ORIGIN AND EVOLUTION OF PLANETARY ATMOSPHERES: AN INTRODUCTION TO THE PROBLEM*

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Abstract—Planetary atmospheres have their birth in certain physical and chemical events in the primitive solar nebula. These events involve irreversible volatile retention through condensation and accretion of planetesimals and giant planets whose volatile inventory can survive the subsequent dissipation of the nebula. Clues to these earliest processes are inferred not without difficulty from the observed volatile compositions of present-day planetary and satellite atmospheres, meteorites and comets. The origins of terrestrial-type atmospheres appear to have involved outgassing of the solid planet with compositions and rates intimately connected to the late growth and thermal evolution of the planet itself. Subsequent evolutionary processes such as escape of certain light elements and cometary and meteoritic infall appear to be of general significance; others such as atmosphere-hydrosphere-crust interactions and development and influence of living organisms are highly specific. Our knowledge of these highly specific areas is largely restricted to the last 3.8 billion years on earth and is based upon analyses of the geologic record which are not presently available for Venus, Titan or the pre-Archean earth and are only available in a superficial way for Mars. In this introductory paper we attempt to draw an integrated picture of the atmospheric evolutionary process being careful to define the outstanding problems, to differentiate theory from fact, and to emphasize the strengths and weaknesses of a priori and a posteriori approaches to these problems.

1. INTRODUCTION

In the last few years we have witnessed through planetary probes a quantum jump in our knowledge of the atmospheres of the planets and their satellites. During this time the goals of atmospheric scientists and the foci of relevant planetary science conferences have for obvious reasons been to explain the presently observed states of these atmospheres. A good deal of the initial analysis of data from this recent epoch is now complete and we have reached a new and much more informed vantage point. In addition, the comparatively quieter solar system missions program of the next several years makes it unlikely that this present vantage faces imminent change. It therefore seems timely to use our new-found knowledge to address the broad and inherently interdisciplinary problems of atmospheric origin and evolution in a comprehensive way.

Recent data from planetary probes do not of course comprise the only motive for our interest in the origin and evolution of planetary atmospheres at this time. There have been significant advances over the past few years in our understanding of the origin of the solar system based on chemical and isotopic analyses of meteorites and on the development of working models of the primitive solar nebula, planetary accretion and planetary thermal histories. There has also been an increasing awareness of the susceptibility of our own atmosphere and climate to change as a result of man's activities and extraterrestrial influences including in the past the chance collision with earth of a comet or asteroid.

The magnitude of the challenge which faces us is amply demonstrated in Fig. 1. Here we have plotted the masses of the dominant forms of the volatile elements observed in each atmosphere as fractions of the total planetary mass. A cursory examination of this diagram leaves one impressed with the surprising diversity of atmospheres in our solar system and leads one to immediately ask why different planets were apparently endowed with such different mixtures of the volatile elements. A closer examination yields underlying patterns which would suggest four categories: oxidized terrestrial atmospheres (Venus, Earth and Mars), reduced terrestrial atmospheres (Titan), reduced gaseous giant atmospheres (Jupiter, Saturn), and finally atmospheres which exhibit

The observed masses of the dominant chemical compounds of the more abundant volatile elements in planetary and satellite atmospheres are shown as fractions of the total planetary or satellite mass. Also shown are the surface pressures on each solar system object. The data for Uranus and Neptune assume a core size inferred from theory.

For the atmospheres in the first category we must explain the enormous differences in their surface pressures, the lack of water on Venus relative to earth, and the surprisingly large decrease in the abundances of the primordial (as opposed to radiogenic) inert gases as we move from Venus to Earth to Mars. Further scrutiny yields further puzzles. The presence of sulfuric acid clouds and significant amounts of HCl and HF on Venus, the existence of reduced species such as CH₄, NH₃, and H₂S in the oxygen-rich atmosphere on earth, and the anomalously large $^{15}$N to $^{14}$N ratio on Mars, have all demanded and received significant attention. We should add that we are still largely ignorant concerning the amounts of the various volatile elements seques-
tered in minerals on Venus and in minerals or ices on Mars; there may be further surprises once this knowledge is gained.

Titan, the atmosphere in our second category, bears its own share of intriguing questions. What is the source of \( \text{N}_2 \)—photodissociation of \( \text{NH}_3 \) or outgassing? How has \( \text{CH}_4 \) survived reduction to higher hydrocarbons over geologic time? What are its clouds composed of and what is the source of HCN observed in its upper atmosphere? What volatiles remain in its core? Did this moon of Saturn evolve in the solar nebula or in a circum-Saturnian nebula?

From an evolutionary viewpoint, the giant and probably solar-composition atmospheres in our third category are perhaps the least surprising. However, the precise manner in which such massive planets as Jupiter and Saturn formed within the low-pressure primitive solar nebula, and the nature of their deep interiors are far from understood. There are also questions concerning the observed presence of non-equilibrium species in their visible atmospheres, in particular, some or all of the species \( \text{C}_2\text{H}_2, \text{C}_2\text{H}_6, \text{CO}, \text{PH}_3 \) and \( \text{GeH}_4 \). The colorations in the clouds of both planets and the Great Red Spot on Jupiter have also fascinated and challenged planetary scientists for many years.

Unfortunately, we are not yet blessed with planetary probe data for the "hybrid" atmospheres of Uranus and Neptune which lie in our fourth and last category. Current models incorporate roughly solar composition atmospheres overlying massive cores containing ices and rocks in solar proportions. What little we know from earth-based observations already suggests that relative to solar proportions, \( \text{NH}_3 \) may be depleted on Uranus, and \( \text{CH}_4 \) may be enhanced on both Uranus and Neptune.

I will avoid an obvious temptation to define a fifth category containing the evanescent and extremely thin atmospheres on Io and Mercury. These bodies are more interesting at least to me, as examples of objects which have failed to evolve significant atmospheres despite the presence of identifiable volatile sources (volcanoes on Io and the solar wind and perhaps outgassing on Mercury).

Studies of the origin and evolution of planetary atmospheres have traditionally involved one of two approaches which have not yet been fully reconciled. On the one hand, presently known facts about the solar system are used to extrapolate back in time with the aim of solving the problem \textit{a posteriori}. On the other hand, present astrophysical information on the formation of stars and solar systems is used in evolutionary models which attempt to solve the problem \textit{a priori}. If we are to be successful, both approaches must ultimately converge on a single and hopefully correct evolutionary theory. As with any effort at unraveling the past we may never possess sufficient information to allow this convergence. However, if we are to maximize the information which we do possess we must develop a comprehensive theory which explains simultaneously all the atmospheres in our solar system.

Planetary-specific hypotheses are useful only to the extent that the same hypotheses applied to other planets yield conclusions conversant with observations. For example, proposals concerning the way atmospheric volatiles combined to form the elements of living organisms on earth, and the remarkable evolutionary events which followed this occurrence, must also relate the ubiquitous presence of life on earth to its lack on other planets.

In this paper I will attempt to outline the elements of a comprehensive approach to the problem of atmospheric origin and evolution. I will leave the far more difficult task of elucidating specific themes within this approach to the talented group of scientists whose papers follow this one.

\section*{2. ORIGIN OF VOLATILES}

It is generally postulated that the volatile elements giving rise to atmospheres were present in the dust and gas of the interstellar cloud which collapsed to form our primitive solar nebula. Spectroscopic observations of dense interstellar clouds indicate that the gas contains a rich assortment of carbon, oxygen and nitrogen-containing compounds in addition to molecular hydrogen which is the probable principal constituent (Herbst, 1978). Observations of the dust in these clouds are less definitive but there is tantalizing evidence that silicates, magnetite, carbonaceous compounds including graphite, and ices are all present (Knacke, 1978). The dust thus bears some resemblance to the so-called "primitive" material in our present solar system (carbonaceous chondrites, comets and interplanetary dust). A summary of the typical composition of a dense interstellar cloud is given in Table 1. The elemental composition of the cloud which collapsed to form our own solar system is inferred largely from data on the composition of the sun for the volatile
elements and of Type 1 carbonaceous chondrites for the less volatile ones (Cameron, 1973).

By one postulated mechanism or another, the interstellar cloud which preceded our solar system was induced to collapse. Recent meteoritic evidence for the presence of the relatively short-lived isotope $^{26}\text{Al}$ in the early solar system strongly suggests that this collapse (and the transient presence of $^{26}\text{Al}$) was due to a nearby supernova explosion (Lee et al., 1976). Collapse of the cloud into a rotating disk-shaped primitive solar nebula was accompanied by increasing temperatures and densities within the nebula. Temperatures in the formation regions for each of the planets are shown in Fig. 2 as a function of time from initial collapse as deduced from a recent model for the accreting nebula disc (Cameron, 1978). As emphasized by the author, these calculations are basically exploratory. However, they serve to illustrate at least qualitatively the important changes to be expected over time and space of the thermodynamic conditions in the nebula.

An important question ultimately impinging on atmospheric composition concerns the extent to which the interstellar dust and gas metamorphosed as it was accreted by the nebula. In the absence of radial mixing within the disc, accreting dust grains may have only partially evaporated or never

![Fig. 2. The temperatures in the regions of formation of the planets as deduced in a model for the primitive solar nebula are shown as a function of time from initial collapse (after Cameron, 1978).](image-url)
evaporated at all depending on distance from the protosun. Similarly, accreting gases as they were warmed and compressed may have chemically re-equilibrated only in part or not at all. In fact, Cameron (1978) presents arguments for expecting strong radial mixing of the gas. Thus, complete evaporation and re-equilibration of interstellar material is possible to the extent that the material can be transported from the cool outer to the warm inner nebula before it accumulates into objects which no longer advect with the gas. These arguments, combined with inferences from meteorites (Wasson, 1978), suggest that evaporation and re-equilibration were very probable in the inner solar system. However, the arguments become less and less convincing as we move out into the far reaches of the solar system where comets may have formed. This should be kept in mind since chemical models of the nebula usually assume complete evaporation or re-equilibration of the grains and complete re-equilibration of the gas.

Once accretion of the nebula was complete, cooling began with net condensation replacing net evaporation of nebula grains. At this juncture, a physical picture of the nebula proves invaluable and we have plotted in Fig. 3 typical isobars during the warmest phase of Cameron’s (1978) nebula model (see Fig. 2). We have added isobars for a Jovian subnebula model (Prinn and Fegley, 1981) since there is evidence that events in the Jovian system may have imitated to some extent the events in the surrounding solar system.

A parcel of material in this nebula model can be cooled either by moving outward or by a decrease in temperature of the entire nebula. Let us denote the time scale for such cooling by $\tau_{\text{cool}}$. As this material parcel cools, three chemical time scales are of interest for determining the partitioning of volatiles between gas and condensate:

(a) if the time scale for gas phase reactions $\tau_g < \tau_{\text{cool}}$ then we can reasonably assume gas-phase equilibrium,

(b) if the time scale for gas to permeate into and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{Isobars (units are common logarithms of pressure in bars) are plotted as a function of radial distance (in Astronomical Units) from the protosun and altitude (in Astronomical Units) above the central plane in the warmest phase of the Cameron (1978) model of the primitive solar nebula. Nebular temperatures and present positions of the planets are indicated. An isobar for a Jovian subnebula model is also shown (Prinn and Fegley, 1981). The respective points in a chemical equilibrium model at which metallic iron (and calcium and magnesium silicates) condense, troilite formation occurs, metallic iron is totally oxidized to troilite and ferrosilicates, calcium and magnesium silicates are hydrated to tremolite, and ice condenses, are shown with dashed lines.}
\end{figure}
react with condensed material $r_{eq} < r_{cool}$ then we have gas-condensate equilibrium.

(c) finally, if the time scale for migration and reaction of elements within the condensed material $r_c < r_{cool}$ then we expect condensate equilibrium.

The opposite inequalities in these three cases imply the possibility for the appropriate dis-equilibrium case. The three equilibrium cases are favored by high temperatures, slow radial mixing and nebula cooling, and in cases (b) and (c), by small grain sizes and slow accretion rates for these grains. In equilibrium case (c) and often in equilibrium case (b) the condensed material remains homogeneous over scales much larger than the single crystal scale. Such cases are usually referred to as homogeneous accretion scenarios. The converse is heterogeneous accretion which can result from either dis-equilibrium cases (b) or (c) and leads to distinct layering of condensed material.

The importance of these definitions is amply demonstrated by considering the manner in which metallic Fe, sulfur and H$_2$O can be incorporated into condensed grains. Imagine the condensation sequence in a material parcel which begins in Fig. 3 inside the orbit of Mercury and moves outwards sufficiently slowly so that equilibrium is always maintained. Metallic iron and calcium and magnesium silicates condense near 0.3 a.u. As the parcel moves out, H$_2$S permeates the iron and converts some of it to troilite (FeS). At the same time H$_2$O also permeates the condensate and oxidizes the remainder of the iron which is incorporated into ferrosilicates. At 1.2 a.u. no metallic iron remains and further permeation of water causes hydration of the calcium and magnesium silicates to form tremolite (Ca$_2$Mg$_5$Si$_8$O$_{22}$H$_2$) and other hydrated silicates at and beyond 1.3 a.u. At this point all of the sulfur is condensed as troilite and a few per cent of the H$_2$O is incorporated into hydrated silicates. The remaining H$_2$O condenses as ice at 5.5 a.u.

Conversely, if the parcel moves outwards sufficiently fast so that equilibrium cannot be maintained, the iron remains as the metal, a few per cent of the H$_2$S is condensed as Na$_2$S and the remaining H$_2$S and all the H$_2$O do not condense until ice and solid H$_2$S form at and beyond 5.5 a.u. A plethora of possibilities lie between these extremes. Current evidence points to sequences closer to the equilibrium than to the disequilibrium case at least in the warmer inner nebula. However, even in the gas phase there are important examples of dis-equilibrium, with major implications for retention of carbon and nitrogen in condensed material (Lewis and Prinn, 1980; Prinn and Fegley, 1981).

3. PLANETARY FORMATION

Two somewhat antithetical models of planetary formation in the nebula are usually visualized. On the one hand, slow accumulation of grains beginning in the nebula leads to successively larger and larger bodies. These may ultimately reach earth-like dimensions but only well after dissipation of the nebula. The larger bodies while in the nebula can capture temporary solar-composition "primordial" atmospheres which would however generally be lost upon dissipation of the nebula. Indeed, if this model is to explain the Jovian planets, we require perhaps improbably large accumulation rates in order to form a body massive enough to capture a primordial atmosphere which can survive the subsequent loss of the nebula.

On the other hand, proposed gravitational instabilities in the nebula could lead to rapid collapse of both gas and grains to immediately form massive Jupiter-like "proto-planets". These proto-planets would possess solar composition overall, but internal differentiation would lead to massive volatile-rich atmospheres and small volatile-poor cores. However, in order to explain the terrestrial planets, this model requires a catastrophic loss of the massive proto-planetary atmosphere.

The manner in which the terrestrial planets could arise through the slow accumulation model has been ably reviewed by Wetherill (1978). Stevenson (1982) discusses competing theories for formation of gaseous giant planets and Mizuno et al. (1982) discuss how inert gases in a sufficiently massive "primordial" atmosphere could dissolve in the planetary core and thus survive subsequent loss upon nebula dissipation.

Although the solar composition "primordial" or "proto-planetary" atmospheres are attractive for explaining the origin of the present-day atmospheres of the major planets, they cannot be the progenitors of the present-day atmospheres on the terrestrial planets. In particular, escape loss of hydrogen and helium from a solar composition atmosphere would leave in the residual atmosphere comparable amounts of $^{14}$N and $^{20,22}$Ne and about a 25 times lesser amount of $^{36,38}$Ar. This is clearly at odds with the observed atmospheric composition on Venus, Earth and Mars as reviewed in Fig. 1. It is also at odds with the observed upper limit for Ne in Titan's atmosphere.
(Owen, 1982). Thus primordial atmospheres if they existed on these terrestrial objects must have subsequently been largely lost. It is useful to remember however that even a temporary primordial atmosphere could enable significantly higher temperatures on the object’s surface than in the surrounding nebula with obvious consequences for devolatilization of accreted condensates.

Mechanisms for the loss of these “primordial” or “proto-planetary” atmospheres are not well understood. Large disruptive tidal forces may play a role for planets close to the proto-sun. Also, as the nebula loses mass, the outflowing gas could serve to sweep away atmospheres. This nebula mass loss is usually referred to as the T-Tauri phase after the presumably young T-Tauri stars which appear to be exhibiting just such behaviour. Finally, if the bodies were small enough, they may have simply been incapable of retaining an atmosphere once the nebula dissipated.

Whatever the mechanism for “primordial” atmospheric loss, the present atmospheres of Venus, Earth, Mars and Titan must be derived largely from other sources. There is now a general consensus that the origin of these terrestrial-type atmospheres involved outgassing of the solid planet. It is for this reason that such close attention has been given in this review to questions concerning retention of volatiles in the condensed material which accreted to form these planets.

A useful way to view planetary formation models is to categorize them as either homogeneous or heterogeneous just as we discussed earlier for grains in the nebula. In this respect, capture of a primordial atmosphere by a solid body is a heterogeneous process whereas collapse formation of a protoplanet is an initially homogeneous process even though subsequent differentiation might lead to a layered heterogeneous structure.

If we focus on the accretion of the solid material of the terrestrial planets, the process would be homogeneous if it involved accumulation of material produced under equilibrium conditions over a relatively narrow range of temperatures in the nebula. For example, for nebula temperatures near 600 K, the body might be composed of an intimate mixture of iron-nickel alloy grains and crystals of forsterite (Mg$_2$SiO$_4$), troilite (FeS), enstatite (MgSiO$_3$), feldspar [(Na, K)AlSi$_3$O$_8$], diopside (CaMgSi$_2$O$_6$), olivine [(Fe, Mg)$_2$SiO$_4$] and pyroxene [(Fe, Mg)SiO$_3$]. If the body became large enough, subsequent differentiation into a core, mantle and crust could then occur.

Conversely, the process would be heterogeneous if initial accumulation involved material condensed at very high temperatures in the nebula or proto-planetary atmosphere followed by material condensed out at successively lower temperatures. This distinctly dis-equilibrium process might yield, for example, a body with a core of refractory minerals covered with subsequent layers of iron-nickel-silicon alloy, forsterite, enstatite, quartz and sulfides and oxides of Na and K. Clearly, the manner in which the terrestrial planets accreted has major implications for their composition and thus for the nature of their outgassed atmospheres.

4. SOURCES, CYCLES AND SINKS OF PLANETARY VOLATILES

When the vapor pressure of a volatile species over its condensed phase exceeds the pressure due to the overlying solids, liquids or gases, devolatilization of the condensate can proceed. Obviously this is favored by high temperatures and low pressures. Thus, significant devolatilization may occur even as a planet or satellite accretes due to the surface melting caused by high energy impacts. Once an atmosphere develops, incoming material may be devolatilized before reaching the surface due to frictional heating. Also, as the atmospheric opacity and thus surface temperatures increase, devolatilization of surface material by solar heating can begin. Temperatures in the interior are governed by stored heat due to the accretion process itself, to radio-active decay of $^{26}$Al, $^{40}$K, $^{232}$Th, $^{235}$U, $^{238}$U and other isotopes, and to the release of gravitational potential energy as dense material sinks during planetary differentiation. Thus devolatilization of the interior is intimately connected with the thermal history of the planet itself. Since accretion rates, radionuclide abundances and degrees of differentiation were undoubtedly all different for each of the terrestrial planets and satellites the times and rates of outgassing of these bodies may have differed widely.

Depending on what models for accretion of terrestrial bodies are adopted, the composition of their outgassed volatiles may also have differed widely. For example, consider the model for volatile retention recently developed by Barshay (1981). This model assumes equilibrium conditions in the nebula (or Jovian or Saturnian subnebula), but because it allows accretion by the body of material equilibrated over a range of temperatures
it is effectively a mildly heterogeneous or "pseudo-homogeneous" accretion model. In Tables 2 and 3 we show the volatiles which could be outgassed by the rocky and icy bodies of the solar system in this model. Results are also given assuming dis-equilibrium conditions for carbon and nitrogen species in the gas phase (Lewis and Prinn, 1980; Prinn and Fegley, 1981).

For the rocky bodies, we see that Mercury will be very volatile-poor with 4He, N2 and 40Ar in very small amounts providing the only potential for forming an atmosphere. Venus, in contrast, has

**Table 2. Potential Outgassing by Rocky Bodies in the Solar System in a Model Assuming an Equilibrium Nebula and Pseudo-Homogeneous Accretion**

<table>
<thead>
<tr>
<th>Body</th>
<th>Condensate</th>
<th>Potential volatile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury</td>
<td>U, Th in Ca-rich refractories</td>
<td>4He</td>
</tr>
<tr>
<td></td>
<td>C, N in Fe-Ni alloy**</td>
<td>N2</td>
</tr>
<tr>
<td></td>
<td>Schreibersite (Fe2P)</td>
<td>P</td>
</tr>
<tr>
<td></td>
<td>Feldspar ([Na, K]AlSi3O6)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Olivine ([Fe, Mg]3SiO4)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>and pyroxene ([Fe, Mg]SiO3)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sodalite (3NaAlSi3O7·NaCl)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fluorpapatite (Ca5(PO4)3·F)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tantalite (FeS)</td>
<td></td>
</tr>
<tr>
<td>Venus</td>
<td>Water (H2O)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Carbon monoxide hydrate (CO·H2O)**</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquefied water (CH4·7H2O)**</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methane hydrate (CH4·7H2O)**</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrogen cyanide (HCN)**</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dry ice (CO2)*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ammonium bicarbonate (NH4·HCO3)*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ice (H2O)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ammonium carbonate (NH4·COONH3)*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ammonia hydrate (NH3·H2O)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydrogen cyanide (HCN)**</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dry ice (CO2)*</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Methane hydrate (CH4·7H2O)**</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Carbon monoxide hydrate (CO·H2O)**</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nitrogen hydrate (N2·7H2O)**</td>
<td></td>
</tr>
</tbody>
</table>

*In this equilibrium nebula model many of the high temperature condensates re-equilibrate at lower temperatures.

**Only very small amounts of carbon (and nitrogen) are retained in this alloy at Mercury but much larger amounts at Venus and Earth and also at Mars if dis-equilibrium conditions apply for gas-phase carbon compounds.

***If dis-equilibrium conditions apply for gas phase nitrogen compounds these are negligible.

**Table 3. Potential Outgassing by Icy Bodies in the Solar System in a Model Assuming an Equilibrium or Dis-equilibrium Nebula or Subnebula and Pseudo-Homogeneous Accretion**

<table>
<thead>
<tr>
<th>Body</th>
<th>Condensate</th>
<th>Potential volatile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triton</td>
<td>Rock</td>
<td>(see Table 2)</td>
</tr>
<tr>
<td></td>
<td>Ammonium bicarbonate (NH4·HCO3)*</td>
<td>NH3, CO2</td>
</tr>
<tr>
<td></td>
<td>Ice (H2O)</td>
<td>H2O</td>
</tr>
<tr>
<td></td>
<td>Ammonium carbonate (NH4·COONH3)*</td>
<td>NH3, CO2, HCN</td>
</tr>
<tr>
<td></td>
<td>Ammonia hydrate (NH3·H2O)</td>
<td>NH3</td>
</tr>
<tr>
<td></td>
<td>Hydrogen cyanide (HCN)**</td>
<td>HCN</td>
</tr>
<tr>
<td></td>
<td>Dry ice (CO2)*</td>
<td>CO2</td>
</tr>
<tr>
<td></td>
<td>Methane hydrate (CH4·7H2O)**</td>
<td>CH4</td>
</tr>
<tr>
<td></td>
<td>Carbon monoxide hydrate (CO·7H2O)**</td>
<td>CO</td>
</tr>
<tr>
<td></td>
<td>Nitrogen hydrate (N2·7H2O)**</td>
<td>N2</td>
</tr>
</tbody>
</table>

*Assumes dis-equilibrium conditions in solar nebula. Retained at lower temperatures or not at all for dis-equilibrium in a planetary subnebula.

**Assumes dis-equilibrium conditions in a planetary subnebula.

***Assumes dis-equilibrium conditions in solar nebula or planetary subnebula and also that residual H2O exists after CH4 and NH3 hydrates form.
both relatively large amounts of carbon dissolved in iron-nickel alloy and significant quantities of FeO which can oxidize the carbon to CO and CO₂. In addition, we expect N₂, ⁴⁰Ar, F₂, Cl₂ and sulfur-containing gases. The earth can capture hydrated silicates from beyond its orbit. Thus, in addition to the outgassing potentials of Venus, it has a source of water and the ability to outgas H₂ and the hydrides of C, N, P, Cl, F and S. At Mars, even greater quantities of hydrated silicates are expected with similar inferences. However, in contrast to the earth most or all of its iron-nickel alloy will be oxidized so that H₂ and the hydrides will be relatively depressed. The asteroids and Europa are expected to have their silicates almost or totally hydrated and their iron totally oxidized. Retention of carbon on these bodies would have to rely on dis-equilibrium production of involatile organic compounds from CO in the nebula perhaps by Fischer-Tropsch type reactions.

The icy bodies have the potential of evaporation of their ice in addition to the devolatilization of their rocky portions. Conclusions for carbon and nitrogen sources depend on distance from the sun in the solar nebula or distance from the planet in a planetary subnebula, and on whether equilibrium or dis-equilibrium conditions apply. For example, if Titan formed under dis-equilibrium conditions in the nebula it would have the potential to outgas only small amounts of NH₃ and CO₂ and, if it condensed below ~55 K, much larger amounts of N₂ and CO. In contrast, if it formed in a subnebula of Saturn under dis-equilibrium conditions we expect very large amounts of NH₃ and CH₄ and smaller amounts of HCN, CO and N₂ with the latter two appearing only if condensation again occurred below ~55 K.

The presence of these volatiles in condensed bodies should not of course be construed as a guarantee that these particular volatiles will outgas. A body composed of serpentine can evolve H₂O only if internal temperatures are high enough to decompose the serpentine into olivine and pyroxene. Often melting is required before any significant devolatilization can occur and the initial products of devolatilization may be chemically altered or even removed before they reach the surface.

Some possible paths for outgassing are illustrated in Fig. 4. Sublimation, evaporation, volcanism and slow upward permeation and effusion all serve to deliver volatiles into the atmosphere.
In general, mineral devolatilization at depth is followed by further reactions with gas, liquid or solid phases which can add or subtract species or change their oxidation state. We can conveniently denote the effective levels at which such reactions cease as the gas, gas-magma and gas-rock “quench levels”. These levels occur where the time scales for the appropriate chemical reactions \( \tau_{\text{chem}} \) equal the time scales for upward transport of the volatiles \( \tau_{\text{tran}} \). Different volatiles may have widely different quench levels depending on their reactivity. In general the \( \tau_{\text{chem}} \) values will decrease rapidly as the temperature increases with depth. Also the \( \tau_{\text{tran}} \) values will obviously be very much smaller when volcanism occurs than when upward permeation is the sole means of vertical progress.

Remarkably little quantitative work has been done even for the earth on the chemical kinetics of outgassing. Chemical equilibrium approaches have progressed further, but offer only a relatively crude picture of the relevant chemical paths. The most comprehensive study published to date of chemical equilibrium ideas applied to volcanism on earth is that of Gerlach and Nordlie (1975a-c). They point out the importance of gas-magma reactions in determining the elemental composition and oxidation state of the outgassed material, and of gas-gas reactions in determining the molecular composition of this material. A simple example of the sensitivity of molecular composition to merely changing the temperature is shown in Fig. 5. Here we show the chemical equilibrium composition of a gas with elemental abundances typical of terrestrial fumaroles and with a total pressure of 1 bar. If this gas were “quenched” at a temperature of 400 K, it would have for example \( \sim 10^2 \) times less \( \text{H}_2 \), \( \sim 10^4 \) times less \( \text{CO} \), and \( \sim 10^7 \) times more \( \text{CH}_4 \) than the same gas quenched at 1000 K! The importance of accurately determining \textit{a priori} the quench level is very clear. In fact, a theoretical framework which can be applied to determining quench levels does exist (Prinn and Barshay, 1977) and the kinetics of many of the important reactions have been studied in the laboratory so the task is far from being insurmountable.

Once outgassed from the interior or from incoming meteoroids, volatile species can suffer a wide variety of fates. These range from simple accumulation in the atmosphere to complex physical and chemical transformations resulting ultimately in their return to the planetary crust or to their escape from the top of the atmosphere. Some of the possibilities for the cycling of volatile elements are summarized in Fig. 4. Permanent retention in the atmosphere is not the common fate of outgassed material. Indeed, many pristine outgassed molecules may find themselves in a remarkably hostile environment characterized by dissociating ultraviolet (u.v.) radiation, temperatures either too low or too high for their

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**Fig. 5.** The chemical equilibrium composition (specifically mole fractions) of a gas at 1 bar total pressure containing elements in relative abundances typical of terrestrial fumaroles is shown as a function of the quench temperature of the gas mixture (Prinn and Barshay, unpublished work).
gaseous existence and gravitational fields too weak to prevent their permanent loss to space.

Permanent loss processes are associated with escape of atoms or ions which have been translationally excited by collisions (thermal escape), exothermic reactions, and interactions involving electromagnetic fields in polar regions (polar wind) and the solar wind. The solar wind plasma itself may also interact with the atmosphere and either be absorbed by it or erode it away. There are also important constraints on the rate at which these escape processes can proceed including thermospheric energy inputs, rates of photochemical transformations, rapidity of vertical transport, and outgassing fluxes. These ideas and their applications to various solar system bodies are reviewed by Hunten (1982).

Over the past decade considerable strides have been made in our ability to quantitatively predict atmospheric escape rates. As discussed by Hunten (1982), these advances have in turn enabled interpretation of the presently observed isotopic composition of atmospheres (e.g. the \(^{14}\)N: \(^{15}\)N and H:D ratios) in terms of the original volatile inventory and outgassing history of the planet. This has proven to be a powerful tool in studies of atmospheric evolution and will no doubt continue to be fruitful as further planetary atmospheric data are obtained.

The molecular composition of the atmosphere is partly controlled by a wide variety of \textit{in situ} chemical reactions. Most of these are driven directly or indirectly by the sun and include photochemical reactions and reactions in lightning strokes and thundershocks. One of the most intriguing questions faced by biochemists and atmospheric chemists alike is to ask whether such abiogenic chemical reactions can produce amino acids, sugars, phosphates and simple organic bases, whether conditions exist for these to condense to form polypeptides and polynucleotides, and finally whether these can in turn serve as precursors for the first self-replicating structures (i.e. living organisms). In view of the fact that the biosphere plays the major role in modulating the present atmosphere on earth, and in view of the fact that we have no evidence of life on any of the other planets, it is of paramount importance to understand the apparently profound constraints on planetary environment necessary for the evolution of life. Chang \textit{et al.} (1982) provide considerable insight into what a fascinating yet extremely difficult problem this really is.

In addition to \textit{in situ} reactions, exchange processes between the atmosphere and surface serve to further modulate molecular composition and the overall accumulation of outgassed species. These processes include gas to particle transformations, condensation, sublimation, sedimentation, rainout and dissolution. They may be reversed by evaporation or sublimation and by the recycling of sediments. The latter can be accomplished by weathering of the sediments by wind, water and chemical reactions or by subduction of the sediments into a fluid asthenosphere followed by their decomposition and reappearance in volcanic and ridge emanations. It should be emphasized that recycling rates for sediments on the various planets are expected to differ widely with important implications for the long-term survival of the less volatile atmospheric species (e.g. will nitrogen survive as \(\text{N}_2\) in the atmosphere or be removed as nitrates?).

5. PLANETARY-SPECIFIC MODELS AND INVERSE PROBLEMS

Although many aspects of the evolutionary problem are usefully considered in generalized terms, the differing physical and chemical environments on each planet dictate that they be studied individually as well as collectively. Recalling the discussion in the introduction concerning \textit{a priori} and \textit{a posteriori} approaches it is inevitable that the \textit{a posteriori} approach plays a major role in understanding the evolution of specific planetary atmospheres. In this respect it is useful to consider the evolution of each atmosphere as presenting an inverse problem with its present state, and the geological and biological relics of its earlier states contained in sedimentary records, as essential constraints on the inversion process.

Not surprisingly, the \textit{a posteriori} approach is most successful when applied to the last 3.8 billion years on Earth; that is over the life-span of the oldest known rocks. As reviewed by Holland (1982) considerable progress has been made in recent years in understanding the post-Archean history of the oceans and atmosphere including the early development of oxygen in the atmospheres. There is no doubt that living organisms have played and will continue to play a dominant role in controlling many aspects of atmospheric evolution. Whether such control has been passive or active is a topic of current debate (Lovelock and Watson, 1982). The time at which life first appeared on Earth is also controversial, and it is not inconceivable that simple prokaryotic cells may have evolved in pre-Archean times. Our lack of
geological evidence of events in the first billion years of the Earth's existence is particularly unfortunate since it was during this period that the organochemical precursors of life must presumably have evolved. Questions concerning the oxidation state of the earliest out-gassed atmosphere on Earth still remain unanswered. At best we can make inferences based on ideas about the presence or absence of metallic iron in the pre-Archean crust and on experiments delineating the degree of atmospheric reduction which is most advantageous for abiotic syntheses of the organochemical precursors.

Our knowledge of the sedimentary record is largely superficial for Mars and totally negligible for Venus. The high temperatures at the surface of Venus and the probable presence of significant subsurface reservoirs of water and carbon dioxide on Mars, make interactions between the surfaces and atmospheres of these planets of considerable importance in the evolution of their atmospheres. These topics are discussed in more detail by Khodakovsky (1982) for Venus and by Fanale et al. (1982a,b) for Mars.

The Voyager 1 mission increased enormously our knowledge of the composition and structure of Titan's atmosphere. We remain ignorant however of the precise chemical composition of its crust and interior and must presently rely on inferences gained from a priori models of its formation in the nebula to provide insight in these areas. Nevertheless, the intriguing organic reactions proceeding in Titan's atmosphere, and their possible relevance to a pre-Archean reduced atmosphere on the Earth, make its atmospheric chemistry and evolution which are discussed by Strobel (1982) of great current interest.

Meteorites have played an important role in the a posteriori approach both to condensation in the nebula and to accumulation of the planets and their atmospheres. Indeed, even the current a priori approaches to condensation processes in the nebula implicitly begin with the assumption that the Type 1 carbonaceous chondrites contain the less volatile elements with relative abundances typical of the primitive solar nebula. Pseudo-homogeneous accretion models have been proposed in which the terrestrial planets are formed exclusively from carbonaceous or ordinary chondritic material followed by massive escape of volatiles (Ringwood, 1966). Distinctly heterogeneous accretion models have also been proposed in which an achondritic volatile-poor bulk planet receives a late-infalling surface veneer of volatile-rich carbonaceous chondritic material (Turekian and Clark, 1975; Anders and Owen, 1977). Such approaches are instructive to the extent that the meteorites which have fallen on the Earth are truly representative of the bulk of the material from which the planets formed.

Collisions with the terrestrial planets of asteroids and comets well after their initial formation are also expected to influence atmospheric evolution both through the volatiles which they contribute to the planet and through the physical and chemical consequences of the impacts themselves (shock waves, surface pulverization and melting, etc.). Indeed, there are recent suggestions that such a collision may have been responsible for the remarkable events apparent at the boundary of the Cretaceous and Tertiary eras including the extinction of many species of life (Alvarez et al., 1980).

6. CONCLUDING REMARKS

Our current perspective emphasizes that atmospheres when viewed at any one time in their history are entities in only approximate balance between volatile sources and sinks. Over geologic and sometimes shorter time scales they have chemically evolved due to specific imbalances between these sources and sinks. These imbalances may be due to sudden or sporadic events (e.g. cometary and asteroidal impacts, explosive volcanic eruptions, origin of life and anthropic combustion of fossil fuel) or to chronic phenomena (solar evolution, weathering, atmospheric photochemical reactions, atmospheric escape, metabolic evolution and ionospheric convection). Chemical evolution of atmospheres is also connected perhaps very intimately with the climatic changes which have occurred on Earth and also, with some probability, on other planets (Pollack, 1979).

The study of the source-sink imbalances and their causes and effects in planetary atmospheres must play a central role in the future development of the subject of atmospheric evolution. This study is inherently interdisciplinary and demands the differing approaches of several branches of the Earth sciences, biology, physics and chemistry. This paper and the ones which follow will hopefully serve as an incentive to those presently unfamiliar with the subject to apply their wits to the problem, in addition to providing a useful review of the state of this art for the experts in the field.
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