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HOW WELL DO WE KNOW THE MARTIAN ABUNDANCES OF HIGHLY VOLATILE ELEMENTS ?

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Some popular models of planetary formation predict that among the terrestrial planets, Mars should contain the highest concentrations of the highly volatile, or atmophile elements. All Martian volatile abundance data are not consistent with these models, however. If SNC meteorite data are representative of Mars as a planet, they suggest that readily volatilized elements such as K, Pb, halogens, etc. are enriched on Mars over Earth by approximately a factor of two (1,2). Geomorphology of the Martian surface suggests abundant liquid water in the ancient past. On the other hand, the concentrations of noble gases, nitrogen, and carbon (as CO_2) in the Martian atmosphere per unit mass of the planet are orders of magnitude less than those of other solar system objects, including the total Earth and chondrite parent bodies (Fig. 1), which bracket Mars in heliocentric distance. The fact that the ^{40}Ar/^{36}Ar isotopic ratio on Mars is an order-of-magnitude larger than that of Earth indicates that at least part of the lower noble gas concentration of Mars is due to a smaller, original endowment of noble gases, and not just due to a lesser degree of planetary degassing into its atmosphere. But what about N, C, and H_2O? It has been suggested that large quantities of carbonates and water-ices or hydrated minerals exist in the upper Martian crust as a result of the present cold temperatures and extensive weathering of rocks over geological time (e.g. 3). It has been proposed that the unusually large ^{15}N/^{14}N isotopic ratio on Mars was caused by fractionation during massive atmospheric loss of atomic N over geologic history from an initial N abundance 10 to 20 times greater than that presently (4). These models suggest that Mars contains (or once contained) significant inventories of C, N, and H_2O.

All reservoirs of the highly volatile elements presumably were derived from the solar composition by various processes, which may have fractionated elements according to mass, ionization potential, adsorption properties, or other factors. Among the Earth, Mars's atmosphere, and carbonaceous and ordinary chondrites, the Ne/Ar and Kr/Ar elemental ratios each differ by less than a factor of three, but differ from solar values by a factor of ~100. Likewise, the C/N and H_2O/N ratios are each similar for the Earth and C1 chondrites. In contrast, Fig. 2 shows that the C/Ar and N/Ar ratios vary by a factor of ~10^6 between the sun and carbonaceous meteorites, with Mars, Earth, and other objects showing intermediate ratios which lie approximately along a linear correlation. Three values of N/Ar shown for Mars correspond to the measured atmospheric ratio (left datum), and the lower and upper ratios (middle and right data) for the original volatile inventory with the assumption that massive N loss occurred to produce today's ^{15}N/^{14}N. Unless the volatile component in Mars underwent a fundamentally different element fractionation process than those components in Venus, Earth, and chondrites, or unless the Martian degassing of N and ^{36}Ar were somehow decoupled (both unlikely), early Mars should lie near the trend defined by Fig.2. If Mars has lost significant amounts of atmospheric N, Fig.2 suggests that it contains a C/^{36}Ar ratio between those of the Earth and C1 chondrites. Because the Earth and C1 chondrites have nearly identical H_2O/C ratios of ~4, the Martian H_2O/C ratio is also expected to lie between those of the Earth and C1 chondrites.

The table below summarizes four models based on the above observations and gives some reasonable inferences of each for Martian volatiles. The table columns give 1) the volatile assumptions of the model, 2) the inferred Martian volatile concentrations relative to Earth, 3) the N/^{36}Ar and C/^{36}Ar ratios, 4) the percentage of Martian degassing inferred by the model, and 5&6) the equivalent global column heights of liquid water and solid $CaCO_3$ over the entire surface of Mars that would be formed from the model quantities of degassed volatiles. The Sub-Earth model (#1) is extreme and can probably be excluded because of the very low quantities of degassed H_2O it predicts and because it leaves no explanation for the high ^{15}N/^{14}N. Models 2 and 3 predict a Mars that has considerably lower concentrations of atmophile elements than the Earth (e.g. Fig.1). These two models differ in their C/^{36}Ar and N/^{36}Ar ratios, and by a factor of 20 in concentrations of N,C, &H_2O. The amount of liquid water predicted on the surface of Mars by models 2 and 3 (11 and 50 meters) might be marginally large enough to produce the observed geomorphological features ascribed to water, but requires 100% planetary degassing. The SNC model (#4) has several advantages: 1) It is consistent with those planetary formation models that predict Mars to be a more volatile-rich planet than the Earth (at least in N,C,H_2O,K, etc., if not noble gases); 2) only a small fraction of the Martian volatiles have degassed into its atmosphere, consistent with the lower tectonic and volcanic activity of Mars compared to Earth; 3) the 50 meters of degassed liquid water is probably enough to produced observed features, yet small enough to be incorporated into crustal rocks; the 5 m of $CaCO_3$ could be mixed to relatively low concentrations into a deep regolith; 4) the fractional degassing of radiogenic ^{40}Ar (3%) is not larger than the fractional degassing of inherited gases (4%); 5) no special degassing of noble gases from pre-Mars planetesimals is required to explain the low abundances of noble gases in the present Martian atmosphere; this low abundance is explained as due to a difference in the ratio of noble gases to N,C,H_2O, i.e., more like C1 meteorites than like the Earth. Models #3 and #4 are based on the highest observed solar system ratios of $H_2O/^{36}Ar$ and $C/^{36}Ar$, yet each predict that no more than about 50 meters of liquid water ever existed at the surface of Mars. Model #4 predicts that Mars is enriched over Earth in volatile elements (except noble gases), whereas the other models require that Mars is depleted in all atmophile elements. If C,N, and H_2O were fractionated from noble gases during accretion of Mars, then a hybrid of models 3 and 4 is permitted. Unless H_2O was further fractionated from N, however, the layer of degassed liquid water at the surface would still be limited to about 50m.

These models predict a range of possible volatile contents and elemental ratios for Mars, and good estimates of the C,N, and H_2O contents of the Martian crust and regolith may be necessary to choose among them. These considerations emphasize the importance of collecting 1) subsurface samples which may contain these volatiles in weathered silicates, 2) shock-lithified regolith breccias near old craters which may preserve early volatiles characteristic of either the atmosphere or the regolith, and 3) young volcanic rocks which may indicate the concentrations of C, N, and K in the Martian interior. Recent studies (5) suggest that impact into porous material may have been an efficient mechanism of implanting ancient Martian gases into regolith breccias, and such breccias might contain evidence of compositional differences in past atmospheres.

(1) G. Dreibus & H. Wanke, Meteoritics 20, p367-382, 1985. (2) J. Chen & G. Wasserburg, G.C.A. 50, p955-968, 1986. (3) F. Fanale, Icarus 28, p179-202, 1976. (4) M. McElroy & M. Prather, Nature 293, p535-539, 1981. (5) D. Bogard, F. Horz, & P. Johnson, J.G.R. 91, No.B12, pE99-E114, 1986.

MODEL ASSUMPTIONS FOR MARS VOLATILES	VOLATILE CONC.	N,$C/^{36}Ar$ RATIOS	DEGASSING ASSUMED	PLANET-TOTAL H_2O	PLANET-TOTAL $CaCO_3$
1. Sub-Earth	<< Earth	< Earth	100%	0.6m	0.05m
Obs.[N] "Real"; ($^{15}N/^{14}N$ Not Due to N Loss)					
2. Volatile-Poor, Earth-Like	<< Earth	= Earth	100%	11m	1m
[N]= 1.8X Lower Calc.					
3. Intermediate	< Earth	=C1 Chon	100%	50m	5m
[N]= Higher Calc.			(^{40}Ar=6%)		
4. SNC-Like	[N,C,H_2O,K] =2X Earth	=C1 Chon	4%	1250m	125m
	[^{36}Ar] =17% of Earth		(^{40}Ar=3%)	(50m)*	(5m)*

(The two water & $CaCO_3$ values for Model #4 give total planet & surface inventory (in parenthesis)).

Figure 1 (below left). Concentrations (per gram of object) of several volatile elements or isotopes for the Martian atmosphere, C1 carbonaceous chondrites, and the total Earth inventory. Figure 2 (below right). Log plot of the element ratios $C/^{36}Ar$ and $N/^{36}Ar$ for the Sun, lunar regolith, Venus, Earth, Mars, C1 carbonaceous chondrites, and C3V chondrites. The three values for Mars represent (from left to right) the observed atmosphere and the lower and upper limits to the initial planetary inventory, calculated assuming that massive nitrogen loss caused the observed increase in $^{15}N/^{14}N$ (4).