N89 - 10786

156600

COMETS, VOLCANISM, THE SALT RICH REGOLITH AND CYCLING OF VOLATILES ON MARS; Benton C. Clark, Planetary Sciences Laboratory, Martin Marietta Denver Aerospace, Denver, CO 80201.

Many independent estimates of the total volatile inventory in the surface and near-surface of Mars have been made based upon noble gas measurements and analogies with terrestrial and/or meteorite data. As compiled in Table I, volatile inventory models range from 1100 to over 24,000 g/cm^2 for the elements C, H, O, and N (the "CHON" group). Of this, H_2O is estimated variously to comprise 46% to 80% of the total. The spread in the CO_2 component is much larger, from 5% to 53%, while N is consistently estimated at less than 1% of the total for the CHON group. The predictions for the ratio C/N (weight/weight) vary from 4 to 28. Two other elements, S and Cl, are often found at significant concentration in volcanic and fumarolic gases. Inventory predictions for these two elements are less common, but as discussed below, they may drastically alter the fate of molecules incorporating the CHON elements.

Table I. Volatile Inventories

	A	B	C	D	E	F	G
Total CHON (g/cm^2)	16-27	300 to 30,000	1108	2021	9423	18,058	24,000
H_2O	0.02%	0.5-10%	53%	47%	80-94%	74%	66-86%
CO_2	96%	0-10%	46%	52%	5-11%	26%	13-33%
N	2.6%	0-10%	0.7%	0.5%	0.2%	0.3%	1%
Reference	Atmos.	Regolith	1 RHK	2 A & O	3 C & B	4 MKY	5 P & B
C/N ratio	10	-	18	28	7-15	24	4-9

<u>The role of comets</u>. From remote observations, it has been known for some time that comets contain abundant H_2O as well as organic compounds and N-containing molecules, particularly HCN. The total predicted volatile inventories for Mars could be produced by the impact with only 10^4 to 10^5 comets, following the primary accretion of the planet.

During the recent flyby of Comet Halley, a variety of organic molecules in the gas phase were apparently detected, although the CO_2/H_2O ratio inferred for the ices was less than 0.035 [6]. Particle composition analysis discovered grains with C and S, as well as grains with CHON composition [7]. If cometary material is of the same overall average composition (including both ices and dust grains) as the sun, the ratios will be C/N=4 and S/Cl=102. Further analysis of the Giotto and Vega measurements may permit reasonably accurate estimates of these ratios, irrespective of the complexity of the distribution of these elements among various chemical phases. The results published so far are not inconsistent with these predictions.

As listed in Table I, the current Mars atmospheric ratio for C/N is

10. Allowing for a relatively large loss in N due to exospheric escape [4], the starting ratio could have been as low as 2. On the other hand, virtually all authors predict large amounts of "missing" CO_2, which apparently is stored in the regolith. Such storage, either as carbonate minerals or as cryo-adsorbed gas, is much easier than with N because of the greater problem of formation of the nitrates and the lower partial pressure and adsorption energy of N_2 gas from the atmosphere. Whether the C/N ratio can be used as a discriminator for or against a major contribution by cometary material to the volatile inventory on Mars must await more definitive results on the chemical composition of cometary nuclei and accurate information on the C and N-bearing molecular components in the martian soil.

Use of H or O in constructing discriminating atomic ratios is almost certainly more difficult because of the distribution of O among many chemical phases, the incorporation of H_2O and OH into the regolith, and the uncertain magnitude of the losses of H by escape during the history of the planet.

More useful should be the S/Cl ratio, which on earth is only 0.3, but is 4 in the martian soil [8], still some 25 times lower than predicted for comets on the basis of solar and chondritic meteorite abundances. Clearly, only if comets are found to be anomously halogen-rich can they be the major source of these volatile elements, and presumably the others as well, on Mars. Their effect, however, could be to raise the S/Cl ratio if planetary outgassing mimics the terrestrial proportion; about a 3-4% contribution to the volatile inventory would be sufficient. An equivalent cometary contribution to the 30x higher inventory on earth would be undetectable.

The salt-rich regolith. At both Viking lander sites, the fines contain abundant S and Cl, almost certainly as sulfate and chloride salts, respectively. Based upon spectroscopic limits for active gases in the atmosphere, more than 99.999% of the S and Cl inventories reside in the regolith of Mars.

Likewise, all estimates of volatiles place the majority of the CHON materials in the regolith fines, since the atmosphere and polar cap reservoirs are demonstrably too small. Neither the Viking XRFS nor the GCMS instruments were capable of detecting carbonates or nitrates, although it was often suggested during development of the latter that soil acidification be added to the experiment. Remote-mapping infrared spectroscopy has placed some upper limits on these minerals, but unambiguous and quantitative detection by this means probably must await the Mars Observer mission. Thermal adsorption processes could be the primary mechanism for uptake of the C and N gases; quantitative predictions are extremely model dependent because of the wide range in properties of the silicate minerals which may or may not be present.

Whichever salts are present, they are sure to be hygroscopic when the temperature and H_2O partial pressure are appropriate. Modeling of climatic cycling of water through the regolith has generally avoided this consideration because the rates of the hydration reactions at low temperatures are presumably not well knwon. In addition, the ubiquitous duricrust can, in principle, form a relatively impermeable barrier by virtue of salt-filling of pore spaces, although the Viking duricrusts are surprisingly friable. Of special interest in this connection is the recent deduction that the duricrust in the vicinity of the Viking sites is unusually "thin" with respect to the other widespread occurrences on Mars [9].

The roles of volcanism. The worldwide eruptive emissions of volcanoes combine to add gases to earth's atmosphere at an average S/Cl ratio of about 5-to-1 [10], a value quite close to the observed ratio in soil on Mars, as previously noted [8]. Furthermore, these gases are chemically very active; even in the cold, dry environment of Mars it has been shown that SO_2, for example, rapidly and quantitatively destroys carbonates and nitrates [11]. Thus, with every volcanic eruption, these minerals will be forced to release C and N (in gases) to the atmosphere. Additional carbonates and nitrates may form, via very slow reactions under contemporary conditions [12], with unreacted igneous minerals in the soil. Even at one-tenth the terrestrial rate [10], some 660 g/cm^2 of SO_2 would be released over geologic time, adequate to recycle much or all of the CO_2 at least once.

Volcanic activity can also serve to irreversibly remove volatiles by sealing over regolith deposits with lava flows. Although some volatiles may be thermally released at the contact zones, this will be small compared to the amounts buried. Without tectonic subduction or aqueous errosion processes, it is unlikely these volatiles can ever be recycled to the atmosphere. Impact blanketing can similarly bury volatile-rich sediments.

Note on returned sample handling strategies. Most sample return studies have focused on the rocks of Mars. The enormously pivotal question of the history of the climate hinges upon the fine-grained component of the regolith. For it is here that the chemically and physically trapped volatiles will be found. Perturbations of the sample during the sampling process will be much more likely than with the taking of rock. Relatively small deviations from the ambiant temperature and vapor conditions could destroy key mineral phases and cause the loss of adsorbed volatile species. On-site studies, such as of thermally-induced gas release, combined with experiments on earth, such as measurement of adsorption isotherms and their hysteresis characteristics, may help resolve such problems. Nonetheless, the preservation of the physico-chemical state of regolith cores should receive the highest priority.

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