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Volatiles on Earth and Mars: A Comparison*

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Based on our new and previous determinations of halogens in SNC meteorites, the bulk concentrations of halogens in the SPB, which is thought to be Mars, are estimated. The two-component model for the formation of terrestrial planets as proposed by A. E. Ringwood (*Geochem. J.* 11, 111–135 (1977) and *On the Origin of the Earth and Moon*, Springer-Verlag, New York, 1979) and H. Wänke (*Philos. Trans. Roy. Soc. London, Ser. A* 303, 287–302 (1981)) is further substantiated. It is argued that almost all of the H_2O added to Mars during its homogeneous accretion was converted on reaction with metallic Fe to H_2, which escaped. By comparing the solubilities of H_2O and HCl in molten silicates, the amount of H_2O left in the mantle of Mars at the end of accretion can be related to the abundance of Cl. In this way an H_2O content in the Martian mantle of 36 ppm is obtained, corresponding to an ocean covering the whole planet to a depth of about 130 m.

The huge quantities of H_2 produced by the reaction of H_2O with metallic iron should also have removed other volatile species by hydrodynamic escape. Thus it is postulated that the present atmospheres of Venus, Earth, and Mars were formed by degassing the interiors of the planets, after the production of H_2 had ceased, i.e., after metallic iron was no longer available. It is also postulated that the large differences in the amounts of primordial rare gases in the atmospheres of Venus, Earth, and Mars are due mainly to different loss factors.

Except for gaseous species, Mars is found to be richer in volatile (halogens) and moderately volatile elements than the Earth. The resulting low release factor of ^{40}Ar for Mars is attributed to a low degree of fractionation, leading to a relatively small crustal enrichment of even the most incompatible elements like K.

INTRODUCTION

Rare gases represent without any doubt the most volatile group of elements. The Viking data show that the Martian atmosphere contains only 1.6×10^{-10} cm^3 ^{36}Ar per gram of the planet's mass. The ^{36}Ar concentrations observed in carbonaceous and enstatite chondrites range between 3×10^{-7} and 8×10^{-6} cm^3/g; even ordinary chondrites without obvious argon loss contain about 2×10^{-8} cm^3/g ^{36}Ar. Hence, in the Martian atmosphere we have a factor of 100 less ^{36}Ar than in any class of unfractionated meteorites. A huge gas loss from the primitive atmosphere during the accretion of Mars seems the almost inevitable conclusion. The gas loss is also evident from the high abundance of rare gas isotopes formed by radioactive decay (^{40}Ar and ^{129}Xe) relative to the primordial rare gas nuclides. The ^{40}Ar/^{36}Ar ratio in the Martian atmosphere is 3000 compared to the 10 times smaller ratio in the terrestrial atmosphere. Only about a factor of 2 could be attributed to the higher K abundance on Mars. There is no doubt that accretion is the most effective degassing stage in the

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evolution of planets (Arrhenius *et al.* 1974, Lange and Ahrens 1983). Consequently a smaller release factor of argon on Mars over geological time as compared to on the Earth would yield a decrease of $^{40}Ar/^{36}Ar$ in the atmosphere as it would mainly affect ^{40}Ar, which is produced by radioactive decay over geological time.

Considering radiogenic components only, the ratio $^{129}Xe_{rad}/^{132}Xe$ in the Martian atmosphere exceeds the terrestrial value by a factor of 22. However, the case of $^{129}Xe_{rad}$ differs from ^{40}Ar in the large difference of the half-lives of the parent nuclides and their different geochemical behavior.

The estimates of the abundance of volatiles on Mars presented in this paper are based on the composition of SNC-meteorites. The SNC-meteorites (4 *s*hergottites, 3 *n*akhlites, and *C*hassigny) represent a small group of differentiated meteorites distinct from all other meteorites. Within the last seven years a number of observations have been made which point towards Mars as the parent body of SNC-meteorites (*S*hergotty *p*arent *b*ody = SPB), their low crystallization ages being the most striking one (Wasson and Wetherill 1979, Wood and Ashwal 1981). The recent discovery of trapped Martian atmosphere with its characteristic $^{40}Ar/^{36}Ar$, $^{40}Ar/^{14}N$, $^{14}N/^{15}N$, $^{129}Xe/^{132}Xe$ ratios in the shergottite EETA 79001 (Bogard and Johnson 1983, Becker and Pepin 1984, Pepin 1985) almost certainly proves that Mars is indeed the parent body of the SNC-meteorites, although as yet there is no generally accepted model for the dynamical problems involved (Wetherill 1984).

BULK COMPOSITION OF MARS

With the assumption that the SNC-meteorites are indeed Martian rocks, these meteorites allow very definite conclusions about the bulk composition of Mars. Our previous estimates of bulk composition (Dreibus and Wänke 1984, 1985, Wänke and Dreibus 1984) were restricted to refractory and moderately volatile elements. The results are given in Table I. In this paper we will concentrate on volatile elements and will only briefly outline the approach used in our previous estimates.

From studies of the bulk compositions of the Earth, the Moon, and the EPB (*e*ucrite *p*arent *b*ody, possibly the asteroid Vesta; Chapman 1976), the consensus has evolved that Si, Mg, and all lithophile refractory elements have been fractionated from each other in the solar nebula to only a rather small degree (Ganapathy and Anders 1974, Morgan *et al.* 1978, Dreibus and Wänke 1980, Wänke 1981). Hence, the chemical composition of a planet is already fixed for 90% of its total mass. We neglect here drastic metal/silicate fractionation as in the cases of the Moon and Mercury. What remains to be evaluated are the moderately volatiles (sulfur being the most abundant element of this category) and the highly volatiles, as well as the ratio of metallic iron to iron oxide and more generally the concentrations of siderophile elements in the planetary mantles.

As both La and Al are refractory elements, their correlations to moderately volatile and volatile elements, as reflected in ratios such as K/La, Na/Al, Ga/Al, and Br/La, directly reveal the bulk concentrations of these elements (Figs. 1 and 2).

Under normal planetary conditions, where olivine, orthopyroxene, and clinopyroxene are the major FeO- and MnO-bearing phases, the liquid–solid partition coefficients for FeO and MnO are only slightly above 1. A chondritic abundance of Mn in the Martian mantle would correspond to 0.46% MnO. The MnO concentrations in SNC-meteorites vary between 0.45 and 0.55%. Hence, as in the EPB, but contrary to Earth and Moon (Dreibus and Wänke 1979), Mn is not depleted on Mars and it is justified to assume a Mn abundance of 1.00. The FeO/MnO ratio of shergottites and nakhlites is 39.1 ± 1.5. Compared to the *C*1 FeO/MnO ratio of 100.6, an abundance of 0.39 is found for FeO in the mantle of Mars. The difference from the *C*1 value

TABLE I

ESTIMATES OF THE BULK COMPOSITION OF MARS

	Mars as SPB,[a,b] this work	Anderson (1972)	Morgan and Anders (1979)	Ringwood (1981)	Mars as SPB rel. to Si and *C*1	Earth[c,d] rel. to Si and *C*1
Mantle and crust (%)						
MgO	30.2	27.4	29.78	29.9	1.00	1.18
Al_2O_3	3.02	3.1	6.39	3.1	1.00	1.35
SiO_2	44.4	40.0	41.60	36.8	1.00	1.00
CaO	2.45	2.5	5.16	2.4	1.00	1.40
TiO_2	0.14	0.1	0.33	0.2	1.00	1.53
FeO	17.9	24.3	15.85	26.8	0.39	0.16
Na_2O	0.50	0.8	0.10	0.2	0.38	0.29
P_2O_5	0.16	0.34	—	—	0.36	0.032
Cr_2O_3	0.76	0.6	0.65	0.4	1.00	0.56
MnO	0.46	0.2	0.15	0.1	1.00	0.28
K (ppm)	315	573	77	218	0.31	0.22
Rb (ppm)	1.12		0.26		0.28	0.18
Zn (ppm)	74		41.8		0.11	0.070
Ga (ppm)	6.6		2.43		0.37	0.21
In (ppb)	14		0.095		0.090	0.115
Tl (ppb)	3.6		0.17		0.013	—
Cl (ppm)	38		0.88		0.029	0.0087
Br (ppb)	145		4.73		0.029	0.0090
I (ppb)	32		0.59		0.029	0.012
La (ppm)	0.48		0.93		1.00	1.06
Th (ppb)	56	77	125	60	1.00	1.30
U (ppb)	16	17	35	17	1.00	1.30
Core (%)						
Fe	77.8	72	88.12	63.7	—	—
Ni	7.6	9.3	7.99	8.2	—	—
Co	0.36	—	0.37	—	—	—
S	14.24	18.6	3.51	9.3	—	—
O	—	—	—	18.7	—	—
Core mass (%)	21.7	11.9	19.0	18.2	—	—

[a] Dreibus and Wänke (1984).

[b] Dreibus and Wänke (1985).

[c] Wänke (1981).

[d] Wänke *et al.* (1984).

of the total iron abundance (i.e., 0.61) is obviously present in the form of metal and sulfide in the Martian core. (For the estimation of the sulfide portion of Fe, respectively the absolute sulfur abundance, see the next section.)

The correlations between refractory and nonrefractory elements clearly indicate 2–3 times higher abundances of moderately volatile and volatile elements on Mars as compared to the Earth. Moderately volatile elements like K are lowest in the lunar samples and highest in the shergottites; hence we can expect a similar sequence in the relevant planetary parent bodies (Fig. 1).

The Br–La correlation couples Br to a refractory lithophile element. Figure 2 shows that the Br abundance on Mars exceeds the terrestrial abundance by a

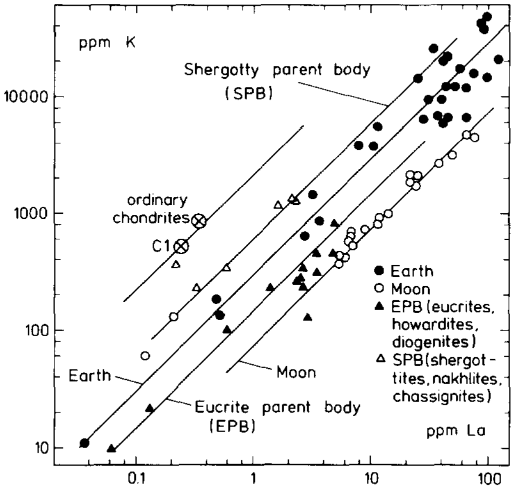

FIG. 1. Correlation of the incompatible moderately volatile element K with the incompatible refractory element La in four planets. All planets show a depletion of K compared to the chondritic value.

factor of 3.2. The oceans of the Earth represent such an excellent store for halogens that in fact the Br/La ratio in glasses of midocean ridge basalts (MORB) may be somewhat lower than the bulk Earth ratio. On Earth the halogens Cl, Br, and I are present in close to their *C*1 abundance ratios (Wänke *et al.* 1984). In Table I, we have assumed *C*1 abundances for chlorine and iodine relative to Br for Mars also. The measured Cl and I abundances might be influenced by contamination, as two of the four shergottites were found in Antarctica and high contamination levels are observed in many Antarctic meteorites for chlorine and iodine, but not for bromine (Dreibus and Wänke 1983). The data points for SNC-meteorites in Fig. 2 are based on new determinations as well as on determinations previously published by us. The data are listed in Table II.

Using data from Smith *et al.* (1984) on Tl and Br from our laboratory we also find that Tl correlates satisfactorily with Br. The Tl/Br ratio points towards a high Tl abundance, which originally may have been even higher as Tl has chalcophile tendencies and might have been affected by sulfide segregation. A rough estimate for In can be made assuming a constant In/Ga ratio (Table I). The In abundance might also have been somewhat lowered by sulfide segregation.

A detailed discussion of our estimates for moderately volatile, siderophile, and chalcophile elements is given elsewhere (Burghele *et al.* 1983, Dreibus and Wänke 1984, 1985). The results of these estimates, with only minor additions and revisions, are given in Table I together with estimates from other authors.

ACCRETION OF EARTH AND MARS

According to the two-component model for the formation of terrestrial planets as introduced by Ringwood (1977, 1979) and slightly modified by Wänke (1981), the composition of these planets can successfully be described as mixtures of two components.

Component A. Highly reduced and free of all elements with equal or higher volatility than Na, but containing all other elements in *C*1 abundance ratios. Fe and all

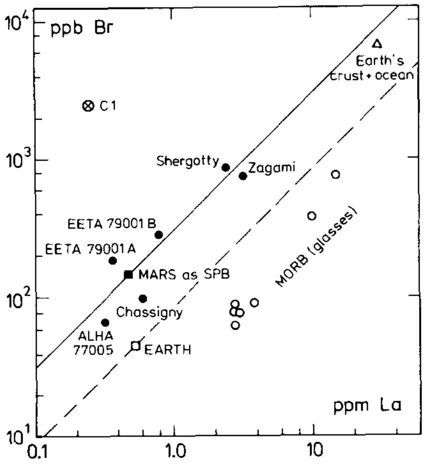

FIG. 2. Br versus La in SNC-meteorites and terrestrial samples. The data point for the Mars' mantle is obtained from Br/La correlation line, assuming a Si normalized *C*1 abundance of La. Data for MORB glasses from Hertogen *et al.* (1980), Palme and Rammensee (1981), Schilling *et al.* (1980), and this work. All other data from this laboratory.

TABLE II

^{129}Xe/^{132}Xe IN MARTIAN AND TERRESTRIAL ATMOSPHERES AND BASALTS IN COMPARISON TO THE HALOGEN AND La CONCENTRATIONS AS DETERMINED IN THIS WORK[a]

	^{129}Xe/^{132}Xe	I (ppb)	Br (ppb)	Cl (ppm)	La (ppm)	I/La ($\times 10^{-3}$)	Br/La ($\times 10^{-3}$)
Mars							
Atmosphere	2.5^{b}						
Basalts							
Shergotty	1.341^{c} 1.48^{d}	36	890	108	2.44	16	400
Zagami		<4	760	145	3.2	—	240
Nakhla	1.576^{c}	17	3460^{e}	1891^{e}	2.14	10	—
		24	3410^{e}	563^{e}			
		<10	4080^{e}	1145^{e}			
EETA 79001A		<100^{f}	189	26	0.37	—	510
EETA 79001B		960^{f}	287	48	0.80	—	360
EETA 79001C (glass)	2.231^{b} 2.39^{d}	<12	378	35	0.30	—	1180
ALHA 77005	1.13^{d}	1720^{f}	69	14	0.32	—	220
Chassigny	1.029^{c}	<10	97	34	0.59	—	160
Earth							
Atmosphere	0.98^{g}						
Sp-Lherzolite		4.2	12	1.4	0.36	12	33
Basalts							
MORB							
DR 11	1.002^{h}	11	90	28	2.75	4	33
DR 12	1.015^{h}	<6	64	22	2.81	<2	23
OIB							
1699	0.988^{h}	20	344	177	10	2	34
1701	0.989^{h}	27	310	233	10	3	31
1712	0.989^{h}	61	550	200	9.7	6	57

[a] Details of the analytical methods used are given in Dreibus *et al.* (1979).
[b] Becker and Pepin (1984).
[c] Ott and Begemann (1985).
[d] Swindle *et al.* (1986).
[e] Terrestrial contamination as Cl and Br are completely water-leachable.
[f] Terrestrial contamination from Antarctica (Dreibus and Wänke 1985).
[g] Nier (1950).
[h] Staudacher and Allègre (1982).

siderophile elements are metallic, and even Si is present partly in metallic form.

Component B. Oxidized and containing all elements—including the volatiles—in *C*1 abundances. Fe and all siderophile and lithophile elements are present mainly as oxides.

However, in reality these two components may in fact only represent end-members of a fractionation sequence. Loss of volatiles from component A may in some cases have affected only the most volatile species like rare gases, halogens, S, Pb, Cs, etc., but not the moderately volatiles (Na, K, etc.).

As seen from Table I and Fig. 3, the SNC-meteorites indicate abundances of moderately volatile (Na, K, Rb, Zn) and volatile elements (Cl, Br, I) on Mars in excess of those on Earth, except for chalcophile elements (Tl, In).

Hence, Dreibus and Wänke (1984, 1985)

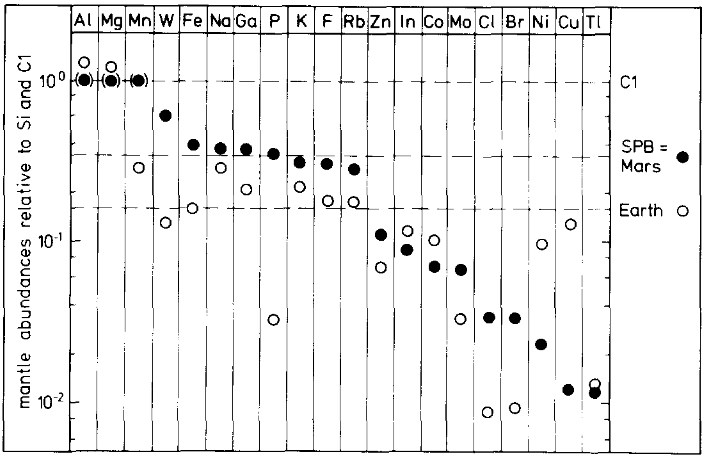

FIG. 3. Estimated abundances of moderately volatile and moderately siderophile and chalcophile elements in Mars' mantle together with the respective data for the Earth's mantle.

concluded that the mixing ratio of component A/component B for Mars is 60:40, compared to a ratio of 85:15 for the Earth. They further concluded that Mars accreted almost homogeneously, contrary to the inhomogeneous accretion of the Earth proposed by Jagoutz *et al.* (1979) and in more detail by Wänke (1981). In the case of the Earth, the high mantle abundances of Ni, Co, Cu, etc. (Fig. 3), which for Ni by far exceeds the amount to be expected from the metal–silicate partition coefficient assuming equilibration with a pure FeNi phase (core), point towards inhomogeneous accretion. The argument for the homogeneous accretion of Mars is the obvious depletion of all chalcophile elements (Cu, Ni, Co., etc.) in the Martian mantle (Fig. 3). It was assumed that sulfur supplied by component B was responsible for formation of a sulfur-rich FeNi alloy, leading to a sulfide–silicate equilibrium. During core formation, extraction of elements from the mantle took place according to their sulfide–silicate partition coefficients rather than their metal–silicate partition coefficients (Burghele *et al.* 1983, Dreibus and Wänke 1984).

In order to explain the different types of accretionary scenarios for Earth and Mars, Dreibus and Wänke (1984) suggested that the volatile-free component A formed mainly at and inside the orbit of the Earth, while the oxidized, volatile-containing component B formed in the asteroidal belt. Mars, located at the transition of the region dominated by component A and the region dominated by component B, was thought to have been fed from both components simultaneously and in approximately equal proportions, while in the case of Earth and Venus the material of component B was added only during a late phase of accretion, since the transfer of material from the region outside of Mars' orbit required additional time. As this transfer may have been influenced by the perturbation effect of Jupiter, it may also have been coupled to the formation time of Jupiter.

WATER ON EARTH AND MARS

Dreibus and Wänke (1985) suggested that because of the homogeneous accretion of Mars, almost all the H_2O added (from component B) reacted with metallic Fe (and, of course, with other metallic phases like Si in component A) and was reduced to H_2, which escaped. The huge quantities of H_2 would not only have greatly accelerated the extraction of gaseous species from the interior of the planet but also have furthered the removal of these species from the gravity field of the planet due to hydrodynamic escape by keeping the mean molecular weight of the atmosphere low. Hence, in order to estimate the amount of H_2O left on Mars after accretion, Dreibus and Wänke (1985) assumed that at the end of accretion the concentration of H_2O and other volatiles at the surface of the planet was zero (no atmosphere or hydrosphere). In addition to hydrodynamic escape of H_2, removal of all atmospheric constituents, including H_2O, by the accretion process itself—large impacts—has to be taken into account.

Analyses of *C*1 chondrites yield about 20% H_2O. However, the preterrestrial H_2O content is only about 5% (Kaplan 1971); the rest is mainly terrestrial contamination and water formed by hydrocarbons during combustion. Hence, in order to find the composition of component B which we assume to be identical to *C*1 chondrites, we divide the *C*1 values by $1 - (0.20 - 0.05) = 0.85$ to compensate for the mass of extraneous H_2O. During accretion, the hydrocarbon hydrogen in *C*1 material will at an intermediate stage also be present in the form of H_2O. For the following we will use the *C*1 water content of 7.15% measured by Boato (1954). With this value we find a water content of component B of 8.41%. This means that 3.36% H_2O was added to Mars during accretion.

During accretion even the relatively small Mars was heated to temperatures which probably led to partial melting of the silicates (Kaula 1979). We have to expect that the solid or liquid phases of the planet's interior were in solubility equilibrium with the temporary atmosphere during the accretion process.

From the Br/La concentration (Fig. 2), one finds the absolute amounts of Cl, Br, and I on Mars, assuming *C*1 abundance ratios of Cl/Br and I/Br as observed for the Earth (Wänke *et al.* 1984). In this way, we find for Mars an absolute Cl concentration of 30 ppm. Assuming the composition of component B to be identical to that of *C*1 meteorites (see below), 320 ppm Cl was actually added to the planet (Palme *et al.* 1981), of which all except the 30 ppm was lost during the accretion process together with H_2 and other gases. The 30 ppm Cl for the whole planet corresponds to 38 ppm Cl in the Martian mantle.

To estimate the water content on Mars we compare the solubility of H_2O and HCl in basaltic melts. Assuming that the solubility of H_2O and HCl is proportional to the square root of pressure (Anderson 1975), we obtain

$$\sqrt{P_{H_2O}} = 1.04 \times 10^{-3} \times C_{H_2O}$$

(Hamilton *et al.* 1964)

$$\sqrt{P_{HCl}} = 6.67 \times 10^{-5} \times C_{HCl}$$

(Iwasaki and Katsura 1967)

with *P* in bars and *C* in ppm.

With the assumption that during accretion H_2O and HCl in the temporary atmosphere are always present in the *C*1 ratio, we can calculate the ratio of the partial pressures of H_2O and HCl, corresponding to the weight ratio of H_2O and HCl, supplied by component B (assuming *C*1 composition, i.e., 8.41% H_2O and 798 ppm Cl):

$$\frac{P_{H_2O}}{P_{HCl}} = \frac{C_{H_2O}}{18} \times \frac{36}{C_{HCl}} = 205.$$

The 38 ppm Cl (=39 ppm HCl) in the Martian mantle corresponds to a partial HCl pressure of

$$P_{HCl} = (6.67 \times 10^{-5} \times 39)^2 = 6.77 \times 10^{-6} \text{ bar}$$

and with

$$P_{H_2O} = 205 \times P_{HCl}$$

to a partial H_2O pressure of $P_{H_2O} = 205 \times 6.77 \times 10^{-6} = 1.39 \times 10^{-3}$ bar.

For the concentration of H_2O in equilibrium with the partial H_2O pressure we find

$$C_{H_2O} = \sqrt{P_{H_2O}}/1.04 \times 10^{-3} = 36 \text{ ppm } H_2O.$$

Hence, we obtain a H_2O concentration in the Martian mantle of 36 ppm. Making the unrealistic assumption of 100% release, this would yield a water layer of about 130 m depth covering the whole planet.

It has been argued that during 4.5 by, comets might have significantly contributed to the H_2O content of Mars (Clark 1986). With the ad hoc assumption that comets have the same $H_2O/^{132}Xe$ ratio as observed in *C*1 chondrites, the ^{132}Xe content of the Martian atmosphere yields an upper limit of 6.2 ppm H_2O possibly supplied by comets.

The assumptions made above are not as unrealistic as they might appear at first sight. Because of the about threefold smaller Cl abundance on Earth (see Table I) compared to on Mars, only a small fraction of the total H_2O in the Earth's mantle—i.e., about 10 ppm (or 7 ppm for the bulk Earth)—could be explained in this way. However, the Earth probably accreted inhomogeneously. According to the model of Wänke (1981), the accretion of the Earth started with the highly reduced and volatile-free material of component A. After the Earth had reached about 60% of its present mass, more and more of the oxidized component B was added. However, small amounts of metal still present were responsible for the extraction of highly siderophile elements (Ir, etc.). Towards the very end of accretion, metal became unstable. Component B dominated and iron was added only in oxidized form. Hence, even the highly siderophile elements remained in the mantle in their *C*1 abundance ratios. The concentration of 3.2 ppb Ir in the Earth's mantle, equal to 2.1 ppb Ir for the whole Earth, corresponds to 0.44% *C*1 material. With a *C*1 H_2O content of 7.15%, we find that 315 ppm H_2O was added to the Earth after metallic Fe and Ni were no longer available. Thus 322 ppm remained in the form of water, whereas of the much larger amount of water (~1.3%) added before metal became unstable, almost all except about 7 ppm was converted to H_2, which escaped. From the estimate of 6.95% H_2O in the Earth's crust (Larimer 1971), we find that the crustal contribution of H_2O (mainly the oceans) to the bulk Earth is about 280 ppm. Even considering the uncertainty of these estimates, very little H_2O would remain for the mantle. However, it seems likely that the mantle contribution is indeed much smaller than generally assumed. Of the total halogen inventory of the Earth more than 90% was found to be concentrated in the crust (Wänke *et al.* 1984). A similar distribution should be expected for water.

We do not have definite constraints on the amount of water that was once on the surface of Mars. However, we have good reasons to assume that this water was very salty. As mentioned above, the Martian halogen concentration exceeds that of the Earth by a factor of 3.2. During accretion Cl and the other halogens are liberated together with H_2O. On today's Earth most of the total water content is in the oceans, which have an average NaCl concentration of 3.1%. Hence, we have to expect that water on Mars was saturated with NaCl since the early days of the planet and had a freezing point of about −20°C. This very important depression of the freezing point of Martian water was previously pointed out by Anders and Owen (1977). In addition to NaCl, also $MgSO_4$ and $MgCO_3$ (Baird *et al.* 1976) are expected to have been present in Martian water. Upon its evaporation and freezing, huge salt deposits should have formed.

PRIMORDIAL RARE GASES ON VENUS, EARTH, AND MARS

The amount of ^{36}Ar in the Martian atmosphere per gram of the planet's mass is about a factor of 100 lower than that in any class of unfractionated meteorites. On the other hand, the ^{36}Ar content of the Venusian atmosphere exceeds that of the Earth by a factor of about 100 (Table III), and even exceeds that of all primitive meteorites except the E4,5 chondrite South Oman, with its extraordinary high concentrations of primordial rare gases (Crabb and Anders 1981).

TABLE III

PRIMORDIAL AND RADIOGENIC RARE GASES IN PLANETS AND METEORITES

	^{36}Ar (10^{-10} cm^3/g)	^{40}Ar (10^{-8} cm^3/g)	^{40}Ar/^{36}Ar	^{129}Xe$_{\text{rad}}$ (10^{-12} cm^3/g)	^{129}Xe (10^{-12} cm^3/g)	^{132}Xe (10^{-12} cm^3/g)	^{129}Xe$_{\text{rad}}$/^{132}Xe	^{129}Xe/^{132}Xe
Mars								
Atmosphere[a]	1.6	48	3,000	1.12	1.88	0.75	1.49	2.5
EETA 79001 glass[b]			2,300					2.231
Earth[a]	210	612	291	1.04	15.3	15.6	0.067	0.983
Venus[c,d]	21,000	225	1.07	—		—	—	
Chondrites								
C1[e] (Orgeuil)	7,800	480	6.2	380	8,130	7,600	0.050	1.07
C3V[e]	3,500	1,350	39	460	3,250	2,460	0.19	1.32
E4[f]	3,310	8,600	260	3,800	4,770	961	3.95	4.96
S. Oman,E4-5[g]	76,000	6,080	8	980	3,930	2,900	0.34	1.36
Krymka, L3[h,i]	3,630	4,070	112	100	2,609	2,450	0.041	1.06
Baratta, L4[h,i]	450	377	84	1,031	2,822	1,750	0.59	1.61
Farmington, H5[k,i]	80	375	470	37	127	88	0.42	1.442

[a] Anders and Owen (1977).
[b] Becker and Pepin (1984).
[c] von Zahn *et al.* (1983).
[d] Morgan and Anders (1980).
[e] Mazor *et al.* (1970).
[f] Wacker and Marti (1983).
[g] Crabb and Anders (1981).
[h] Heymann and Mazor (1968).
[i] Marti (1967).
[k] Heymann (1967).

From SNC-meteorites a value of 247 ppm K for bulk Mars is obtained (Dreibus and Wänke 1984, 1985), leading to a total of 1840×10^{-8} cm^3/g ^{40}Ar produced in 4.5×10^9 years. The observed amount of ^{40}Ar in the Martian atmosphere corresponds to 48×10^{-8} cm^3/g. Hence, if we neglect a possible loss of ^{40}Ar from the atmosphere into space, we find a release factor for ^{40}Ar of 0.026. For the Earth, with a bulk K content of 154 ppm (Wänke *et al.* 1984), one finds a release factor for ^{40}Ar of 0.53. It had been argued that the Martian atmosphere was partly removed by energetic impacts over geologic time (Watkins and Lewis 1984). However, in light of the following discussion we feel that after the accretion stage, the removal of atmosphere by this process was probably minute. The amount of ^{40}Ar in the terrestrial atmosphere corresponds very closely to the amount produced during 4.5 by from the decay of K present in the crust. This means that of the ^{40}Ar produced in the mantle only a small fraction found its way to the atmosphere.

Under the assumption that ^{40}Ar is released only from the planetary crusts is justified at least in respect to a first-order approach, the low release factor of 0.026 for ^{40}Ar on Mars seems to be mainly the consequence of the low concentration of only 787 ppm K (mean K concentration in SNC-meteorites) in the Martian crust. This comparatively low K concentration is in line with the more mafic character of the Martian surface rocks (Baird *et al.* 1976). If we assume 100% release of ^{40}Ar from the crust and no release at all from the mantle, for both Earth and Mars the resulting release factor would be

$$R = \frac{[\mathrm{K}_{\text{crust}}] \cdot M_{\text{crust}}}{[\mathrm{K}_{\text{bulk}}] \cdot M_{\text{planet}}}$$

$[\mathrm{K}_{\text{crust}}]$ and $[\mathrm{K}_{\text{bulk}}]$ being the concentration of K in the crust and the bulk planet and M_{crust} and M_{planet} the masses of the crust and the planet. Also,

$$\frac{M_{\text{crust}}}{M_{\text{planet}}} = f.$$

In the case of the Earth, $f_{\mathrm{Earth}} = 0.004$. Denoting Earth by E and Mars by M, we find

$$R_{\mathrm{E}} = \frac{[\mathrm{K}_{\mathrm{E,crust}}] \cdot f_{\mathrm{E}}}{[\mathrm{K}_{\mathrm{E,bulk}}]} = \frac{17{,}630 \times 0.004}{154} = 0.46,$$

with

$[\mathrm{K}_{\mathrm{E,crust}}] = 17{,}630$ (Wedepohl 1981)
$[\mathrm{K}_{\mathrm{E,bulk}}] = 154$ (Wänke *et al.* 1984).

The resulting value of $R_{\mathrm{E}} = 0.46$ comes very close to the value $R = 0.53$ (see above) derived from the argon content of the terrestrial atmosphere and the bulk K content of the Earth. Accordingly,

$$R_{\mathrm{M}} = \frac{[\mathrm{K}_{\mathrm{M,crust}}]}{[\mathrm{K}_{\mathrm{M,bulk}}]} \cdot f_{\mathrm{M}} \quad \text{or} \quad f_{\mathrm{M}} = R_{\mathrm{M}} \cdot \frac{[\mathrm{K}_{\mathrm{M,bulk}}]}{[\mathrm{K}_{\mathrm{M,crust}}]}.$$

If we take the mean value of the K concentration observed in SNC-meteorites of 787 ppm (Burghele *et al.* 1983, Dreibus *et al.* 1982, Laul *et al.* 1986) to be representative for the Martian crust, and with $R_{\mathrm{M}} = 0.026$ and $[\mathrm{K}_{\mathrm{M,bulk}}] = 247$ ppm, we find that the mass fraction of the Martian crust is

$$f_{\mathrm{M}} = 0.026 \left(\frac{247}{787}\right) = 0.008.$$

The mass fraction of the Martian crust estimated in this way is a factor of 2 higher than the value $f_{\mathrm{E}} = 0.004$ for the Earth's crust and would correspond to a crustal thickness of 13 km compared to 17 km on Earth.

Contrary to the situation of Earth, a considerable portion of the Martian crust seems to be old (Neukum and Hiller 1981) and may have kept ^{40}Ar generated since solidification. Hence, the figures for the mass of the Martian crust are in fact only lower limits. However as 50% of ^{40}Ar was produced during the first 1.3 by, the true values should not be more than a factor of 2 higher.

In light of the low release factor of ^{40}Ar for Mars one might argue that the low abundances of the primordial rare gases are at least in part due to a similar inefficient release. However, we feel that only a small part of the factor of 130 between the ^{36}Ar concentrations in the atmospheres of Earth and Mars can be explained by a smaller degassing efficiency for Mars.

The highly reduced enstatite chondrites generally have primordial ^{36}Ar concentrations within the range of the oxidized carbonaceous chondrites. However, there are exceptions, the most striking being the primordial rare gas content of South Oman (Crabb and Anders 1981), which even exceeds that of Venus. With respect to its state of reduction, component A in the model of Ringwood (1977, 1979) and Wänke (1981) is similar to enstatite chondrites. Clearly all terrestrial planets are dominated by the reduced component A. It is interesting to note that the ^{84}Kr/^{132}Xe ratio in the enstatite chondrite South Oman is closer to the ratios in the atmospheres of Earth (Wacker and Anders 1984) and Mars than those of *C*1 and other carbonaceous chondrites. Hence, one could even speculate that the rare gases on the terrestrial planets were not primarily supplied by carbonaceous-type material. It might also be that the abundances of primordial rare gases in carbonaceous chondrites changed from loss by diffusion, which should be largest in the case of Ne and Ar, while Xe would be least affected.

In the model of Ringwood (1977, 1979) and Wänke (1981) it is assumed that the reduced component A is almost free of moderately volatile and volatile elements. Enstatite chondrites are undepleted or only slightly depleted in moderately volatiles. They may in fact be mixtures of even more reduced matter and oxidized volatile-containing material (component B). In any case, the elemental abundances of enstatite chondrites (Baedecker and Wasson 1975) are puzzling and cannot be explained in a straightforward way. With respect to rare gases, we have to keep in mind that even in South Oman the concentration of ^{36}Ar normalized to the solar value and Si corresponds to an abundance of 6×10^{-7}, a very high depletion indeed.

In fact it may be that the solids from which the inner planets formed contained rare gases proportional to their partial pressure in that region of the solar nebula (Pollack and Black 1979). In the model of Cameron and Pine (1973), the total nebula pressure decreases from 0.72 AU (Venus orbit) to 1.52 AU (Mars orbit) by a factor of 4. A similar factor applies to solar wind-implanted rare gases, which differ, however, in their element ratios (Wetherill 1981). Nevertheless, the total variation we might obtain in this way is very small compared to the observed differences.

To explain the observed differences in the primordial rare gas contents of Venus, Earth, and Mars, we propose large differences in gas loss during accretion. As discussed by various authors, two quite different processes are thought to be of importance for the removal of primitive atmospheres:

(1) Hydrodynamic escape due to the presence of large amounts of H_2 so that the mean molecular weight remains low (Zahnle and Kasting 1986, Hunten *et al.* 1986).

(2) Removal by large impacts (Watkins and Lewis 1984).

On Mars, because of its lower gravity, both processes will clearly act more efficiently than on Earth and Venus. Homogeneous accretion as proposed for Mars (Dreibus and Wänke 1984) will not only generate large amounts of H_2 but could also make impact-induced gas loss more efficient, as impacts of bodies from both populations (components A and B) will be effective. In the case of inhomogeneous accretion, the oxidized, volatile-containing component B is added only towards the end of accretion and gas loss by impact is restricted to that period. This is, of course, only relevant if the rare gases are supplied solely by component B. On Earth and Venus, accretional energy leads to formation of huge magma oceans (Kaula 1979), in which substantial portions of rare gases redissolved and subsequently were even carried into the solid regions of the highly convecting mantles. On Mars, melting occurred on a much smaller scale, as the energy of accretion and core formation per unit mass are about 5 times lower (Solomon 1981). In this respect we note that the amounts of gases redissolved depend on the thickness of the layers which equilibrate with the atmosphere and only to a lesser degree on the gas/solid partition coefficients.

Impact-induced fission of the proto-Earth seems the most likely model for the origin of the Moon (Hartmann and Davis 1975, Cameron and Ward 1976, Ringwood 1979, 1986, Melosh and Sonnett 1986, Wänke and Dreibus 1986, Wetherill 1986). The mass of the projectile probably considerably exceeded that of the Moon, and its impact towards the end of terrestrial accretion would probably have completely removed any atmosphere present at that moment. Clearly gas loss also has to be expected in the case of Venus. However, unlike the Earth, Venus was probably not hit late in its accretion history by an object of sufficient mass to form a moon. It has been suggested by Cameron (1983) that the primordial rare gas concentrations of the atmospheres of Earth and Venus may have been similar prior to the removal of the terrestrial atmosphere by the giant Moon-forming impact. Consequently all other atmospheric constituents (including H_2O) would also have been removed.

The observed amounts of primordial rare gases on Venus can be taken as a lower limit on the amounts added. Relative to Venus, the Earth has then lost 10^2, and Mars 10^4, times more of its primordial rare gas contents. The low concentration of ^{36}Ar on Mars can be brought into agreement with the obviously high concentrations of moderately volatile and volatile elements such as K, Rb, Cl, Br, and Pb by assuming that the different rare gas concentations in Venus, Earth, and Mars are due to different loss factors during accretion.

On Earth the large amounts of H_2 generated during accretion may have removed most of the primordial rare gases delivered by component B. Assuming that the observed amounts of primordial rare gases on Earth were contributed predominantly by the 0.44% *C*1 material added at the very end of accretion after iron was no longer present in reduced form (see the preceding section), the 0.44% *C*1 material would bring about 33×10^{-12} cm^3/g ^{132}Xe to the bulk Earth compared to 16×10^{-12} cm^3/g ^{132}Xe present in the atmosphere. As the portion of the Earth's inventory of ^{132}Xe, which is in the atmosphere, is probably not less than about 50% (Allègre *et al.* 1986/1987), this is in surprisingly good agreement considering the large uncertainties in our exercise. In this case of ^{36}Ar, only about 20% of the 210 $\times 10^{-10}$ cm^3/g ^{36}Ar in the Earth atmosphere could be derived from 0.44% *C*1 material. However, we have the strong suspicion that with respect to rare gases the *C*1 chondrites of today do not represent the material actually added at the accretion stage of the terrestrial planets. Because about 90% of the radiogenic ^{40}Ar produced during the past 4.5×10^9 years was obviously lost from *C*1 chondrites by diffusion, a similar loss of ^{36}Ar may be inferred (Mazor *et al.* 1970). Preferential diffusion loss of Ne, Ar, and Kr relative to Xe would also explain the striking difference of Kr/Xe ratios in Earth and Mars from that in *C*1 chondrites (Anders and Owen 1977). In this way, the "Xe problem" might be solved (Canalas *et al.* 1968, Fanale and Cannon 1971, Bernatowicz and Podosek 1978, Podosek *et al.* 1980, Wacker and Anders 1984). However, as discussed above, it might be that *C*1 material (or component B) may not be the sole source of the rare gas inventory of terrestrial planets.

The most precise value for the ratio $^{129}Xe/^{132}Xe$ in the Martian atmosphere is obtained from the trapped component in the shergottite EETA 79001, for which Becker and Pepin (1984) gave a value $^{129}Xe/^{132}Xe = 2.23$ and Swindle *et al.* (1986) a value of 2.39. As pointed out by Ott and Begemann (1985), it seems that the $^{129}Xe/^{132}Xe$ ratio in the interior of Mars, as reflected in SNC-meteorites, is lower than the ratio in the Martian atmosphere. In contrast, the $^{129}Xe/^{132}Xe$ ratio in terrestrial rocks is equal or higher than the atmospheric ratio (Table II).

Because of the short ^{129}I half-life of 16 my, $^{129}Xe_{rad}$ is produced early in the history of planets. Iodine is not only a highly incompatible element, but also highly volatile. Like the other halogens, iodine is easily extracted from heated rock samples in the presence of H_2O. Hence, it might be that under accretion conditions on Mars, iodine was removed from the interior of the planet very efficiently and was incorporated into the crustal rocks present at that time. Clearly primordial rare gases, including xenon, would have been extracted together with iodine. However, rare gases would mostly have entered the atmosphere and been lost. After the end of accretion, $^{129}Xe_{rad}$ produced from ^{129}I in the crust would have been released into the atmosphere over geologic time, leading to the observed high $^{129}Xe/^{132}Xe$ ratio. As it seems unlikely that iodine from the interior of Mars was extracted more efficiently than xenon, the $^{129}Xe/^{132}Xe$ ratio in the atmosphere will become larger than in the interior only, if most of the early atmosphere was removed very efficiently during accretion.

For terrestrial rocks (MORB and mantle xenoliths) one finds Cl, Br, and I in *C*1 abundance ratios (Fig. 4), while in shergottites iodine is depleted relative to *C*1 halogen ratios. Shergottites are young basalts and probably reflect the composition of the Martian mantle in modern time. Thus, their iodine depletion could be an indication of an early extraction of iodine from the

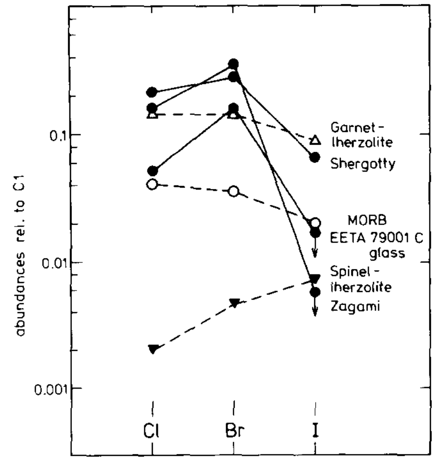

FIG. 4. Halogen concentrations relative to *C*1 in rocks from Earth and Mars. In Shergotty, Zagami, and the glass samples from EETA 79001, iodine is considerably depleted relative to Br and Cl, whereas in terrestrial MORB glasses and upper mantle samples (i.e., garnet- and spinel-lherzolite), iodine is not depleted.

Martian mantle. On Earth, continuous recycling might have led to this preservation of the *C*1 ratio in mantle-derived samples (Staudacher and Allègre 1982).

In this paper we have repeatedly favored scenarios in which planetary atmospheres created during accretion were also almost completely lost during the accretion. Hence, the present atmospheres and hydrospheres should be formed by degassing of the planet after the end of accretion.

Such a loss of volatiles during accretion is manifested by the low abundances of halogens and $^{129}\mathrm{Xe}_{\mathrm{rad}}$ on Earth. The concentration of Cl, Br, and I in the bulk Earth (Cl = 7.8 ppm, Wänke *et al.* 1984) is lower than in any of the primitive meteorites. It is also lower than the contribution of 15% component B, assuming *C*1 abundances (798 ppm × 0.15 = 120 ppm).

We do not know the amount of primordial rare gases originally added to the Earth, but we know at least roughly the amount of iodine in the Earth (I = 8.8 ppb, Wänke *et al.* 1984). With a $^{129}\mathrm{I}/^{127}\mathrm{I}$ ratio of 1.09×10^{-4} for Bjurböle (Podosek, 1970), we calculate an amount of 167×10^{-12} cm^3/g $^{129}\mathrm{Xe}_{\mathrm{rad}}$ produced by decay of $^{129}\mathrm{I}$. Compared with the value of 1.04×10^{-12} cm^3/g $^{129}\mathrm{Xe}_{\mathrm{rad}}$ in the Earth's atmosphere, one calculates an interval of 115 my between time of retention of $^{129}\mathrm{Xe}_{\mathrm{rad}}$ in Bjurböle and the time of retention of $^{129}\mathrm{Xe}_{\mathrm{rad}}$ in the Earth's atmosphere. Even assuming a release factor for $^{129}\mathrm{Xe}_{\mathrm{rad}}$ as low as that for $^{40}\mathrm{Ar}$, i.e., about 0.5, the time difference would only shrink by one half-life of $^{129}\mathrm{I}$, i.e., by 15.7 my. As seen from Table III, all primitive meteorites contain $^{129}\mathrm{Xe}_{\mathrm{rad}}$ in amounts far exceeding the amounts of $^{129}\mathrm{Xe}_{\mathrm{rad}}$ on Earth. The same holds, of course, for primordial rare gases which, however, can in principle be lost prior to or simultaneous with accretion. The loss of $^{129}\mathrm{Xe}_{\mathrm{rad}}$ produced from $^{129}\mathrm{I}$ added to the Earth can only occur after the decay of $^{129}\mathrm{I}$ and the release of its daughter product from the interior of the planet.

As long as H_2O was able to react with metallic iron and be converted to H_2 during accretion, no *permanent* atmosphere could develop and even volatiles from the interiors of terrestrial planets were extracted with high efficiency and lost. Thus the present atmospheres of Earth, Venus, and Mars were only formed after metallic iron was no longer available, by outgassing of the planets. Volatiles added after this stage were retained to a much larger extent.

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