
Chemistry and Accretion History of Mars [and Discussion]

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Chemistry and accretion history of Mars

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Using element correlations observed in SNC meteorites and general cosmochemical constraints, Wänke & Dreibus (1988) have estimated the bulk composition of Mars. The mean abundance value for moderately volatile elements Na, P, K, F, and Rb and most of the volatile elements like Cl, Br, and I in the Martian mantle exceed the terrestrial values by about a factor of two. The striking depletion of all elements with chalcophile character (Cu, Co, Ni, etc.) indicates that Mars, contrary to the Earth, accreted homogeneously, which also explains the obvious low abundance of water and carbon.

SNC meteorites and especially the shergottites are very dry rocks, they also contain very little carbon, while the concentrations of chlorine and especially sulphur are higher than those in terrestrial rocks. As a consequence we should expect SO₂ and HCl to be the most abundant compounds in Martian volcanic gases. This might explain the dominance of sulphur and chlorine in the Viking soils. In turn SO₂, being an excellent greenhouse gas, may have been of major importance for the warm and wet period in the ancient Martian history. Episodic release of larger quantities of SO₂ stored in liquid or solid SO₂ tables in the Martian regolith triggered by volcanic intrusions as suggested here could lead to a large number of warm and wet climate periods of the order of a hundred years, interrupted by much longer cold periods characterized by water ice and liquid of solid SO₂. Sulphur (FeS) probably also governs the oxygen fugacity of the Martian surface rocks.

1. Chemical composition of the Martian mantle and core

There are two main sources of information about the chemical composition of planet Mars. First, the direct analysis of the Martian surface soil by the Viking landers, and second, the information contained in the SNC meteorites which are generally believed to represent a suite of altogether 10 rocks expelled from the Martian surface by large impacts. The SNC meteorites comprise a small group of differentiated meteorites (shergottites, nakhlites and chassigny). From their composition it has been possible to obtain estimates on the composition of the Martian mantle and with some assumption even on the composition of the Martian core (see table 1 and figure 1).

It has been argued that the abundances of elements in the Martian mantle – especially the similar abundances of several geochemically very different elements (W to Rb in figure 1) – indicate that the two-component model put forward to explain the composition of the Earth's mantle is also well suited for Mars. According to the two-component model as formulated by Ringwood (1979) and

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285

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Table 1. Bulk composition of Mars as derived from SNC meteorites (Dreibus & Wänke 1984) (H₂O added during accretion = 3.4%; H₂O retained in the mantle = 36 ppm equivalent to a surface layer of 130 m on 100% degassing.)

mantle + crust				core	
MgO %	30.2	Cl ppm	38	Fe %	77.8
Al ₂ O ₃	3.02	Br ppb	145	Ni	7.6
SiO ₂	44.4	I	32	Co	0.36
CaO	2.45	Co ppm	68	S	14.24
TiO ₂	0.14	Ni	400		
FeO	17.9	Cu	5.5		
Na ₂ O	0.50	Zn	62	core mass	
P ₂ O ₅	0.16	Ga	6.6	21.7%	
Cr ₂ O ₃	0.76	Mo ppb	118		
MnO	0.46	In	14		
K ppm	305	Tl	3.6		
Rb	1.06	W	67		
Cs	0.07	Th	56		
F	32	U	16		

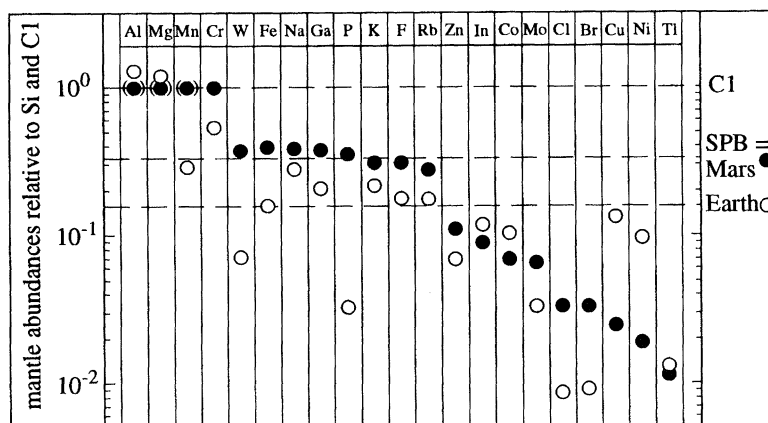


Figure 1. Estimated elemental abundances in the mantle of Mars (SPB) together with the respective data for the Earth's mantle.

Wänke (1981) both Earth and Mars, and probably also Venus and Mercury, were formed by two chemically distinct components but with different mixing ratios for the individual planet. These components are:

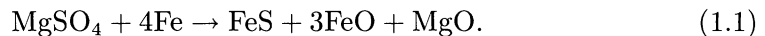
(i) Component A: highly reduced and free of all elements with equal or higher volatility than Na, but containing all other elements in Cl abundance ratios. Iron and all siderophile elements in metallic form, even Si may be partly present as metal.

(ii) Component B: oxidized and containing all elements – including volatiles –

in Cl abundances. Iron and all siderophile and, of course, all lithophile elements present as oxides.

Looking at figure 1, the low abundances of all elements with chalcophile character in the Martian mantle is obvious. It has been taken as evidence for the extraction of these elements from the Martian mantle by FeS segregation to the core during the accretion process of the planet which allowed a nearly perfect equilibration of component A and component B. The mixing ratio (component A/component B) was estimated to 60:40. In the equilibration process two reactions were thought to be of special importance:

(i) Sulphur supplied in the form of FeS and sulphates by component B and metallic FeNi from component A formed a sulphur-rich FeNi alloy:



During core formation (segregation of the (Fe, Ni)S alloy) extraction of elements from the mantle took place according to their sulphide–silicate partition coefficients rather than their metal–silicate partition coefficients.

(ii) Water from component B reacted with the metallic iron of component A:



The large amounts of H₂ (corresponding to about 0.4% of the planet's mass) led to hydrodynamic escape of heavier species like rare gases, etc. Only trace amounts of water remained in the Martian mantle. Carbon from component B at least partly dissolved in the remaining metallic iron and was extracted into the core (Kuramoto & Matsui 1994).

The high contribution of component B led via reaction (1.1) to a sulphur-rich core (about 14% S), while the total mass of the core became considerably smaller. Reaction (1.2) was responsible for the Martian mantle becoming FeO rich but H₂O poor.

The sulphide–silicate equilibrium in the Martian mantle indicates its saturation with FeS. The FeO content of the Martian mantle is about a factor of 2 higher than that of the terrestrial mantle. As a consequence, the sulphur abundance in the Martian mantle is expected to be substantially above the S abundance in the Earth's mantle as the solubility of FeS in silicates increases with the FeO content. Hence, the observed high concentrations of sulphur in mantle-derived magmas as represented by the shergottites (sulphur content between 600 and 2800 ppm) is not surprising.

The size and the composition of the Martian core, with its over 14% of S as given in table 1, fits not only well with the geophysical data, i.e. the Martian moment of inertia factor and the planet's density, but also falls within the error to a value of 16% S, obtained by Schubert & Spohn (1990) for a completely fluid core that is only weakly convecting, which in turn could explain the very weak magnetic field of Mars.

2. Abundance of water and other volatiles on Mars

Two of the five known shergottites, i.e. Shergotty and Zagami, have a composition very similar to the Viking soil (table 2). The large concentrations of sulphur (3.5%) and chlorine (0.8%) in the Viking soil (Clark *et al.* 1976) seem not be noticeably accompanied by respective cations, as the most likely cations for the

Table 2. Comparison between Shergotty and Martian soil

	Shergotty	Martian soil
SiO ₂ %	51.4	43.0
FeO	19.4	16.2
CaO	10.0	5.8
MgO	9.28	6.0
Al ₂ O ₃	7.06	7.2
TiO ₂	0.87	0.6
Na ₂ O	1.29	–
S	0.13	3.5
Cl	0.01	0.8
CO ₃	< 0.2	< 2
H ₂ O	< 0.02	< 1
Sr ppm	51	58

sulphates, Mg and Ca, have even higher concentrations in Shergotty and Zagami as has the Viking soil. This observation speaks for a direct introduction of SO₂ and probably also HCl to the Martian regolith via gas–solid reactions.

To estimate the water content of the Martian mantle, Dreibus & Wänke (1989) used data on the water content of Shergotty of 180 ppm measured by Yang & Epstein (1985). Shergotty is enriched in La by a factor of 5 relative to the Martian mantle. Assuming a similar enrichment for H₂O, a mantle concentration of $180:5 = 36$ ppm was found. This is exactly the value obtained earlier by Dreibus & Wänke (1987), comparing the solubility of H₂O and HCl in silicate melts and using the abundance of chlorine in the Martian mantle as deduced from SNC meteorites. The exact match is, of course, purely fortuitous considering the uncertainties.

To exclude a possible loss of H₂O from the Shergotty magma during ascent and before crystallization, we compare the ratios of volatile, respectively moderately volatile, elements (figure 2). The K/Cl ratio of Cl chondrites is 0.8, while in MORB and other terrestrial basalts this ratio varies between 13 and 26, indicating the large depletion of the volatile element chlorine compared to the moderately volatile element K. For Shergotty a K/Cl ratio of 15 is found, indicating no significant loss of Cl from the magma if we assume similar K/Cl ratios for Earth and Mars, an assumption not absolutely proven but well justified (Dreibus & Wänke 1987). No loss of Cl indicates no substantial loss of H₂O either.

Over the years, the dry Martian mantle as proposed by Dreibus & Wänke (1989) has been questioned in light of water-rich inclusions observed in SNC meteorites (Johnson *et al.* 1991; McSween & Harvey 1993). However, it was not known if the host phases of these inclusions have crystallized from mantle-derived magmas or represent material from a water-rich Martian crust taken up by intrusions and overplating of mantle-derived magmas. The contradictory evidence of a dry Martian mantle as indicated by the low water content of SNC meteorites and the erosional Martian surface features, which seem to require large amounts of water, has recently been discussed by Carr & Wänke (1992).

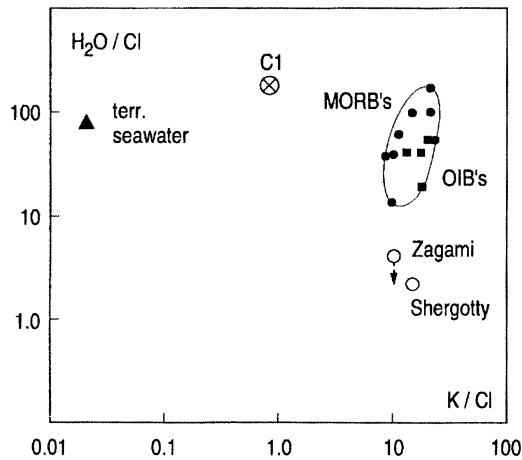


Figure 2. $\text{H}_2\text{O}/\text{Cl}$ against K/Cl . While terrestrial seawater and basalts have $\text{H}_2\text{O}/\text{Cl}$ ratios close to the Cl value, the shergottites (Martian rocks) have more than an order of magnitude lower $\text{H}_2\text{O}/\text{Cl}$ ratios, but K/Cl ratios identical to terrestrial basalts. Evidently no substantial loss of either Cl or H_2O has occurred before crystallization in the shergottites (Shergotty and Zagami).

The value of 180 ppm H_2O for Shergotty used by Dreibus & Wänke (1989) for their estimate of the water in the Martian mantle could be considered to be too low as the sample was preheated to 350°C to remove water of terrestrial origin. Karlsson *et al.* (1992) have shown that indeed SNC meteorites give off considerable amounts of water below 350°C , but both H/D analyses (Watson *et al.* 1991) as well as oxygen isotopes (Karlsson *et al.* 1991) indicate a large portion of terrestrial water contribution below 350°C .

In total, Karlsson *et al.* (1992) extracted 640 ppm H_2O from Shergotty without preheating and 260 ppm above 350°C . However, the oxygen isotopes indicate that for all the SNC meteorites, apart from the presence of terrestrial contamination, a large fraction of the water, although Martian, is not derived from the Martian mantle, but obviously represents Martian surface water with an oxygen isotope composition up to three times further away from the terrestrial isotope fractionation line than the oxygen in the silicates of SNC meteorites. At the high temperatures during magma generation in the Martian mantle isotopic equilibration between oxygen of the silicates and of water would certainly have been established. Hence, only a fraction of the water found in SNC meteorites can be mantle derived and the other non-terrestrial part must come from the Martian surface. The oxygen isotopes of the surface component might have been created by nonlinear isotope fractionation by non-thermal escape of oxygen to space (Jakosky 1992).

Of course, it could also be that the water added to Mars during accretion had oxygen isotopes much further away from the terrestrial isotope fractionation line than the oxygen of Martian mantle silicates and that isotopic equilibration of these two oxygen reservoirs never took place. Such a scenario has severe consequences for the accretion processes; it is discussed in more detail by Carr & Wänke (1992). Even in the case of the Earth, if it has received most of its present water by a late veneer, it might be that this water had oxygen isotopes very different from those of the oxides in the mantle. Later on, subduction and recycling of the

oceanic crust might have continuously brought water from the surface into the originally dry mantle and isotopic equilibration with the oxygen of the silicates took place there.

As subduction of crustal material seems not to occur on Mars, material from a late veneer could have been added to the upper crust only and would remain unrecognized in mantle-derived magmas. Clearly, the amount of water, CO₂, etc., added to the crust in this way cannot be a constraint from mantle-derived basalts.

3. On the expected dominance of SO₂ in the Martian volcanic gases

As discussed above, shergottites contain mantle-derived concentrations of about 200 ppm H₂O, about 100 ppm CO₂, but between 1200 and 5600 ppm SO₂, while terrestrial MORB contain about 2000 ppm H₂O and similar concentrations of CO₂ and SO₂.

Reflecting the similar abundances of H₂O, CO₂ and SO₂ in terrestrial magmas, these three compounds are also found in about equal abundances in the gases of terrestrial volcanoes. On a planet with a mantle considerably poorer in water than the Earth but similar or richer in SO₂, it is to be expected that SO₂ should dominate the exhalation gases although part of the sulphur might degas in the form of H₂S and elemental S.

In order to explain the run-off channels and valley networks present on the ancient, heavily cratered Martian terrain, it was suggested that Mars was warmed by the greenhouse effect of a dense CO₂ atmosphere (Moroz & Mukhin 1978; Pollack *et al.* 1987). However, recent work by Kasting (1991) has shown that this mechanism was not efficient enough because of the formation of CO₂ clouds especially in the early solar system history when the luminosity of the Sun was about 25 to 30% lower than today. SO₂ is a very efficient greenhouse gas and its importance for heating of the Martian atmosphere was pointed out by Postawko & Kuhn (1986). Trace amounts of SO₂ would lead to substantial warming of the Martian atmosphere. However, the atmosphere lifetime of SO₂ is limited by its photochemical oxidation to SO₃ and atmosphere–surface reactions.

At present, the mean surface temperature of Mars at low latitudes is 218 K or –55°C, while on the poles the temperature drops to less than –140°C. Considering the lower solar luminosity 3.5 by ago, the equatorial mean temperature would drop to about 200 K or –73°C or close to the freezing point of SO₂. Thus without an appreciable greenhouse effect, H₂O should have been a solid at all latitudes, CO₂ a solid or gas depending on latitude and SO₂ a liquid or solid depending on latitude (figure 3). On Earth, the CO₂ from erupting lavas amounts to less than 10% of the amount of CO₂ emitted to the atmosphere from fracture zones and diffusive loss through volcano flanks. Under similar conditions on Mars SO₂, CO₂ and H₂O would migrate through the (mega)-regolith towards the surface (figure 4). Most of the CO₂ will be quickly transferred to the atmosphere, while SO₂ gas would feed solid, respectively liquid, SO₂ tables at low depths. Water vapour will be trapped at even greater depth and correspondingly higher temperatures.

The degassing rate of SO₂ from erupting magmas is probably too small for a substantial contribution of SO₂ to greenhouse warming on a global scale. However, local warming of SO₂ tables in the Martian regolith by a volcanic intrusion will drive SO₂ to the surface as a liquid at temperatures close to its triple point

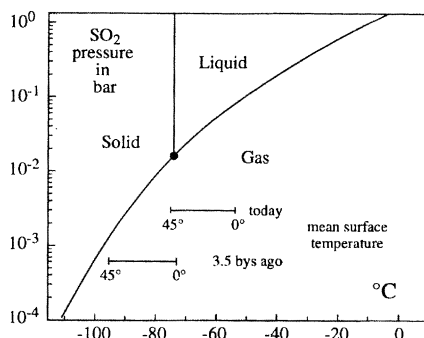


Figure 3. Phase diagram of SO_2 and the range of the mean surface temperature between 0° and 45° latitude on Mars.

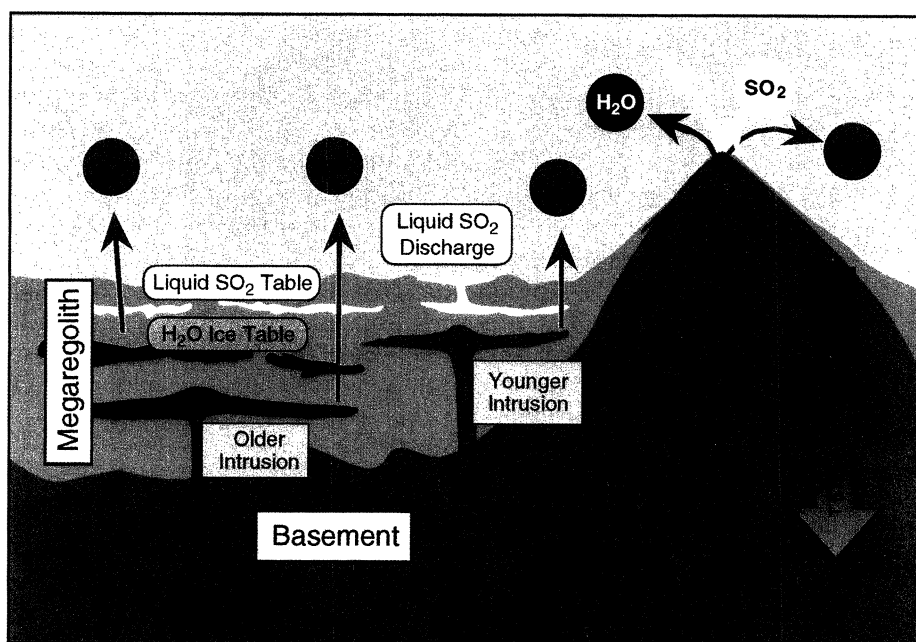


Figure 4. On Mars gases from volcanic intrusions migrating through the megaregolith will be trapped according to their condensation temperatures and form H_2O ice tables and liquid or solid SO_2 tables at different depths. Only CO_2 will directly migrate to the atmosphere under normal conditions.

(16 mbar and -73°C). Evaporation of stored liquid or solid SO_2 could lead to a sudden release of enough SO_2 into the atmosphere for a global temperature rise.

The feedback of evaporation and release to the atmosphere of SO_2 and H_2O stored in reservoirs at shallow depth to global warming might considerably prolong the periods of a warm, wet climate. Hence, we suggest that the erosional features observed at the Martian surface are the result of many temporally separated events which were followed by much longer cold periods during which the water retreated to subsurface ice layers until being liquidized again by the next SO_2 eruption.

The total amount of carbonates in the Martian soil is not known. Water, SO_2 ,

CO₂ as well as HCl are volcanic exhalation gases, dominantly produced between 4.5 and 3.5 billion years ago. The presence of SO₂ which will, at least partly, quickly be transformed to SO₃ together with even minimal amounts of water, makes carbonate formation only possible if CO₂ is in excess of SO₂ which seems unlikely according to what was said above. Hence, the proposition of carbonate layers as a sink for atmospheric CO₂ might have to be reconsidered.

Like the water from volcanic intrusions, water supplied to the Martian surface by a late veneer might also be stored in the near-surface layers in the form of ice. Temporary greenhouse warming by SO₂ after large SO₂ discharges may have been responsible for the melting of ice and break-out of water in areas not directly connected to volcanic activity. Aside from water, liquid SO₂ could in fact explain some of the erosion features on the Martian surface.

We know that Mars contains considerable amounts of FeS (Dreibus & Wänke 1985). Although today most of the FeS resides in the Martian core a certain fraction has remained in the mantle, from which sulphur-rich magmas were formed. Formation of SO₂ requires a source of oxygen. The Martian soil contains about 3.5% S, most probably in the form of sulphates. The oxygen required to transform FeS to SO₃, respectively sulphate, should have had an important influence on the oxygen fugacity of the Martian surface and might well be the limiting factor for water. As water is the most likely source of oxidation to transform SO₂ released into the atmosphere to SO₃, we have to ask how much of the water once present at the Martian surface was used up for this process. In general the processes for the transformation of SO₂ to sulphate demand an exact quantitative analysis (Settle 1979). On the other hand, contact metamorphism or direct infiltration of magma into the regolith containing sulphates would lead to their decomposition and generation of SO₂. In this way, one might even visualize recycling of SO₂.

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Discussion

I. P. WRIGHT (*Department of Earth Sciences, Open University, U.K.*). Terrestrial mid-ocean ridge basalts are thought to form at typically 40 km depth (i.e. 12 000 bar), and are subsequently emplaced under 5 km of sea water (i.e. 500 bar pressure). During this process a basalt can be erupted rapidly and subsequently quenched to form a glass, which contains a large proportion of the original volatile content of the magma. Martian magmas probably form under pressures similar to those on Earth. However, the shergottites are thought to have been erupted close to the surface of the planet under an atmospheric pressure that was presumably not different to that in evidence today (i.e. 0.006 bar). Is the apparently low volatile content of the shergottites simply due to the fact that they are degassed?

H. WÄNKE. Compared to terrestrial MORB samples, the shergottites have factor of 10 lower water abundances, whereas their sulphur and halogen concentrations are about twice the terrestrial values. The twofold higher K/La ratio of the martian basalts compared to terrestrial basalts also indicates a higher proportion of moderately volatile elements on Mars. The similar K/Cl ratio in terrestrial and martian basalts (Dreibus & Wänke 1989) suggests a similar enrichment of moderately volatile and volatile elements on Mars relative to Earth. However, the H₂O/Cl and H₂O/K ratios in terrestrial basalts exceed those on Mars by factors of 6–25. No loss of the highly volatile Cl excludes substantial degassing of the basaltic magma during eruption. Therefore the 10 times lower H₂O/Cl ratio for shergottites relative to MORBs indicates a dryer magma for Martian basalts.

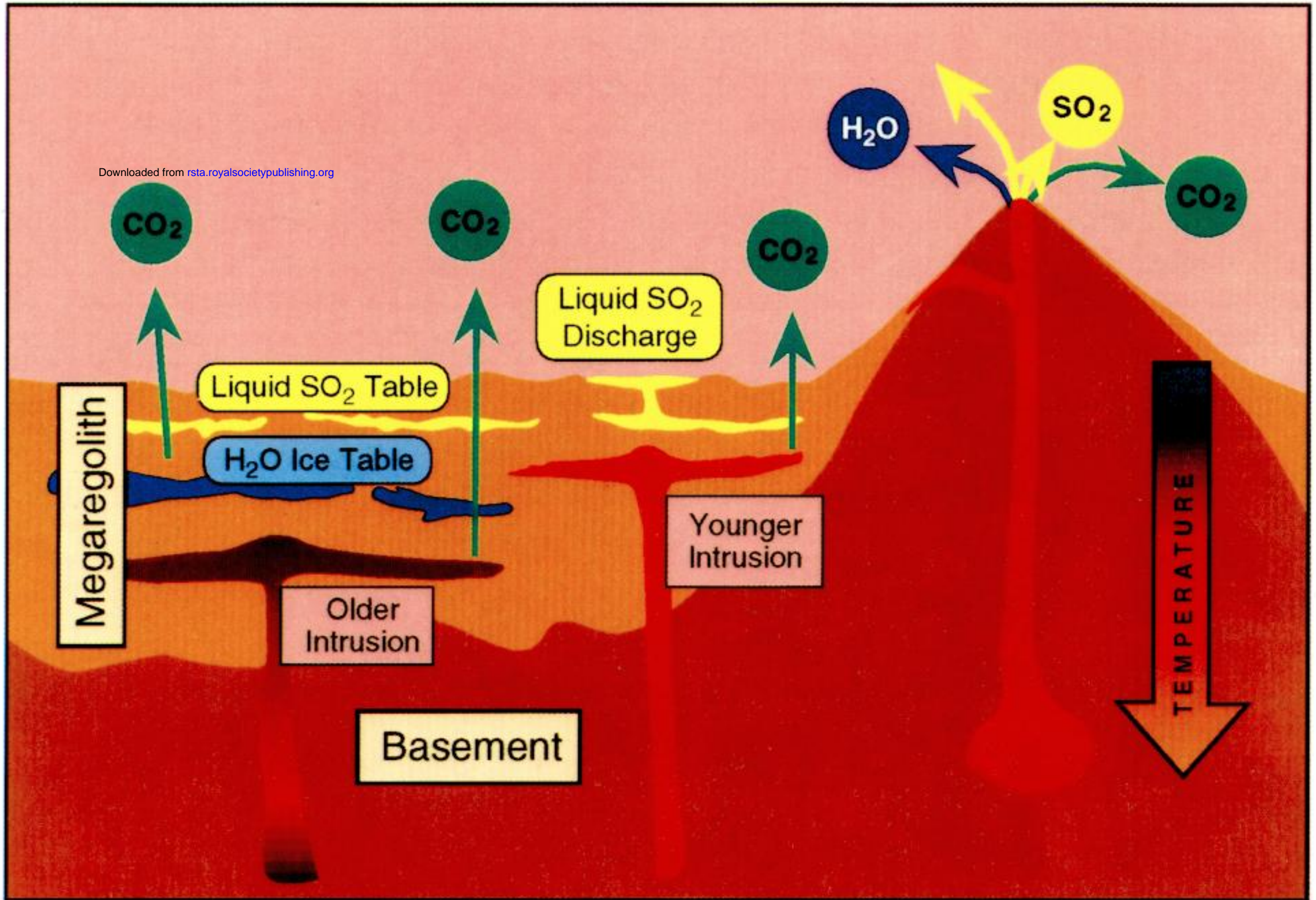


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