2 Provenance and Cosmochemistry

In this chapter, we consider the relationship between the composition of a planet and the origin of the material from which it was made. Since this is not a book about planet formation, there is no intent here to be comprehensive; it is merely enough background so that one can appreciate the link between these different subjects.

2.1 How should we think about a Planet?

If you wanted to understand the taste of an apple or the merits of a particular wine vintage, you would surely take at least two approaches: One is to consider the biochemical processes that make an apple or a grape distinctive and cause it to develop in a particular way—in living things, this is the genetic code; the other is to consider provenance—the character of the apple or the grapes depends on the soil in which the plant grew, the climate, the particular vagaries of the seasonal weather, the tender loving care provided, and perhaps even whether the plant grew on a sun-facing slope. In many ways, this is akin to the argument in the social sciences about what determines the type of a person that a child grows up to become. The main factors can be divided into nature, the child’s genetic makeup, and nurture, how the child is raised by her parents or society. In a similar way, we should think about the two aspects of a planet: The planet as an engine, processes that operate within and change the materials from the form in which they were delivered; and the cosmic provenance of the planet, the material it was built from and how these are determined by the location and conditions where the planet formed. Unlike living things, the planetary engine is not genetically determined, but it is nonetheless strongly constrained by the laws of physics and chemistry. The most striking lesson we have learned from planetary exploration is that a remarkably wide range of outcomes and behaviors is possible, and recent exoplanet discoveries provide strong confirmation of this picture of diversity.

2.2 What are Planets made of?

The best way to answer this question is to “ask the planet,” which means deducing planetary composition from its observed properties. In practice, this often does not work that well even for Earth. So far as we know, there are no rocks at Earth’s surface that were delivered from Earth’s core (and maybe not even any that were delivered from the core-mantle boundary, though claims have been made). Consequently, we do not have direct observational evidence that Earth’s core is mostly iron; it could be an alloy of niobium (which can have similar density, compression properties, and electrical conductivity—indeed all of the properties attributed to Earth’s core by remote sensing). To make the argument that Earth’s core is mostly iron, we must appeal, at least in part, to cosmochemical arguments like “What is abundant as a planet forming material?” These arguments are necessarily plausible rather than rigorous, but they still make a strong case due to the large differences in cosmic abundance among materials of similar chemistry. Cosmic abundances of elements are determined by nuclear physics. Hydrogen overwhelmingly dominates because it is an elementary particle; helium is also abundant because it is stable and can be formed in the Big Bang era. Heavier elements (what
astronomers call “metals”) are formed in stars and then ejected into the interstellar medium, where the material then becomes available to form solar systems. Combinations of alpha particles, multiples of 4 mass units with proton number equal to neutron number, are very favorable at low mass; oxygen, formed by combining four alphas, is especially favorable because of its nuclear shell structure. So oxygen is the next most abundant element followed closely by carbon. Neon (five alphas) and nitrogen (not a combination of alphas) follow somewhat behind. It is more complicated as one goes to larger masses, but magnesium, silicon and iron are particularly favored by nuclear physics. Iron is the “endpoint” of equilibrium nucleosynthesis in the sense that all more massive nuclei are less stable.

Cosmic abundances can be estimated by observations of the interstellar medium and other stars. However, they are not spatially uniform because of differences in stellar activity from place to place. These abundances are continuously evolving in response to both ongoing thermonuclear synthesis and the sudden recycling of material back into the interstellar medium after a star dies; since both of these processes occur at different rates depending on the local environment, abundances themselves evolve in both space and time. This means that planets forming around other stars could have significantly different properties, even though the fundamental classes of materials (discussed in the next chapter) are surely universal.

Solar system abundances are determined from the solar photosphere and correlate well with the relative abundances measured in meteorites, except for the most volatile elements. Accordingly, the ratio of hydrogen to silicon is enormously different in the Sun from the value in a meteorite or in Earth, but the ratio of Ca to Al, say, is very similar between the Sun and a meteorite. This comparison is not easy to do at high precision for many reasons, most of all that meteorites vary from one class of meteorite to another (though often only by small amounts), and determination of solar abundances from spectroscopy is not straightforward (and still debated for some important ratios, e.g., C/O, Ne/H).

Meteorites are not truly primitive; they consist of materials that have been processed in some way. This processing is sometimes “planetary” in character. For example, iron meteorites are created when the parent body is large enough to have formed a core, separating its silicate and metallic iron components. Sometimes the processing involves loss of volatiles or irradiation by cosmic rays. The most primitive rocks delivered to us from space are called Type One Carbonaceous Chondrites (written CI chondrites). It is popular to suppose that meteorites provide a guide to materials in the nebula from which the solid planets formed, at least inward of the asteroid belt. It is important to understand, however, that this is really little more than a hypothesis, but it is one that has proven to have substantial explanatory power.

Of course, elemental abundances do not tell you all you want to know; one also needs to know the chemical form that the materials take. Here is a summary list, useful for understanding the most abundant elements:
Table 2.1: Solar System Abundances

<table>
<thead>
<tr>
<th>Element</th>
<th>Number Fraction</th>
<th>Mass Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.92</td>
<td>0.71</td>
</tr>
<tr>
<td>He</td>
<td>0.08</td>
<td>0.27</td>
</tr>
<tr>
<td>O</td>
<td>7 x 10^-4</td>
<td>0.011</td>
</tr>
<tr>
<td>C</td>
<td>4 x 10^-4</td>
<td>0.005</td>
</tr>
<tr>
<td>Ne</td>
<td>1.2 x 10^-4</td>
<td>0.002</td>
</tr>
<tr>
<td>N</td>
<td>1 x 10^-4</td>
<td>0.0015</td>
</tr>
<tr>
<td>Mg</td>
<td>4 x 10^-5</td>
<td>0.001</td>
</tr>
<tr>
<td>Si</td>
<td>4 x 10^-5</td>
<td>0.0011</td>
</tr>
<tr>
<td>Fe</td>
<td>3 x 10^-5</td>
<td>0.0016</td>
</tr>
<tr>
<td>S</td>
<td>1.65 x 10^-5</td>
<td>0.0004</td>
</tr>
<tr>
<td>Ar</td>
<td>5 x 10^-6</td>
<td>1.5 x 10^-4</td>
</tr>
<tr>
<td>Al</td>
<td>4 x 10^-6</td>
<td>1.2 x 10^-4</td>
</tr>
<tr>
<td>Ca</td>
<td>3 x 10^-6</td>
<td>1.2 x 10^-4</td>
</tr>
</tbody>
</table>

There are some indications of solar system composition that arise from looking at comets or looking at the interstellar medium, but these are never as reliable as those obtainable from actual rock samples. It is always better to have a sample in hand (in the lab), than to infer composition remotely through spectroscopy. Material from the interstellar medium may survive partly unaltered in comets and more distant planets. This kind of inference is quite imprecise (even aside from uncertainty of survival). There are interstellar and interplanetary dust particles whose compositions have been examined in detail in the lab but these are not necessarily representative because they have lost their volatile component. The Stardust mission gives us some idea of how representative these materials may be and the Genesis mission has told us about isotopic ratios (especially the differences and similarities between the Sun and planetary materials).

2.3 What is the Connection between Planetary Materials and Our Ideas of Solar System Origin?

An important but wrong idea in this field is the “minimal mass solar nebula equilibrium condensation model”. Wrong ideas play an important role in science. There is nothing bad about discussing a wrong idea provided you understand that it is wrong: It forms a benchmark from which you can progress to a more precise understanding.

2.3.1 Minimal Mass Solar Nebula and Equilibrium Condensation

The idea is this: Planets formed from a solar nebula, a disk of gas and dust in approximately Keplerian orbit around the newly forming Sun. The disk contains an amount of material sufficient to explain the planets. This disk is assumed to be of solar composition. In the terrestrial planetary zone, you need enough material to provide several Earth masses of rock. This suggests a total mass in that region of order a thousand Earth masses, since “rock” is several hundred times less abundant than hydrogen by mass. In the outer solar system, the giant planets are not of solar composition and one
needs as much as an order of magnitude more mass of solar composition than the combined mass of the planets in order to explain their heavy element component. This argument, discussed in more detail in subsequent chapters, suggests a “minimal nebula” (defined as the minimal amount of solar composition material needed to form the observed planets) of maybe ~ ten thousand Earth masses, or at least 3% of the mass of the Sun.

Let’s take this total mass and distribute it as a disk that has surface density (mass per unit area) $\Sigma(r)$, where $r$ is distance from the Sun. This surface density must fall off with distance from the sun, though in a way that is not well understood. We suppose that

$$\Sigma(r) \sim (3000 \text{ g/cm}^2) \left( \frac{\text{1AU}}{r} \right)^{1.5}, \quad 0 < r < 40\text{AU}$$

(2.1)

where 1AU = $1.5 \times 10^{13}$ cm is the Earth-Sun distance and the pre-factor is chosen so that the integrated mass of the disk is $6 \times 10^{31}$ g = 0.03 solar masses. The power law is somewhat arbitrary, but very roughly represents the observed mass distribution of the planets. We further suppose that the temperature distribution, given that it must also fall off with distance, at some typical epoch is

$$T(r) = 700 \left( \frac{\text{1AU}}{r} \right)$$

(2.2)

This is designed to give rocks condensing at small $r$, and water ice at a few AU and beyond. (Precise numbers are not important for the purposes of illustrating the general character of the model).

### Figure 2.1

At each radius, the local pressure must balance the weight of the disk and thus

$$P(r) \sim \Sigma(r) g_{\text{disk}}(r),$$

where $g_{\text{disk}}$ is the local gravitational acceleration perpendicular to the disk. Unless the disk is very massive, $g_{\text{disk}}$ is simply the small component of central gravity that is directed to the disk midplane. We can thus write,

$$g_{\text{disk}} = g \sin \theta = \frac{GM}{r^2} \sin \theta \approx \frac{GM}{r^2} \left( \frac{H}{r} \right)$$

(2.3)

where $H$ is a typical height above the disk, $\theta$ is the angle above the midplane, and we can approximate $\sin \theta \approx \tan \theta \approx H/r$, since $H/r << 1$. We know that the disk is pressure supported, and thus we can equate the pressure due to the weight of the disk (at the midplane) to the thermal pressure using the ideal gas equation $P = \rho k_B T / \mu = g_{\text{disk}} \Sigma(r)$. 

We can simplify this equation by realizing that the volume density is roughly related to surface density by \( \rho(r) \sim \Sigma(r)/H(r) \). Thus we can write

\[
P = \frac{\Sigma(r)}{H(r)} \frac{k_B T(r)}{\mu} = \frac{GM}{r^2} \left( \frac{H}{r} \right) \Sigma(r)
\]

where \( \mu \) is the mean molecular weight (dominated by molecular hydrogen). This equation can then be simplified to solve for the disk dimensions, which using the simple temperature law above results in a disk with \( H/r \sim 0.1 \). (Note that we have chosen the temperature law’s exact dependence on radius to simplify this approximate calculation. In more careful calculations, the disk can be flared with \( H/r \) depending on \( r \) rather than constant.) We can then substitute this back into the pressure and density equations to find

\[
\rho(r) \sim 3 \times 10^{-9} \left( \frac{1 \text{AU}}{r} \right)^{2.5} \text{g/cm}^3
\]

\[
P(r) \sim 100 \left( \frac{1 \text{AU}}{r} \right)^{3.5} \text{dyn/cm}^2
\]

For comparison, atmospheric pressure on Earth is \( \sim 10^6 \) dynes/cm\(^2\). Notice that disk pressures and densities are much lower than everyday experience with Earth or indeed most planetary atmospheres.

**Figure 2.2**

We can now extend this model using the idea of equilibrium condensation, which states that you can figure out the materials that should exist at each radius by knowing the temperature and pressure at that radius. You may recall from basic chemistry that any component of a mixed gas will condense once the partial pressure for that component
exceeds the vapor pressure, i.e. when $P_{\text{partial}} = fP > P_{\text{vapor}}$, where $f$ is the number fraction of the component and $P$ is the total pressure. For example, water will condense at all radii external to where $10^{-3} P(r) > P_{\text{vapor}}$, since water comprises about $10^{-3}$ of the molecules. This “snowline” is at about 4.2 AU (in the model described here) because the vapor pressure of water at $700/4.2 = 165$K is roughly $5 \times 10^{-4}$ dyn/cm$^2$ $\sim (10^{-3})(100)/(4.2)^{3.5}$.

The game of “equilibrium condensation sequences” postulates a static disk environment that cools from an initial hot state. As it cools, materials condense out in accordance with equilibrium thermodynamics. The game proceeds as follows: Take your expected elemental abundance and specify a temperature and pressure. Take the set of molecules and condensed phases that minimizes Gibbs energy. In the terrestrial zone, this requires consideration of many different possible mineral assemblages.

![Figure IV.26](Taken from J. Lewis; “Physics and Chemistry of the Solar System”.)
This can be done for gradually decreasing temperature to see what condenses out. It can be done for rock and also for ice. Simplistically, one could imagine using this as a guide to the composition of planets.

2.3.2 Why should you not believe equilibrium condensation stories?

There are at least six pitfalls:

(i) The model is based on a “static picture” of the nebula. In reality, it evolves with time, not merely by changing temperature but by redistributing mass. Solids do not have to follow gases with the result that solar abundance is not necessarily a good guide to the local composition except, perhaps, in respect of the relative abundances of materials of similar volatility.

(ii) Equilibrium thermodynamics may be irrelevant. This is certainly so at low temperatures (the reactions don’t “go” because they are kinetically inhibited). For example, methane is the preferred carrier of carbon at low temperature and high relative hydrogen abundance but the reaction $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ has negligible rate at low $T$ and low density. As a result, CO entering from the interstellar medium may stay in that form.

(iii) Even when equilibrium is possible in principle, it may not proceed in practice. For example, suppose I accumulate a large chunk of metallic iron that condenses at high $T$. Thermodynamics tells me that it wants to become oxidized as I lower the temperature. But this requires that the oxygen (as water or CO) have access to the inside of my iron body. It might instead merely rust the outer surface. This is another form of kinetic inhibition, though in this case it is the kinetics of diffusion rather than the kinetics of reaction rate that prevents equilibration.

(iv) Materials in a given zone of condensation need not necessarily be used at that location to make a planet; mixing of materials may occur... this depends on (imperfectly understood) aspects of the planetary formation process. [As an example of this, see the simulations of John Chambers, Making more terrestrial planets, Icarus, 152, 205(2001).]

(v) Other chemistry may take place in the solid body precursors (“meteorite parent bodies”) that alters the planet makeup. For example, water-rock reactions may take place on even quite small bodies. The equilibrium condensation story predicts that you can never have liquid water as a condensate (it is always either ice or vapor).

(vi) There might even be “physical sorting” (i.e. some material may survive more readily in the planet accumulation process, depending on how easily they are busted up in collision or lost by evaporation). Of course, this will only change the average planetary composition if some material is completely lost (into the Sun; or out back to the interstellar medium). A proposed example of this is the high iron content of Mercury.

In any event, the speciation inside the planet will be at least partly determined by the chemistry inside of the planet, regardless of the details of the materials used to build the planet.


2.3.3 **Are there Examples Where the Nature of the Source Material had Major consequences for Planetary Structure?**

The most obvious example is the “snow line” effect: We see no bodies with a lot of water ice inward of 5 AU (except maybe Ceres) while water ice is as abundant or more abundant as rock for most bodies at Jupiter orbit or beyond. Before we knew about exoplanets, this was naturally explained as a consequence of formation conditions, especially the decline in temperature with distance. Now that we see many close in exoplanets that are Jupiter-like, we are more cautious. We say instead that these planets formed far out and then migrated inwards to their current locations. (Since this is not a text about planetary dynamics, we will not make the effort here to give details on how this migration arises, but it is possible because of angular momentum transfer between the forming planet and the disk in which it is embedded.) You will sometimes see the statement that ice formation is “needed” to make the core of a giant planet but this claim is questionable. It is true however that giant planet formation is more difficult at higher temperatures, since this may make accretion of gas more difficult. It is also likely that you need more mass in the giant planet zone than in the terrestrial planet zone; the surface density given above (eq 2.1) has this property.

A major difference in planetary composition can arise in a system where C/O exceeds unity. (In our solar system it is below unity). In that case, some C may condense directly (as graphite or as a carbide or be compressed to diamond).

One possible, though controversial, connection between source material properties and the resulting planet composition is the ratio of magnesium to silicon in terrestrial bodies. According to elemental abundances, \( \text{Mg}/\text{Si} = 1.07 \). This is closer to pyroxene composition (e.g. MgSiO\(_3\)) than olivine. Yet we think Earth’s upper mantle (and perhaps entire mantle) is more predominantly olivine composition (Mg\(_2\)SiO\(_4\)), which has a higher Mg/Si ratio. Maybe something happened during planet formation that decreased Si relative to Mg (e.g. partial evaporation?) Or maybe there is Si in earth’s core? In any event, you would seek to understand the connection between Earth’s Mg/Si and what we see in space.

2.3.4 **Are there Examples of where the Nature of the Source Material is Not Preserved in the Planetary Structure?**

A likely example is the behavior of carbon. Oxygen may have accreted onto Jupiter as both H\(_2\)O and CO. But CO is not stable (relative to CH\(_4\)) deep in Jupiter’s atmosphere, so the form that O takes in this planet does not depend on the form in which it arrived. (The total amount of water might then be determined by the amount that arrives as ice plus the amount obtained by conversion of CO.

Another possible example is the behavior of water ice. At sufficiently low temperature, water ice may accrete onto icy satellites in amorphous form but it will revert to crystalline form under the action of both heating and pressure inside the body. Ice is generally observed (spectroscopically) to be in crystalline form, even for small bodies in the Kuiper belt (e.g. Quaoar). The reasons for this are not understood.
Ch. 2 Problems

2.1) Ganymede and Io are believed to have Fe-S cores. (The notation “Fe-S” means an alloy of Fe and S; you can think of it as an intimate mixture of Fe and FeS in variable proportions). Assume the core contains no oxidized iron. Estimate the mass and composition of these cores by carrying out the following cosmochemical reasoning (which is called a mass balance argument): These bodies formed from relatively low temperature assemblages in which all the Fe was either in the form Fe$_3$O$_4$ (magnetite) or FeS. (The assumption of magnetite is a simplification of a more complicated reality). Assume all the cosmic abundance of sulfur is tied up in FeS. Using the solar system abundance tables you can determine how much of the remaining Fe is in the form of Fe$_3$O$_4$. (Remember that O is copiously abundant so you never have to worry about having sufficient oxygen in these kinds of calculations.) Now suppose that the mass of reduced carbon (think of it as elemental carbon) in the satellite building material is 10% the mass of iron. (By “iron” I mean of course iron in all chemical forms.) For comparison, there is a famous CI meteorite, called Orgueil, that has about~ 20% carbon relative to iron by mass. Assume this carbon is available to reduce the magnetite. [Assume Fe$_3$O$_4$ + 2C → 3Fe +2CO$_2$ inside these bodies once they form. Incidentally, these satellites show some evidence for the presence of carbon dioxide. Will your result change if you assume instead Fe$_3$O$_4$ + 4C → 3Fe +4CO?

The mass of Io is 8.93 x 10$^{26}$ g. Assume Io has cosmic Mg/Fe ratio and the non-core part of Io is MgSiO$_3$. Your answer for Io will be applicable also to Ganymede because Galileo data tell us that Ganymede minus all its water ice is identical to Io in mass and mean density and moment of inertia.

Answer: From abundances, the number of sulfur atoms relative to iron atoms is 0.55, so only 0.45 of the Fe atoms are available to form Fe$_3$O$_4$. The mass of reduced carbon is 0.1 of the iron mass so the number of reduced carbon atoms is about 0.5 the number of iron atoms. In the reduction reaction, we need only 2 carbon atoms to reduce 3 Fe atoms. Therefore we have an excess of the required number and Io will consist only of Fe(metal), FeS and MgSiO$_3$. The ratio of the mass of the mantle to the mass of the core is easily computed from the ratio of magnesium atoms to total iron atoms (~1.2) and the result is about 1.6. Accordingly, the Io core mass is around 3.5 x 10$^{26}$ g. If we had assumed the second proposed reaction then some un-reduced (oxidized) iron will remain in the mantle and the core will be smaller. (This is actually quite likely).

2.2) Equation 2.2 for the temperature is offered without any physical justification. Neither the absolute value nor the radial dependence is obvious and will depend on the physical process responsible for determining the temperature. But one way to get a feeling for the possible temperature is to suppose that the disk is radiating like a black body at some temperature $T_d$ and from a total area $2\pi R_d^2$ where $R_d$ is the disk radius. Assuming the energy available is that provided by material falling from infinity to a typical radius ~0.5$R_d$, find an estimate for $T_d$ in terms of the typical formation time $\tau$ for a solar mass and estimate the actual
value for \(R_d=10\text{AU}, \tau=10^6\text{ years}\). (This is only intended to give you a sense of numbers in the earliest phase. Subsequently there is much more energy available form the luminosity of the newly forming sun or the energy released as the disk evolves.

2.3) What is the predicted ice/rock mass ratio and mean density of small, cold bodies that form for the following four cases: (a) All carbon is in the form of \(\text{CH}_4\) and methane condenses; (b) As in (a) but methane does not condense; (c) All carbon is in the form of \(\text{CO}\) and condenses; (d) As in (c) but with the \(\text{CO}\) not condensing.

“Small” means you can ignore the effects of pressure.

Assume “ice” = \(\text{H}_2\text{O} + \text{condensed methane} + \text{condensed CO}\).

Assume anhydrous rock. Use the simple abundances table I gave you. Assume that to an adequate approximation the cosmic abundance of \(\text{O}\) is locked up either in \(\text{H}_2\text{O}\) or \(\text{CO}\) (i.e., very little is in the rock, even though oxygen is the most abundant element in rock! Make sure you understand why this is so and explain it in words. The other alternative for \(\text{O}\) is \(\text{CO}_2\) but I’m asking you to ignore that. You can certainly exclude \(\text{O}_2\) because it is thermodynamically and kinetically ridiculous. I’m also asking you to ignore the fact that some \(\text{C}\) is not in a volatile phase at all.

Assume “rock” density =3.6 g/cm\(^3\). (It’s higher than Earth mantle because all the iron is included.) Assume this rock is anhydrous and contains the entire cosmic abundances of Mg, Si and Fe, and with about 3 oxygens per Mg. Water ice density =0.92 g/cm\(^3\); methane ice density =0.6 g/cm\(^3\); CO ice density = 1.1 g/cm\(^3\). (These numbers are only roughly right.)

[Case (b) is thought to correspond roughly to Ganymede, etc. Of course you won’t get the correct density for Ganymede since pressure is important in that body. Case (d) is thought to correspond to Triton and Pluto. We don’t know of any objects in category (a) or (c). Incidentally, we don’t know the C/O ratio with sufficient precision to really do this right. In other words, the table I gave you may not be quite right.]

2.4) The Galilean satellite system is sometimes thought of as a “miniature” solar system. Construct the equivalent of the minimum mass solar nebula for the Galilean satellites by finding the equations equivalent to 2.1-2.5. Use Jupiter’s radius (not 1 AU) as the natural lengthscale. Assume the disk extends out to 30 Jupiter radii; use the same power law exponents as for the solar nebula and assume that the value of \(T\) is \(\sim 250\text{K}\) at 10 Jupiter radii (in order to explain why Io and Europa must have mostly formed inside Jupiter’s “snow line”). Notice I used 250K rather than 170K (the solar nebula snowline number). Why? You will not be able to answer this until after you have constructed the model for pressure and density. Useful information: The total satellite mass (Io+Europa+Ganymede+ Callisto) is \(\sim 4\times 10^{26}\) g and about 2/3 of this is rock. Jupiter radius is \(7 \times 10^9\text{cm}\), surface gravity is \(\sim 2500\text{cm/s}^2\). Table 2.1 tells you that you need roughly 100 times more gas than rock by mass.[As with the solar
nebula, this is not thought to be what actually happened but it is a useful benchmark.