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Mars and Earth: Origin and Abundance of Volatiles

Mars has only 3 percent of Earth's share of volatiles, but got them from the same meteoritic source.

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The thinness of the martian atmosphere has been one of the great disappointments of the space age. Early estimates by P. Lowell, A. Dollfus, G. de Vaucouleurs, and others suggested a surface pressure near 80 millibars (*1*), about one-tenth the terrestrial value, and thus possibly dense enough to sustain advanced life (*2*). But beginning with the observations of Spinrad and Münch in 1963 (*3*), this value dropped relentlessly and leveled off near 8 millibars (*4*) 11 years before Viking 1 supplied the definitive figure of 7.65 millibars (*5*).

Five processes, in combination, may be responsible for the tenuous nature of the martian atmosphere: (i) a small initial endowment of volatiles, (ii) incomplete outgassing from the interior, (iii) recondensation or trapping in surface regions, (iv) catastrophic loss of an early atmosphere, and (v) gradual escape of the lighter constituents. At least the first four are well shielded from human inquiry by their remoteness in time and space, and so all pre-Viking attempts to understand the origin of the martian atmosphere ended on an inconclusive note. They did show, however, that important and perhaps decisive clues might come from isotopic and elemental abundances of noble gases on Mars (*6, 7*).

Such data are now available, thanks to the success of the Viking missions. In this article we have tried to combine these new data with other facts and ideas from meteoritics and planetology into a detailed, quantitative model. We conclude that the first process was dominant, but that the second, third, and fifth processes also played a role. Mars was poor in volatiles from the start and fell further behind Earth by less complete outgassing, by extensive retrapping, and by partial loss of lighter gases. Those predictions of our model that can be tested at this time agree or at least are consistent with current data on Mars, Earth, and Venus. Time will tell whether the remaining predictions are true.

Noble Gases on Earth and Mars

Let us begin by comparing noble-gas abundances in the atmospheres of the two planets (Fig. 1). Both patterns are remarkably similar, although the abundances on Mars are two orders of magnitude lower. Both differ strikingly from the solar pattern, but resemble the patterns of various chondrite classes (*8, 9*), except for the lower xenon abundance. It has been shown, however, that much of Earth's xenon is locked up in shales (*10, 11*), and if this effect is allowed for, the match to the chondrites becomes very close.

Apparently chondrites, Earth, and now also Mars represent a common "planetary" pattern (*8, 12*). Because chondrite parent bodies were only $\sim 10^{-6}$ times as massive as Earth, the basic fractionation that produced the planetary pattern from a solar gas must have occurred prior to the formation of the planets—probably during condensation of dust grains from the solar nebula.

Admittedly, the match between the terrestrial and chondritic patterns is not perfect. As Fig. 1 shows, the planetary pattern in chondrites is not quite uniform, but varies slightly between and within classes (*8, 9*). And there are substantial isotopic differences between terrestrial, chondritic, and solar neon and xenon, for reasons which are not yet fully understood, but seem to depend on the nature of the host minerals and the temperature of trapping (*8, 11, 13, 14*). Following earlier authors, we shall optimistically assume that the isotopic fractionations will somehow take care of themselves, once the right process for the elemental fractionations has been found (*11, 14-16*).

If dust with a planetary noble-gas pattern was common in the inner solar nebula, one would expect to find the same pattern in the atmospheres of Venus and Mars (*7, 17, 18*). Presumably this dust was also the principal carrier of carbon, nitrogen, and hydrogen, and if we knew the proportions of these volatiles to noble gases then we could predict a planet's total inventory of volatiles from noble-gas abundances alone. This will be the major task of this article.

Condensation of Noble Gases and Other Volatiles

It is generally agreed that chondritic meteorites are primitive condensates from the solar nebula, modified by only a few additional processes before accretion to their asteroidal parent bodies (*19-21*). Presumably Earth and Mars accreted from similar condensates. Let us compare two classes of chondrites, C (carbonaceous) and H (high-iron ordinary), spanning a wide range of volatile-element contents (Table 1).

The petrologic types (given by numerals 1 to 6) have slightly different mean-

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Table 1. Mean abundances of highly volatile elements in chondrites.

Class and type	Approximate condensation temperature (°K)	^{36}Ar (10^{-8} cm^3/g)	C (ppm)	N (ppm)	H (ppm)	Tl (ppm)
C1	360	87	36,000	2,800	7,900	146
C2	400	130	23,000	1,500	8,900	92
C3V	410–430	33	6,700	61	500	58
C3O	420–440	164	4,700	60	1,000	49
H3	430	9.8	2,280	86	10*	82
H4	450	2.9	1,310	47	5*	1.59
H5	460	1.4	1,100	43	4*	0.77
H6	470	0.9	1,060	50	4*	0.81
H (weighted average)		2.0	1,190	47	5*	4.4
References	(*23*)	(*8, 9, 14*)	(*116*)	(*117*)	(*40*)	(*25, 118*)

*These values are rather uncertain. They were estimated from carbon content, on the assumption that 8 percent of the carbon is present as a polymer of C/H = 1 (*45*).

ings in the two classes: as originally assigned (*22*), they represent decreasing volatile content from C1 to C3 and increasing recrystallization from H3 to H6. However, more relevant to our purposes, they also happen to be correlated with condensation temperatures of these meteorites (column 2 in Table 1), as determined by various chemical and isotopic thermometers (*23-25*). Apparently these meteorites typify a range of nebular condensates, analogous although not necessarily identical to those from which the planets accreted (*26*).

It is obvious on inspection of Table 1 that the ratios of volatiles vary from type to type. The reason is the diverse condensation chemistry of these elements. Argon dissolves in solid solution in several trace minerals of Fe, Cr, and Ni (*14, 16, 27, 28*), whose amounts, variety, and solvent capacity increase with decreasing temperature. In contrast, C and N condense first in small amounts as solid solutions in nickel-iron (*29*), and at lower temperatures, together with H, as organic polymers on the surfaces of catalytically active grains (*30*). Their high abundances in C1 and C2 chondrites reflect the large-scale formation of catalytically active clay minerals and magnetite below 400°K. (The abundance of H is further boosted by the presence of structural OH in these clay minerals.) Similarly, Tl condenses first as a solid solution in minor sulfide (*28, 31*) or nickel-iron (*24*) phases and then as a surface coating of pure Tl or Tl_2S.

It is naive to expect any one of these condensates to be the sole building material of a particular planet. In the absence of a thermostat, temperatures of the nebula must have fallen during accretion of the planet (or its constituent planetesimals), and so the nebular dust must have become steadily richer in volatiles. (Even the small chondrite parent bodies show this effect; note the trend from H6 to H3 in Table 1.) Moreover, gravitational scattering by the growing planets must have led to considerable exchange of material among different parts of the nebula, especially a late inflow of volatile-rich material from the Jupiter zone (*32*). Thus a continuum of condensates, spanning or even exceeding the gamut of Table 1, may have contributed to the inner planets.

A model including all these condensates would have more parameters than constraints. We shall therefore begin by simply evaluating the limiting cases of homogeneous and heterogeneous accretion (*33*). Homogeneous accretion (*34*) builds each planet from a single kind of material that has the right content of volatiles throughout. Heterogeneous accretion (*35, 36*) adds the volatiles mainly at the end of the accretion process, in the form of a thin "veneer" of volatile-rich material.

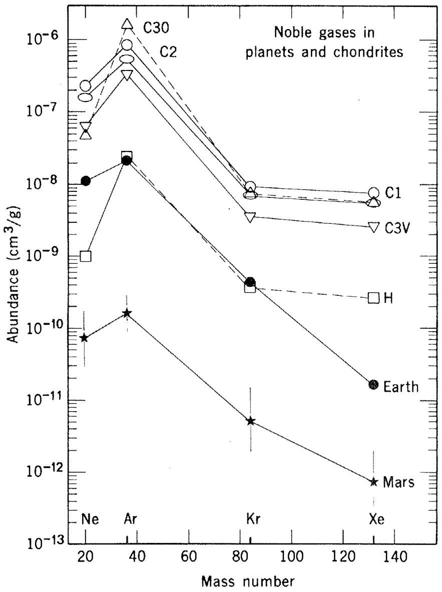


Fig. 1. Noble gases in chondrites show a distinctive "planetary" pattern, strongly fractionated with respect to solar ratios [^{20}Ne/^{36}Ar = 40, ^{36}Ar/^{84}Kr = 2500, ^{84}Kr/^{132}Xe = 10 (*83*)]. Earth and Mars show a similar pattern, except for a deficiency at Xe that may reflect trapping in shales (*10, 11*) as well as the martian regolith or polar caps (*17*). Presumably this pattern was established during condensation of dust grains from the solar nebula. Error bars on the martian values are preliminary but conservative estimates (*69*), to be replaced by final values when the necessary calibrations have been completed. The martian ^{20}Ne value was calculated from the observed ^{22}Ne value, for an assumed ^{20}Ne/^{22}Ne ratio of 10 ± 3 (*69*).

Sources of Earth's Volatiles

There is good reason to believe that most of Earth's ^{36}Ar is now in the atmosphere (*37*), and we can therefore use it as an index to compare meteoritic and terrestrial noble-gas inventories. The amount of atmospheric ^{36}Ar per gram of planet is 2.1×10^{-8} cubic centimeter (standard temperature and pressure) (*38*). In terms of homogeneous accretion, this figure could be matched by a grand average of H-chondrites, weighted according to the proportions of the petrologic types (Table 1). In terms of heterogeneous accretion, a few percent of any of the carbonaceous chondrites would do (column 2 of Table 2). Having chosen the amounts needed to account for the ^{36}Ar, let us now extend the comparison to a few other volatiles (Table 2).

Columns 3 to 5 in Table 2 provide no strong constraints. The Ar/Kr ratio is too high, but by less than 2 standard deviations, except for C1's and C3O's. Carbon and nitrogen also are too high (except for nitrogen in C3O's), but the excess can probably be hidden in Earth's core.

Ordinary chondrites. Hydrogen poses more serious problems, especially for H-chondrites (or for the other two kinds of ordinary chondrites, L and LL). Chemical analyses of ordinary chondrites typically show ~ 0.1 percent water, but mineralogical and isotopic data make it very doubtful that any of this water is extraterrestrial (*39, 40*). No hydrated mineral such as tremolite, predicted by Lewis (*34*), has ever been seen in ordinary chondrites; the most likely prospect, amphibole (*41*), apparently contains O^{2-} and F^- in place of OH^- (*42*). Indeed, no hydrated silicates would be expected to coexist with the water-sensitive minerals actually present, such as nickel-iron. Moreover, the water is released below 180°C (*39*) and hence seems to be adsorbed rather than chemically bound. Isotopic studies of carbonaceous chondrites (*39, 40*) and lunar soils (*43*) have shown that such loosely bound water is of terrestrial origin.

A much smaller amount of potential water is present in the form of hydrogen in the organic polymer (*18, 44*). From the very scanty published data (*45*), it appears that less than one-tenth of the total carbon is present as an aromatic organic polymer with a C/H ratio of ~ 1; the remainder presumably occurs as graphite and mainly as a solid solution in γ-nickel-iron (*46*). The hydrogen contents of H-chondrites in Table 1 were estimated on the assumption that 8 percent of the carbon is present as a polymer of C/H = 1 (*45*).

Table 2. Chondrites as a source of Earth's volatiles. Column 2 gives the mass required to supply the observed amount of ^{36}Ar in the atmosphere (2.1×10^{-8} cm^3/g).

Class	Mass (Earth = 1)	^{36}Ar/^{84}Kr	C (ppm)	N (ppm)	H (ppm)	δD (%)	$\delta^{13}C$ (per mil)
*Observed**		*48*	*23*	*830*	*31*	*−1.8*	*−6.4*
H	1	66 ± 42	1,190	47,000	5	?	−24
C1	0.024	90 ± 12	870	68,000	190	+24	−7/−11
C2	0.039	77 ± 23	910	59,000	350	+5/−17	−4/−10
C3O	0.013	211 ± 67	60	770	13	−12	−16
C3V	0.063	83 ± 26†	420	3,800	31	+18	−18

*Earth's crust, atmosphere, and oceans. †Excluding two meteorites with ^{36}Ar/^{84}Kr = 210 and 270.

This estimate is too uncertain to prove that another source of volatiles is needed. However, isotopic data on hydrogen and carbon do require just that. Kokubu *et al.* (*35*) have shown that juvenile water from Earth's interior contains less deuterium ($\delta D = -15$ percent) than either mean ocean water ($\delta D \equiv 0$ percent) or mean surface water ($\delta D = -1.75$ percent). Because deuterium enrichment of surface waters by preferential escape of protium is implausible (it requires loss of >4 percent of the oceans, with concomitant production of unreasonably large amounts of O_2), they suggested C1 or C3V chondrites ($\delta D = +18.3$ to $+26.9$ percent) as the source of the heavy surface waters and C2 or C3O chondrites ($\delta D = -15.3$ to $+4.2$ percent) as the source of the light interior waters (*47*). Even if we assume without proof that ordinary chondrites can serve as the source of the light water, we still need C1, C2, or C3V chondrites for the heavy water.

The carbon data point in the same direction, but more conclusively. Carbon of H-chondrites is markedly lighter ($\delta^{13}C = -24$ per mil relative to the PDB standard) than average terrestrial carbon [$\delta^{13}C = -6.4 \pm 1.3$ per mil (*48*)], whereas carbon of C-chondrites brackets the terrestrial value [−3.7 to −18.8 per mil (*39*)]. If crustal carbon is to be made by mixing H-chondrites with the most ^{13}C-rich C-chondrites, then C-chondrites would have to provide no less than 87 percent of the crustal carbon and even larger percentages of other volatiles. It thus seems that some mix of C-chondrite–like materials was the main source of Earth's volatiles.

Carbonaceous chondrites? This mix cannot have consisted mainly of C1 or C2 chondrites because they are too rich in water. Larimer (*49*) has pointed out that no more than half of Earth's total water can still be in the mantle, otherwise basaltic lavas from the upper mantle would contain more water than they actually do. The global abundance of hydrogen thus must be less than 62 parts per million (ppm), which rules out C1 and C2 chondrites (H = 190 and 350 ppm) as major components of the C-chondrite mix.

This leaves C3V's as the sole remaining alternative. They have a passable Ar/Kr ratio, fairly modest excesses of C and N, and about the right amount of H (*50*). However, we again emphasize that they are not a perfect match isotopically and would have to be complemented by C2's or similar material to bring H, C, and N into isotopic balance.

It thus appears that we cannot account for the volatiles either with a homogeneous planet composed of any of the known meteorite types, or with a veneer or ordinary chondrites only. The latter model, proposed by Rasool and LeSergeant (*51*), will not satisfy the hydrogen and carbon constraints. On the other hand, we can supply Earth's volatiles in about the right proportions with a late-accreting veneer of a few percent C3V-chondrite–like material (*52*). Ganapathy and Anders (*53*) have used C3O's for this purpose, but Table 2 shows that C3V's are superior.

Our neighboring planets, Mars and Venus, should have acquired their volatiles from a similar veneer. This veneer might be a local, late condensate or an alien material scattered from the Jupiter zone (*32*). In either case, it would be a late addition, confined to the planet's outermost layers.

Bulk Composition of Earth

Before trying to resolve the Mars data in terms of initial endowment, outgassing, and loss, we must find a way to do this for Earth. The central question is the bulk composition of the planet. Ganapathay and Anders (*53*) have recently shown that plausible compositions for Earth and the moon can be obtained by assuming that these bodies (or their precursor planetesimals) formed by the same cosmochemical processes as did the chondrites. Four such processes have been recognized (*20, 21*), leading to a total of about five components. Each of these components contains a group of elements of similar volatility (Fig. 2) in more or less constant, generally cosmic, proportions. Thus one only needs to know the global abundances of some four index elements to estimate the abundances of all 83 naturally occurring elements (Fig. 3).

For a differentiated planet such as Earth or the moon, two index elements can be estimated directly: Fe from the bulk density and U from heat flow data [see (*53*) for details]. Two others, K and Tl, can be estimated from their ratios to U in surface rocks. As first shown by Wasserburg *et al.* (*54*), the K/U ratio in Earth's surface rocks is remarkably constant at 1×10^4, well below the cosmic ratio of 6.2×10^4 (*55*). This constancy suggests that these two elements do not separate readily in igneous processes, and so this ratio may be representative for the whole Earth. Because ^{40}K is one of the main sources of radiogenic heat in Earth, the heat flow data, coupled with the K/U and Th/U ratio, tightly constrain the global abundances of both K and U. Later work has shown that the K/U ratio is similarly constant but lower in lunar rocks [~1600 versus ~10,000 (*53, 56*)], and so is the Tl/U ratio [0.0023 versus 0.27 (*53, 57*)].

Release of Volatiles from Earth

Various tests against petrologic and chemical data (*58*) have shown that the compositions in Fig. 3 are reasonable first approximations, although undoubtedly in need of further refinement. For our purposes, a test of sorts is provided by the "release factors" (*49, 59*), defined as the ratio of crustal abundance to global abundance. (Here and elsewhere in this article, we express crustal abundance per unit mass of planet, rather than in the conventional manner, per unit of mass of crust. This merely requires multiplication by 0.004, the mass fraction of Earth's crust.) If the model is valid, then the release factors for volatiles should never exceed unity and should resemble those of geochemically similar but less volatile elements, which are much less depleted according to the model (Fig. 3).

Figure 4 shows data for all 16 volatiles of nebular condensation temperature less than 600°K, for four elements of higher condensation temperature (K, Rb, Ba, and La) that are likewise incompatible with mantle mineralogy and are therefore concentrated in the crust (*49, 59, 60*), and for radiogenic ^{40}Ar. Elements are arranged according to ionic charge.

By and large, the results look reasonable. Of the first 14 elements, 12 have very similar release factors, between 0.11 and 0.36. (The standard deviation of the mean, a factor of 1.4, is comparable to the errors in crustal abundances.) There is no systematic difference between the ten volatiles and the four less volatile elements, although their global depletions differ greatly. According to Fig. 3, refractory Ba and La are enriched in Earth by a factor of 1.6 relative to solar abundances, whereas moderately volatile K and Rb are depleted by a factor of 0.22 and the ten highly volatile elements by a factor of 0.024. Only the two most volatile metals, Cd and Hg, fall below the general trend, but there is no lack of possible excuses for this anomaly (*61*). The generally flat trend of Fig. 4 is another argument in favor of a carbonaceous veneer as the main source of volatiles. A higher-temperature condensate such as H-chondrites would have given a sloping trend, with progressively smaller release factors for the more volatile elements.

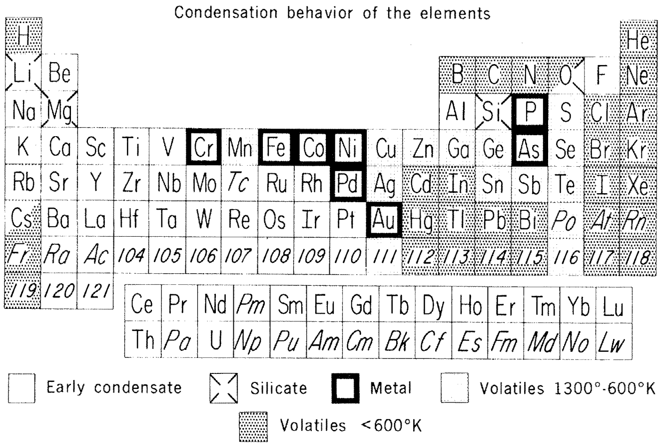
Of the last seven elements, ^{40}Ar, ^{36}Ar, Kr, and H show larger release factors than the preceding 14, consistent with their chemical inertness and the dryness of the Earth's mantle, respectively (*49*). [Krypton, with a physically impossible release factor of 1.26, has overshot the mark, but this merely reflects the fact that we knowingly used a source material with ^{36}Ar/^{84}Kr greater than the atmospheric ratio, 83 rather than 48 (Table 2). Had we used some of the lower ratios among C3V chondrites (67, 70, and 74) rather than the mean for the group, this discrepancy would have been reduced.] Xenon falls out of line, apparently due to trapping in sedimentary rocks, as mentioned earlier.

For C and N, virtually no meaningful tests are available. Both elements are soluble in metallic iron, and hence may have been extracted into the core to a substantial degree. According to Turekian and Clark (*18*), the upper mantle contains no more C and N than does the crust. About 14 ppm N and 1600 ppm C thus would have to be accommodated in the core—not an unreasonable amount.

Clues to the Volatile Endowment of Mars

Our key data for Mars are the abundances of the two argon isotopes: $^{36}\text{Ar} = 1.6 \times 10^{-10}$ cm^3/g and $^{40}\text{Ar} = 4.8 \times 10^{-7}$ cm^3/g (*62*). Argon is the most informative of the noble gases, being too heavy to escape, too unreactive to be trapped in sediments, and yet volatile enough to be outgassed more completely than most other elements (Fig. 4). Moreover, the two isotopes are coupled to two cosmochemical element groups: ^{36}Ar to 16 highly volatile elements and ^{40}Ar (daughter of ^{40}K) to 15 moderately volatile elements (Figs. 2 and 3).

However, we cannot interpret this surface abundance of Ar in terms of initial endowment and outgassing without knowing the global abundance of Ar or at least one other element from each group. Such information is lacking at the present time; we know neither the K/U and Tl/U ratios, nor the global U abundance on Mars. Under the circumstances, we shall resort to an intuitive approach:



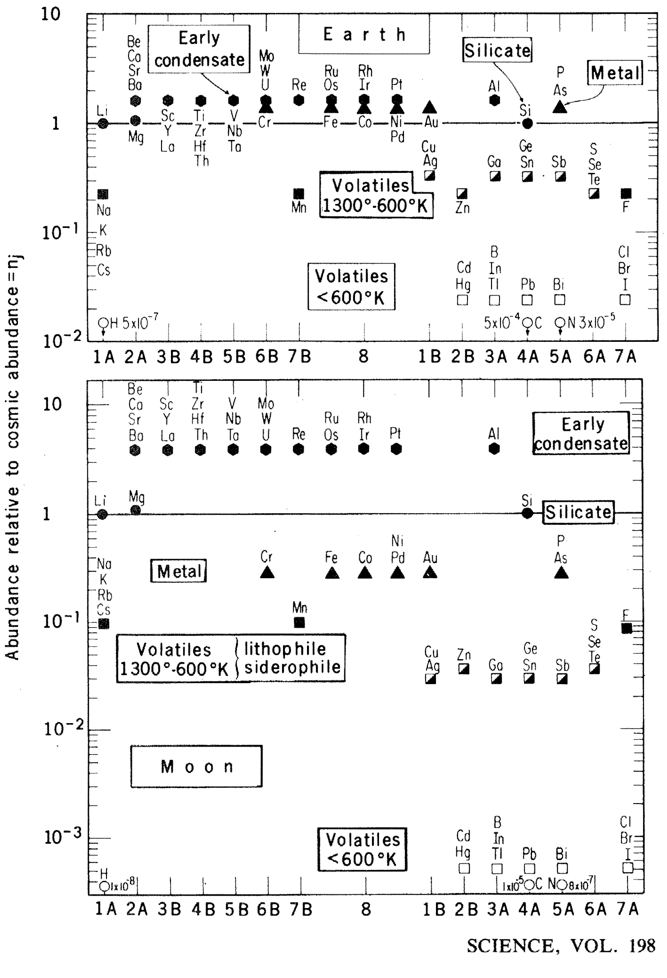


Fig. 2 (left). Elements can be divided into five groups, on the basis of condensation temperature from a solar gas and fractionation behavior in chondrites (*20, 21*). Elements of the same group usually fractionate by about the same factor, and so the abundance of each group in a given planet can be estimated from that of a single index element. Italic symbols denote radioactive elements that do not occur in nature. Fig. 3 (right). Bulk composition of Earth and the moon, according to the model of Ganapathy and Anders (*53*). The highly volatile elements are assumed to have been brought in by material of C3V chondrite composition.

guess the martian abundances of the index elements Tl and K from the available data on other planets, use these values to predict various elemental and isotopic abundances, and then check these predictions against observation to verify the initial guesses.

Table 3. Compositional data on differentiated planets. Values in roman type are observed, those in italic type are calculated from a model (*53*), and those in bracketed italics are guessed.

Planet	Mass (Earth = 1)	Distance from sun (Earth = 1)	$\frac{K}{U}$	K (ppm)		^{36}Ar (10^{-10} cm^3/g)		Tl, global (ppb)	Reference
				Surface	Global	Surface	Global		
Earth	1	1	9,400	13,000	*170*	210	*285*	*4.9*	(*53*)
Venus	0.815	0.72	12,000	19,000					(*66*)
Mars	0.108	1.52		800	[*100*]	1.6		[*0.14*]	(*62*)
Moon	0.012	1	2,000	600	*96*		*7.9*	*0.14*	(*53*)
EPB*	4×10^{-5}	2.36	3,000	360	*36*		*3.2*	*0.056*	(*64*)
H-chondrites	10^{-6}	2.2?	70,000	830	830		240	4.4	(*8, 9, 25*)

*EPB = eucrite parent body, probably the asteroid 4 Vesta.

We have data of varying completeness for five differentiated planets (Table 3). The last is the parent body of the eucrites, also known as basaltic achondrites. Although not yet conclusively located in the sky [the best candidate is the asteroid 4 Vesta (*63*)], at least its composition seems to be fairly well known. Four independent attempts to reconstruct its composition have given remarkably consistent results (*64*).

There is at least one good reason to treat the differentiated planets as a distinct group. Isotopic studies by Clayton and co-workers (*65*) show that Earth, the moon, eucrites, and several other classes of differentiated meteorites contain oxygen of identical isotopic composition, whereas most kinds of undifferentiated meteorites (chondrites) contain different and variable proportions of ^{16}O, apparently from an alien, presolar component. This distinction carries over to certain chemical traits. All three differentiated bodies for which global K abundances are available are depleted relative to undifferentiated bodies (for instance, H-chondrites; last row of Table 3). Data for Venus are still incomplete, but the K/U ratio is lower than the solar value of 62,000 at all three sites analyzed by Venera 8, 9, and 10: 22,000, 7,800, and 6,500 (*66*). Similarly, the K abundance in martian dust is apparently no higher than that in H-chondrites (≤800 versus 830 ppm), although the Ca and Al contents are two to three times greater than chondritic, and hence imply an igneous differentiation that should have enriched K to an even greater degree (*67*).

Two lines of evidence thus suggest a low global K content for Mars: the low surface abundance and the consistently low K content of other differentiated planets, which bracket Mars in both size and heliocentric distance. The total variation in Table 3 is only a factor of 4, and we therefore feel justified in adopting a value of 100 ppm, close to the mean. Regrettably, statistics for terrestrial planets will never be much better. [After this article was written, we learned of gammaray measurements by the Soviet orbiter Mars 5 giving the following mean surface abundances for Mars (*68*): K = 3000 ppm, U = 1 ppm, and Th = 5 ppm. Both the low potassium abundance and the low K/U ratio of 3000 place Mars partway between Earth and the moon in Table 3 and support our choice of a global potassium abundance below the terrestrial value.]

For our second index element, Tl, the variation is much greater, and there are no data whatsoever for Mars. Anything between the terrestrial and lunar values would seem to be acceptable. However, the ^{40}Ar/^{36}Ar ratio points to a low Tl value. The martian ratio of 3000 is a factor of 10 higher than the terrestrial ratio of 296. This difference cannot be due to preferential outgassing of ^{40}Ar on Mars because ^{40}Ar, having formed gradually and at a greater average depth, should be released less completely than ^{36}Ar, which was present from the start, and mainly in surface regions. Nor can the difference be blamed on loss of an early ^{36}Ar-rich atmosphere or on more retentive mineralogical siting of the ^{36}Ar. Loss of an early atmosphere is unlikely on various grounds, as shown by Owen *et al.* (*69*) and later in this article. The mineralogical sites occupied by K and ^{36}Ar certainly are not identical in chondrites, as shown by the preferential release of ^{40}Ar upon heating (*70*). However, material falling on Mars in the last stages of accretion would be vaporized because of the high infall velocity (≥ the escape velocity, 5 kilometers per second), and so the initial mineralogy would be destroyed. Eventually, the volatiles were reincorporated in crustal and mantle rocks, and although very little is known about the siting of ^{36}Ar in such rocks, data on terrestrial mantle rocks and well gases consistently show ^{40}Ar/^{36}Ar ratios greater than atmospheric (*15, 37, 71*). Evidently, much of the ^{36}Ar released during accretion of Earth remained in the atmosphere, rather than being retrapped in rocks. Thus the high ^{40}Ar/^{36}Ar ratio on Mars strongly suggests a low intrinsic abundance of ^{36}Ar, Tl, and other highly volatile elements.

Before using the low ^{36}Ar abundance to justify the choice of a low Tl abundance, we must make sure that these two elements are in fact correlated during nebular condensation, in view of the dif-

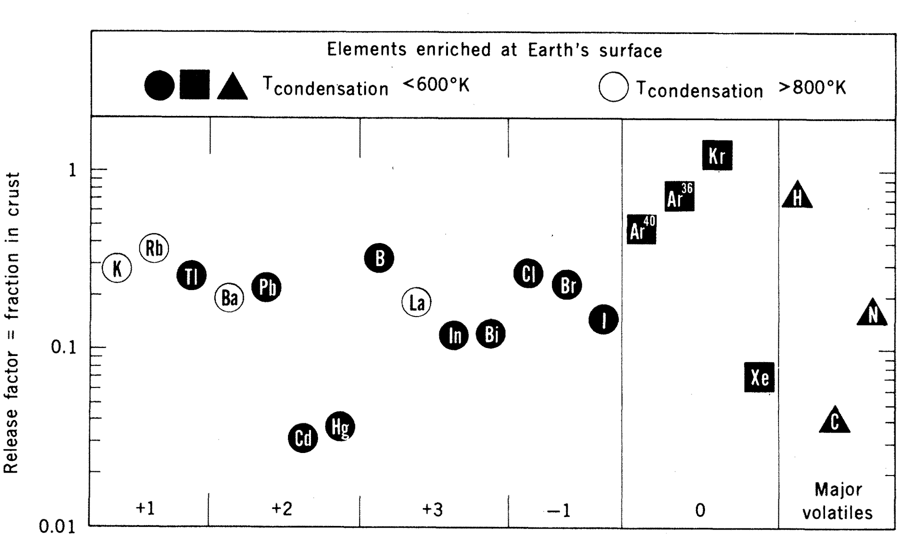


Fig. 4. Most elements forming large ions (and hence incompatible with the mineralogy of the mantle) are present in Earth's crust at about 0.2 to 0.3 of their global abundance (Fig. 3). The relative constancy of these "release" or "outgassing" factors supports the model composition in Fig. 3, particularly the assumption that the highly volatile elements were brought in by material of approximately C3V chondrite composition.

ferences in trapping mechanisms and host phases. Data on chondrites (Fig. 5) show a passable correlation over three orders of magnitude, and both Earth and a gas-rich mineral fraction from the Allende C3V chondrite (*14*) more or less fit the general trend.

If ^{36}Ar had outgassed to the same degree on Mars and Earth, we could infer a 130-fold lower Tl abundance of 0.04 part per billion (ppb) from the 130-fold lower ^{36}Ar abundance (Table 3). However, we might expect a priori that Mars has outgassed to a smaller extent than Venus or Earth, because of its smaller size, and consequently is richer in volatiles than implied by the atmospheric ^{36}Ar abundance. Photographs of the martian surface indeed provide qualitative support for this idea. The lack of evidence for crustal motion and associated tectonic activity—the huge volcanoes and the remnants of a primitive crust (*72*)—are consistent with a low amount of postformation outgassing, as is the fact that the ^{40}Ar content of the atmosphere is less than 10 percent of the value predicted by a strict terrestrial analogy (*62*). And the trend in Table 3 does not support a Tl content as low as 0.04 ppb: on the basis of size, one would expect Mars to have a Tl value at least as high as that of the moon, 0.14 ppb. Let us therefore tentatively adopt 0.14 ppb for the Tl content of Mars and reconsider our choice later on.

An Abundance Table for Mars

Having chosen values for the two index elements Tl and K, we are now in a position to calculate global and crustal abundances of 29 other volatiles that are correlated with them (Table 4). Global abundances for Earth were taken from (*53*), with adjustments of H, C, N, and noble gases to C3V rather than C3O chondrite proportions, whereas crustal abundances were taken from (*49, 53*). Global abundances for Mars were scaled downward from those for Earth, using factors of 1.7 for the K group and 35 for the Tl group.

Martian crustal abundances were estimated by dividing Earth's crustal abundances by the same scaling factors, 1.7 for the K group and 35 for the Tl group (Table 4). These are the abundances expected if Mars and Earth had differentiated and outgassed to the same degree—that is, if the elements were partitioned in the same ratio between crust and interior of the two planets. Judging from a comparison of terrestrial and lunar basalts (*53*), partition coefficients on the two planets indeed are similar, and so this may not be a bad assumption, even for those elements of the K group that have very small release factors (Table 4). Larger errors may be expected for the atmophiles, whose abundance is not controlled by simple distribution equilibriums.

Comparison with Observations

At the present stage of exploration, much less is known about the crust than about the atmosphere of Mars. Consequently, our comparison is restricted to a few, mainly atmophile elements, marked by asterisks in Table 5. Unfortunately, these are the very elements for which our predicted crustal abundances are least accurate.

Even these limited data suggest strongly that Mars has outgassed less than Earth. The "predicted" values are based on minimal, moonlike global abundances of volatiles and release factors equal to those for Earth. Unless we are prepared to assume still lower global abundances, we must attribute the preponderance of ratios less than 1 to less complete outgassing. Let us consider the elements in detail, focusing on the ratio observed/predicted ("relative release factor").

Argon, krypton, and xenon. The ratios for the three gases rise progressively from 0.27 to 1.7, which suggests that the heavy gases on Mars are less completely sequestered in sedimentary rocks than they are on Earth. This effect should be minimal for argon, and so the ^{36}Ar value of 0.27 probably is the best estimate of relative outgassing of atmophiles.

Argon-40. The ratio for ^{40}Ar is 0.13, one-half the value for ^{36}Ar. This difference certainly is in the right direction. Radiogenic ^{40}Ar should be outgassed less than primordial ^{36}Ar because it formed only gradually over geologic time and at a greater average depth. On Earth, ^{40}Ar also has a smaller release factor, 0.48 versus 0.74.

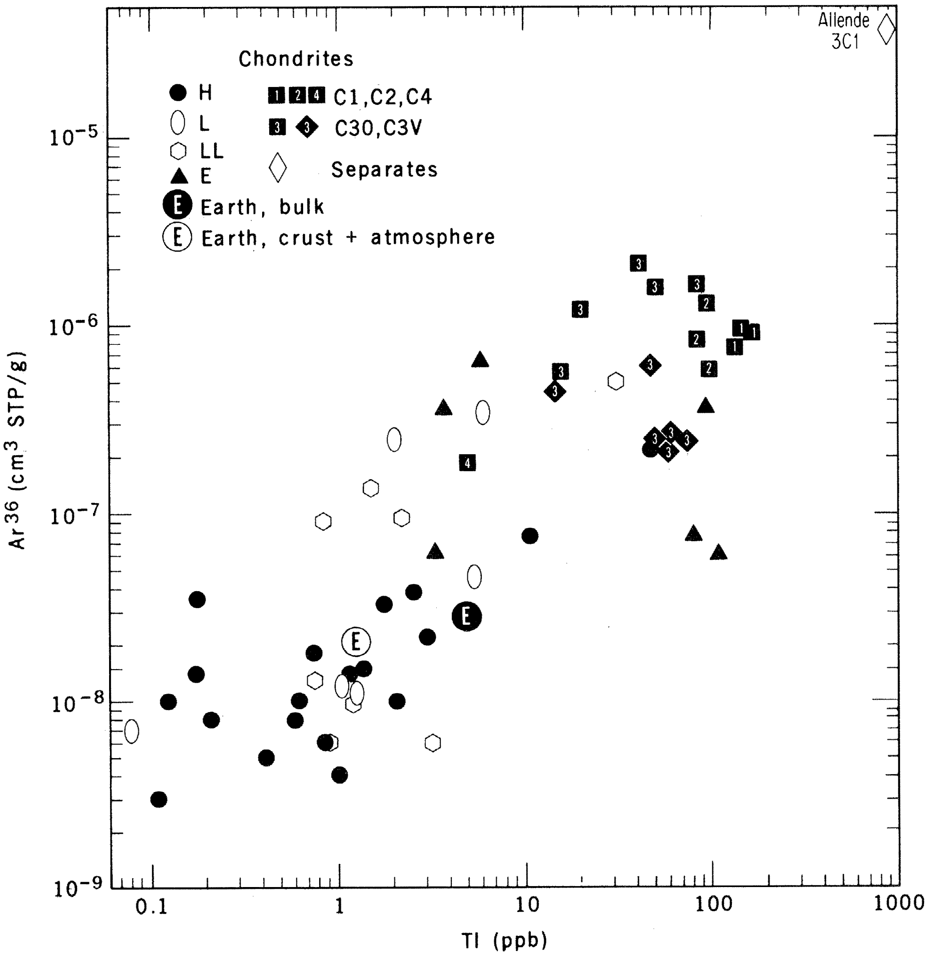


Fig. 5. Argon-36 and thallium are roughly correlated in chondrites, in spite of differences in condensation mechanisms. We can therefore use one or both of them as index elements for the highly volatile elements in Fig. 2.

Nitrogen. The observed ratio of 0.026 is an order of magnitude lower than the value for ^{36}Ar. However, nitrogen has an atomic mass of only 14, and so we must also consider atmospheric escape (*73, 74*). In fact, we know the present atmosphere of Mars does not contain all the nitrogen degassed by the planet because of the 70 percent enrichment of ^{15}N relative to ^{14}N (*75*). If escape is the only nitrogen sink, then an initial abundance ten times the present value would be required to achieve the present ratio of ^{15}N/^{14}N. [Deposition of nitrogen compounds in the martian soil would require an increase in this factor (*76*).] Corrected for this loss, the one-time surface abundance becomes 6.2 ppb, and the relative release factor 0.26, essentially identical to the value of 0.27 for ^{36}Ar. Within the framework of our model, this agreement between two completely independent efforts to assess the total nitrogen abundance suggests that escape has dominated deposition as the means for nitrogen removal.

Water. We can estimate the total outgassed water vapor in a similar manner. We assume that the relative release factor for hydrogen should also be close to 0.27 (the release factors for H and ^{36}Ar are identical on Earth; see Table 4), which would imply a value of 0.24 ppm for the total outgassed hydrogen. This in turn corresponds to a layer of liquid water 9.4 meters deep over the entire planet, or the equivalent of 0.35 bar of atmospheric water vapor. Loss of water vapor by photodissociation and escape should remove only ~2.5 m over 4.6 aeons (*77*). From the fact that the ^{16}O/^{18}O ratio in the CO_2 on Mars appears to be identical with the terrestrial value to a precision of ±5 percent (*78, 79*), McElroy *et al.* (*75*) have concluded that there must be a reservoir of oxygen equivalent to 0.5 bar of water vapor that can exchange with the oxygen in the CO_2 (*80*). Thus we again find good agreement between our model and the calculation of abundances from escape processes—better than we have a right to expect, considering that the hydrogen abundance in C3V chondrites is poorly determined (*50*).

Chlorine and sulfur. A further test is offered by the detection of chlorine and sulfur in the martian soil (*67*). We cannot compare these analyses with the crustal abundances in Table 5, without knowing the thickness of the dust layer and the thickness and composition of the underlying crust. However, these factors largely cancel when element ratios are compared, and since this windblown dust has a similar composition at the two Viking sites, it may be representative enough for such a comparison. The mean Cl/S ratio of the dust is 0.75 percent/3.3 percent = 0.23, identical to the predicted ratio of 0.20 ppm/0.88 ppm = 0.23 but much lower than the terrestrial ratio of 4.7. Some caution may be needed here because Earth's release factor for S is exceedingly small (8.2 × 10^{-5}), and so our tacit assumption that it is similar on Mars may not be justified. However, if we accept the agreement at face value, it does constitute an interesting test of the model, because Cl and S belong to different volatility groups and hence scale by very different factors (Fig. 3 and Table 4).

Salt-bearing dust layer. Baird and coworkers (*67*) have argued that chlorine and sulfur are present on Mars as water-soluble NaCl and $MgSO_4$. The abundances of Cl and S thus permit us to estimate the thickness of the surface layer on Mars within which these apparent evaporites have deposited. Our predicted crustal abundances of Cl and S are 88.5 and 390 g/cm², so material of the mean Cl and S content analyzed by Viking (0.75 and 3.3 percent) can comprise a layer 72 m deep (for the reported density of 1.65 g/cm³).

A 10-m layer of water at 0°C could dis-

Table 4. Abundances on Earth and Mars.

Element	Earth			Mars	
	Global, predicted	Crustal, observed	Release factor	Global, predicted	Crustal, predicted
Tl Group (condensation temperature < 600°K)					
H, ppm	42.6	31	0.73	1.22	0.89
B, ppb	79.2	25.7	0.32	2.26	0.73
C, ppm	571	23	0.040	16.3	0.66
N, ppb	5,190	830	0.16	148	24
Cl, ppm	25	7.0	0.28	0.71	0.20
Br, ppb	134	30.5	0.23	3.83	0.87
Cd, ppb	21	0.66	0.032	0.60	0.019
In, ppb	2.7	0.32	0.119	0.077	0.009
I, ppb	17	2.52	0.148	0.48	0.072
Hg, ppb	9.9	0.36	0.036	0.28	0.010
Tl, ppb	4.9	1.24	0.25	0.14	0.035
^{204}Pb, ppb	1.97	0.44	0.22	0.056	0.013
Bi, ppb	3.7	0.448	0.121	0.106	0.013
^{36}Ar, 10^{-10} cm³/g	285	210	0.74	8.1	6.0
^{84}Kr, 10^{-12} cm³/g	340	430	1.26	9.7	12.3
^{132}Xe, 10^{-12} cm³/g	217	15.6	0.072	6.2	0.45
K group (condensation temperature = 1200° to 600°K)					
F, ppm	53	1.8	0.034	31	1.06
Na, ppm	1,580	85.6	0.054	930	50
S, ppm	18,400	1.50	8.2 × 10^{-5}	10,800	0.88
K, ppm	170	47.2	0.28	100	28
Mn, ppm	590	4.56	7.7 × 10^{-3}	350	2.7
Cu, ppm	57	0.272	4.8 × 10^{-3}	34	0.16
Zn, ppm	93	0.352	3.8 × 10^{-3}	55	0.21
Ga, ppb	5,500	60	0.011	3,200	35
Ge, ppb	13,800	5.8	4.2 × 10^{-4}	8,100	3.4
Se, ppb	6,100	0.31	5.1 × 10^{-5}	3,600	0.18
Rb, ppb	580	208	0.36	341	122
Ag, ppb	80	0.32	4 × 10^{-3}	47	0.19
Sn, ppb	710	5.6	7.9 × 10^{-3}	418	3.3
Sb, ppb	64	1.04	0.016	38	0.61
Cs, ppb	59	6	0.10	35	3.5
^{40}Ar, 10^{-8} cm³/g	1,270	612	0.48	718	360

Table 5. Volatile elements on Mars.

Element	Earth		Mars		Observed
	Bulk, predicted	Crust, observed	Crust, predicted	Surface, observed	Predicted
^{36}Ar,* 10^{-10} cm³/g	285	210	6	1.6	0.27
^{84}Kr,* 10^{-12} cm³/g	340	430	12.3	5.0	0.41
^{132}Xe,* 10^{-12} cm³/g	217	16	0.45	0.75	1.7
N,* ppb	5,190	830	24	0.62	0.026
H, ppm	43	31	0.89		
C, ppm	571	23	0.66	0.009	0.014
Cl, ppm	25	7.0	0.20		
^{40}Ar,* 10^{-8} cm³/g	1,270	610	360	48	0.13
S, ppm	18,400	1.5	0.88		

*Atmophile.

solve all the NaCl and one-eighth the $MgSO_4$ present. Such a solution has a freezing point of about −13°C and a eutectic temperature presumably less than −20°C, and so the presence of the salts would somewhat extend the stability range for liquid water on Mars. Future life detection experiments on Mars should therefore use nutrient media based on saturated NaCl-$MgSO_4$ brines.

Carbon. It is evident from Table 5 that carbon is more deficient than nitrogen in the martian atmosphere. An obvious sink for the missing carbon is deposition as carbonates, and Baird and co-workers (*67*) have in fact concluded that the dust contains 5 percent $CaCO_3$. A 72-m layer, as inferred above, could thus store 71 g of carbon per square centimeter, or about 25 percent of the predicted crustal abundance of 290 g/cm^2. The combination of a surface dust layer (or perhaps an even deeper regolith) of this composition with one or two large sedimentary basins of the type found at Chryse (*81*) in which the carbonate content could be considerably higher (on Earth, values of 50 percent are common) would effectively hide the missing carbon. Some CO_2 might also be stored in the water ice reservoir as a hydrate (*82*).

Past atmospheric pressure. From the predicted crustal abundances in Table 5, we can calculate a maximum value for the pressure, on the assumption that Mars outgassed to the same degree as Earth, and that the CO_2 was all in the atmosphere. The result is 525 mbar CO_2 plus 8 mbar N_2. But as we argued above, Mars apparently outgassed less than Earth by a factor of ~ 0.27, and so a more realistic estimate would be 140 mbar CO_2 plus 2 mbar N_2. This is more than enough to permit the existence of liquid water. With a reservoir of water equivalent to a 9-m layer of liquid over the surface of the entire planet, we should have the wherewithal for cutting the famous dendritic channels.

Isotopic Data on Noble Gases

Neon. We have no information on isotopic ratios for Mars because $^{20}Ne^+$ is masked by $^{40}Ar^{2+}$ in the mass spectrum (*79*). The detection of ^{22}Ne allows us to determine that $^{22}Ne/^{36}Ar \sim 0.045^{+0.050}_{-0.025}$ on Mars (*69*). This is close to the terrestrial value of 0.05, but somewhat higher than the mean value of 0.023 ± 0.015 in C3V chondrites. There are at least two reasons for this difference.

1) Earth and Mars may have accreted solar wind-irradiated dust, with a characteristically higher $^{20}Ne/^{36}Ar$ ratio [40 (*83*) or 28 ± 9 (*84*)].

2) This may be an expression of a possible difference in composition between the veneer-forming material on the two planets and the C3V chondrites. The planetary $^{22}Ne/^{36}Ar$ ratio in chondrites is a sensitive function of mineralogy and formation temperature (*14, 27*), and actually varies between 0.008 and 0.049 in C3V chondrites alone. We reiterate that we are using these meteorites only as the closest available approximation for the veneer-forming material, not as its actual surviving relics.

One way to decide among these and other alternatives is to evaluate the $^{20}Ne/^{22}Ne$ ratio, which is distinctly different for "solar" and "planetary" neon (12.5 and 8.2). Once isotopic data for martian neon become available, a unique interpretation may emerge. But for the time being, this potentially informative clue remains uninterpreted.

Argon. The isotopic data for Ar and Xe are shown in Table 6. Let us focus our attention on the isotopic ratios in the last two columns. The global $^{40}Ar/^{36}Ar$ ratios predicted by the model are slightly higher than the observed atmospheric ratios, for both Mars and Earth. As we have stressed repeatedly, this is just the trend expected, in view of the later production and deeper origin of the ^{40}Ar.

Krypton. Within experimental error, the isotopes of krypton appear to have the same relative abundances on Mars as on Earth (*79*). In view of the rather limited isotopic variations in meteoritic krypton, however, this consistency between Mars and Earth is neither surprising nor informative. Xenon is a much more useful element in this respect.

Xenon-129 on Mars and Earth

The observed $^{129}Xe/^{132}Xe$ ratio for Mars, 2.5^{+2}_{-1}, is distinctly larger than the primordial ratio of about 1.02 and implies a substantial contribution from the decay of extinct 16.4-million-year ^{129}I (*85*). However, it agrees well with the predicted ratio of 2.96, based on the assumption that the $^{129}I/^{127}I$ ratio in proto-Mars material at the onset of ^{129}Xe retention was 1.46×10^{-4}, the highest value seen in carbonaceous chondrites and hence presumably the initial value for the earliest condensates from the solar nebula (*86*). If the difference between 2.96 and 2.5 is taken at face value despite the large errors, it could mean either that ^{129}I decayed for 6 million years before retention of radiogenic ^{129}Xe began, or that radiogenic ^{129}Xe was less completely outgassed than primordial ^{132}Xe, as for the analogous pair ^{40}Ar and ^{36}Ar. Both alternatives are plausible: chondrites show a ~15-million-year spread in xenon retention ages (*87*), and the release factor of ^{129}Xe is some 25 percent smaller than that of ^{132}Xe, not unlike the somewhat larger difference of 65 percent between ^{40}Ar (whose parent ^{40}K is longer-lived) and ^{36}Ar.

In making this comparison, we have tacitly assumed that the xenon in the martian atmosphere is isotopically similar to the bulk of the planet's xenon, trapped in sediments or in the interior. This is tantamount to assuming that any xenon-rich rocks formed during the first few half-lives of ^{129}I were largely reworked afterwards, so that radiogenic and primordial xenon were homogenized. From the extreme scarcity of rocks older than 4×10^9 years on the moon, a smaller and geologically less active planet, it would seem that this is not a bad assumption.

The $^{129}Xe/^{132}Xe$ ratio for Earth is drastically lower than the predicted value, 0.98 versus 2.96 (Table 6). Actually, the discrepancy is even greater than these ratios suggest, because only 6.7 percent of the ^{129}Xe in Earth's atmosphere is believed to be radiogenic (*88*). For a more realistic picture, we compare the predicted abundance of radiogenic ^{129}Xe, 434×10^{-12} cm^3/g, to the observed atmospheric abundance of 1.04×10^{-12}. Even after correction for xenon trapped in shales or in the interior (using a release factor of 0.072, as for ^{132}Xe), the discrepancy is no less than a factor of 30. And the missing ^{129}Xe is not hidden in Earth's interior, because only a few samples of well gases show so much as a 10 percent enhancement in ^{129}Xe (*89*).

There is little doubt that it is Earth and not Mars which is anomalous in this respect. The C3V and similar chondrites, the assumed source of volatiles for both planets, generally show enhanced $^{129}Xe/^{132}Xe$ ratios around 1.5 or 2, but occasionally reaching up to 6 or greater (*8, 9, 14*). Thus it is the lack of such enhancement in Earth which needs to be explained, not the presence of an enhancement on Mars.

Indeed, the contrast between Earth and the chondrites was noted even in the early days of iodine-xenon dating, and has generally been attributed to a later start of ^{129}Xe retention (*88, 90*), perhaps related to the longer accretion time of planets compared to asteroids. This was a tenable explanation as long as Earth was the only planet for which ^{129}Xe data

Table 6. Isotopic data on argon and xenon.

Planet	^{40}Ar (10^{-8} cm^3/g)	^{36}Ar (10^{-10} cm^3/g)	^{129}Xe$_r$ (10^{-12} cm^3/g)	^{132}Xe (10^{-12} cm^3/g)	$\frac{^{40}\text{Ar}}{^{36}\text{Ar}}$	$\frac{^{129}\text{Xe}}{^{132}\text{Xe}}$
Mars						
Global (model)	720*	8.1	12†	6.2	8900	2.96
Surface (observed)	48	1.6	1.12	0.75	3000	2.5^{+2}_{-1}
Release factor	0.067	0.20	0.093	0.12		
Earth						
Global (model)	1270*	285	434†	217	446	2.96
Surface (observed)	612	210	1.04‡	15.6	296	0.98
Release factor	0.48	0.74	0.0024	0.072		

*Amount produced in 4.55×10^9 years for global K contents of 100 and 170 ppm. †For an initial ^{129}I/^{127}I ratio of 1.46×10^{-4} and global I contents of 0.48 and 17 ppb. ‡See (*88*).

were available. But now that Mars has turned out to have a chondrite-like excess of ^{129}Xe, it appears that accretion time cannot be the only variable.

The chondrites provide an important and perhaps decisive clue. Unmetamorphosed meteorites with hydrous, fine-grained matrices (C1 and C2) contain much of their iodine in labile, even water-soluble form, unaccompanied by ^{129}Xe, whereas metamorphosed meteorites with anhydrous, coarse-grained matrices (C3's and higher petrologic types) generally contain much of their iodine in retentive sites, accompanied by their normal complement of ^{129}Xe (*8, 9, 87, 91*). Perhaps a similar difference in grain size and thermal history of the veneer material is responsible for the difference between Earth and Mars. Let us try to explain the planets in these terms.

Iodine is one of the most volatile elements (Fig. 2) and would therefore be forced to condense on the surfaces of previously formed grains as the solar nebula cools. Suppose these grains are not allowed to accrete into bodies large enough to be metamorphosed. As the ^{129}I decays, the ^{129}Xe$_r$ daughter would not be retained in this surface film but would escape. If such material is swept up by a planet during the final stages of its formation on a time scale of 10^8 years, a veneer will be acquired that has all its volatiles intact except for ^{129}Xe$_r$. This is the process postulated for Earth.

But now consider the alternative situation, in which the grains form bodies that are big enough to experience metamorphism. The primary grains react with each other, atoms diffuse into the interior, and the iodine ends up inside its favorite host minerals. Now the ^{129}Xe$_r$ will be retained as the ^{129}I decays, awaiting subsequent release during accretion by a planet or during later outgassing activity. This is the process postulated for Mars.

We can provide some support for this ad hoc distinction between the two types of veneer material. Collision lifetimes in the Earth zone will be much shorter than in the Mars zone, so many planetesimals will fragment after a brief period of growth before they have been metamorphosed. This effect would tend to be increased if (as we believe) the volatile-rich material came from a region near the outer asteroid belt so the encountering orbits would have been more eccentric near Earth than near Mars. Finally, new observations of Phobos provide what amounts to experimental evidence that volatile-rich bodies did grow large enough for metamorphism in the vicinity of Mars. According to the best current information, this satellite has a mean density that must be less than 2.5 g/cm^3, with a most probable value of 2.0 g/cm^3, a low albedo, and a flat, featureless reflected-light spectrum, all of which suggest that it is much more like a carbonaceous chondrite than a basalt (*92*). In situ chemical analysis of this object would be most interesting.

Could Mars Be Volatile-Rich After All?

We have built an elaborate model on the assumption that thallium and other highly volatile elements are depleted 35-fold on Mars relative to Earth. Let us reexamine this assumption and see whether a less extreme depletion is consistent with the observations.

A firm upper limit comes from the ^{40}Ar/^{36}Ar ratio (Table 6). The predicted global value for this ratio is 8900 (for Tl = 0.14 ppb), compared to the observed value of 3000. If we accept the argument that the release of ^{40}Ar can never be greater than that of ^{36}Ar, in view of its later production and greater depth of origin, then we could raise the abundances of ^{36}Ar and the entire Tl group by up to a factor of 3 but no more. Even a factor of 3 would imply equal outgassing of the two isotopes, in contrast to the manifestly greater outgassing of ^{36}Ar on Earth, and so a factor of 2 might be more realistic.

All other observations can be reconciled with such a two- to threefold increase. The predicted crustal abundances in Table 4 increase in proportion, whereas the relative release factors in Table 5 drop. The amounts of N, H_2O, and C to be lost or hidden would double or triple, but these amounts can still be reconciled with the independent estimates of original N or exchangeable H_2O cited earlier. The predicted ^{129}Xe/^{132}Xe ratio remains the same because I and Xe both belong to the Tl group. The Cl/S ratio, on the other hand, changes by a factor of 2 or 3, and hence no longer fits the observed value. However, this ratio need not be the same in evaporites as in the weathered source rocks because S and Cl may be retained in the residual clays to different degrees, and so a modest discrepancy may not be significant.

Although a two- to threefold increase in volatile abundances can be readily accommodated, a tenfold, let alone 35-fold increase (to terrestrial levels) cannot. Not only is the ^{40}Ar/^{36}Ar ratio wholly inconsistent with such an increase, but the amounts of N, H, and C to be lost or hidden become excessive, and the Cl/S ratio becomes discordant by a factor of 10 or 35.

Loss of an Early Atmosphere?

We next consider the possibility that Mars was initially volatile-rich and extensively outgassed, but then lost its massive early atmosphere in a catastrophic event. The primitive atmosphere that was lost must have included a major fraction of the carbon and nitrogen, but much of the water might have been retained if it was in the form of ice at the time of the catastrophe.

There are two arguments against this model. The first is more aesthetic than substantive: except in Velikovskian cosmogonies, one does not invoke catastrophes to clear up ambiguities unless several independent lines of evidence point to such a solution. We do not yet have any indication from other planetary observations for such an occurrence—for instance, an intense, T-Tauri type solar wind that would have stripped an atmosphere from a planet unprotected by a magnetic field. In fact, Handbury and Williams (*93*) have argued from momentum considerations that it is not possible for a T-Tauri solar wind to dissipate the solar nebula, which makes its ability to strip off a planetary atmosphere even more questionable. Thus, even if the T-Tauri phase is a normal stage in the evolution of solar-type stars, it is not clear that it plays an important role in the present context. The internal evidence is not compelling either, which leads to the second argument. It would appear that any process that removed the atmosphere must have stopped very abruptly to avoid fractionating the martian noble gases from the meteoritic pattern that they presently exhibit. A detailed model of the escape process must be worked out by its advocates to see if this is a more reasonable requirement than it appears.

This model can also be tested by a similar investigation of the atmosphere of Venus, another inner planet with no magnetic field, since the rate of solar wind-induced mass loss from the atmosphere of Venus is larger than that from Mars (*94*). Data on noble-gas abundances are not yet available for Venus, but the fact that the amount of CO_2 presently in the atmosphere of that planet appears to be comparable to or even slightly larger than the amount equivalent to all the terrestrial carbon suggests that Venus has not lost a massive, early atmosphere. The similarity between terrestrial and venusian N_2/CO_2 ratios also supports this conclusion (Table 7).

Evolution of the Atmosphere of Mars

The orientation of this article is to provide a scheme for predicting the total abundances of volatiles; we are not prepared to give a detailed model for how the martian atmosphere passed from an early, dense state to the condition in which we now behold it. But a schematic scenario may be useful in order to demonstrate the plausibility of our argument. The basic notion is that the atmosphere gradually decreased in density as a result of the deposition of carbon dioxide in the form of carbonates and the escape of nitrogen from the upper atmosphere. While the latter process was critical for the ultimate nitrogen abundance and isotope ratio, it should have played a small role in determining the total atmospheric pressure, since carbon dioxide was probably always the most abundant gas. The depositional process (which may have included formation of nitrates or nitrites) was most active during the time when liquid water was most abundant—the cutting of the sinuous channels was thus a premonition of the end of the dense atmosphere. The apparent absence of an active martian biota (*95*) has prevented the recycling of volatiles through biological processes. Moreover, there is evidence that carbonates may form even under the present arid conditions on Mars (*96*).

Table 7. Atmospheres of Earth and Venus.

Component	Earth		Venus now (*119*)
	Now	Total*	
N_2, percent	78	1.5	1.8
O_2, percent	21	Trace	Trace
Ar, ppm	9000	190	200
CO_2, percent	0.03	98	98
H_2O, km	3	3	Trace
Pressure, bars	1	70 †	88 ± 3

*No carbonates, no life. †For a crustal carbon abundance of 9×10^{22} g (*120*).

There may have been climatological cycles similar to those suggested by Ward (*97*) and Sagan *et al.* (*98*) during this early period, but we have to admit that the details of atmospheric processes remain obscure. For example, it is not obvious how the necessary warming of the planet was achieved. It is not enough to have a high surface pressure in order to get the water running; one must also increase the average temperature. It may be that carbon dioxide and water vapor worked symbiotically to produce an enhanced greenhouse effect. It may also be that the major water activity occurred at a time when the atmosphere was much more reducing than it is now, and ammonia rather than nitrogen was present to add its particularly appropriate infrared absorptivity to the planetary greenhouse (*99*). These ideas and others can be tested by atmospheric models, a task we leave for others to pursue.

Venus

Being approximately the same size as Earth, Venus may be expected to have had a similar accretion and outgassing history. Its bulk composition may well be different from Earth's, however, since it formed closer to the sun. But in our model the resulting fractionation (relative to Earth) should not have affected the most volatile elements—including the noble gases—because we expect them to be delivered in a late-accreting veneer. Hence the noble gases should again be present in planetary (that is, chondritic) proportions (Fig. 1), a conclusion already reached by Turekian and Clark (*18*).

The high surface temperature of Venus and the large atmospheric CO_2 abundance both imply thorough degassing of the postulated veneer. At a mean temperature of 747° ± 50°K (*100*), the planet's surface is hot enough to maintain the observed amount of CO_2 in the atmosphere by the Urey equilibrium (*73, 101*) between silica and carbonates

$$CaCo_3(s) + SiO_2(s) \rightleftarrows CaSiO_3(s) + CO_2(g)$$

The bulk of the water contributed by the veneer was removed by the "runaway greenhouse" effect (*102*). In fact the ratio of the mass of CO_2 in the atmosphere of Venus to the mass of the planet is very similar to the same ratio for Earth, when the total terrestrial CO_2 inventory is assessed (1×10^{-4} versus 0.7×10^{-4} g/g). This coincidence not only supports the idea of thorough outgassing, it suggests that the materials that formed the surface layers of both planets were actually quite similar in their total mass and volatile content. We would therefore predict a ratio for $CO_2 : N_2 : {}^{36}Ar$ in the atmosphere of Venus that is very close to that observed in the full volatile inventory on Earth. The results from the Venera 10 probe support this view [Table 7; the values are in excellent agreement with the predictions of Turekian and Clark (*18*)], but we must await a more detailed analysis that includes the abundances of the primordial isotopes of argon and the other noble gases before we will have a rigorous test. These constituents should also be present in absolute amounts similar to those on Earth, not 100 times depleted as on Mars. No gross depletion of Xe from the meteoritic value is anticipated on Venus in the absence of sedimentary processes (and the presence of a high mean temperature on the surface of the planet).

But we anticipate that the volatile abundances will not be identical with any of the other data sets presently available. Our model only predicts a veneer that has a composition similar to that of the C3V chondrites; in fact this veneer must have been a mixture of constituents that differed slightly in composition from planet to planet. It may even have included mineral assemblages that are not currently represented among meteorites falling on Earth.

Venus may provide several tests of the mechanisms we invoked to explain the differences between Mars and Earth. We attributed the postulated depletion of volatiles on Mars to the planet's smaller size. Thus Venus should contain nearly the same mass fraction of volatiles as does Earth. We suggested that the deficiency of ${}^{129}Xe_r$ on Earth could be explained by the smaller size and gentler thermal history of the volatile-bearing bodies. If our moon played a critical role in keeping the size small, then Venus should show a martian equivalent of $^{129}Xe_r/^{132}Xe$. But if this was a general property of the formation of veneers on large inner planets, Venus should again resemble Earth. We have hypothesized that the higher value of $^{20}Ne/^{36}Ar$ on Earth and Mars compared with the C3V chondrites could reflect the infall of solar wind-irradiated interplanetary dust on these planets, a process that should also increase the ratio $^{20}Ne/^{22}Ne$. Since Venus is still closer to the sun, the infall should be greater, hence both ratios may be even higher than they are on Earth.

We shall soon know the answers to these and other questions, since a full-scale in situ exploration of the atmosphere of Venus is planned as part of a 1978 National Aeronautics and Space Administration mission (*103*).

Why Are Small Planets Volatile-Poor?

Whether or not we accept the exact numbers in Tables 3 and 7, the general trend is clear: three small differentiated planets in the inner solar system, from Mars on down, are poorer in volatiles than are the two large planets, Earth and Venus. Heliocentric distance certainly is not the relevant variable: on the contrary, the two planets closest to the sun are richest in volatiles. This tends to speak against the condensation model of Lewis (*34*), which predicts a simple correlation of volatile content with heliocentric distance. Apparently a model relying on local nebular temperature as the sole variable cannot account for the observed compositions. Additional fractionation processes seem to be needed, such as those inferred for meteorites (*20, 21*), and particularly a mechanism for the depletion of volatiles in some, but not all, small planets. [Shergottites, a differentiated meteorite class resembling eucrites but of distinctive oxygen isotope composition (*65*), are much less depleted in volatiles (*104*). Their parent body, although only of asteroidal size, seems to have had a more Earth-like abundance of volatiles (*104*).]

Lower influx. The most obvious such mechanism is the larger gravitational capture cross section of larger bodies (*105*), which would enable them to collect a greater share of late-accreting, volatile-rich material (*33*). However, this mechanism is quantitatively inadequate to explain the difference between Earth and the moon (*106, 107*).

For the moon, there exists an additional mechanism that can account for the difference: the aerodynamic wind created by its motion in a satellite orbit (*108*). But this mechanism is obviously unavailable for the other bodies in Table 3. In principle, one could invoke lower fluxes of volatile-rich material for the more distant bodies, but the available data suggest that the difference in fluxes was not large enough. Models of the solar nebula (*109*) predict only a small decrease in surface density between Earth and Mars, and crater counts on Mars, the moon, and Mercury (*110*) as well as dynamical calculations (*111*) suggest that the flux of crater-forming objects in the very last stages of accretion was roughly constant between 0.38 and 1.52 astronomical units.

Volatile loss on impact. Small bodies have small escape velocities, and so one might expect them to lose volatiles on impact. However, data on lunar and meteoritic regoliths suggest that this effect is not important for bodies as large as the moon or even the eucrite parent body. Lunar soils quantitatively trap many volatiles from bombarding micrometeorites (for example, Bi, Br, Ge, In, and Pb) except for noble gases, light elements such as C and N, and a few heavier elements such as S and Se that form hydrides with solar-wind hydrogen (*106, 112*). Lunar highland breccias, reflecting an earlier bombardment by larger bodies, show the same trend (*113*), and so does the gas-rich howardite Kapoeta, which is believed to come from the regolith of the eucrite parent body (*104*). Because Mars has a higher escape velocity as well as an atmosphere, it is likely to retain even the gaseous elements lost from the moon and the eucrite parent body.

Dissipation of the solar nebula. The solar nebula was dissipated somehow [although probably not by the T-Tauri solar wind (*93*)], and one may wonder if the atmospheres of small planets were not swept away at the same time. However, if this mechanism is to deplete not only atmophiles such as H, C, N, and noble gases but also metals such as Pb, Bi, Tl, and the halogens (Fig. 3), then several unlikely conditions must be met. The crust of the planet must be hot enough to vaporize these elements, it must be permeable enough to allow their complete escape to the surface, and the atmosphere must be hot enough to prevent them from recondensing (~1000°K).

Thus we are left without an adequate explanation for the depletion of volatiles on small bodies. On a purely qualitative level, the trend can be explained by a quasi-circular argument: small bodies are small because they grew more slowly than the large ones; the difference should have been greatest in the final stages, when the volatiles accreted; hence the small bodies contain a smaller share of volatiles. But the actual mechanism still eludes us, and the mystery is deepened by the fact that not all small bodies are so depleted. The parent bodies of chondrites (Tables 1 and 3) and shergottites (*104*) are not much poorer in volatiles than is Earth.

Summary

Mars, like Earth, may have received its volatiles in the final stages of accretion, as a veneer of volatile-rich material similar to C3V carbonaceous chondrites. The high $^{40}Ar/^{36}Ar$ ratio and low ^{36}Ar abundance on Mars, compared to data for other differentiated planets, suggest that Mars is depleted in volatiles relative to Earth—by a factor of 1.7 for K and 14 other moderately volatile elements and by a factor of 35 for ^{36}Ar and 15 other highly volatile elements.

Using these two scaling factors, we have predicted martian abundances of 31 elements from terrestrial abundances. Comparison with the observed ^{36}Ar abundance suggests that outgassing on Mars has been about four times less complete than on Earth. Various predictions of the model can be checked against observation. The initial abundance of N, prior to escape, was about ten times the present value of 0.62 ppb, in good agreement with an independent estimate based on the observed enhancement in the martian $^{15}N/^{14}N$ ratio (*78, 79*). The initial water content corresponds to a 9-m layer, close to the value of ≥13 m inferred from the lack of an $^{18}O/^{16}O$ fractionation (*75*). The predicted crustal Cl/S ratio of 0.23 agrees exactly with the value measured for martian dust (*67*); we estimate the thickness of this dust layer to be about 70 m. The predicted surface abundance of carbon, 290 g/cm^2, is 70 times greater than the atmospheric CO_2 value, but the $CaCO_3$ content inferred for martian dust (*67*) could account for at least one-quarter of the predicted value. The past atmospheric pressure, prior to formation of carbonates, could have been as high as 140 mbar, and possibly even 500 mbar. Finally, the predicted $^{129}Xe/^{132}Xe$ ratio of 2.96 agrees fairly well with the observed value of 2.5^{+2}_{-1} (*85*).

From the limited data available thus far, a curious dichotomy seems to be emerging among differentiated planets in the inner solar system. Two large planets (Earth and Venus) are fairly rich in volatiles, whereas three small planets (Mars, the moon, and the eucrite parent body—

presumably the asteroid 4 Vesta) are poorer in volatiles by at least an order of magnitude. None of the obvious mechanisms seems capable of explaining this trend, and so we can only speculate that the same mechanism that stunted the growth of the smaller bodies prevented them from collecting their share of volatiles. But why then did the parent bodies of the chondrites and shergottites fare so much better?

One of the driving forces behind the exploration of the solar system has always been the realization that these studies can provide essential clues to the intricate network of puzzles associated with the origin of life and its prevalence in the universe. In our own immediate neighborhood, Mars has always seemed to be the planet most likely to harbor extraterrestrial life, so the environment we have found in the vicinity of the two Viking landers is rather disappointing in this context. But the perspective we have gained through the present investigation suggests that this is not a necessary condition for planets at the distance of Mars from a solar-type central star. In other words, if it turns out that Mars is completely devoid of life, this does not mean that the zones around stars in which habitable planets can exist are much narrower than has been thought (*114*). Suppose Mars had been a larger planet—the size of Earth or Venus—and therefore had accumulated a thicker veneer and had also developed global tectonic activity on the scale exhibited by Earth. A much larger volatile reservoir would now be available, there would be repeated opportunities for tapping that reservoir, and the increased gravitational field would limit escape from the upper atmosphere. Such a planet could have produced and maintained a much thicker atmosphere, which should have permitted at least an intermittently clement climate to exist. How different would such a planet be from the present Mars? Could a stable, warm climate be maintained? It seems conceivable that an increase in the size of Mars might have compensated for its greater distance from the sun and that the life zone around our star would have been enlarged accordingly.

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