An Oxygen Isotope Model for the Composition of Mars

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We derive the bulk chemical composition, physical properties, and trace element abundances of Mars from two assumptions: (1) Mars is the parent body for the Shergottite–Nakhlite–Chassignite (SNC) meteorites, and (2) the oxygen isotopic composition of Mars was determined by the oxygen isotopic compositions of the different types of nebular material that accreted to form Mars. We use oxygen isotopes to constrain planetary bulk compositions because oxygen is generally the most abundant element in rock, and is either the first or second (after iron) most abundant element in any terrestrial planet, the Moon, other rocky satellites, and the asteroids. The oxygen isotopic composition of Mars, calculated from oxygen isotopic analyses of the SNC meteorites, corresponds to the accretion of about 85% H-, 11% CV-, and 4% CI-chondritic material. (Unless noted otherwise, mass percentages are used in this paper.) The bulk composition of Mars follows from mass balance calculations using mean compositions for these chondrite groups. We predict that silicates (mantle + crust) comprise about 80% of Mars. The composition of the silicate fraction represents the composition of the primordial martian mantle prior to crustal formation. The FeO content of the mantle is 17.2%. A metal–sulfide core, containing about 10.6% S, makes up the remaining 20% of the planet. Our bulk composition is similar to those from other models. We calculate the abundances of siderophile ("metal-loving") and chalcophile ("sulfide-loving") elements in the martian mantle from the bulk composition using (metal–sulfide)/silicate partition coefficients. Our results generally agree with predictions of the SNC meteorite model of Wänke and Dreibus for the composition of Mars. However, we predict higher abundances for the alkalis and halogens than those derived from SNC meteorite models for Mars. The apparent discrepancy indicates that the alkalis and halogens were lost from the martian mantle by hydrothermal leaching and/or vaporization during accretion. Geochemical arguments suggest that vaporization was only a minor loss process for these elements. On the other hand, aqueous transport of the alkalis and halogens to the surface is supported by the terrestrial geochemistry of these elements and the high K, Rb, Cl, and Br abundances found by the Viking XRF and Phobos gamma ray experiments on the surface of Mars. © 1997
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INTRODUCTION

Oxygen is generally the most abundant element in rock (e.g., see Ehmann 1971), and depending on the existence and size of an Fe-bearing core, is either the first or second most abundant element in any of the terrestrial planets, the Moon, asteroids, and rocky satellites. During the past two decades, analyses of lunar samples, meteorites, and terrestrial rocks have shown that different types of meteorites have oxygen isotopic compositions distinct from those of the Earth–Moon system (e.g., Clayton 1993). In particular, the Shergottite–Nakhlite–Chassignite (SNC) meteorites, which are generally believed to come from Mars (e.g., McSween 1994), and the eucrites, which are believed to come from the asteroid 4 Vesta (McCord *et al.* 1970), have oxygen isotope compositions that are distinct from those of the Earth and Moon. This is illustrated in Fig. 1 which shows the oxygen isotopic compositions of the major types of rocky meteorites, the Earth, and Moon in a three isotope plot. The two axes express the oxygen isotopic composition relative to Standard Mean Ocean Water (SMOW) where

$$\delta^{18}O = [(^{18}O/^{16}O)_{sample}/(^{18}O/^{16}O)_{SMOW} - 1] \times 1000 \quad (1)$$

$$\delta^{17}O = [(^{17}O/^{16}O)_{sample}/(^{17}O/^{16}O)_{SMOW} - 1] \times 1000 \quad (2)$$

and the ratios $^{18}O/^{16}O = 2.0052 \times 10^{-3}$ and $^{17}O/^{16}O = 3.7288 \times 10^{-4}$ in SMOW.

Another important point illustrated by Fig. 1 is that different types of chondritic meteorites, which are samples of relatively unaltered nebular material (Sears and Dodd 1988), also have different oxygen isotopic signatures. For example, the oxidized carbonaceous (CI, CM2, CV3) chondrites, the less oxidized ordinary (H, L, LL) chondrites, and the highly reduced enstatite (E) chondrites plot at different locations in Fig. 1. This indicates that chondritic material in the solar nebula had different oxygen isotope compositions, as well as having different volatile contents and redox states. As a result, the accretion of different amounts of chondritic matter, such as oxidized carbona-
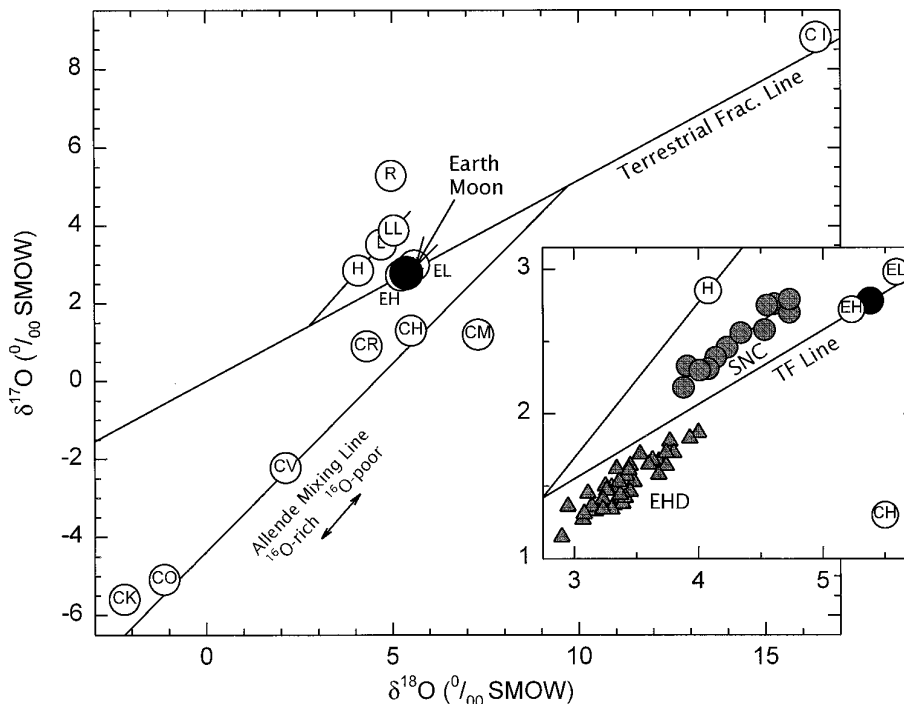
FIG. 1. Oxygen isotope systematics for chondrites and the Earth–Moon system. The terrestrial fractionation line and the mixing line of Allende components are also shown. The insert shows an enlarged region for differentiated meteorites such as EHD (eucrites, howardites, diogenites) and SNC (shergottites, nakhlites, chassignites), which plot parallel to the terrestrial fractionation line. All data are from Clayton and co-workers (e.g., Clayton 1993, Clayton *et al.* 1991, Clayton and Mayeda 1983, 1984, 1996 and references therein).

ceous chondrite matter and less oxidized ordinary chondrite matter, plausibly led to different oxygen isotopic compositions for the different terrestrial planets.

The accretion of varying proportions of oxidized, volatile-rich material (similar to CI carbonaceous chondrites) and reduced material (similar to enstatite chondrites) is explicitly postulated in two component models for the accretion of the terrestrial planets (e.g., Ringwood 1979, Wänke 1981). However, the reduced component in these models is believed to be volatile poor while enstatite chondrites are relatively volatile rich. Other models also postulate that a mixture of nebular materials were accreted during formation of the terrestrial planets. For example, in Lewis' equilibrium condensation model (Barshay 1981; Lewis 1974, 1988), the terrestrial planets accreted material in a feeding zone extending from inside to outside the present orbit of each planet. In general, more reduced, volatile-poor material came from the inner edge of the feeding zone while more oxidized, volatile-rich material came from the outer edge of the feeding zone. In contrast to the two component models of Ringwood and Wänke, Lewis' model uses a continuum of compositions, taken from chemical equilibrium condensation calculations to form each planet. The two component models can be viewed as an extreme endmember of Lewis' equilibrium condensation–accretion model.

Models by Anders and colleagues postulated that the Earth, Moon, and Mars formed from a mixture of chondritic materials that were subject to the same cosmochemical processes (i.e., condensation, metal–silicate fractionation, volatile element loss, etc.) as the chondritic meteorites (e.g., Anders and Owen 1977, Morgan and Anders 1979). In these models a veneer composed of CV3 chondrites provided the volatiles to the accreting bodies.

Independently, geochemists have used seismic profiles, chemical analyses of relatively unaltered rocks thought to come from the mantle (fertile peridotites, spinel–lherzolites, and garnet lherzolites), petrological models of peridotite–basalt melting, and element ratios to derive the composition of the primordial terrestrial mantle (prior to crustal formation) and the bulk Earth (e.g., Jagoutz *et al.* 1979, Hart and Zindler 1986, Kargel and Lewis 1993, Allegre *et al.* 1995). A key conclusion of this modeling is that the Earth has a kinship to chondritic meteorites, although it cannot be identified with any one chondrite group. As noted by Hart and Zindler (1986): ''In other words, the Earth is not like any chondrite (in major elements) but is composed of its own blend of accretion products, with a bias toward a higher proportion of the high temperature refractory components (or, equivalently, a lower proportion of the volatiles and partially refractory components).'' It appears likely that the Earth accreted from a mixture

of chondritic material, as proposed in the cosmochemical models of Anders, Lewis, Ringwood, and Wänke.

As mentioned above, chondritic material in the solar nebula had different oxygen isotope compositions, as well as different volatile contents and redox states. Here we use the distinctive oxygen isotope compositions of chondrites and of the SNC meteorites to constrain the mass fractions of different types of chondritic material accreted by the planet Mars. Then, using mass balance calculations and the mean chemical compositions of the different types of chondrites (CI, CM2, CV3, H, L, LL, E, etc.), we can calculate the bulk chemical composition, oxidation state, density, and so on for Mars.

Here we adopt the widely held view that after condensation, small planetesimals formed by agglomeration of chondritic material. These planetesimals grew in size by collisional accretion and eventually accreted to form the Earth and other terrestrial planets (e.g., Wetherill 1980). Our choice of chondritic meteorites as the building blocks of the terrestrial planets allows us to use the isotopic signature of oxygen, the most abundant element in chondritic meteorites, to constrain the mixture of nebular materials accreted by Mars (or other objects) for which we have oxygen isotopic data. Although at present chondritic meteorites are believed to come from parent bodies in the asteroid belt, it is implausible that *all* chondritic meteorite groups originally formed in this region of the solar nebula. The wide range of oxygen isotopic compositions, redox states, volatile abundances, and chemical fractionations displayed by the carbonaceous, ordinary, and enstatite chondrites are more plausibly the result of processes operating over a distance of several astronomical units in the solar nebula than of processes operating over the restricted range currently occupied by the asteroid belt (also see Wasson (1988) for similar arguments). In fact, the planetary accretion models of Anders, Lewis, Ringwood, Wänke, and colleagues discussed above postulate that a mixture of oxidized, volatile-rich material from further out in the nebula and reduced, volatile-poor material from the inner regions of the nebula was accreted by the terrestrial planets during their formation.

The present paper expands upon the concept originally presented by Lodders (1991) that "Die mittlere O-Isotopenzusammensetzung der größeren terrestrischen planetaren Körper wird durch Akkretion von isotopisch unterschiedlich zusammengesetztem, chondritischem Material (kohlige, gewöhnliche- und Enstatit-Chondrite) in unterschiedlichen Verhältnissen definiert (the mean oxygen isotopic composition of the terrestrial planetary bodies is determined by the oxygen isotopic composition of the mixture of chondritic material accreted to form these bodies)." Preliminary results of the oxygen isotope mixing (OIM) model for the composition of Mars were given by Lodders (1995) and Lodders and Fegley (1996).

This paper is organized as follows. We first use oxygen isotope data for chondrites and the SNC meteorites to constrain the mixture of chondritic matter accreted by Mars. We then calculate the bulk chemical composition of Mars, the compositions of the silicate fraction (mantle +crust) and core, and the bulk density and mean moment of inertia. The composition of the silicate fraction represents the composition of the primordial martian mantle prior to crustal formation. Henceforth we refer to the silicate fraction as the mantle. The abundances of siderophile ("metal-loving") and chalcophile ("sulfide-loving") elements in the martian mantle and core are calculated from the bulk composition using literature data for elemental partitioning between silicate and metal+sulfide. We compare our results to those from other models, in particular to the SNC meteorite model of Wänke and Dreibus for the composition of Mars. Their model, which is described in a series of papers (Dreibus and Wänke 1984, 1985, 1987, 1989; Wänke *et al.* 1984; Wänke and Dreibus 1988, 1994), is henceforth referred to as the Wänke-Dreibus (WD) model.

One conclusion of our model is that higher abundances for the alkalis and halogens are predicted than those derived from the SNC meteorite model for Mars. We interpret this apparent discrepancy in terms of alkali and halogen loss from the martian mantle by hydrothermal leaching and/or vaporization during accretion. Geochemical arguments suggest that vaporization was only a minor loss process for these elements. On the other hand, aqueous transport of the alkalis and halogens to the surface is supported by the terrestrial geochemistry of these elements and the high K, Rb, Cl, and Br abundances found by the Viking XRF and Phobos gamma ray experiments on the martian surface.

OXYGEN ISOTOPE MIXING MODEL CALCULATIONS

McSween (1994) summarizes the strong evidence indicating that the SNC meteorites come from Mars. Here we explicitly assume that Mars is the source of the SNC meteorites. The Wänke–Dreibus model also assumes that Mars is the source of the SNC meteorites, but they do not use oxygen isotopes to constrain the bulk composition of Mars. Instead, as described later, the Wänke–Dreibus model uses chemical analyses of the SNC meteorites and ratios of different elements to derive the bulk composition of Mars.

Figure 1 shows that the oxygen isotopic composition of the SNC meteorites is distinct from that of the Earth–Moon system or any chondritic meteorite group. However, the SNC meteorite field plots within a triangle formed by the volatile-rich CI chondrites, the H group ordinary chondrites, and less volatile-rich CV carbonaceous chondrites. This suggests that Mars accreted from a mixture of carbonaceous chondrite (i.e., oxidized, volatile-rich) mate-

TABLE I
**Mean Oxygen Isotopic Compositions[a] Used
in the Calculations**

	$\delta^{18}O^0/_{00}$	$\delta^{17}O^0/_{00}$
CI	16.35(±0.50)	8.81(±0.37)
CV	2.12(±1.57)	-2.33(±1.53)
H	4.08(±0.22)	2.85(±0.15)
SNC	4.31(±0.31)	2.51(±0.21)

[a] Relative to SMOW. Data from Clayton *et al.* 1991; Clayton and Mayeda, 1983, 1984, 1996.

rial and ordinary chondrite (i.e., less oxidized, volatile-poor) material. Although oxygen isotopes were not used as a constraint, Anderson (1972) also proposed that Mars accreted from a mixture of ordinary (~75%) and carbonaceous (~25%) chondrites.

The necessary mass fractions (X) of each chondritic group (CI, CV, H) forming the SNC parent body were obtained by solving the following mass balance equations:

$$^{18}O_{SNC} = {}^{18}O_{CI} X_{CI} + {}^{18}O_{CV} X_{CV} + {}^{18}O_H X_H \quad (3)$$

$$^{17}O_{SNC} = {}^{17}O_{CI} X_{CI} + {}^{17}O_{CV} X_{CV} + {}^{17}O_H X_H \quad (4)$$

$$^{16}O_{SNC} = {}^{16}O_{CI} X_{CI} + {}^{16}O_{CV} X_{CV} + {}^{16}O_H X_H \quad (5)$$

$$1 = X_{CI} + X_{CV} + X_H. \quad (6)$$

The percentages of atomic ^{18}O, ^{17}O, and ^{16}O in each meteorite group were needed for the calculations. The necessary oxygen isotopic data for chondrites and the SNC meteorites were taken from Clayton *et al.* (1991) and Clayton and Mayeda (1983, 1984, 1996) and are listed in Table I. The mass fractions of CI, CV, and H chondrites obtained by solving the equations and considering the ranges in mean chondrite O-isotopic compositions are $X_{CI} = 0.036^{+0.024}_{-0.028}$, $X_{CV} = 0.109^{+0.032}_{-0.028}$, and $X_H = 0.854^{+0.004}_{-0.003}$, respectively.

Although the selection of CI, CV, and H chondrites may seem arbitrary at first, it was found that a CI chondritic component was necessary to obtain a solution to the mass balance equations. Many models for the composition of the Earth and other terrestrial planets use a CI component to supply volatiles. However, we require a CI component in our model because of constraints imposed by the oxygen isotopic composition of Mars. We also found that unreasonable results (negative mass fractions resulting from solving Eqs. (3)–(6)) were obtained if enstatite chondritic matter were involved (e.g., in a combination of CI, H, and EH chondrites). Physically meaningful solutions (i.e., positive values between 0 and 1) for the accreting mass fractions of chondritic material are only obtained if the SNC isotopic composition plots inside a triangle formed by three different chondrite groups (e.g., CI, CV, H chon-

drites). An additional criterion for the selected mixture is that the resulting chemical composition and physical parameters must be reasonable.

Substituting H chondrites by L chondrites also gave a numerical solution but this mixture led to martian core sizes around ten mass percent, which are below currently accepted estimates (e.g., Longhi *et al.* 1992). Substitution of H chondrites by LL chondrites or substitution of CV chondrites by CM chondrites gave solutions involving negative mass fractions. Other combinations yielded solutions such as $X_{CI} = 0.007$, $X_{CV} = 0.181$, $X_L = 0.812$ or $X_{CM} = 0.094$, $X_{CV} = 0.037$, $X_H = 0.870$ similar to the preferred selection of a mixture of CI, CV, and H chondrites.

The choice of CI, CV, and H chondritic material was given preference because these chondritic groups can be regarded as "extreme endmembers." The CI chondrites are the most water-rich, and the CV chondrites the most refractory-rich carbonaceous chondrites, while the H chondrites are the most metal-rich among ordinary chondrites. This preferred mixture of chondrites also gave the best agreement with predictions from the Wänke–Dreibus SNC meteorite model for the composition of Mars.

BULK COMPOSITION OF MARS

The oxygen isotope calculations above constrain the mass fractions of CI, CV, and H chondrite matter accreted by Mars. The bulk composition of Mars was then calculated from the general mass balance equation

$$C_{Mars} = C_{CI}X_{CI} + C_{CV}X_{CV} + C_HX_H, \quad (7)$$

where C_i is the mean concentration by weight of each element in CI, CV, or H chondrites, and X_i is the respective mass fraction of CI, CV, or H chondritic matter. Elemental abundance data for CI chondrites were taken from Anders and Grevesse (1989) with the exception of sulfur and Se which are from Dreibus *et al.* (1995). The mean H_2O content of CI chondrites was taken from Boato (1954), which was also selected by Dreibus and Wänke (1987) in their model. Compositional data for CV and H chondrites are from the compilation by Wasson and Kallemeyn (1988), except for Li in CV chondrites, which was taken from Nichiporuk and Moore (1970). The mean Na abundance of 6400 ppm for H chondrites listed by Wasson and Kallemeyn (1988) is higher than other Na determinations in H chondrites. For example, Schmitt *et al.* (1972) obtain 5800 ppm as a mean Na concentration for H chondrites and many other authors also obtain lower values for Na than listed by Wasson and Kallemeyn (1988). Therefore, a value of 6000 ppm was adopted here for the mean Na abundance in H chondrites.

We also need to consider uncertainties in the calculated bulk abundances obtained from Eq. (7). The uncertainties

in the mass fractions introduced from the observed ranges in O-isotopic composition are largest for the mass fractions of CI and CV chondritic matter. However, because the contributions of CI and CV chondritic matter are relatively small and the H chondritic material dominates, the total abundance of an element obtained from Eq. (7) is mainly governed by its abundance in H chondritic material. The total abundances computed from Eq. (7) are affected more by the uncertainties in the average elemental abundances of chondrites than by the uncertainties in the accreted mass fractions of each type of chondritic matter.

Abundance determinations for the elements in individual chondrite groups generally vary by ±10%. This variation reflects several factors. One factor is that volatile elements such as Tl or In have large abundance variations in chondrites (Laul *et al.* 1973). Another factor is that some elements are very difficult to determine and only a few analyses have been done (as, for example, is the case for Li and the halogens). The overall uncertainties in the calculated bulk abundances from Eq. (7) are therefore taken as ±10% except for some elements such as Li, the halogens, or very volatile elements (Tl, In) where larger uncertainties, similar to those observed in chondrites, are appropriate. No bulk elemental abundances were calculated for Be, Nb, and Hg because the average abundances of these elements in CV and H chondrites are unknown.

The three chondrite groups have different metal, sulfide, carbon (carbon in metal, graphite, organic matter, etc.), and water contents, and also different 'FeO' concentrations in their silicates. The initially accreted 'FeO,' metal, sulfide, and water concentrations can be obtained from mass balance equations similar to Eq. (7):
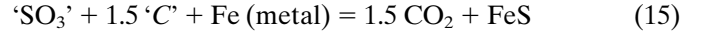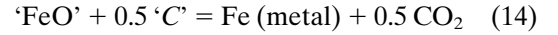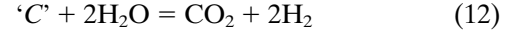
$$C(\text{'FeO'})_{\text{bulk}} = C(\text{'FeO'})_{\text{CI}}X_{\text{CI}} + C(\text{'FeO'})_{\text{CV}}X_{\text{CV}}$$
$$+ C(\text{'FeO'})_{\text{H}}X_{\text{H}} \tag{8}$$

$$C(\text{Fe, met.})_{\text{bulk}} = C(\text{Fe, met.})_{\text{CI}}X_{\text{CI}} + C(\text{Fe, met.})_{\text{CV}}X_{\text{CV}}$$
$$+ C(\text{Fe, met})_{\text{H}}X_{\text{H}} \tag{9}$$

$$C(\text{FeS})_{\text{bulk}} = C(\text{FeS})_{\text{CI}}X_{\text{CI}} + C(\text{FeS})_{\text{CV}}X_{\text{CV}}$$
$$+ C(\text{FeS})_{\text{H}}X_{\text{H}} \tag{10}$$

$$C(\text{H}_2\text{O})_{\text{bulk}} = C(\text{H}_2\text{O})_{\text{CI}}X_{\text{CI}} + C(\text{H}_2\text{O})_{\text{CV}}X_{\text{CV}}$$
$$+ C(\text{H}_2\text{O})_{\text{H}}X_{\text{H}}. \tag{11}$$

The initially accreted assemblage is not an equilibrium assemblage. During accretion the growing planet heats up and redox reactions involving metal, sulfide, carbon, water, and 'FeO' in the silicates readjust the amounts of these compounds present. We model the amount of metal, sulfide, and 'FeO' left, using the redox reactions

$$\text{'C'} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2 \tag{12}$$

$$\text{Fe (metal)} + \text{H}_2\text{O} = \text{FeO} + \text{H}_2 \tag{13}$$

$$\text{'FeO'} + 0.5\,\text{'C'} = \text{Fe (metal)} + 0.5\,\text{CO}_2 \tag{14}$$

$$\text{'SO}_3\text{'} + 1.5\,\text{'C'} + \text{Fe (metal)} = 1.5\,\text{CO}_2 + \text{FeS} \tag{15}$$

and assume that all H_2O and carbon are converted to CO_2 and H_2, which escape. Because Eqs. (12)–(15) involve loss of H_2 and CO_2, the bulk composition calculated from Eq. (7) is then renormalized to 100%.

Jeans escape of CO_2 from Mars would require high temperatures but simultaneous production of CO_2 and H_2 allows hydrodynamic escape of CO_2 (and also other heavier noble gases) as discussed by Dreibus and Wänke (1987) and as shown by the detailed modeling of Pepin (1991). One might also ask if the abundance of sulfur would be affected by these reactions. Sulfur loss could occur if significant amounts of sulfur would be present in the gas (e.g., as S_2, H_2S, SO_2, OCS) but as long as excess carbon and Fe metal are present, the formation of FeS retains sulfur and prevents sulfur loss from the planet.

The resulting bulk composition from Eq. (7) is listed in Table II. The corresponding compositions for the mantle and core of Mars are listed in Table III. The data in Table III are simply derived from Table II by mass balance. The lithophile elements (Si, Al, Mg, Ca, etc.) are assigned to the silicate portion and the amount of Fe needed to use up excess oxygen is put into the mantle as 'FeO.' The rest of the Fe and all S, Ni, and Co are put into the core. Phosphorus is partitioned between silicate and metal on the basis of partition coefficient data described later. The mantle makes up 79.37% and a metal–sulfide core is the remaining 20.63% of Mars in our model.

MAJOR ELEMENT COMPOSITION OF THE MARTIAN MANTLE

Elemental concentrations in the mantle of Mars were calculated from the basic mass balance equation

$$C_{\text{mantle}} = C_{\text{bulk}}/X_{\text{mantle}} \tag{16}$$

and are listed in Table IV. As mentioned earlier, these estimates are for the primordial martian mantle, prior to any crustal formation and extraction of incompatible elements. Tables III and IV compare our results to other Mars composition models, and to Kargel and Lewis' (1993) model for the composition of the Earth.

The mantle density in each model was estimated by converting the elemental composition (Table IV) into a normative high pressure assemblage (30 kbar) using an algorithm similar to that described by McGetchin and Smyth (1978). Mineral densities were taken from Robie

TABLE II
Predicted Elemental Abundances in Bulk Mars (Mantle, Crust, and Core)

		OIM (a)	M&A (b)			OIM (a)	M&A (b)
Li		1.69	1.94	Pd		0.86	0.74
B		0.5	0.00226	Ag	ppb	60	37.9
C		(2960) (c)	16.3	Cd	ppb	80	0.62
N		(180) (c)	0.148	In	ppb	16	0.077
O	wt%	33.75	34.11	Sn	ppb	915	258
F		33	19.1	Sb	ppb	76	23.4
Na		5770	574	Te	ppb	430	13.8
Mg	wt%	14.16	14.55	I	ppb	100	0.48
Al	wt%	1.21	2.73	Cs	ppb	120	21
Si	wt%	16.83	15.74	Ba		4.3	8.0
P		1100	1608	La		0.320	0.75
S		22000	6660	Ce		0.890	1.99
Cl		120	0.71	Pr		0.130	0.25
K		730	62	Nd		0.670	1.38
Ca	wt%	1.33	2.98	Sm		0.200	0.41
Sc		8.4	19	Eu		0.078	0.157
Ti		650	1580	Gd		0.310	0.56
V		77	162	Tb		0.055	0.105
Cr		3680	3620	Dy		0.360	0.71
Mn		2250	940	Ho		0.078	0.156
Fe	wt%	27.24	26.72	Er		0.240	0.455
Co		795	702	Tm		0.040	0.068
Ni	wt%	1.58	1.52	Yb		0.220	0.451
Cu		87	210	Lu		0.035	0.076
Zn		66	33.9	Hf		0.180	0.451
Ga		6.3	1.97	Ta		0.023	0.0455
Ge		15	5	W		0.16	0.356
As		2.0	2.68	Re		0.07	0.118
Se		8.5	2.22	Os		0.82	1.71
Br	ppb	740	3.83	Ir		0.76	1.66
Rb		2.7	0.209	Pt		1.40	3.28
Sr		10.7	28.4	Au		0.21	0.214
Y		2.2	5.19	Tl	ppb	14	0.14
Zr		6.5	30.8	Pb	ppb	460	0.056
Mo		1.7	1.57	Bi	ppb	25	0.106
Ru		1.1	4.65	Th	ppb	44	101
Rh		0.22	0.50	U	ppb	12.6	28

Note. ppm if not noted otherwise.

(a) This work. Mixture of 4% CI, 11% CV, and 85% H chondrites. No data for Be, Nb, and Hg because no analyses are available for CV or H chondrites.

(b) Morgan and Anders 1979.

(c) Calculated C and N abundances after equilibration of chondritic mixture. Because CO_2 and N_2 are volatile, abundances are given in parenthesis.

a lower Mg/(Mg + Fe) ratio) than the terrestrial mantle and that the martian core is smaller than the terrestrial core. The higher predicted 'FeO' contents in the martian mantle lead to densities higher than that of the terrestrial mantle. All of the models assume a chemically homogeneous mantle. As noted by Longhi *et al.* (1992), chemical homogeneity is probably an oversimplification, which has to be assumed in the absence of any useful constraints on the extent of heterogeneity. The similarities between the Mars composition models in Tables III and IV are consequences of the lower bulk density of Mars and the larger reduced moment of inertia of Mars compared to those of the Earth.

The major element chemistry derived here is similar to that of the Wänke–Dreibus (WD) model, which uses chemical analyses of the SNC meteorites and ratios of different elements to constrain the bulk composition of

TABLE III
Predicted Abundances in Bulk Mars: Major Elements in the Mantle and Core and Comparison to the Earth

wt%	OIM (a)	WD (b)	W81 (c)	R81 (d)	MA79 (e)	MG78 (f)	A72 (g)	Earth (h)
SiO_2	36.03	34.8	32.6	30.1	33.70	22.50	34.9	31.38
Al_2O_3	2.29	2.3	2.4	2.5	5.18	2.63	2.7	2.72
MgO	23.58	23.6	23.2	24.5	24.12	27.78	23.9	24.78
CaO	1.87	1.9	2.2	2.0	4.18	2.29	2.2	2.33
Na_2O	0.78	0.4	1.0	0.2	0.08	0.43	0.7	0.27
K_2O	0.088	0.03	0.10	0.02	0.008	0.09	0.06	0.02
TiO_2	0.108	0.1	0.12	0.2	0.27	0.53	0.1	0.13
Cr_2O_3	0.538	0.6	n.d.	0.3	0.53	n.d.	0.5	0.29
MnO	0.290	0.4	n.d.	0.08	0.12	n.d.	0.2	0.092
FeO	13.66	14.0	12.4	21.9	12.84	17.09	21.2	5.47
P_2O_5	0.14	0.13	n.d.	n.d.	n.d.	n.d.	0.3	0.012
Mantle & Crust	79.37	78.3	74.3	81.8	81.0	85.0	87.8	67.5
*Mg/(Mg+Fe)**	*0.76*	*0.75*	*0.77*	*0.67*	*0.77*	*0.75*	*0.67*	*0.89*
Fe	16.74	16.88	15.5	11.6	16.74	13.62	8.47	27.88
Co	0.080	0.078	n.d.	n.d.	0.07	n.d.	n.d.	0.07
Ni	1.58	1.65	1.5	1.5	1.52	n.d.	1.1	1.59
S	2.18	3.09	8.7	1.7	0.67	1.38	2.23	0.88
O	0	0	0	3.4	0	0	0	1.69
P	0.05	0	0	0	0	0	0	0.11
Core	20.63	21.7	25.7	18.2	19.0	15.0	11.8	32.5
Metal (Fe,Co,Ni)	14.6	13.2	1.9	10.1	17.2	11.2	5.7	22.1
Sulfide (FeS)	6.0	8.5	23.8	4.7	1.8	3.8	6.1	2.4
*X(S)**	*0.17*	*0.23*	*0.47*	*0.11*	*0.06*	*0.15*	*0.29*	*0.05*

(a) This work. Mixture of 4% CI, 11 wt% CV, and 85% H chondrites.

(b) SNC model, Dreibus and Wänke 1984, Wänke and Dreibus 1988, Longhi *et al.* 1992. Abundances from element correlations in SNC meteorites using CI-chondritic abundances for refractory elements from Palme *et al.* 1981.

(c) after Weidenschilling (see BVSP 1981).

(d) 30% CI + 70% high temperature component, after Ringwood (see BVSP 1981).

(e) Four component meteorite model, Morgan and Anders 1979.

(f) Pyrolite plus 12.8 wt% FeO, McGetchin and Smyth 1978 who used a core composition from Johnston and Toksöz 1977. Silicates also 0.67 wt% Fe_2O_3.

(g) 75% C3 chondrite + 25% ordinary chondrites, Anderson 1972.

(h) Kargel and Lewis 1993. The core also contains 0.15% Cr and 0.13% Mn in their model.

* Mole fraction.

n.d.: Not determined.

and Hemingway (1995). Both the calculated densities and normative mineralogies are listed in Table IV. Longhi *et al.* (1992) discussed several of the bulk composition models listed in Table IV, but list mantle densities which vary slightly from those in Table IV. This may be due to different definitions of normative compositions and use of different densities for the individual minerals.

All of the Mars composition models in Tables III and IV predict that the martian mantle is more oxidized (i.e.,

TABLE IV
Predicted Mantle and Core Composition, High Pressure
Densities, and Estimated Moment of Inertia

	OIM (a)	WD (b)	G83 (c)	W81 (d)	MA79 (e)	MG78 (f)	A72 (g)
Silicate Portion wt%							
SiO_2	45.39	44.4	45.07	43.9	41.6	39.41	39.8
Al_2O_3	2.89	2.9	3.26	3.2	6.39	3.09	3.1
MgO	29.71	30.1	32.08	31.2	29.78	32.68	27.2
CaO	2.35	2.4	3.03	3.0	5.16	2.69	2.5
Na_2O	0.98	0.5	1.4	1.4	0.10	0.50	0.8
K_2O	0.11	0.04	0.12	0.14	0.01	0.11	0.07
TiO_2	0.14	0.13	n.d.	0.16	0.33	0.62	0.1
Cr_2O_3	0.68	0.8	n.d.	n.d.	0.65	n.d.	0.6
MnO	0.37	0.5	n.d	n.d	0.15	n.d.	0.2
FeO	17.22	17.9	15.07	16.7	15.85	20.11	24.2
Fe_2O_3	0	0	0	0	0	0.79	0
P_2O_5	0.17	0.17	n.d.	n.d.	n.d.	n.d.	0.3
H_2O	n.d.	0.004	n.d.	0.44	0.001	n.d.	0.9
High Pressure Norm (wt%)							
pyroxene	42.63	37.75	34.28	30.5	21.55	12.06	18.8
olivine	50.91	51.87	62.32	65.8	48.98	73.21	71
garnet	4.82	8.61	3.43	3.1	25.86	11.41	7.2
oxides	0	0	0	0	2.05	2.14	0
other (h)	1.64	1.37	n.a.	0.3	1.58	1.2	1.8
ρ (STP) g cm^{-3} (i)	3.50	3.52	3.46	3.48	3.58	3.57	3.61
Core wt%							
Fe	61.48	53.1	45.60	1.5	82.02	74.77	39.0
Co	0.38	n.d.	n.d.	n.d	0.37	n.d.	n.d.
Ni	7.67	8.0	6.20	5.8	7.99	n.d.	9.3
Fe_3P	1.55	0	0	0	0	0	0
FeS	28.97	38.9	48.20	92.7	9.62	25.23	51.7
ρ (STP) g cm^{-3} (j)	7.27	7.04	6.81	5.92	7.85	7.34	6.74
Mantle & Core							
Silicates wt%	79.37	78.3	n.d.	74.3	81.0	85.0	87.8
Core wt%	20.63	21.7	n.d.	25.7	19.0	15.0	11.2
bulk ρ(STP) g cm^{-3}	3.92	3.95	--	3.89	3.99	3.87	3.85
r_{core}/R_{total}	0.481	0.496	--	0.552	0.458	0.430	0.425
$C/(MR^2)$	0.367	0.367	--	0.371	0.368	0.375	0.380

(a) This work.
(b) SNC model by Dreibus and Wänke 1984, Wänke and Dreibus 1988, 1994, see also Longhi *et al.* 1992.
(c) Goettel 1983.
(d) after Weidenschilling (see BVSP 1981).
(e) Morgan and Anders 1979.
(f) McGetchin and Smyth 1978. Core composition $Fe_{85}S_{15}$ from Johnston and Toksöz 1977 is used.
(g) Anderson 1972.
(h) Other normative minerals include ilmenite, chromite, whitlockite.
(i) Densities are for a high pressure assemblage calculated using an alogithm similar to that descibed by McGetchin and Smyth 1978.
(j) Core densities were calculated using high pressure densities of Fe ($\rho=8.09$) and FeS ($\rho = 5.77$) as listed by Goettel 1981 and $\rho = 8.9$ for Co, Ni, and 6.74 for Fe_3P.
n.d. Not determined.
n.a. Not applicable.

Mars. There are two major differences between our oxygen isotope mixing (OIM) model and their SNC meteorite model. One is that Wänke and Dreibus assume CI chondritic abundances of refractory lithophile elements (e.g., Ca, Al, Ti, REE, U, Th, Mg, Si) in their modeling. We do not make this assumption, or indeed any assumption, about the abundances of refractory lithophiles in the OIM model.

The abundances of these elements are calculated solely from mass balance and Eq. (7). The second difference is the higher Na_2O and K_2O abundances in our model. We address this difference later when we present evidence for aqueous leaching and hydrothermal transport of alkalis and halogens from the martian mantle to the surface of the planet.

The other Mars composition models in Tables III and IV predate the evidence linking the SNC meteorites to Mars and are based on different assumptions. The meteorite mixing models of Anderson (1972) and Ringwood (1981) assume (as we do) that Mars accreted from chondritic material. However, these models are designed to fit older values for the reduced moment of inertia ($C/MR^2 \sim$ 0.370–0.377) that are higher than the currently accepted value of 0.365 (Reasenberg 1977, Kaula 1979). Because the reduced moment of inertia of a homogeneous spherical planet is 0.400, these models yield fairly small cores (11.8–18.2%) and FeO-rich mantles with Mg/(Mg + Fe) $\sim$ 0.67, versus 0.75 in the OIM and WD models. McGetchin and Smyth (1978) used FeO-enriched pyrolite models to derive their bulk composition. Their model was designed to give a mantle density of $\sim$3.55 g cm^{-3}, taken from the internal structure models of Johnston and Toksöz (1976). Morgan and Anders (1979) used Viking atmospheric composition data and XRF analyses plus the Mars 5 orbital gamma ray data to constrain the abundances of four index elements. The elemental abundances of all the other naturally occurring elements were then calculated using the abundances of the index elements. The key assumption in the Morgan and Anders model is that the index elements accurately represent the cosmochemical fractionations undergone by all the other elements. These two models both have Mg/(Mg + Fe) $\sim$ 0.75, about the same as in the OIM model. McGetchin and Smyth (1978) predict a smaller core size and a significantly lower SiO_2 abundance in the mantle. Morgan and Anders (1979) predict a core size (19%) comparable to the OIM model, but also have a lower silica content in the mantle. The last model (Weidenschilling 1981) is a modification of Lewis' equilibrium condensation model in which Weidenschilling's estimates for planetary accretion zones are used to constrain the composition of the nebular condensates accreted by Mars. Although the oxidation state of the mantle (Mg/(Mg + Fe) $\sim$ 0.77) is similar to our result, the condensation model gives a larger core size (25.7%) because the core is predominantly FeS. This is a direct consequence of assuming that Mars accreted from equilibrium condensates whose composition was determined by the radial temperature gradient in the solar nebula (Lewis 1974).

For all models the normative calculations gave mineral assemblages mainly consisting of olivine, pyroxene, and garnet, plus some minor ilmenite, whitlockite, and phosphates. (The minor phases could only be calculated for

models predicting the TiO_2, Cr_2O_3, and P_2O_5 abundances.) The models by Morgan and Anders (1979) and McGetchin and Smyth (1978) also yield normative periclase and wüstite. Morgan and Anders (1979) used the same algorithm as we did but also allowed oxides to react with garnet to form olivine and spinel. Including this transition leads to bulk densities that are 0.5–1% lower than calculated otherwise (see Morgan and Anders 1979).

As expected from the major element chemistry, the normative compositions of the OIM and WD models are similar. Both models give about 51% olivine. However, because the OIM model has higher Na and K abundances, more jadeite is present, leading to higher pyroxene and lower garnet abundances than in the WD model. The bulk silicate densities for the OIM and WD models are 3.50 and 3.52 g cm^{-3}, respectively. This is within the range of 3.46–3.58 g cm^{-3} obtained for the other models in Table IV.

COMPOSITION OF THE MARTIAN CORE

The elemental composition of the core was calculated from the amount of Fe, Co, and Ni present as metal and sulfur in the bulk assemblage

$$C_{core} = C_{bulk(metal\ and\ sulfide)}/X_{core}, \qquad (17)$$

where $X_{core} = 0.2063$ is the mass fraction of the core from Table III. Our predicted bulk composition of the martian core is 89.4% Fe, Co, and Ni, 10.6% sulfur, and 0.05% phosphorous, or equivalently 29.0% FeS, 1.6% Fe_3P, and 69.4% FeCoNi–metal (Table IV). An estimate of the core density was obtained by computing the bulk core density from the high pressure densities of Fe and FeS (8.09 and 5.77 g cm^{-3}, respectively, Goettel 1981) and the densities of Fe_3P (6.74 g cm^{-3}) and Ni, Co (8.9 g cm^{-3}). These values were also used to calculate the core densities for the other models in Table IV.

The predicted sulfur contents of the martian core are 10.6% (OIM) and 14.2% (WD) in the two models. These differences are potentially significant because the sulfur content of the martian core has important implications for the physical state of the present-day core (totally liquid, totally solid, or two phase), the temperature of the core, thermal convection in the core, and the existence of a magnetic field on Mars today (Longhi et al. 1992, Schubert et al. 1992). In particular, Schubert et al. (1992) estimated that the present martian core would be completely liquid if the sulfur content of the core were ~15% or more. While the WD model predicts about this much sulfur, the OIM model does not.

The lower sulfur content predicted for the martian core by the OIM model gives a core density of 7.3 g cm^{-3}. In comparison, the higher sulfur content predicted for the martian core by the WD model gives a somewhat lower

density of 7.0 g/cm^3. Longhi et al. (1992) list a core density of 6.8 g cm^{-3} for the WD model and generally give lower core densities than we calculate for the other models in Table IV. This difference is partly due to somewhat higher densities for Fe and FeS used here.

However, there also seems to be a computational error in the work by Longhi et al. (1992). For example, in their Table 5, Longhi et al. compute the density of Fe + 14.5% sulfur (60.2% Fe metal and 39.8% FeS) as 7.0 g cm^{-3} from Fe metal with $\rho = 8.0$ and FeS with $\rho = 5.6$ g/cm^3. It seems that they used

$$\rho_{core} = \Sigma F_i \rho_i \qquad (18)$$

to compute the bulk densities, where $F_i = M_i/M_{tot}$ is the fractional mass and ρ_i is the density for Fe metal and FeS. However, the density needs to be calculated from

$$\rho_{core} = \frac{\Sigma M_i}{\Sigma V_i} = \frac{M_{total}}{\Sigma(F_i M_{total}/\rho_i)} = \frac{1}{\Sigma(X_i/\rho_i)}. \qquad (19)$$

Using Eq. (19), we obtain a density of 6.8 g cm^{-3} instead of 7.0 g cm^{-3} for the example in their Table 5. Therefore, the density calculations in Longhi et al. (1992) may be incorrect.

It is important to keep in mind that the calculated core densities here do not include any dependence on temperature. Better estimates for the densities require more detailed geophysical modeling. However, the approach taken here should be sufficient to allow a reasonable estimate of the densities and to compare the results of the different Mars bulk composition models.

BULK DENSITY AND ESTIMATED MOMENT OF INERTIA

We calculated bulk densities for the OIM model and other models in Table IV using an equation similar to (19). The OIM model predicts that the bulk density of Mars is 3.92 g cm^{-3} and the WD model gives a bulk density of 3.95 g cm^{-3}. Bulk densities from the other models range from 3.87 to 3.99 g cm^{-3}. For comparison, the current value for the observed mean bulk density of Mars is 3.9335($\pm$0.0004) g cm^{-3} (Esposito et al. 1992).

Fractional core radii (r_{core}/R_{total}) for different Mars models were calculated from

$$\frac{r_{core}}{R_{total}} = \left(\frac{\rho_{bulk} - \rho_{mantle}}{\rho_{core} - \rho_{mantle}}\right)^{(1/3)} \qquad (20)$$

and are listed in Table IV. The OIM model and the WD model predict core sizes of 48 to 50% of Mars' radius,

respectively. The other models give core radii of 43 to 55% of the total.

The reduced moment of inertia follows from

$$\frac{C}{MR^2} = \frac{\rho_{\text{mantle}} + (\rho_{\text{core}} - \rho_{\text{mantle}})(r_{\text{core}}/R)^5}{2.5\,\rho_{\text{bulk}}} \quad (21)$$

and is also listed in Table IV. The OIM model and the WD model both give $C/MR^2 \sim 0.367$ and are closest to the currently accepted value of 0.365 (Reasenberg 1977, Kaula 1979), while the other models yield higher values. However, as discussed earlier, some of the older models are based on the older values of $C/MR^2 \sim 0.370$–0.377 (Anderson 1972, Ringwood 1981).

MINOR AND TRACE ELEMENT CHEMISTRY OF THE MARTIAN MANTLE

Here we use the OIM model to predict the abundances of minor and trace elements in the martian mantle. Lithophile elements, which do not enter the core, as well as chalcophile and siderophile elements, which partition between the mantle and core, are considered. Later, we use our own calculations of element ratios in SNC meteorites to make independent predictions of minor and trace element abundances in the martian mantle. We then compare our two sets of predicted elemental abundances (OIM and SNC element ratios) with each other and with prior element ratio calculations by Wänke and Dreibus and Treiman et al. (1986, 1987). Our predicted abundances agree well with each other and with those from the prior element ratio calculations.

The abundances of the lithophile trace elements (e.g., alkalis, halogens, Ba, REE) in the mantle were computed from Eq. (16) using $X_{\text{mantle}} = 0.7937$ and taking elemental abundances in bulk Mars (C_{bulk}) from Table II. This is the same procedure used earlier for Ca, Al, Mg, and the other lithophile major elements. No assumptions other than mass balance are needed to predict lithophile element abundances in the mantle.

Siderophile and chalcophile elements partition between the silicate mantle and the metal–sulfide core during planetary differentiation. Thus, we need to use partition coefficients, which are concentration ratios of an element between two components (such as metal and silicate, or two different silicates, or silicate and melt, or sulfide and silicate) to take this redistribution into account. This is described in more detail below.

The siderophiles Ni and Co are compatible in olivine and have olivine/melt partition coefficients, D_{ol} of about 9 and 3, respectively (e.g. Kennedy et al. 1995). On the other hand, other siderophiles such as Mo and W are incompatible in olivine and have olivine/melt partition coef-

TABLE V
(Metal & Sulfide)/Silicate Partition Coefficients 'D' Used to Calculate Chalcophile & Siderophile Element Distribution in Mars

	D	Ref.		D	Ref.		D	Ref.		D	Ref.
Ga	3	1	P	3.3	4	Cu	100	1	Ni	2730	6
In	3	est.	As	700	1	Ag	>200	1	Ru	10000	est.
Tl	3	est.	Sb	1000	1	Au	20000	1	Rh	10000	est.
Ge	500	2*	Bi	1000	est.	Mo	250	1	Pd	10000	7**
Sn	20	3*	S	1000	5	W	3	1	Os	10000	est.
Pb	2.1	4	Se	1000	1	Re	71000	4	Ir	710000	4
			Te	1000	est.	Co	100	1	Pt	10000	7**

Note. Partition coefficients (D) for a core containing about 30 mass% FeS and 70 mass% FeNi. Partition coefficients are listed for weight ratios (D = $C_{\text{metal\&sulfide}}/C_{\text{silicate}}$). In some cases the partition coefficients are calculated from 'pure' D(metal/silicate) and D(sulfide/silicate) partition coefficients using D = $Y_{\text{met}}D_{\text{met/sil}} + Y_{\text{sulf}}D_{\text{sulf/sil}}$ where Y_{met} and Y_{sulf} are the mass fraction metal and sulfide in core. (1) Lodders and Palme 1991a,b; Lodders 1991. (2) Schmitt et al. 1989. (3) Capobianco et al. 1995. (4) Jones and Drake 1986. (5) A. Holzheid, unpublished data from this laboratory. (6) Hillgren 1991. (7) Stone et al. 1990. est.: Estimated value.
* D(metal/silicate) only.
** D(sulfide/silicate) only; similar values are assumed for D(metal/silicate).

ficients $D_{\text{ol}} \ll 1$. Thus, during core formation, Ni and Co were partly scavenged by olivine while other siderophiles such as Mo and W were more efficiently partitioned into the metal–sulfide melt that sank to form the martian core. Taking possible olivine fractionation into account, we calculated the concentration of siderophiles and chalcophiles in the mantle from

$$C_{\text{mantle}} = C_{\text{bulk}} (D_{\text{ol}}X_{\text{ol}} + X_{\text{sil}})/[(D_{\text{ol}}X_{\text{ol}} + X_{\text{sil}} + D_{\text{core}}X_{\text{core}})(X_{\text{ol}} + X_{\text{sil}})]. \quad (22)$$

The OIM model predicts that the martian mantle is about 51% olivine (Table IV). Thus, the mass fraction of olivine, X_{ol} is $0.51 \times 0.7937 \simeq 0.40$, the mass fraction of other silicates is ~ 0.39, and the mass faction of the core is ~ 0.21. The D_{core} values in Eq. (22) are the Nernstian (metal–sulfide)/silicate partition coefficients, which are defined as

$$D_{\text{core}} = C_{(\text{metal\&sulfide})}/C_{\text{silicate}}. \quad (23)$$

The partition coefficients used here are listed in Table V. These partition coefficients are for a metal–sulfide melt containing $\sim 30\%$ FeS. The predicted FeS contents of the martian core are ~ 29 and $\sim 39\%$, respectively, in the OIM and WD SNC meteorite models (Table IV). Only the "pure" metal/silicate ($D_{\text{met/sil}}$) and "pure" sulfide/silicate ($D_{\text{sulf/sil}}$) partition coefficients are available for some elements. In these cases, partition coefficients appropriate for a core containing about 30% iron sulfide were calculated from

$$D_{\text{(metal\&sulfide)/silicate}} = Y_{\text{met}}D_{\text{met/sil}} + Y_{\text{sulf}}D_{\text{sulf/sil}}, \quad (24)$$

where Y_{met} (0.7) and Y_{sulf} (0.3) are the mass fractions of metal and sulfide in the core. No partition coefficients are available for In, Tl, Bi, Te, and some noble metals. In these cases partition coefficients were estimated by comparison with partition coefficients for other elements in the same chemical group in the periodic table (e.g., In and Tl from Ga, Bi from As and Sb, Te from S and Se). Indium, Tl, Bi, and Cd are normally assumed to be lithophile, but chalcophile behavior increases with increasing atomic number down a group in the periodic table. However, we did not attempt to estimate the partition coefficient for Cd.

The olivine/liquid partition coefficients for Ga and Ge were taken from Malvin and Drake (1987). Unfortunately, olivine/liquid partition coefficients are not known for some siderophiles. Following Jones and Drake (1986), we take $D_{\text{ol}} = 0.01$ for Mo and W, and take the same value for Cu. For all other siderophile elements, we take $D_{\text{ol}} = 1$, assuming that they partition homogeneously among all mantle silicate phases.

Our predicted abundances for lithophile, chalcophile, and siderophile elements in the mantle of Mars are listed in Table VI. The data for the chalcophiles and siderophiles are listed with a capital 'D' to show that their distribution between the martian mantle and core was estimated using partition coefficients. Before discussing these results in any detail, we first describe our element ratio calculations which give independent predictions of minor and trace element abundances in the martian mantle.

UPDATED ELEMENT RATIO CALCULATIONS FOR MINOR AND TRACE ELEMENT ABUNDANCES IN THE MARTIAN MANTLE

The SNC meteorites are igneous rocks which underwent varying degrees of differentiation and elemental fractionation (e.g., McSween 1994). Their elemental compositions are related to, but are not identical to, the elemental composition of the martian mantle. SNC meteorite models for the composition of Mars, such as the Wänke–Dreibus model, use a method called element correlation, or element ratios, to derive the elemental composition of the martian mantle from chemical analyses of the SNC meteorites.

The element ratio method is based upon Goldschmidt's observations that elements with similar ionic radii and similar silicate/melt partition coefficients (i.e., similar compatibility) fractionate to about the same extent during igneous processing. Although the absolute concentrations of a pair of elements may be different in a mantle source and the igneous rock formed from it, the relative concentrations of the two elements in the rock and mantle source are approximately constant. Then, if the absolute mantle concentration of one element in the pair can be determined

by some other means, the mantle abundance of the second element can easily be calculated from the element ratio using the abundance of the "reference" element.

A simple example given by Hofmann (1988) is useful for illustrating the element ratio concept. Consider two elements 1 and 2, with concentrations $c°$ and c, respectively, in a mantle source and melt. (The igneous rock is assumed to form by crystallization of the melt.) If F is the fraction of melting (ranging from 0 for no melting to 1.0 for complete melting) and D_i is the silicate/melt partition coefficient for either element then we can write

$$\frac{c_1}{c_2} = \frac{c_1^0}{c_2^0} \cdot \frac{F + D_2(1 - F)}{F + D_1(1 - F)} \quad (25)$$

for the elemental concentrations in the melt and mantle source. As long as $D_1 \sim D_2 \ll F$, then

$$\frac{c_1}{c_2} \sim \frac{c_1^0}{c_2^0} \quad (26)$$

and the concentration ratio in the melt and mantle source are approximately constant. For example, in the case of highly incompatible elements with $D_i \sim 0.001$, Eq. (26) holds for all F values greater than about 0.01 (that is 1% melting or more). Larger degrees of melting are required for Eq. (26) to be valid for ratios of more compatible elements with larger silicate/melt partition coefficients. But even for elements with $D_i \sim 0.01$, only 10% melting is needed for element ratios to be constant in the source and melt. Over time, geochemical analyses and modeling of terrestrial rocks, lunar samples, and basaltic achondrites (eucrites) have shown that several element pairs such as K/La, Ba/La, and W/U display good correlations and satisfy Eq. (26).

We used the element ratio method to give independent estimates of elemental abundances in the martian mantle. This helps to provide a check on the mantle abundances calculated from the OIM model, particularly for the siderophile and chalcophile elements where partitioning between the mantle and core had to be considered. Our calculations include newly discovered SNC meteorites (e.g., Mittlefehldt 1994) and more recent elemental analyses that were unavailable when the calculations by Wänke and Dreibus (1988, 1994) and Treiman *et al.* (1986) were done.

Analyses for 11 SNC samples (counting the two lithologies of EETA79001) were collected from the literature. Mean elemental abundances were calculated for all samples and used to compute element ratios. The Appendix lists the element pairs, the calculated ratios, the uncertainties of each ratio ($\pm 1\sigma$ range and the percent deviation from the mean), and the number of samples used to calculate each ratio. This table also lists the element ratios ob-

TABLE VI
Predicted Elemental Abundances in the Martian Mantle and Crust

	OIM (a)	Element Ratios (b)	W&D (c)	Tr. et al. (d)	M&A (e)		OIM (a)	Element Ratios (b)	W&D (c)	Tr. et al. (d)	M&A (e)
Li	2.1	0.9 (Li/La)*	2.8	1.2	2.4	Ag ppb	< 1.4 D	7 (Ag/La)*	--	6	--
B	0.63	--	--	--	0.003	Cd ppb	110	--	--	--	0.76
F	41	23 (F/Li, Li = 2.1)	32	23	23.6	In ppb	(~12 D)	18 (In/Al, Al=15300)	14	6.8	--
Na	7270	1470 (Na/Ti)	3700	1740	710	Sn ppb	190 D	--	--	--	--
Mg wt%	17.84	= 17.84	18.2	--	18.0	Sb ppb	0.4 D	5 (Sb/La)*	--	0.9	--
Al wt%	1.53	0.58 (Al/Ti)	1.6	0.67	3.4	Te ppb	(~2.1 D)	--	--	--	--
Si wt%	21.20	--	20.8	--	19.4	I ppb	120	20 (I/La)*	32	--	0.59
P	740 D	590 (P/Tb)	700	580 $	.--	Cs ppb	154	76 (Cs/La)	70	92	26
S	110 D	250 (S/Ti)	--	255	--	Ba	5.4	6.3 (Ba/La)	--	8.8	9.9
Cl	150	19 (Cl/La)	38	24	0.88	La	0.400	= 0.400	0.48	=0.46	0.93
K	920	246 (K/La)	305	345	77	Ce	1.12	--	--	--	2.46
Ca wt%	1.68	--	1.75	--	3.7	Pr	0.167	--	--	--	0.31
Sc	10.5	8.2 (Sc/Ti)	--	7.7	23.5	Nd	0.850	= 0.850	--	--	1.70
Ti	815	= 815	840	=850	1950	Sm	0.250	--	--	--	0.51
V	97	42 (V/Ti)	--	28	200	Eu	0.099	0.082 (Eu/Ti)	--	0.102	0.19
Cr	4640	6240 (Cr/Mg)	5200	2660	4450	Gd	0.395	--	--	--	0.69
Mn	2840	3480 (Mn/Fe)	3560	--	1160	Tb	0.069	= 0.069	--	--	0.13
Fe wt%	13.38	= 13.38	13.9	--	12.3	Dy	0.454	--	--	--	0.88
Co	67 D	87 (Co/Mg)	68	50	--	Ho	0.098	--	--	--	0.19
Ni	140 D	290 (Ni/Mg)	400	90	--	Er	0.300	--	--	--	0.56
Cu	2.0 D	2.9 (Cu/Ti)	5.5	2.9	--	Tm	0.050	--	--	--	0.084
Zn	83	60 (Zn/Fe)	62	66 $	42	Yb	0.277	--	--	--	0.56
Ga	4.4 D	6.3 (Ga/Al, Al=15300)	6.6	2	2.4	Lu	0.044	--	--	--	0.094
Ge	0.14 D	--	--	--	--	Hf	0.229	0.224 (Hf/Ti)	--	--	0.56
As	0.014 D	0.04 (As/La)*	--	0.064	--	Ta ppb	29	35 (Ta/La)	--	50	56.2
Se	0.04 D	0.06 (Se/Ti)	--	0.071	--	W ppb	80 D	62 (W/U)	67	52 $	--
Br	0.94	0.12 (Br/La)	0.145	0.16	0.0047	Re ppb	0. 005D	--	--	0.04	--
Rb	3.5	0.94 (Rb/La)	1.06	1.34	0.26	Os ppb	(~0.4 D)	--	--	--	--
Sr	13.5	--	--	--	35	Ir ppb	0.05 D	--	--	--	--
Y	2.8	--	--	--	6.4	Pt ppb	~0.7 D	--	--	--	--
Zr	8.3	--	--	--	38	Au ppb	< 0.05 D	1.5 (Au/La)*	--	0.55 $	--
Mo	0.017 D	0.054 (Mo/Ti)*	0.118	0.059 $	--	Tl ppb	(~10 D)	3.7 (Tl/Al, Al=15300)	3.6	2.8	0.17
Ru ppb	(~0.5 D)	--	--	--	--	Pb ppm	0.38 D	--	--	--	--
Rh ppb	(~0.1 D)	--	--	--	--	Bi ppb	(~0.1 D)	--	--	0.9	--
Pd ppb	(~0.4 D)	--	--	--	--	Th ppb	56	80 (Th/La)*	56	96	125
						U ppb	16	17 (U/La)	16	31	35

Note. Data in ppm if not noted otherwise. No data for Be, Nb, and Hg because their average abundances in chondrites are unknown. --: Data not available.

(a) This model. Numbers followed by 'D' are obtained assuming core-mantle partitioning. Data in parenthesis are calculated using estimated partition coefficients (see text).

(b) Data obtained from element ratios (see Appendix) using the element pair listed in parenthesis. Adopted values for the reference element are marked by '='. * Element ratios show strong scatter and are not very reliable.

(c) Dreibus & Wänke 1984, Wänke & Dreibus 1988, 1994. Data from element ratios in SNC meteorites and assuming relative CI-chondritic abundances for refractory elements on the SPB. CI data from Palme *et al.* 1981 were used.

(d) Treiman *et al.* 1986, 1987. Data from element ratios in SNC meteorites, see Appendix. La and Ti mantle abundance of 1.95xCI were used here to calculate abundances of elements other than La or Ti from element ratios, as was done by Treiman *et al.* 1987 for some elements.

($) Following corrections were made: *P*: Using an absolute Ti abundance of 1.95x CI and the P/Ti ratio given by Treiman *et al.* 1986 (see Appendix) yields 580 ppm P instead of 690 ppm as listed by Treiman *et al.* 1987. *Zn*: Treiman *et al.* 1986 take Zn abundances in SNC meteorites as representative for the whole mantle. Their measurements yield a mean Zn abundance of 66 ppm in SNCs. From their listed CI and refractory element normalized value of 0.25, an absolute Zn abundance of 150 ppm results. *W*: Treiman *et al.* 1987 list ppm instead of ppb. *Mo*: See comment in Appendix. Treiman *et al.* 1987 list Mo = 50 ppb. *Au*: Treiman *et al.* 1987 list 0.15 ppb, the 0.55 ppb listed here is from their Au/La ratio (see Appendix).

(e) Four component meteorite model by Morgan & Anders 1979. If no mantle abundance is given by Morgan & Anders, a silicate portion of 81% is used to compute mantle abundances for elements which do not partition into the core.

tained by Treiman *et al.* (1986) and Wänke and Dreibus (1988, 1994) for comparison.

We converted the element ratios from the Appendix into absolute elemental abundances in the martian mantle using the refractory lithophile elements (La, Ti, Al, Mg, Nd, Tb) and Fe as reference elements. These reference elements were chosen because past work shows that they display good correlations. The mantle abundances of these reference elements were taken from our OIM model calculations in Table VI. The mantle abundances calculated from the element ratio method are also listed in Table VI, along with the element pair used in each computation. This method is very similar to that of Wänke and co-workers (Laul *et al.* 1986, Wänke and Dreibus 1988, 1994), who determined the mantle and core size and then used element ratios in SNC meteorites to determine the mantle abundances of several elements.

COMPARISONS TO PRIOR WORK

Table VI summarizes predictions for the composition of the primordial martian mantle. Results from the OIM model and our updated element ratio calculations are compared to the WD SNC meteorite model (based on element ratio calculations), element ratio calculations by Treiman *et al.* (1986, 1987), and to predictions from Morgan and Anders (1979). As noted earlier, the latter model does not use SNC meteorites to model Mars but assumes instead that Mars formed from chondritic material that underwent the same cosmochemical fractionations as experienced by chondritic meteorites. Below we discuss comparisons between our results and the prior work in more detail. We divide this discussion into three groups of elements: refractory lithophile elements, siderophile and chalcophile elements, and volatile lithophile elements. These divisions are assigned on the basis of elemental volatilities in the solar nebula (Larimer 1988).

Refractory Lithophile Elements

Figure 2 shows the predicted abundances of refractory lithophile elements in the mantle of Mars. The elements are plotted in order of increasing volatility (decreasing condensation temperature) in the solar nebula and their abundances are normalized relative to the La abundance in CI chondrites. Zirconium to calcium are highly refractory, while Eu to Mn are refractory lithophiles. The Wänke–Dreibus model assumes that all refractory lithophiles (Zr to Mn in Fig. 2) have CI chondritic relative abundances and are not fractionated from one another. The points for their model all fall in a straight line at unity in Fig. 2. Morgan and Anders (1979) assume that the highly refractory lithophiles are unfractionated, and their data points also fall at unity. The minor deviations, such as Hf, are
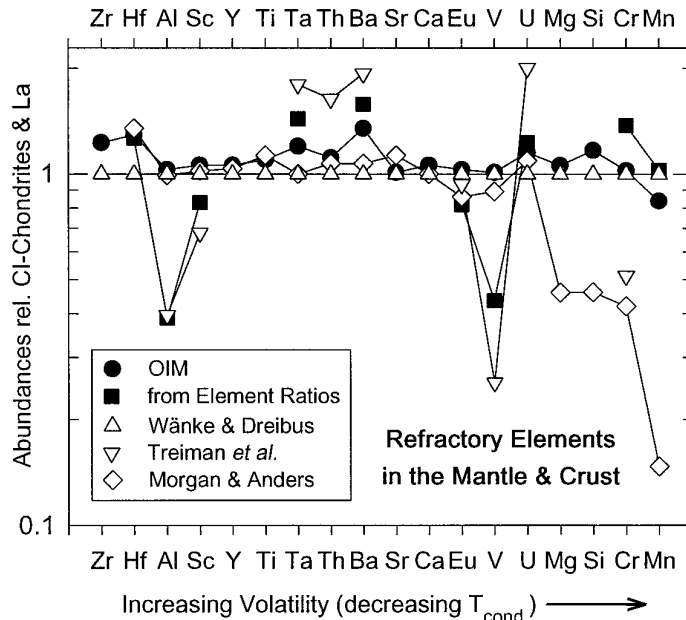

FIG. 2. Abundances of refractory elements in the silicate portion (mantle and crust) of Mars. Elements are listed in order of increasing volatility, as indicated by their decreasing condensation temperatures. Abundances of refractory elements from the OIM model reflect abundance variations in CI, CV, and H chondrites (Table VI). For comparison, the elemental abundances from the model by Morgan and Anders (1979) and the Wänke and Dreibus model are shown. Relative to CI and La, the abundances in the Wänke and Dreibus model are defined as unity, while Morgan and Anders assign lower abundances to less refractory elements. Also shown are abundance data obtained from SNC meteorites using element ratios (Treiman *et al.* 1986 and this study). The variations in the data from the element ratio method reflect elemental fractionations in the source regions of the SNC meteorites (see text for more details).

due to revisions in CI elemental abundances since their paper. However, Morgan and Anders (1979) predict lower abundances for Mg, Si, Cr, and Mn. The OIM model predicts relative abundances close to CI chondritic for most of the refractory lithophiles in Fig. 2. These abundances are determined solely by mass balance without the assumptions made in the WD model.

Our updated element ratio calculations and the older calculations by Treiman *et al.* (1986, 1987) predict fractionated refractory lithophile abundances for several elements. The fractionations arise because the refractory lithophiles are not constrained to have CI chondritic relative abundances in these calculations. However, the apparent depletions (for Al, Sc, V) and enrichments (for Ta, Th, Ba, U) may be an artifact of assuming that the SNC meteorites provide representative samples of the entire martian mantle. Earlier, we noted that garnet and possibly also spinel are constituents of the martian mantle. Aluminum, Sc, and V are more compatible in garnet and spinel than La, the normalizing element. If the source regions of the parental

magmas for the SNC meteorites contained garnet or spinel, the magmas would have been depleted in Al, Sc, and V relative to the mantle source. During crystallization of the SNC meteorites from these depleted magmas, "new" element ratios for Al, Sc, and V were established. However, these new element ratios are lower than the ratios in the mantle source region. Treiman *et al.* (1986) also noted that the presence of spinel can explain the apparent Al depletion.

On the other hand, Ta, Th, Ba, and U are more incompatible than La (e.g., Hofmann 1988) and thus, these elements easily become enriched in any melts. Again, once crystallization of these melts forms the minerals in SNC meteorites, well defined U/La or Ta/La ratios may appear but these ratios do not necessarily reflect the ratio of the bulk mantle.

Another interesting element shown in Fig. 2 is Cr. Treiman *et al.* (1986) obtained low normalized Cr abundances of about 0.5 which they ascribed to evaporative loss. Chromium and Li have similar volatilities and Treiman *et al.* (1986) calculated a normalized Li abundance of 0.4 from the Li/La ratio in SNC meteorites. However, the Li/La ratio in SNC meteorites is very unreliable and the data scatter strongly (see Table VI and Appendix). Therefore, Treiman *et al.* (1986) may have underestimated the Cr abundance, although their value is close to that of Morgan and Anders (1979).

It is also interesting to compare the Cr and Mn abundances. Nebular condensation calculations predict that Mn is more volatile than Cr (Fegley 1993). Therefore, if Cr were depleted by volatilization, Mn should be depleted as well. However, Wänke and Dreibus (1988) pointed out that the Mn abundances in SNC meteorites are close to those expected assuming the CI relative abundance of Mn in the martian mantle. Their arguments indicate that Mn is not depleted. We also predict that Mn is essentially undepleted. The OIM model predicts a slight Mn depletion ($\sim$0.85 × the CI Mn/La ratio), while our updated element ratio calculations predict the CI ratio.

On the other hand, our element ratio calculations predict a slight Cr enrichment in the bulk mantle. However, this is based on the Cr/Mg ratio, which may be affected by Mg removal. Olivine is a good candidate for removing Mg from the source regions of SNC parent melts because Mg has an olivine/liquid partition coefficient about six times larger than that of chromium (Kennedy *et al.* 1995). Fractionation of the Cr/Mg ratio by pyroxene removal is less likely because Mg and Cr have similar pyroxene/liquid partition coefficients.

Chalcophile and Siderophile Elements

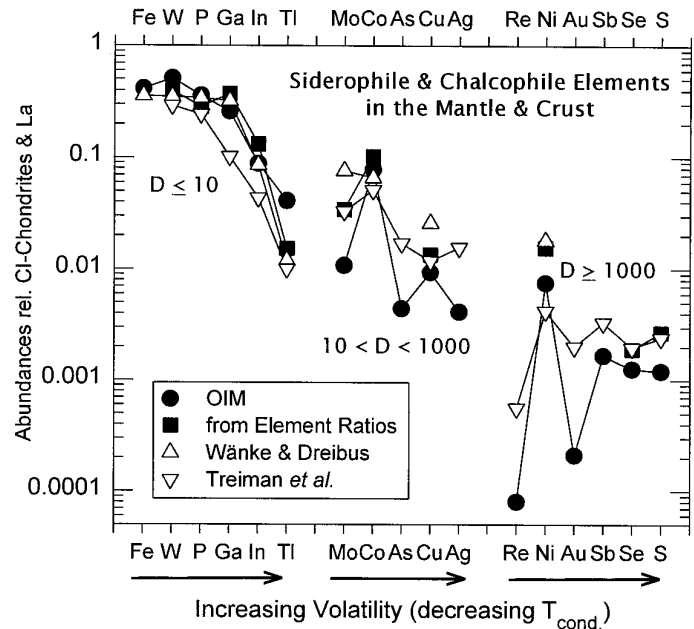The normalized mantle abundances for the chalcophile and siderophile elements are plotted in Fig. 3. The ele-

FIG. 3. Elemental abundances of siderophile and chalcophile elements in the martian mantle. Elements are grouped according to their (metal and sulfide)/silicate partition coefficient (D) and within a group are arranged by increasing volatility. The data from the OIM model were calculated using bulk elemental abundances and partition coefficients (Table V) assuming core–mantle equilibrium. The other data shown for comparison are all obtained using the element ratio method. See text for a more detailed discussion.

ments are further classified according to their (metal and sulfide)/silicate partition coefficients. Elements are listed in order of increasing volatility within each group. Morgan and Anders (1979) did not predict mantle abundances, but only bulk Mars abundances. We included their predictions for lithophiles (which reside only in the mantle) in Fig. 2. However, without making further assumptions we cannot discuss their predictions for chalcophiles and siderophiles, which partition between the core and mantle of Mars.

Not surprisingly, Fig. 3 shows that the three sets of element ratio calculations done by us, Treiman *et al.* (1986, 1987), and by Wänke and colleagues generally agree (with some exceptions). In contrast, the abundances predicted by the OIM model rely on partition coefficients (D values) to determine the distribution of siderophiles and chalcophiles between the martian mantle and core. Overall, the abundances from the element ratio calculations and from the OIM model show similar trends, although there are some variations which we will discuss next.

First we consider slightly siderophile and chalcophile elements with $D \leq 10$ for partitioning between metal and sulfide and silicate. The abundances of Ga, In, and Tl show the largest disparity among the different models. The three sets of element ratio calculations yield different abundances, although one would expect better agreement since

all three sets of calculations use similar data sets for the SNC meteorites. However, Treiman *et al.* (1986) predict systematically lower abundances for Ga, In, and Tl. This can easily be understood because Treiman *et al.* (1986) used Ga/Ti, In/Ti, and Tl/Ti ratios while our element ratio calculations and those by Wänke and coworkers used elemental ratios relative to Al.

As discussed earlier, the Al/Ti ratio in SNC meteorites is probably fractionated because Al was incorporated into spinel or garnet in the mantle source regions. Because Ga, In, and Tl correlate well with either Ti or Al (see Appendix), the question arises of which ratios should be preferred for determining absolute mantle abundances for these elements. A guide to answering this question is the compatibility of Ga, Al, and Ti, for which partition coefficients of mantle minerals provide a measure. Gallium easily replaces Al in spinel and the $D_{sp/liq.}$ is about 4.6 for Ga and 3.3 for Al (Malvin and Drake, 1987), while Ti is not compatible in spinel. The same may hold for garnet, however, we are not aware of any determinations of Ga partition coefficients between garnet and silicate melt. Thus, the bulk Ga/Al ratio is probably insensitive to garnet or spinel fractionation and the Ga/Al ratio in SNC meteorites probably more closely resembles the bulk planetary value. On the other hand, the Ga/Ti ratio from SNC meteorites probably leads to Ga abundances which are too small, because some Ga, but no Ti, can be kept in the source regions of the SNC parent melts by garnet or spinel fractionation. A similar situation may hold for In and Tl, which may also replace Al. Unfortunately, no partition coefficients for In and Tl for garnet or spinel are available.

The OIM model predicts Ga and In abundances that agree within a factor of 2 with abundances from the element ratio calculations. In fact OIM predicts Ga and In abundances in between the high and low values from the different element ratio calculations. Our model predicts a Tl abundance about 4 times higher than obtained from element ratios. The Tl abundance in the OIM model was calculated using an estimated (metal and sulfide)/silicate partition coefficient of 3, which may be too low. Experimental determinations of the metal/silicate and sulfide/silicate partition coefficients for Tl are needed to test this explanation. (Experimental data are also needed for In partition coefficients.) Another possibility is that Tl was depleted by volatilization during accretion. However, In and Tl have similar condensation temperatures in the solar nebula (Fegley 1993), indicating similar volatility. It seems unlikely that Tl but not In, which is lighter, would be lost during the accretion of Mars.

Now we consider siderophile and chalcophile elements with (metal and sulfide)/silicate partition coefficients in the range from 10 to 1000. Molybdenum, Co, As, Cu, and Ag are in this group. The Co and Cu abundances obtained from element correlations agree well with those predicted

by the OIM model. The comparison is somewhat difficult for Mo, because Mo has been only analyzed in three SNC meteorites. As a result the element ratios are not well defined. It seems that Mo/Ti ratios (used by Treiman *et al.* 1987 and in this work) are better suited than Mo/Nd ratios (used by Wänke and co-workers) to estimate the Mo abundance in the silicate mantle because the variations in the Mo/Ti ratios (30%) are smaller than for the Mo/Nd ratios (65%, see Appendix). However, more Mo analyses of SNC meteorites are necessary to estimate the Mo abundance from element ratio calculations.

The mantle abundance for Co from the OIM model, our element ratio calculations, and the SNC meteorite model of Wänke and Dreibus yield the same value within uncertainties. We used the Co/Mg ratio to calculate a Co abundance of 87 ppm, while Wänke and Dreibus (1988) used a better suited correlation of Co vs (FeO + MgO) to determine a Co abundance of 68 ppm. The value by Wänke and Dreibus is close to the value of 67 ppm predicted by the OIM model using partition coefficients. The abundance of 50 ppm Co obtained by Treiman *et al.* (1986) is not based on an element ratio. Instead, Treiman *et al.* (1986) assumed that the martian mantle has similar abundances of Co, Bi, F, Re, and Zn as found in SNC meteorites because these ''indifferent'' elements apparently distribute homogeneously among mantle silicates.

The estimated Cu abundances in the martian mantle range from 2.0 to 5.5 ppm. Treiman *et al.* (1986) used the Cu/Ti ratio to estimate a Cu abundance of 2.9 ppm, which is the same value we calculated in our updated element ratio calculations. Wänke and Dreibus took the Cu abundance of 5.5 ppm in ALH77005, a shergottite close in composition to their bulk mantle composition, as representative for the martian mantle. The OIM model yields a Cu abundance of 2.0 ppm in the martian mantle, closer to the values obtained from the Cu/Ti ratios.

A comparison of the As and Ag abundances predicted by the OIM model and element ratio methods is more complicated because no well defined correlations exist for these two elements. Treiman *et al.* (1986) calculated As/La and Ag/La ratios and used them to estimate the mantle abundances of As and Ag. Their results are included in Fig. 3 along with the abundances predicted by the OIM model. In both cases OIM predicts abundances about a factor of five lower than the element ratios. Given the uncertainties in the element ratios and in the partition coefficients for Ag, these data should not be overinterpreted.

Next, we consider the highly siderophile and chalcophile elements with *D* values of 1000 and larger. Sulfur, Se, Te, Sb, Ni, Re, Au, and the noble metals are in this group. The best comparisons can be made for Ni, S, and Se because good element correlations exist for them. The abundance of S and Se from the element ratios of S/Ti or Se/

Ti are within a factor of two of the abundances obtained from the OIM model.

Nickel abundances calculated from the Ni/Mg ratio are 290 ppm Ni (our results) or 400 ppm Ni (Wänke and Dreibus 1988). The difference is probably due to the more recent data set of SNC meteorite analyses that we used. Treiman *et al.* (1986) obtained 90 ppm Ni from the Ni/Cr ratio. However, as mentioned above, they assumed that Cr is depleted due to volatility. As a consequence, using their lower mantle abundance for Cr then leads to a lower Ni abundance. Taking our updated Ni/Cr ratio of 0.055 (see Appendix) and the Cr abundance of 4640 ppm predicted from the OIM model, we calculate a Ni abundance of 255 ppm in the mantle. This is close to the Ni abundance we calculated from the Ni/Mg ratio. However, the Ni mantle abundance derived from the OIM model is only 140 ppm. This value is derived by considering partitioning of Ni between the martian core, olivine, and other mantle silicates. The OIM model value may be too low because Ni partitioning into pyroxenes, in which Ni also shows some compatibility, was neglected. More detailed modeling of Ni partitioning among mantle silicates could refine this value.

The element ratio method is not very reliable for other highly siderophile elements like Sb and Au, because the Sb/La or Au/La ratios strongly scatter (see Appendix). For Re, Treiman *et al.* (1986) assume indifferent behavior as they did for Co. Their mantle Re abundance is about 0.04 ppb, while the OIM model prediction is about a factor of ten lower. Again the OIM value requires a calculation of Re partitioning between the core and mantle. (For a recent discussion of the Re and Os abundances in SNC meteorites see Warren and Kallemeyn 1996).

The abundances predicted by OIM for other highly siderophile elements are listed in Table VI. In most cases, the data were obtained using estimated partition coefficients (Table V), so these values are best regarded as first-order estimates.

Leaving aside the problems with some highly siderophile element abundances, it appears that the abundances of siderophile and chalcophile elements calculated from the OIM model taking into account the distribution of these elements between the martian mantle and core are consistent with their elemental abundances obtained from element ratio calculations that we have done. Furthermore, our elemental ratio calculations generally agree well with prior calculations done by Wänke and colleagues, and Treiman *et al.* (1986,1987).

Volatile Lithophile Elements

Figure 4 shows the abundances of volatile lithophile elements (the alkalis, halogens, and Zn) predicted by the OIM model and element ratio calculations. Considerable uncertainty still exists about the nebular condensation tem-
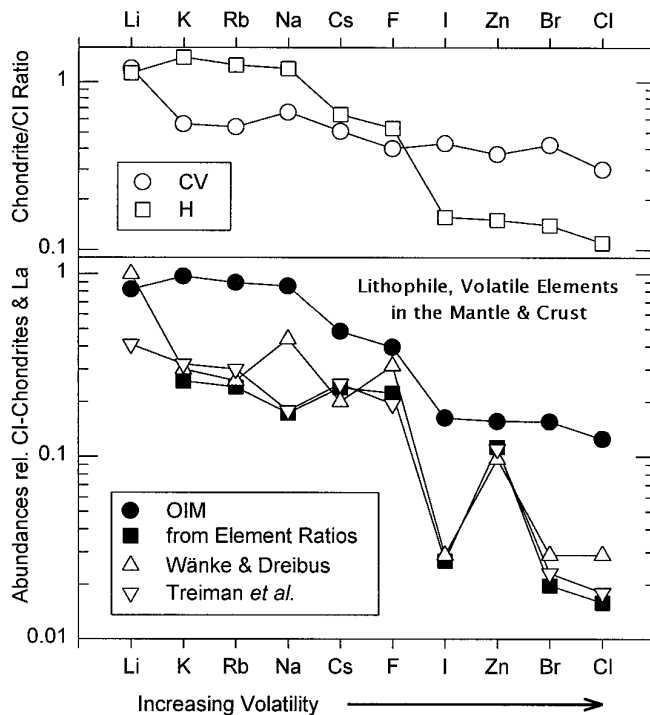

FIG. 4. Abundances of lithophile, volatile elements in the martian mantle. Elements are in order of increasing volatility, as defined by the chondritic CV/CI and H/CI abundance ratios. In particular, the OIM model predicts halogen abundances 6–8 times higher than predicted by element correlations. As discussed in the text, the halogen and alkali abundances in the martian mantle (i.e., the element correlation values) were plausibly depleted by aqueous leaching and hydrothermal transport of these elements from the mantle to the martian surface.

peratures of these elements (Fegley 1993), so we used the CI chondrite normalized abundance trends observed in H and CV chondrites as a measure of volatility. This empirical volatility trend is shown at the top of Fig. 4. Because oxygen isotopes show that H chondritic matter was the main material accreted by Mars, the abundance trend observed in H chondrites is given preference in determining the volatility sequence. However, as can be seen from the top portion of Fig. 4, the volatility sequence derived from CV chondrites is basically the same as that derived from H chondrites.

We now compare the mantle abundances of volatile lithophiles predicted by OIM with those derived from analyses of SNC meteorites and element ratios. Although Zn sometimes behaves as a chalcophile, it is included in this group because its (metal and sulfide)/silicate partition coefficient is only about 0.03, indicating that it is a lithophile element (Lodders and Palme 1990, Lodders 1991).

Overall, the abundances predicted by the OIM model are higher than those from other models. The best comparisons can be made for Na, K, Rb, Cs, F, Cl, and Zn, because their element ratios show less scatter than those for the other volatile lithophiles (see Appendix). The Li, Br, and I element ratios in SNC meteorites show large variations,

so it is difficult for element ratio methods to predict their abundances with any certainty.

The K and Rb abundances from element ratios are 3.7 times lower than those obtained in the OIM model and Cs abundances are 2 times lower. The Na/Ti ratio indicates a Na abundance about 5 times lower than that predicted by the OIM model while the Na/Al ratio used by Wänke and Dreibus indicates Na abundances about two times lower than predicted by OIM. However, as mentioned above, Al is probably depleted in the source region(s) of the parental magmas of the SNC meteorites. In contrast to Ga (see above) Na does not replace Al in spinel or garnet and Na is incompatible in these minerals. As a result the Na/Al correlation established during crystallization of plagioclase from an Al depleted magma gives Na abundances too high for the martian mantle.

In any case, element ratio calculations using analyses of SNC meteorites indicate lower alkali abundances than predicted by OIM. On the other hand, we can see from Tables III and IV that other Mars compositional models based on cosmochemical arguments (e.g., the modified equilibrium condensation model by Weidenschilling 1981) suggest even higher Na and K abundances than the OIM model.

The predicted abundance of F, which is similar in volatility to Cs, is 2 times higher than F abundances obtained from the F/Li ratio in SNC meteorites. Likewise, the abundances of the other halogens I, Br, and Cl obtained from our updated element ratios are about 6 to 8 times lower than predicted from the OIM model. The H/CI and CV/CI chondrite abundances at the top of Fig. 4 indicate that Cl, Br, and I have similar volatilities. How can the larger mantle abundances of alkalis and halogens predicted by OIM be explained?

Evaporative Loss of Alkalis and Halogens during Accretion of Mars?

One possibility is that the differences in the alkali and halogen abundances predicted by the OIM model and element ratio calculations are due to vaporization. The OIM model takes nebular volatility fractionations into account because elemental abundances in chondrites were established by volatility fractionations in the nebula (Larimer and Wasson 1988a, 1988b; Palme et al. 1988; Palme and Boynton 1993). Thus, vaporization of alkalis and halogens could have occurred during planetary accretion.

Vaporization and loss of iodine (with an atomic weight of ~126.9) from the gravity field of Mars may have been possible during very early stages of accretion, when Mars was small or was driven by hydrodynamic escape during early degassing periods. If iodine were lost by vaporization, other volatile elements such as Cl (at. wt. ~35.5), Br (at. wt. ~79.9), and Zn (at. wt. ~65.4), which are lighter than

I, should also have been lost. The CI normalized Zn abundance in CV and H chondrites (Fig. 4) shows that Zn is intermediate in volatility between I and Br. However, analyses of SNC meteorites show that Zn is more abundant than I, Br, or Cl even though Zn, I, Br, and Cl have similar volatilities.

Wänke and Dreibus calculated a Zn abundance of 62 ppm by assuming that ALH77005 closely represents martian mantle abundances. This is the same assumption that they used to calculate the Cu abundance. Treiman et al. (1986) took a similar approach. Assuming that Zn partitions similarly among mantle minerals, Treiman et al. (1986) took the relatively uniform abundance of Zn in SNC meteorites as representative of the martian mantle. We obtain a mean Zn abundance of 66 ± 7 ppm Zn from their analyses of five SNC meteorites. Normalizing to the CI abundance and La gives a value of 0.11 which is shown in Fig. 4 (instead of the 0.25 listed by Treiman et al. 1986). Our updated element ratio calculations used the mean Zn/Fe ratio in SNC meteorites. This ratio is well defined and shows less variance than halogen/La ratios (see Appendix). We calculated a Zn abundance of 60 ppm from the Zn/Fe ratio, which is almost indistinguishable from the 62 ppm calculated by Wänke and Dreibus and the 66 ± 7 ppm calculated from Treiman et al.'s (1986) data. The OIM model predicts a Zn abundance of 83 ppm, which is a factor of 1.4 higher than the Zn abundance from the three independent element ratio calculations. In contrast, even though Cl, Br, and I are as volatile as Zn, the halogen abundances predicted by OIM are a factor of 6–8 higher than the element ratio predictions. Therefore, volatility related losses during accretion cannot account for the apparent discrepancy between the different alkali and halogen abundance estimates. Our conclusion is apparently supported by the potassium isotopic measurements by Humayun and Clayton (1995) which seem to argue against evaporative loss of potassium (and other alkalis) during planetary accretion. However, their results are challenged by Esat (1996) and more work is required to resolve that issue.

Terrestrial Geochemistry of the Alkalis and Halogens and Implications for Mars

Here we explore the possibility that aqueous leaching has depleted alkalis and halogens in the mantle source(s) of the parental magmas of the SNC meteorites. Assuming that the abundances predicted by OIM are representative of the primordial martian mantle, Fig. 4 shows that I, Br, and Cl were removed from the mantle more efficiently than Na, K, and Rb or Cs and F. The terrestrial geochemistry of the alkalis and halogens suggests that aqueous leaching can easily explain the apparent depletions of these elements.

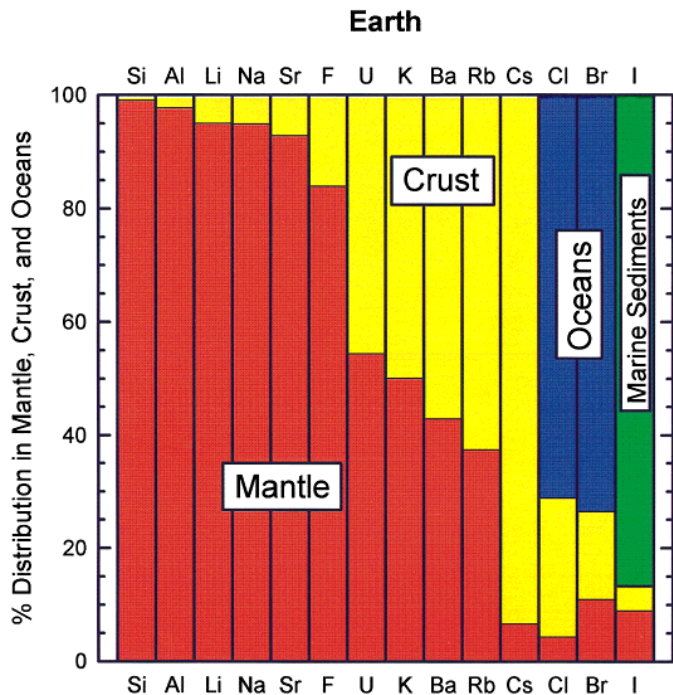Figure 5, which was compiled from several sources (Quinby-Hunt and Turekian 1983, Deruelle et al. 1992,

Earth

FIG. 5. Distribution of some refractory elements, alkalis, and halogens in the Earth. Incompatible elements (K, Ba, Rb, Cs) are highly enriched in the Earth's crust. The terrestrial oceans are the major repository for Cl and Br. Iodine is heavily concentrated in biogenic marine sediments. Among alkalis and halogens, Li, Na, and F are mainly stored in the Earth's mantle. For more explanations and data sources see text.

Wänke *et al.* 1984, Wedepohl 1995), shows the distribution of the alkalis and halogens between the mantle, crust, and hydrosphere of the Earth. The mantle, crust, and hydrosphere make up the bulk silicate Earth (BSE). Most of the Br and Cl are found in sea water, while most of the iodine is found in marine sediments. The crust is the major reservoir of K, Rb and Cs but contains smaller percentages of Na and F, which mainly reside in the mantle.

The relative enrichments of alkalis and halogens in sea water are shown at the top of Fig. 6, where we have plotted sea water concentrations normalized to BSE abundances. This plot shows that Cl and Br are highly enriched in sea water. Iodine is depleted in sea water relative to Cl and Br because I resides mainly in organic-bearing marine sediments, which account for about 80% of the iodine in the bulk silicate Earth (Deruelle *et al.* 1992). Fluorine, which forms less soluble salts than the other halogens, is depleted in sea water relative to its concentration in the BSE. Although Na is enriched in sea water relative to its concentration in the BSE, the enrichment is not large enough for sea water to be the major repository for Na. Potassium is slightly enriched in sea water, while Rb and Cs are depleted relative to their concentrations in the BSE.

The middle of Fig. 6 shows CI-normalized abundance data for the BSE. Also shown are mantle abundances ob-

tained from mantle nodules (Wänke *et al.* 1984). The CI-normalized abundances of the alkalis and halogens for the BSE are about 0.1–0.01, indicating that the bulk silicate Earth is depleted in alkalis and halogens relative to CI chondrites. However, because I is concentrated in marine sediments, while Cl and Br are concentrated in sea water, their CI-normalized mantle abundances are even lower than that. Likewise, because Cs and, to a lesser extent, Rb and K are concentrated in the crust, their abundances are also somewhat lower in the mantle than in the BSE. The
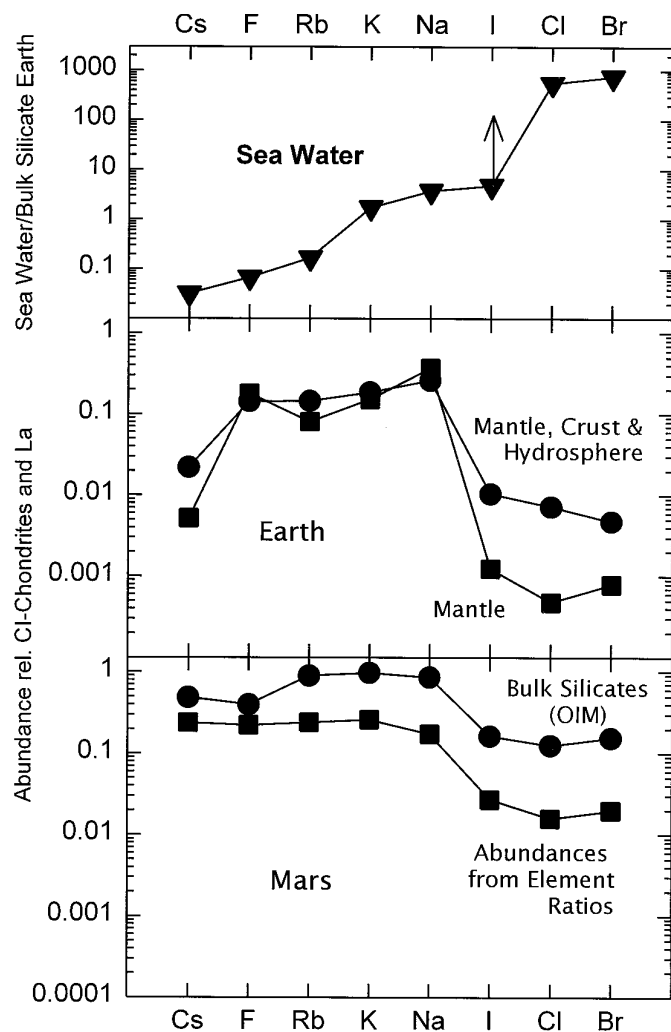

FIG. 6. Abundance of alkalis and halogens in sea water relative to bulk silicate Earth (mantle, crust, and hydrosphere) (top), CI chondrite and La normalized abundances in the bulk silicate Earth and mantle (middle), and abundances for Mars from the OIM model and element correlations (bottom). Most of Cl, Br, and I (and also to a somewhat lesser extent the alkali elements) in the bulk silicate Earth are in the crust and hydrosphere, while their mantle abundances are low. A similar situation may be envisioned for Mars, where the element correlations from the mantle derived rocks of the SNC meteorites only reflect mantle abundances. However, the OIM model predicts the abundances of the alkalis and halogens for the entire silicate portion (mantle plus crust and possible hydrosphere). See text for more discussion and data sources.

halogens (Cl, Br, I) and alkalis (K, Rb, Cs) are depleted from the terrestrial mantle by formation of the crust and hydrosphere.

Figures 5 and 6 show that we would get the "wrong" answer if we tried to determine the composition of the bulk silicate Earth only from element ratios in ultramafic nodules and basalts. Our estimated abundances for K, Rb, Cs, Cl, Br, and I would be lower than the actual abundances of these elements in the bulk silicate Earth. For example, mantle nodules and MORB have Cl/La ratios of about 1.4 and 14, respectively, and Br/La ratios of 0.13 and 0.033, respectively (Jagoutz *et al.* 1979, Hofmann 1988, Jambon *et al.* 1995). However, the Cl/La and Br/La ratios for the bulk silicate Earth are about 67 and 0.17, respectively (taking La from Wänke *et al.* 1984 and Br and Cl abundances from Jambon *et al.* 1995 for BSE). This means that estimates from element ratios from mantle derived basalts alone would lead to estimated abundances about a factor of 5 too low for Cl or Br.

However, we only have mantle derived samples, namely the SNC meteorites, available to estimate elemental abundances on Mars. Based on the known geochemistry of the alkalis and halogens, element ratios in SNC meteorites probably also lead to anomalously small estimated abundances of the alkalis and halogens on Mars. As shown at the bottom of Fig. 6 we propose that the higher alkali and halogen abundances predicted by the OIM model are relevant to the primordial martian mantle prior to crustal formation and aqueous extraction. The lower alkali and halogen abundances predicted by element ratios in the SNC meteorites give us abundances in depleted martian mantle after crustal formation and aqueous extraction. Our proposal naturally leads to two questions: What is the evidence that alkalis and halogens are concentrated at the surface of Mars? What is the evidence for aqueous leaching (or hydrothermal activity) on Mars?

Alkali and Halogen Enrichments on the Surface of Mars and Evidence for Aqueous Leaching and Hydrothermal Activity on Mars

The results of the surface analyses of Mars from the American (Viking 1 and 2) and Russian (Mars 5, Phobos 2) space probes are summarized in Table VII. The similarity of the major element composition of the soil analyses and that of the basaltic Shergottites has been noted by several workers (see, e.g., Banin *et al.* 1992, McSween 1994) and for comparison, Shergotty data are also listed in Table VII, together with the Mars soil/Shergotty concentration ratios.

The concentration ratios of Mg, Al, Si, Ti, and Fe are all around unity, showing the close resemblance of Shergottites and martian soil but martian surface abundances of sulfur, halogens, and alkalis (K and Rb) are higher than in the Shergotty meteorite. In particular, S, Cl, and, although more uncertain, Br, are enriched by more than 20 times on the martian surface than in the Shergotty basalt. If the Shergotty meteorite (or other basaltic Shergottites) are taken as representative material which produced the basaltic martian crust, the high enrichments of the halogens found on the martian surface are unexpected. However, the high S and Cl concentrations on the martian surface are compatible with weathering of mafic rocks and brine formation (e.g., Banin *et al.* 1992). Formation of a crust and early hydrothermal activity on Mars can deplete the halogens and also the alkalis from the source region of the basalts and enrich the alkalis and halogens on the surface by brine formation and subsequent evaporation. Consequently, the alkali and halogen abundances obtained from element correlations of the mantle-derived SNC meteorites are not representative for the bulk silicate portion of Mars, because the important surface reservoir of the halogens and alkalis is not considered. As summarized by McSween (1994) the Rb/Sr and Sm/Nd isotope systematics of the SNC meteorites may require assimilation of the SNC rock forming magmas with an incompatible element rich phase (= crust?) and may thus hint at early crustal formation. Future investigation of these isotope systematics in the framework of our OIM model may help to better understand possible crust formation processes on early Mars.

Secondary minerals (carbonates, sulfates, smectite clays, and other phases often referred to as "iddingsite") from hydrothermal weathering are also present in the SNC meteorites and it has been shown that these alteration products are preterrestrial and most likely formed on Mars (e.g., Gooding *et al.* 1988, 1991). Among the SNC meteorites, the Nakhlites seem to be the most likely samples for containing aqueous alteration products. Very recently, Lindstrom *et al.* (1996) performed analyses on small samples of the weathering products from the Lafayette meteorite. As listed in Table VII, they found that the halogens and alkalis are enriched in the weathering products compared to the bulk Lafayette meteorite.

The occurrence of carbonates, sulfates, and halides in veins in primary silicates in the Lafayette and Nakhla meteorites indicates that aqueous alteration post-dated igneous crystallization, but the igneous minerals of Nakhla and Lafayette are unlikely the sources of the secondary salts as argued by Gooding *et al.* (1991) and Treiman *et al.* (1993). Interestingly, the abundances of K, Rb, and Cl in these alteration products are very similar to those found in the martian soil (Table VII) although S concentrations are lower in the Lafayette (and Nakhla) weathering products than in the soil. The similarity of K, Rb, and Cl abundances may be pure coincidence, but this similarity could also indicate that fluids containing salts circulated between the surface and the near-surface region where Nakhlite primary minerals were present.

We suggest that during early differentiation CO_2 and

TABLE VII
Analyses of Martian Samples

	Mars Space Probe Soil Analyses					SNC - Meteorite Analyses			Concentration Ratios	
	Phobos 2		Viking 1 Chryse (b)	Viking 2 Utopia (b)	Mars 5 (c)	Shergotty (Basalt) (d)	Lafayette (Wehrlite) (d)	Lafayette Weathering Products (e)	Mars Soil/ Shergotty	Lafayette Weathering Prod./Bulk
	Mean (a)	Range								
Mg wt%	4.5	3.0 - 6.0	3.6	(3.6)	--	5.6±0.1	7.8	8.38	0.5 - 1.1	1.1
Al wt%	6.2	5.0 - 7.0	3.9	(4)	5±2	3.6±0.3	1.3±0.7	2.5	1.4 -1.9	1.9
Si wt%	20.0	19.0 - 21.0	21	20	14±3	24.0	20.6±2	23.0	0.8 - 0.9	1.2
K wt%	0.4	0.3 - 0.6	<0.4	<0.4	0.3±0.1	0.14±0.02	0.09±0.01	0.3 - 0.7	2.1 - 4.3	3.3 - 7.8
Ca wt%	6.7	6.0 - 7.0	4.1	4.1	--	6.9±0.4	9.6±0.5	0.50	0.9 - 1.0	0.05
Ti wt%	1.3	1.0 - 1.8	0.37	0.32	--	0.50±0.05	0.25±0.08	0.006	0.6 - 3.6	0.02
Fe wt%	9.0	7.0 - 11.0	12.2	12.1	14±4	15.1±0.5	16.8±1.7	22.5	0.5 - 0.8	1.3
Na wt%	3.3	1.4 - 5.5	--	--	--	1.0±0.2	0.30±0.04	0.21	1.4 - 5.5	0.7
S wt%	--	--	2.7	3.2	--	0.13±0.1	0.041	0.28	21 - 25	6.8
Cl wt%	--	--	0.8	0.4	--	0.01	0.0065	0.36	40 - 80	55
Br ppm	--	--	~ 80	present	--	0.9±0.2	0.4±0.3	2 - 4	~ 90	5 - 10
Rb ppm	--	--	≤30	≤30	--	6.4±0.6	2.8±0.6	34±5	≤5	12
Cs ppm	--	--	--	--	--	0.44±0.5	0.32±0.05	20	--	63
Sr ppm	--	--	60±30	100±40	--	46±8	75	--	1.3 - 2.2	--
Th ppm	2.3	1.2 - 4.0	--	--	2.1±0.5	--	0.15	< 0.3	--	< 2
U ppm	0.7	0.5 - 1.0	--	--	0.6±0.1	0.11±0.03	0.05	< 0.3	4.5 - 9.1	< 6

Note. -- indicates that data are not available.

(a) Surkov *et al.* 1994.

(b) Clark *et al.* 1982, Utopia data in parenthesis estimated by them by analogy with Chryse data; Clark and van Hart 1981 (Br); Toulmin *et al.* 1977 (Rb and Sr).

(c) Surkov *et al.* 1989.

(d) Mean Shergotty data from unpublished data compilation by K. Lodders.

(e) Treiman *et al.* 1993; Lindstrom *et al.* 1996.

some residual water, which did not fully react with metal (see Eqs. (12)–(15) were dissolved in the martian mantle. The amount of water or CO_2 remaining after early differentiation is not easy to constrain because the solubility of water depends on pressure, temperature, and composition of the silicate. Although the exact dissolved water and CO_2 concentrations remain to be modeled, it is clear that the fluid phase can leach the silicates and become enriched in carbonates, sulfates, halogens, and alkalis. During magma ascent toward the surface, water and CO_2 become less soluble in the magmas and can separate from the silicate. An aqueous phase rich in halogens and alkalis would leave a depleted magma behind and if this aqueous phase reaches the surface, later evaporation and brine formation would explain the enrichment of halogens, S, K, and Rb in the martian soil.

Mars may also have experienced early formation of a crustal component rich in incompatible elements such as Rb, because an incompatible element-rich and isotopically distinct component may be required to explain the controversial and poorly understood isotopic systematics of the SNC meteorites (see McSween (1994) for a summary). If such a crustal component exists and if it were permeated by water, extraction of incompatible Rb, K, and halogens from this crust may also have been an important source of the salts observed on the martian surface.

The absence of high pressure minerals indicates that the observed SNC lithologies crystallized near the surface. After crystallization, secondary aqueous alteration products were deposited but these products are not derived from the primary crystallized minerals (e.g., Gooding *et al.* 1991). If the silicates (and/or) magmas from which the SNC lithologies formed were depleted prior to crystallization and if aqueous saline fluids were circulating in the near surface and crust, where SNC host rocks finally crystallized, the deposit of the alteration products in the SNC meteorites can be understood.

The lower sulfur content in the meteoritic alteration products than in the martian soil is consistent with this scenario because sulfates may precipitate preferentially during evaporation on the surface while halogens and carbonates are preferentially removed from the "circulating" fluid. It would be interesting to see hydrothermal compositional models which allow the precipitation of salts observed in the SNC meteorites and also yield the salts inferred from the martian soil analyses. However, if brine formation and salt deposition took place on Mars, the martian soil composition has been influenced by the composition of the early brines and also by the composition of eroding surface rocks. As a result it may be very difficult to decipher evaporite salt and crustal rock signatures. It remains a matter of future study to use the alkali and

halogen abundances obtained from the OIM model and SNC meteorites to learn more about the surface evolution of Mars.

APPENDIX I

Observed Elemental Abundance Ratios in SNC-Meteorites

Element Pair	Conc. Ratio (± 1σ range) (a)	% Dev. from Mean (a)	No. of Pairs (a)	Wänke & Dreibus (b)	Treiman et al. (c)	
Lithophiles						
Li/La*	2.2±0.5	23	7	6.4	2.70	(1.7)
Na/Al	0.248±0.020	8	11	0.235	n.d.	
Na/Ti	1.80±0.10	6	1	n.d.	2.05	(2)
K/La	614±50	8	11	641±100	753	(2)
Rb/La	2.35±0.28	12	10	2.36	2.93	(2)
Cs/La	0.19±0.01	6	10	0.15	0.20	(2)
Ba/La	15.8±0.5	4	9	9.6	19.2	(1.7)
Al/Ti	7.1±0.4	5	1	18.6	7.9	(1.5)
Sc/Ti	$(10.0±1.5)×10^{-3}$	15	10	$13×10^{-3}$	$9.1×10^{-3}$	(2)
Hf/Ti	$(2.75±0.35)×10^{-4}$	13	10	$2.4×10^{-4}$	$2.7×10^{-4}$	(1.5)
V/Ti	0.052±0.007	14	10	n.d.	0.033	(2)
Ta/La	0.087±0.043 (s)	50	6	0.06	0.11	(1.7)
Cr/Mg	0.035±0.003	12	11	0.029	n.d	
Mn/Fe	0.026±0.001	4	11	0.026	n.d.	
Zn/Fe	$(4.49±0.36)×10^{-4}$	8	10	n.d.	n.d.	
Eu/Ti	$(1.01±0.05)×10^{-4}$	5	10	n.d.	$1.2×10^{-4}$	(1.5)
Th/La*	0.20±0.13	65	4	0.12	0.21	(1.7)
U/La	0.042±0.009	20	8	0.034	0.068	(2)
F/Li	11.0±1.1	10	7	12.6	n.d.	
Cl/La	46.5±7.4	16	10	92.6	53.3	(2)
Br/La*	0.31±0.14 (d)	45	8	0.347	0.347	(2.5)
I/La*	0.05±0.03 (e)	64	3	0.07	n.d.	
Siderophiles and chalcophiles						
Ga/Al	$(4.1±0.2)×10^{-4}$	5	10	$4.1×10^{-4}$	n.d.	
Ga/Ti	$(2.94±0.18)×10^{-3}$	7	10	n.d.	$2.3×10^{-3}$	(1.5)
In/Al	$(1.2±0.3)×10^{-6}$	20	9	$0.88×10^{-6}$	n.d.	
In/Ti	$(8.9±1.9)×10^{-6}$	21	9	n.d.	$8.0×10^{-6}$	(2)
Tl/Al	$(2.4±0.5)×10^{-7}$	17	9	$2.3×10^{-7}$	n.d.	
Tl/Ti	$(1.8±0.3)×10^{-6}$	14	9	n.d.	$3.3×10^{-6}$	(2.5)
P/Tb	8600±660	8	10	10140	n.d.	
P/Ti	0.646±0.055	10	10	n.d.	0.68	(2)
As/La*	0.09±0.04	43	8	n.d.	0.14	(2.5)
Sb/La*	0.012±0.007	60	8	n.d.	$1.97×10^{-3}$	(2)
S/Ti	0.31±0.034	11	8	n.d.	0.30	(2)
Se/Ti	$(7.2±0.9)×10^{-5}$	13	9	n.d.	$8.4×10^{-5}$	(2)
Mo/Nd*	0.15±0.11 (d)	65	2	0.128	n.d.	
Mo/Ti	$(6.6±2.0)×10^{-5}$	30	3	n.d.	$6.96×10^{-5}$	(f)
W/La	0.18±0.03	16	8	0.22	0.11	(2)
W/U	3.9±0.6	15	6	4.2	n.d.	
Co/Mg	$(4.90±0.45)×10^{-4}$	9	10	$3.7×10^{-4}$	n.d.	
Ni/Mg	$(1.61±0.27)×10^{-3}$	17	10	$2.2×10^{-3}$	n.d.	
Ni/Cr	0.055±0.007	13	10	n.d.	0.033	(2)
Cu/Ti	$(3.6±0.5)×10^{-3}$	14	5	n.d.	$3.4×10^{-3}$	(2)
Ag/La*	0.017±0.004	20	9	n.d.	0.014	(2.5)
Au/La*	$(3.8±1.4)×10^{-3}$	37	10	n.d.	$1.2×10^{-3}$	(3)

(a) ppm concentration ratios, this work.
(b) Dreibus and Wänke 1984, Wänke and Dreibus 1988, 1994. For refractory lithophile elements the ratios equal the CI-chondritic ratios from Palme *et al.* 1981.
(c) Treiman *et al.* 1986 list ratios relative to CI values from Anders and Ebihara 1982. Absolute ratios listed here were recalculated using the Anders and Ebihara CI data. Numbers in parenthesis are the uncertainty factors (multiplier/divisor) assigned to the ratios by Treiman *et al.*
(d) Data for Nakhla not included.
(e) No Antarctic meteorites included (see Wänke and Dreibus 1988).
(f) Treiman *et al.* 1987 list a CI-normalized Mo/Ti ratio of 0.33 obtained from ratios in ALH77005 and Shergotty. However, the CI normalized ratios are 0.038 and 0.035 respectively. We assume that Treiman *et al.* used a CI-normalized value of 0.033 from which the ratio listed here was computed.
(s) Shergottites only. Nakhlites and Chassigny form separate correlation.
* Very unreliable ratio, strong data scatter.

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