CHEMICAL EVOLUTION OF THE EARLY MARTIAN HYDROSPHERE; M. W. Schaefer, University of Maryland and Goddard Space Flight Center, Greenbelt, MD

Mars today is a cold, dry planet, with a thin atmosphere, largely consisting of carbon dioxide. It may not always have been that way, however. Values of total outgassed CO_2 from several to about 10 bars are consistent with present knowledge (18), and this amount of CO_2 implies an amount of water outgassed at least equal to an equivalent depth of 500 to 1000 meters (3). Pollack et al. (18) have made extensive calculations deriving the amount of carbon dioxide necessary to achieve a strong enough greenhouse effect to raise the surface temperature of Mars above the freezing point of water, and have determined that, for different values of surface albedo, latitude, and orbital position, pressures of from 0.75 to 5 bars are necessary. The geological evidence suggests that any such warm, wet period in Mars' history must have been over by about 3.5 billion years ago.

One may model the early Martian ocean as a body of relatively pure water in equilibrium with a dense (several bars) carbon dioxide atmosphere. The juvenile water outgassed by Mars should have been extremely acidic, based on Earth analogy. In such waters all common components of ordinary rocks are highly soluble, with the exception of SiO_2 and Al_2O_3 (10). The chemical weathering of lavas, pyroclastic deposits, and impact melt sheets would have the effect of neutralizing the acidity of the juvenile water. Equilibrium would be achieved when the weathering rate of the rocks was equal to the dissolution rate of the carbon dioxide in the atmosphere (which dissolution would itself require the water to be quite acidic, with a pH no greater than about 5). There was also an extensive groundwater system at this time (2), which acted to weather even those parts of the regolith far distant from the ocean. On the Earth, about 30% (9) of the outgassed water is thought to be geochemically bound in the crust. One might take this figure as an upper limit to how much of the Martian water budget might have become bound in its regolith during the relatively restricted time available for such processes to occur (no more than about 1 billion years, compared to the 4.5 billion years available on the Earth). Assuming then a total value for outgassed water on Mars of 500 - 1000 m, averaged over the entire planet, and only a few meters of that lost to space through thermal escape (12), at the time when enough carbon dioxide was lost from the atmosphere such that temperatures dropped below the freezing point of water on Mars, there should have been at least 350 - 700 m of water still free and unbound. The formation of the highland-lowland dichotomy is believed to have taken place by the time of the decline of the heavy meteorite bombardment (7), thus providing a natural basin into which this water could collect. The lowland terrain takes up roughly 30% (± 5%) of the surface of Mars; therefore, if the available water was concentrated in the lowland terrain, it would have a depth of some 1000 - 2800 m. This depth is comparable to the height of the boundary scarp between the highland and lowland terrains, similarly (though probably coincidentally) to the way in which water on the Earth is largely contained by the continents to within the lowlands formed by the oceanic crust. There may be geological evidence for such an ocean on Mars (3, 13, 11, 15-17).

As calcium and other cations are added to the water by chemical weathering, they are quickly removed by the precipitation of calcium carbonate and other minerals, forming a deposit of limestone beneath the surface of the ocean. Even in the deepest parts of this ocean, pressure effects will not be enough to prevent the precipitation of carbonates, unlike the present situation on the Earth, where carbonate deposits only form in relatively shallow water. By this process, carbon dioxide is removed from the atmosphere. The time scale on which this occurs can be as little as 10^7 years (3, 6, 18), assuming no reworking of deposited carbonates, or when such reworking is postulated, a time scale of up to about a billion years is reasonable (18). As the carbon dioxide is removed from the atmosphere, the heat trapped due to the greenhouse effect becomes unimportant, the planet's surface cools to below the freezing point of water, and the surface of the ocean freezes. When the surface of the ocean freezes, the removal rate of carbon dioxide from the atmosphere is decreased, due to the decreased rate of regolith weathering caused by the lesser mobility of water through the atmosphere-regolith system, but it is not halted. The ice layer will act to trap beneath it an artificially high concentration of dissolved carbon-bearing species, brought in by the percolation of groundwater. The freezing of the water will have the additional effect of further increasing the cation concentration in the remaining liquid, due to the exclusion of cations from the crystal structure of the ice. This behavior is observed in frozen lakes in the terrestrial Arctic (8) and Antarctic (14), and there results in the precipitation of carbonates on the lake beds.

As the atmospheric carbon dioxide pressure and the temperature continue to decrease, there should come a time when the Martian ocean is almost completely frozen, perhaps overlying a layer of salts or concentrated brines above the carbonate layer. Due to the high expected ratio of calcium (or other cation) concentration relative to HCO_3^- concentration in the water, calcium carbonates are preferentially deposited, and the remaining fluid gradually evolves to form a Ca-Na sulfate-chloride brine (5). If the entire Martian CO_2 budget of, say 1 - 10 bars, were to be used to form this carbonate deposit, it would imply an average thickness for the deposit of 100 to 1000 meters.

Once the ocean is completely frozen, the sublimation and ablation of ice from the uppermost surface of the ocean is no longer compensated for by the freezing of the water below; the ice itself gradually disappears, starting at the warmest areas near the highland-lowland boundary, migrating into the regolith and leaving only a residual cap at the north pole. Or it could be that the ocean would be so reduced in volume by the time it froze completely that it would be not significantly larger than the present polar cap. Also at this time, carbon dioxide from the atmosphere may be adsorbed onto the cold regolith. Eventually, through the action of freezing and the removal of water from the atmosphere-regolith system by irreversible geochemical weathering, the entire water budget of Mars will be tied up in its present reservoirs in the polar caps and regolith.

Given the preceding scenario for the geochemical evolution of the northern lowland plains of Mars, it should be possible to draw a few conclusions about the expected mineralogy and geomorphology of this region. The basement material should be a highly-altered regolith, though it is impossible to say with any certainty whether the original material was mostly basalt flows, ash deposits, or some other volcanic product. One would expect, however, that it should have been highly brecciated by the early, heavy meteorite bombardment of the planet. It should contain a significant proportion of clays and other hydrous minerals. Overlying this basement, and covering most of the northern plains, are carbonate deposits, several hundred meters thick or more. Likely to be primarily calcium carbonate, these deposits would be progressively more sulfate- and salt-rich in their upper layers. The topmost layers of these deposits would be primarily gypsum ($CaSO_4 \cdot 2H_2O$) or mirabilite ($Na_2SO_4 \cdot 10H_2O$), and assorted salts (5). Continued meteoritic impacts, and dust storms, have acted to mix these sedimentary materials with the volcanic materials common over most of the rest of the planet, to form a surficial mantling of dust of uniform composition. Viking chemical analyses indicate that the surficial deposits in Chryse Planitia and Utopia Planitia may contain as much as 8 - 15% sulfates, and up to 10% carbonates (4), consistent with such a volumetric mixing model. It has also been suggested by several researchers that brines may be at least metastable at present in the regolith of Mars (1), particularly in the region of Solis Lacus, where anomalous radar reflectivity has been observed (19,20).

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GLOBAL RELATIONSHIPS BETWEEN VOLCANIC VENTS AND FRACTURES RADIAL TO LARGE IMPACT BASINS ON MARS.

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The relation of volcanic vents on Mars to impact basins has been studied previously (1,2,3,4,5,6). It has been asserted that the concentric fractures around impact basins extend into the crust and might localize some features, including volcanoes (e.g. 4). In this study, we assess the possibility of radial fractures inferred to be associated with impact basins as an additional control on the location of volcanoes on Mars. Geologic mapping at 1:2 million scale enabled 250 central vents and fissure vents to be identified. Patterns of vent distribution (fig. 1) superimposed on a globe show that most are located on three distinct circles. The first is a great circle which passes through Arsia Mons, Pavonus Mons , Ascreaus Mons, and Tempe Fossae, along Protonilus Mensae (an area of fractured terrain), through Syrtis Major, Hadriaca Patera, and a series of fissure vents southwest of Tharsis. A similar great circle trends SW to NE from the Hellas basin, through Hadriaca Patera, Tyrhenna Patera, Elysium, Alba Patera (which is approximately antipodal to the Hellas basin), southern Tempe Fossae, the eastern Valles Marineris chaotic region, and the Amphitrites Patera vents on the southwest rim of the Hellas basin. The third series of vents is on a small circle ~4800 km in diameter centered at ~ 104°W, 2°N. This site is near the center of the Tharsis gravity anomaly (7) and the loci of associated tensile stresses (8). Most fissure vents not located on the Tharsis trend of volcanics are on this small circle, as are Alba Patera and other central vents.

There are two more possible great circles which may be superimposed onto the martian globe. The first can be traced along the escarpment dividing the northern lowlands from the southern highlands, across Isidis Planitia (the site of a possible impact basin at ~ 273°W, 13°N), fractured terrain in Solus Planum (a possible fissure vent source area), and through Juventae Chasma. This circle may reflect the role of inferred radial fractures in modifying the surface without associated volcanism. The second possible great circle passes through the Hellas impact basin, some large unnamed central vent volcanoes (at ~ 205°W, 48°S) , Apollonaris Patera, the escarpment north of Alba Patera and the Tempe Fossae region, and into Acidalia Planitia. Acidalia Planitia is also along the trend of the Tharsis chain of volcanoes and may indicate an impact site centered near 30°W, 60°N.

Although concentric fractures of smaller impact basins may influence local vent sites, the global setting appears to be governed by radial fractures associated with major impact basins. This is supported by the association of one or perhaps two great circles with the Hellas impact basin, and possible great circles associated with the Isidis basin and Acidalia Planitia. The distribution also suggests that larger impacts produce larger fractures and can, therefore, accommodate more

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volcanic vents. Isidis, Argyre, Procellarum, and Hellas basins in that order, have an increasing number of vents inferred to be associated with them.

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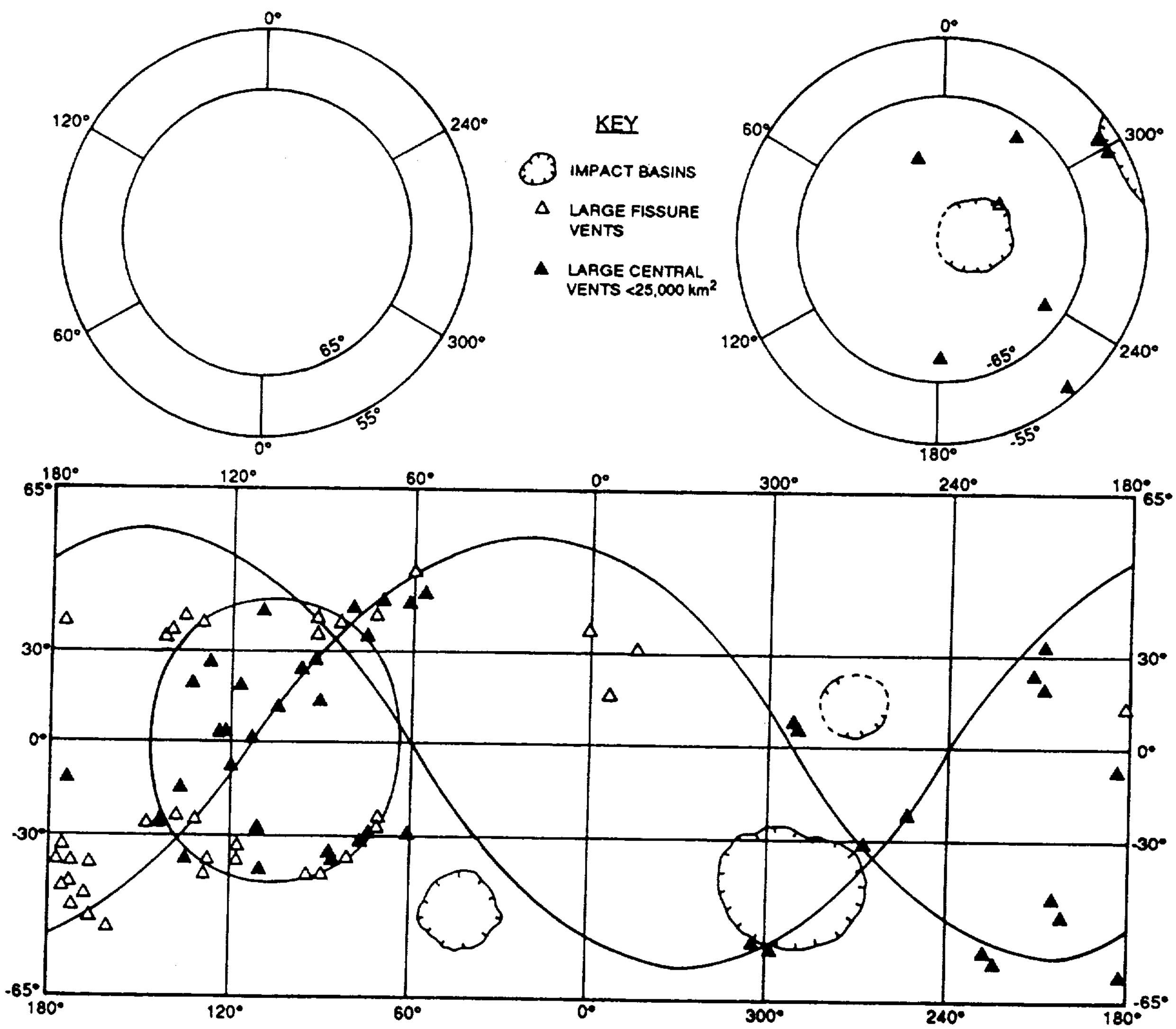

Figure 1. Vent locations, impact basins, and great and small circles.