\text{O}$ signature of Mars.

CHEMICAL COMPOSITION OF MARS

Using the case of accretion of Mars from a mixture of 74% EC and 26% OC, we estimated (Tables 5 and 6) the bulk features (bulk chemical compositions, densities, and sizes) of the martian core and mantle + crust and the planet’s moment of inertia factor (I/MR^2). Below, we discuss some of the salient features of this preliminary geochemical modeling in

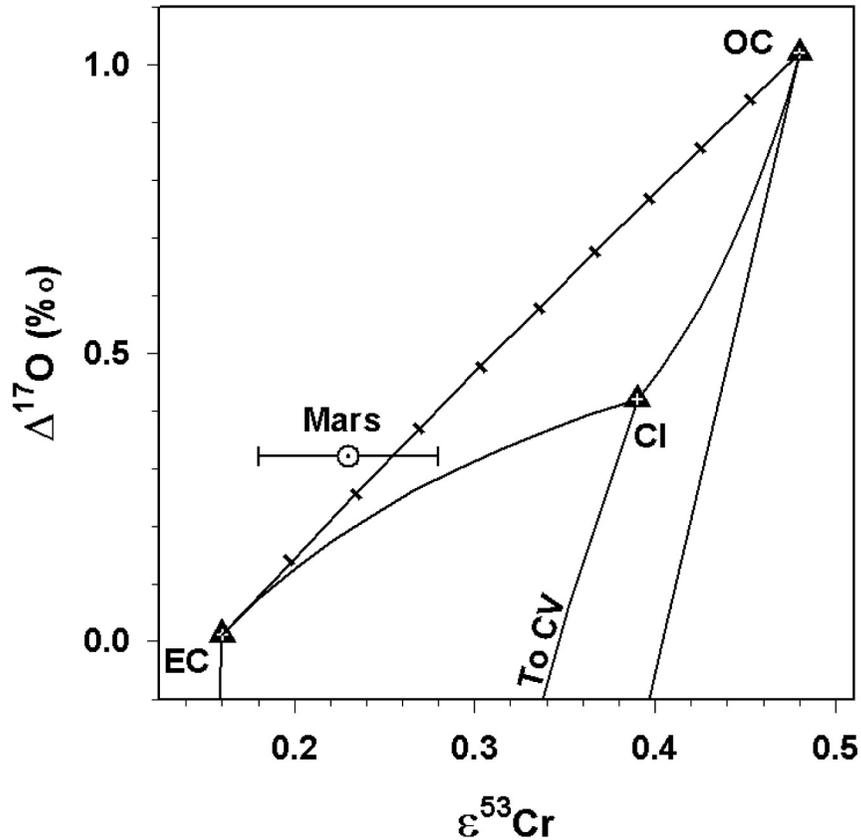


Fig. 4. Plot of $\epsilon^{53}\text{Cr}$ versus $\Delta^{17}\text{O}$. The mean of the martian meteorite data (Lugmair and Shukolyukov 1998) falls on the EC-OC mixing curve, and is consistent with a 75% EC + 25% OC mixing relation as shown by the tick marks (in increments of 10% of OC) on the EC-OC mixing curve. The $\epsilon^{53}\text{Cr}$ values of the carbonaceous chondrites (CI and CV) represent the lower limits (see text for discussion).

relation to the existing knowledge about Mars and terrestrial-planetary interiors.

The bulk planet Fe concentration suggested by the present mixture is 24.7 wt% (Table 5), which is consistent with the range of 23.10 to 26.29% suggested by Bertka and Fei (1998a). If we assume that all the Fe (with a zero pressure density of 7.9 g/cc) inherited from the precursors resides in the martian core, then the present model would predict a core with a radius of 1686 km. But, clearly, a part of this iron has been distributed in the rest of the planet (mantle and crust), as has been indicated by the martian meteorite data (which contain ~17 wt% of FeO, Wänke and Dreibus 1988).

The fraction of Fe in the martian mantle and crust at the end of core formation was governed by the ambient oxygen fugacity. We modeled this using a procedure similar to that commonly adopted by other models (e.g., Lodders and Fegley 1997). In the first step, the oxygen inherited by Mars by accretion was used in stoichiometric amounts for forming the oxides of the major elements (Table 6), the surplus being used to form the oxide of iron (FeO). These oxides formed the bulk of the mantle and crust. The rest of the Fe and all of S, Ni, and Co were assigned to the core. This resulted in high SiO_2 (55 wt%) and low FeO (6 wt%) concentrations in the mantle and

a low I/MR^2 for the planet. But, martian meteorite data predict that the martian mantle should have about 17 wt% FeO (e.g., Longhi et al. 1992). Using this as a constraint, we have examined the effect of the partitioning of silicon and phosphorous in between the mantle and core. The composition of mantle + crust and core presented in Table 6 could thus be obtained by allowing small fractions of the planet's Si into the core and P into the mantle. The core thus produced accounts for 23% of the mass and 52% of the radius of Mars and has 6.7 wt% Si. Iron in the core has been partitioned into the phases Fe, FeS, FeSi, $(\text{Ni, Fe})_5(\text{Si, P})_2$ based on the inferences from the mineralogy of enstatite chondrites (e.g., Lin and El Goresy 2002) and high pressure and melting studies (e.g., Dobson, Vocadlo, and Wood 2002). For the estimation of the density for the core (6.5 g/cc), we have used the densities for Fe, FeS, and Ni from Goettel (1981), and the zero pressure density of Co (8.9 g/cc, e.g., Hammond 1970). The density of FeSi has been calculated from the unit cell parameters determined by Dobson, Vocadlo, and Wood (2002), while that (zero pressure density) for $(\text{Ni, Fe})_5(\text{Si, P})_2$ has been taken to be 7.56 g/cc (Roberts, Rapp, and Weber 1990). By using the constraints imposed by the mass and radius of Mars, the estimated core (above), and a

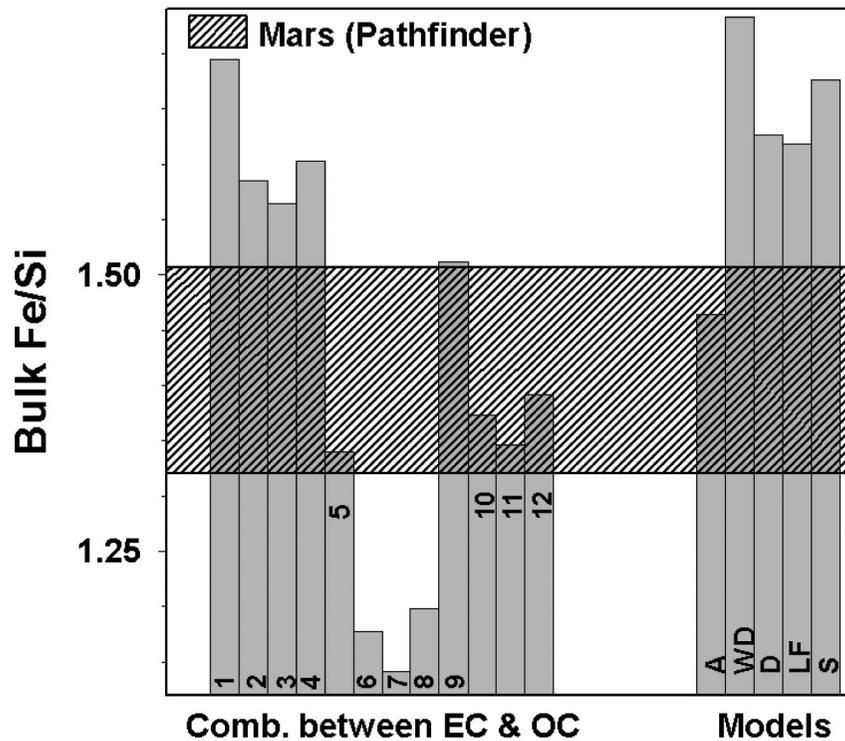


Fig. 5. Plot showing the possible combinations (numbers that corresponds to) of mixing between EC and OC (the numbers correspond to those in Table 4) and the consequent Fe/Si ratios (wt%) against the range of ratios predicted from the Mars Pathfinder data (Bertka and Fei 1998). Also shown are the Fe/Si ratios of different models (A = Anderson (1972); WD = Wänke and Dreibus (1988); D = Delaney (1994); LF = Lodders and Fegley (1997); S = the model: 45% EH + 55% H of Sanloup, Jambon, and Gillet. (1999).

crust with an assumed thickness of 50 km and density of 2.9 g/cc, we derived the density of the mantle to be 3.55 g/cc. This distribution of densities resulted in a moment of inertia factor of 0.368 ± 0.003 , where the uncertainties reflect those involved in the mixing ratios (± 4), densities of the core phases (some used in Table 6 are the zero pressure densities), and finally, the mean thickness of the crust (20 to 80 km) and its density (2.7 to 3 g/cc). Within the uncertainties, the moment of inertia factor is similar to that (0.366 ± 0.002) suggested by Folkner et al. (1997).

We would like to point out here that the model of Mars presented in Tables 5 and 6 and in the discussion above is based on the simplistic approach that assumes a homogeneous accretion. The estimates of the bulk properties (such as chemical compositions, densities, and relative sizes) of the mantle and core (in Table 6) would vary if one considers the case of inhomogeneous accretion. Because, under such an accretion scenario a number of mixing combinations between the two precursors can be possible (as a function of the sequence of accretion), each of which would probably predict a somewhat different set of densities and relative masses of the core. A detailed discussion on these possibilities lies beyond the scope of this paper, and will be presented elsewhere (manuscript in preparation). As can be

realized from Table 6, the consistency of the present model with the bulk geophysical features of Mars and the bulk chemical composition of the mantle, as inferred from the martian meteorites, relies mostly on the possibility of accommodating a small fraction of planet's Si in the core. In the following discussion, we try to evaluate this possibility in light of the present knowledge on the behavior of Si during the core-mantle separation early in the evolution of planets like Mars.

Silicon has commonly not been invoked as a light element in the core of Mars (see Stevenson 2001 for a recent review), although its presence in the terrestrial core has often been suggested from geochemical arguments (see Hillgren, Gessmann, and Li 2000 for a recent review). For example, Wänke and Dreibus (1997) have pointed out that the depletion of Si in Earth's mantle-derived rocks as compared to samples from Mars can be explained by the presence of 14.4 wt% of Si in Earth's core. Although, the presence of significant Si in the Earth below the core-mantle boundary is a matter of debate at the present, recent results from high pressure and temperature melting studies (Dobson, Vocollo, and Wood 2002) and theoretical studies based on ab initio calculations and seismic data (Alfe, Gillan, and Price 2002) suggest as low as 8 mol% of Si in Earth's outer core. Iron silicide as a possible host

Table 5. Bulk chemical composition of Mars obtained from a mixture (12, Table 4) of (74%) EC and (26%) OC. Data source for EC and OC are Wasson and Kallemeyn (1988), except for W in EC, which is from Lee and Halliday (2000).

Elements	Bulk conc.	Elements	Bulk conc.
	(%)		(ppb)
O	31.66	Pb	893
Fe	24.72	Ru	887
Si	17.77	Sn	796
Mg	12.97	Pd	753
S	3.93	Os	610
C	3.10	Ce	584
Ni	1.46	Ir	543
Ca	1.02	Nd	427
Al	1.00	Nb	282
Na	0.64	Au	250
Cr	0.33	La	237
Mn	0.21	Dy	232
P	0.14	Gd	198
	(ppm)	Cd	195
K	775.5	Yb	176
Co	722.5	Cs	161
Ti	541.4	Er	159
Cl	346.7	Sm	152
F	166.4	Hf	151
Cu	131.0	W	133
Zn	111.2	Sb	123
V	61.8	Ag	112
Ge	28.7	Pr	102
Se	16.7	I	91
Ga	11.4	Eu	60
Sr	8.5	Ho	57
Sc	7.0	Bi	54
Zr	5.3	Re	49
Ba	3.0	Tl	41
Rb	2.7	Tb	40
As	2.5	Th	35
Y	1.5	Tm	28
Li	1.5	Lu	26
Br	1.3	In	25
Te	1.2	Ta	17
Pt	1.2	U	10

phase for Si in the core has thus been the focus of a number of experimental and theoretical studies. The results from Guyot et al. (1997), based on both experimental and theoretical observations, show that significant amounts of Si can be dissolved in Fe between the pressures 8 and 15 GPa. A number of similar studies have also shown that, at pressures below 25 GPa, liquid iron can accommodate significant amounts of Si in solution, while at pressures above 25 GPa, Si may exsolve from the solution (Hillgren, Gessmann, and Li 2000). Possible partitioning of Si into the core is also compatible with the chemical data on the opaque phases (metal bearing) in enstatite chondrites. A recent study by Lin and El Goresy (2002), for example, has shown up to 12.5 wt% of Si in such

phases. The expected pressure at the core-mantle boundary of Mars for the present model (Table 6) is about 20 GPa, which falls within the regime of significant Si solubility indicated by the above studies. Therefore, we cannot neglect the possibility of Si being present as a light element in the martian core. The partitioning of Si into the martian core would require a reducing environment to prevail during the core-mantle separation. Although Mars has been earlier pictured as being a volatile rich planet (compared to Earth, e.g., Dreibus and Wänke 1985), recent studies (e.g., Wadhwa 2001; Herd et al. 2002) have indicated the martian mantle to be more reducing than it has earlier been thought. Further, it is not known at what point of time the volatiles were acquired by the planet. If the volatiles were added to Mars in the form of late veneers after the core-mantle separation, then one cannot rule out the possibility of a much more reducing environment prevailing early in Mars' history than that recorded in the martian meteorites.

It is apparent from the above discussion that, at present, it is not possible to prove or disprove the possible presence of Si in the martian core, which in turn is the basis of the model of Mars presented in Table 6. The simple model presented is able to explain the isotopic composition of oxygen, which forms the bulk of Mars, and two other independent elements (which could not be accounted for by the other models), an observation which is hard to ignore. At the same time, with the present state of the model, it is not possible to account for many of the other important issues such as the nature of accretion, planetary differentiation, and the volatiles, which form the subject matter for future study.

SUMMARY

Based on the isotopic compositions of nitrogen and oxygen of martian meteorites, we have shown that Mars could have accreted from enstatite and ordinary chondrite type materials. This was found to be consistent with the chromium isotopic ($\epsilon^{53}\text{Cr}$) signatures of martian meteorites and the bulk planet Fe/Si ratio. However, the detailed nature of precursor materials (particular types of EC or OC) could not be resolved by our approach. Based on the bulk planet Fe/Si, as suggested by the moment of inertia factor for Mars, four potential mixtures (Mean EC:OC::74:26, Mean EC:LL::80:20, Mean EC:L::74:26, and EL:H::62:38) could be identified. A simple homogeneous accretion from the mean EC and mean OC (74:26) has been found consistent with the bulk planet properties of Mars. But it requires the presence of 6.7 wt% Si in the planet's core, which is consistent with the results from both experimental and theoretical studies, as well as with the chemical data for opaque phases in enstatite chondrites.

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Table 6. Bulk planet estimates for Mars, based on accretion from 74% EC and 26% OC.

Mantle + Crust		Core	
Mass fraction = 0.77		Mass fraction = 0.23	
Density (g/cc):		$R_{\text{core}}/R_{\text{Planet}} = 0.52$	
Mantle = 3.55		Density (g/cc) = 6.48	
Crust = 2.9			
<u>Major oxides</u>	<u>Wt%</u>	<u>Major constituents</u>	<u>Wt% of core</u>
MgO	29.1	Fe	21.3
Al ₂ O ₃	2.5	FeS	49.0
SiO ₂	47.1	FeSi	19.2
CaO	1.9	(Fe, Ni) ₃ P	3.4
Na ₂ O	1.2	Ni	3.0
TiO ₂	0.1	(Ni, Fe) ₅ (Si, P) ₂	3.7
Cr ₂ O ₃	0.6	Co	0.3
MnO	0.4		
FeO	16.9	<u>Bulk planet</u>	
P ₂ O ₅	0.01	I/MR ² = 0.368 ($\pm 0.003^a$)	
K ₂ O	0.1	Fe (wt%) = 24.7	
		Fe/Si = 1.391	
<u>Key elemental ratios</u>	<u>Mole fractions</u>		
Mg/(Mg + Fe)	0.755		
Mg/Si	0.92		
Fe/Si	0.30		
Al/Si	0.064		
Mn/Fe	0.022		
Inputs			
<u>Bulk planet parameters</u>	<u>Phases in core</u>	<u>Density (g/cc)</u>	
Mass of Mars = 6.42 ± 10^{23} kg ^b	Fe ^c	8.09	
Mean Radius of Mars = 3390 km ^b	FeS ^c	5.77	
Mean crust thickness = 50 km	FeSi ^d	6.4	
	(Fe, Ni) ₃ P ^e	7.4	
	Ni ^f	8.9	
	(Ni, Fe) ₅ (Si, P) ₂ ^e	7.56	
	Co ^f	8.9	

^aIncludes the uncertainties ($\pm 4\%$) in the mixing ratios, thickness (20 to 50 km) and density (2.7 to 3 g/cc) of the crust.

^bCompilation by Kieffer, Jakosky, and Snyder(1992).

^cCompilation by Goettel (1981).

^dCalculated from the cell parameters given by Dobson, Voadlo, and Wood (2002).

^eZero pressure densities calculated from the cell parameters compiled by Roberts, Rapp, and Weber (1990).

^fCompilation by Hammond (1970).

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APPENDIX

Table 1A. Chemical and isotopic compositions (of interest) of the chondritic^a end-members used in the present study.

	Carbonaceous			Enstatite			Ordinary			
	CI	CM	CV	EH	EL	EC	H	L	LL	OC
Cr/O ($\times 10^{-3}$) ^b	5.8	7.1	9.7	11.3	9.8	10.5	10.3	10.3	9.4	10
N/O ($\times 10^{-3}$) ^c	3.2	3.5	0.1	–	–	1.4	–	–	–	0.03
Fe/Si ^b	1.733	1.628	1.506	1.737	1.183	1.460	1.627	1.162	0.979	1.256
$\delta^{15}\text{N}$ (‰)	+43 \pm 15 ^d	34 \pm 5 ^d	–22 \pm 12 ^e	–	–	–28 \pm 10 ^f	–	–	–	–2 \pm 8 ^g
$\Delta^{17}\text{O}$ (‰)	0.42 \pm .11 ^h	–4.28 \pm .15 ^h	–4.01 \pm .47 ^h	0.010 \pm .118	0.014 \pm .056	0.012 ⁱ	0.73 \pm .09	1.07 \pm .09	1.26 \pm .12	1.02 ^j
$\varepsilon^{53}\text{Cr}$	~0.39 ^k	–	~0.10 ^k	–	–	0.16 ^l	–	–	–	0.48 ^m

^aC = Carbonaceous chondrites (CI, CM, and CV refer to the different types); EC = Enstatite chondrites (EH and EL refer to the two types of EC); OC = Ordinary chondrites (H, L, and LL are the three types of OC). Nomenclature adopted following the commonly used classification of chondrites (e.g., McSween 1999).

^bWasson and Kallemeyn (1988).

^cThe N/O ratios of the different end-members have been calculated based on the nitrogen data from Kerridge (1985) and Kung and Clayton (1978) for the carbonaceous chondrites; Kung and Clayton (1978), Thiemens and Clayton (1983), and Grady et al. (1986) for the enstatite chondrites; and Kung and Clayton (1978), Hashizume and Sugiura (1995), and Sugiura, Kiyota, and Hashizume (1998) for the ordinary chondrites.

^dKerridge (1985).

^eGrand mean of 22 data ($\delta^{15}\text{N}$ range: –45 to +24‰) from Kung and Clayton (1978) and Kerridge (1985).

^fGrand mean of 34 data ($\delta^{15}\text{N}$ range: –47 to –6‰) from Kung and Clayton (1978), Thiemens and Clayton (1983), and Grady et al. (1986).

^gGrand mean of 50 data from Kung and Clayton (1978), Hashizume and Sugiura (1995), and Sugiura, Kiyota, and Hashizume (1998).

^hClayton and Mayeda (1999).

ⁱNewton, Franchi, and Pillinger (2000).

^jClayton et al. (1991).

^kShukolyukov and Lugmair (2000b).

^lShukolyukov and Lugmair (1999).

^mLugmair and Shukolyukov (1998).