Compositional Relationships Between Meteorites and Terrestrial Planets

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Terrestrial planets exhibit a range of core sizes, mantle, and surficial magma compositions. Determining the bulk compositions of terrestrial planets presents a challenge faced by geochemistry and cosmochemistry. Traditionally, chondritic meteorites have been called upon as suitable bulk compositions. Detailed examination of such building blocks, however, frequently results in a problem for any specific meteorite type. In this contribution, we examine whether the terrestrial planets can be made from (1) known meteorite types; (2) familiar types that have been transformed at higher pressures, temperatures, or different $f_{\text{H}_2}$ or $f_{\text{O}_2}$; or (3) from materials no longer falling to Earth because they have all been swept up in the accretion process. Bulk properties such as Mg-Si-Al, D/H ratios, O, Cr, and Os isotopes, and noble gases provide constraints on the bulk composition. The bulk compositions of Mars and asteroid 4 Vesta can be explained by mixtures of known meteorite types. However, the idea is entertained that Earth and perhaps other terrestrial planets are not made from familiar meteorite types, but instead from a material that is not currently represented in our collection. Our limited understanding of terrestrial planet formation and origin is due primarily to the restriction of samples to Earth and Moon, Mars, and some asteroids. Sample return missions such as Genesis will greatly enhance our understanding of planet formation, as would samples returned from Mercury and Venus.

1. INTRODUCTION

In order to elucidate compositional relationships between meteorites and terrestrial planets, it is necessary to identify the mechanisms by which, and the materials from which, the planets accreted and differentiated into their cores, mantles, crusts, oceans, and atmospheres. The problem we face is that we sample planets approximately 4.5 G.y. after they formed. Rocks have been subjected to various differentiation processes, and we need to find a way to “see through” 4.5 G.y. of solar system history. Fortunately, nature has provided us with appropriate samples of some terrestrial objects.

For Earth we have lavas, typically basanites or kimberlites, that transport samples of the mantle to the surface for our study. Mantle nodules and unaltered basanites are particularly useful for deducing the state of the silicate Earth immediately after primordial differentiation into metallic core and silicate mantle. For the Moon, we have mare basalts and feldspathic highland rocks, but no samples of the lunar mantle. For Mars we have martian meteorites and Mars Pathfinder and Spirit and Opportunity in situ analyses of martian rocks but, again, no mantle samples. We have samples of primitive and differentiated meteorites. Unfortunately, we have no samples of Mercury or Venus delivered as meteorites. For Mercury, we must make do with remote sensing measurements of composition (Strom, 1997) and gross geophysical measurements of density. For Venus we must rely on chemical analyses from the Soviet Venera and Vega spacecraft.

Evidence for dependence of composition upon heliocentric distance comes from consideration of metallic core masses of terrestrial planets, along with their mantle FeO content (Fig. 1). Mercury has a very large metallic core, but only a small amount of FeO in its mantle based on spectroscopic measurements (e.g., Emery et al., 1998; Solomon, 2003). Earth and Venus have intermediate core sizes and mantle FeO contents. And Mars has the smallest core of the terrestrial planets, and is thought to have the highest mantle FeO content (e.g., Longhi et al., 1992; Bertka and Fei, 1998a,b). Estimates of the core size in asteroid 4 Vesta [based on HED meteorites (e.g., Righter and Drake, 1997b; Ruzicka et al., 1997)] have converged on values between 10 and 20 mass%, and mantle FeO contents as high as 25 wt% (Fig. 1). Other elements and all but one (Cr) isotopic compositions do not vary systematically with distance from the Sun (e.g., Palme, 2000; Scott and Newsom, 1989; Taylor, 1991), and such fundamental observations must be explained by any model for making terrestrial planets.
There are three approaches that have been adopted for considering the bulk compositions of terrestrial planets. The formation of the Earth has been debated in terms of heterogeneous vs. homogeneous accretion, and both of these fall into the first class of model that terrestrial planets are made of extant meteoritic material that originated in the asteroid belt. Early theories favored homogeneous accretion of Earth, from materials that are represented in our meteorite collections (e.g., Ringwood, 1961). Heterogeneous accretion envisions the material accreting to Earth changing in composition and oxidation state with time. Eucken (1944) first proposed this idea, and later work of Wood (1962), Larimer and Anders (1967), and Cameron (1962) was all consistent with the existence of temperature and compositional gradients imposed by conditions in the early solar system (Turekian and Clark, 1969). Heterogeneous accretion was subsequently modeled in detail by later workers such as Wänke (1981), Newsom and Sims (1991), and O’Neill (1991). For example, driven by the “stairstep” abundance pattern of siderophile (metal-seeking) elements in the terrestrial upper mantle (Fig. 2), Wänke (1981) suggested that the first 80–90% of Earth accreted from very reducing materials. All elements except the refractory lithophile elements such as Sc and the rare earth elements (REE) (Fig. 2) would be quantitatively extracted into the core, and the mantle would be devoid of Fe2+. The next roughly 20–10% of material accreting to Earth would be more oxidizing, and all but the highly siderophile elements (Ir, Os, Au, etc.) would remain stranded in the mantle. The highly siderophile elements were again quantitatively extracted into the core. The last roughly 1% added [the so-called “late veneer” (Chou, 1978)] was so oxidizing that metallic Fe did not exist. The “stairstep” pattern of siderophile elements in Fig. 2 is thus explained.

A second class of model has been devised since the 1990s in light of developments in high-temperature and high-pressure experimental data and dynamical and planetary accretion modeling. The realization that high temperatures (>3000 K) are possible during planetary growth stages is a result of the giant impact theory for the origin of the Moon (Hartmann and Davis, 1975; Cameron and Ward, 1976), and its most recent version (Canup and Asphaug, 2001; Cameron, 2000). In addition, there is general agreement (e.g., Drake, 2000; Walter et al., 2000; Rubie et al., 2003; Wade and Wood, 2005) that Earth developed one or more magma oceans late in its accretion, effectively homogenizing any preexisting material. The bulk geochronal properties of Earth were likely established by magmatic processes in a high-pressure and high-temperature magma ocean environment (see solid symbols in Fig. 2). This second class of model allows for the possibility that Earth is made of known meteorites that have been chemically transformed by high temperature and pressure during growth.

A third class of model holds that terrestrial planets are not made of materials known in our meteorite collections, but rather swept-up material available in the region of the inner solar system in which they formed. Wetherill’s (1975) pioneering dynamical work indicated that, at any stage during the growth of a planet, the largest objects accreting to it were one-tenth to one-third of the mass of the growing planet (e.g., Wetherill, 1975). The modern view is that
“feeding zones” for planets are relatively narrow, with only late-stage accretion sampling material from significant distances (e.g., Chambers, 2001; Drake and Righter, 2002). Thus, chemical and isotopic reservoirs should have been preserved in some form as a function of heliocentric distance, and it is unlikely that any planet was made primarily from material currently existing in the asteroid belt.

In this paper we review these three approaches to terrestrial planet formation: known building blocks, known but transformed building blocks, and unknown building blocks. Where necessary, we review aspects of the meteoritic materials that are potential building blocks for terrestrial planets, the processes that were operating in the early solar nebula, and accretion processes (planetesimal formation and giant impacts). We also review the relative effects of such processes that can transform such materials (temperature, \( f_\text{O}_2 \), pressure, and water content) as planets start to grow. Finally, we illustrate gaps in understanding and sampling, and show that an understanding of the volatile contents of terrestrial planets depends upon all these processes.

2. MATERIALS AND CONDITIONS IN THE EARLY SOLAR SYSTEM

2.1. Chondrites and Their Properties

To understand how the terrestrial planets may be related to the chondrites requires considerable insights into the processes that made the components in chondrites and accreted the chondritic components into planetesimals, as well as how planetesimals evolved into planets and asteroids.

2.1.1. Chondrite groups and chondritic components. Fifteen groups of chondrites are defined primarily by their bulk chemical compositions (Figs. 3 and 4), although secondary parameters such as bulk O-isotopic compositions, chondrule size and abundance, and mineralogy are also useful (Table 1). The redox state of Fe is a fundamental variable in the chondrite groups with the two extremes defined by reduced enstatite chondrites containing FeO-free silicates and Fe metal, and oxidized carbonaceous chondrites containing very little metal and FeO-rich silicates (Table 1,

Fig. 3. Compositional variation in carbonaceous chondrites (top diagrams) and ordinary, enstatite, R, and K chondrites (bottom diagrams) for the lithophile elements (left diagrams) and siderophile and chalcophile elements (right diagrams). Note the close correspondence of most chondritic materials for the lithophile elements, with the greatest disparity being for volatile elements such as Mn, Na, and K. Figure after Krot et al. (2003).
There are four major constituents of chondrites — chondrules, refractory inclusions, metal, and matrix. Chondrules are millimeter- to centimeter-sized largely spherical objects composed primarily of ferromagnesian silicates that were wholly or partly molten in the solar nebula (or protoplanetary disk) and cooled in minutes to hours (e.g., Zanda, 2004). They commonly contain grains of metallic Fe,Ni and, in most but not all groups, troilite. The refractory inclusions, which account for <0.1–10 vol% of the chondrite groups, formed entirely from minerals that were stable above 1400 K in the solar nebula, assuming canonical pressures of 10⁻³–10⁻⁴ bar. Two varieties are recognized: Ca-Al-rich inclusions (CAIs), which are composed entirely of refractory Ca-Al-Ti minerals and may be rimmed by forsterite grains, and amoeboid-olivine aggregates (AOAs), which are mixtures of fine-grained forsterite and Ca-Al-Ti minerals (MacPherson, 2003). The fine-grained and irregularly shaped refractory inclusions probably formed from grains that condensed in the solar nebula, and include so-called “fluffy” type A CAIs and AOAs. Coarse-grained CAIs with igneous textures and spheroidal shapes are probably melted condensates that cooled during crystallization at rates comparable to those of chondrules.

Matrix material is a mixture of grains with sizes of 10 nm to ~5 μm that coated the chondrules and refractory inclusions before they accreted (see Scott and Krot, 2005a). The bulk composition of matrix is approximately CI-like, but the components are derived from diverse locations in the disk and include ~10–50 ppm of presolar silicates and oxides. Because fine-grained material was readily altered in asteroids, only type 3–4 chondrites appear to contain mostly unaltered matrix material and high concentrations of presolar silicates (Brearley, 1993; Greshake, 1997; Nguyen and Zinner, 2004; Kobayashi et al., 2005). Hydrated silicates and Fe-rich olivine, which were once thought to be nebula products, are rare in the least-altered chondrite matrices. These matrices contain instead crystalline Mg-rich silicates, amorphous Fe-rich silicates, plus grains of metallic Fe,Ni, sulfides, and refractory oxides. The minerals in pristine chondrite matrices are surprisingly similar to those in the chondritic, anhydrous interplanetary dust particles (IDPs), which are thought to come from comets, although the latter contain 10x higher concentrations of C and presolar grains (Bradley, 2003). (Hydrated, chondritic IDPs are thought to come from asteroids, but some chondritic IDPs contain both anhydrous and hydrated minerals.) Thus the nebular silicate dust that accreted at 2.5 AU was not fundamentally different from the silicate dust at 5–10 AU, and probably also resembled the dust that accreted inside 2 AU.

The major constraints on the time and location of chondrule, CAI, and matrix grain formation come from isotopic data, especially radiometric ages and O-isotopic compositions, that has been reviewed elsewhere (e.g., Scott and Krot, 2005b).

2.1.2. Chondrite parent bodies. Chondrites come from diverse parent bodies, and evidence from cosmic-ray exposure ages and chondrite breccias suggest that each group is probably derived from one or a few asteroids (see Scott and Krot, 2003). The major clues to the formation locations of the chondrites are those derived from inferred relationships between asteroids and chondrite parent bodies. Carbonaceous chondrites are probably derived from C-type asteroids that are dominant in the belt beyond 2.5 AU (Bell...
TABLE 1. Characteristic properties of the chondrite groups.

<table>
<thead>
<tr>
<th>Group</th>
<th>Type</th>
<th>Refractory Inclusions (vol%)</th>
<th>Chondrites Average Diameter (mm)</th>
<th>Fe,Ni Metal (vol%)</th>
<th>Matrix Frequency (vol%)</th>
<th>Fall Frequency (%)</th>
<th>Refractory Lithophile/Mg Relative CI†</th>
<th>Examples</th>
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<tbody>
<tr>
<td>Carbonaceous</td>
<td></td>
<td></td>
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<td>CI</td>
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<td>&lt;0.01</td>
<td>&lt;5</td>
<td>—</td>
<td>&lt;0.01</td>
<td>95</td>
<td>0.5</td>
<td>1.00</td>
</tr>
<tr>
<td>CM</td>
<td>1–2</td>
<td>5</td>
<td>20</td>
<td>0.3</td>
<td>0.1</td>
<td>70</td>
<td>1.6</td>
<td>1.15</td>
</tr>
<tr>
<td>CO</td>
<td>3</td>
<td>13</td>
<td>40</td>
<td>0.15</td>
<td>1–5</td>
<td>30</td>
<td>0.5</td>
<td>1.13</td>
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<tr>
<td>CV</td>
<td>2–3</td>
<td>10</td>
<td>45</td>
<td>1.0</td>
<td>0–5</td>
<td>40</td>
<td>0.6</td>
<td>1.35</td>
</tr>
<tr>
<td>CK</td>
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<td>4</td>
<td>15</td>
<td>0.8</td>
<td>&lt;0.01</td>
<td>75</td>
<td>0.2</td>
<td>1.21</td>
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<tr>
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<td>0.5</td>
<td>50–60</td>
<td>0.7</td>
<td>5–8</td>
<td>30–50</td>
<td>0.3</td>
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<tr>
<td>CH</td>
<td>3</td>
<td>0.1</td>
<td>~70</td>
<td>0.05</td>
<td>20</td>
<td>5</td>
<td>0</td>
<td>1.00</td>
</tr>
<tr>
<td>CB₁</td>
<td>3</td>
<td>&lt;0.1</td>
<td>40</td>
<td>~5</td>
<td>60</td>
<td>&lt;5</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>CB₂</td>
<td>3</td>
<td>&lt;0.1</td>
<td>30</td>
<td>~0.5</td>
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<td>&lt;5</td>
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<td>Ordinary</td>
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<tr>
<td>H</td>
<td>3–6</td>
<td>0.01–0.2</td>
<td>60–80</td>
<td>0.3</td>
<td>8</td>
<td>10–15</td>
<td>34.4</td>
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<tr>
<td>L</td>
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<td>60–80</td>
<td>0.5</td>
<td>3</td>
<td>10–15</td>
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<tr>
<td>LL</td>
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<td>1.5</td>
<td>10–15</td>
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<tr>
<td>EH</td>
<td>3–6</td>
<td>&lt;0.1</td>
<td>60–80</td>
<td>0.2</td>
<td>8</td>
<td>&lt;0.1–10</td>
<td>0.9</td>
<td>0.87</td>
</tr>
<tr>
<td>EL</td>
<td>3–6</td>
<td>&lt;0.1</td>
<td>60–80</td>
<td>0.6</td>
<td>15</td>
<td>&lt;0.1–10</td>
<td>0.8</td>
<td>0.83</td>
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<tr>
<td>Other</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>3</td>
<td>&lt;0.1</td>
<td>20–30</td>
<td>0.6</td>
<td>6–9</td>
<td>70</td>
<td>0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>R</td>
<td>3–6</td>
<td>&lt;0.1</td>
<td>&gt;40</td>
<td>0.4</td>
<td>&lt;0.1</td>
<td>35</td>
<td>0.1</td>
<td>0.95</td>
</tr>
</tbody>
</table>

* Includes chondrule fragments and silicates inferred to be fragments of chondrites.
† Includes matrix-rich clasts, which account for all matrix in CH and CB₁ chondrites.
‡ Fall frequencies based on 918 falls of differentiated meteorites and classified chondrites (Grady, 2000).
§ Mean ratio of refractory lithophiles relative to Mg, normalized to CI chondrites.
that probably supplied the Tagish Lake chondrite. The chondrites in Table 1 may be reasonably representative of the tougher asteroids. Supporting evidence comes from the Kaidun breccia, which is composed entirely of fragments of seven groups of enstatite, carbonaceous, ordinary, and R chondrites plus some ungrouped carbonaceous samples (excluding CH and CB chondrites) and some achondritic fragments (Zolensky and Ivanov, 2003; Mikouchi et al., 2005).

2.2. Solar Nebula Models

Our knowledge of the conditions in the solar nebula is based on observations of young stars as well as thermodynamic models for the condensation of solids and liquids from a gas of solar composition. Historically, variation in conditions within the nebula has been linked to radial distance from the Sun (e.g., Wasson, 1985; Lewis, 1974). Factors controlling the thermal profile within the nebula have been reviewed by Boss (1998) and include mass accretion rates, opacity (dust/gas ratio), and total mass. Although estimates of nebular midplane temperatures have in the past been typically cool [300–600 K (Woolum and Cassen, 1999)], developments within this field have led to revision to higher midplane temperatures as much as a factor of 3 higher (Humayun and Cassen, 2000). These hotter temperatures most likely led to vaporization of all but the most refractory materials within a few astronomical units of the Sun, but only for a short (10^5 yr) period of time (Humayun and Cassen, 2000). Increasing sophistication has led to models combining gas/dust ratios and thermodynamics (Ebel and Grossman, 2001), as well as treating specific trace-element groups, such as the volatile elements (Humayun and Cassen, 2000) or highly siderophile elements (e.g., Campbell et al., 2001).

Additional evidence for conditions in the solar nebula comes from the meteorites. Virtually all the chondritic components except for the presolar grains and organics formed in the nebula at high temperatures during relatively brief heating events. Refractory inclusions formed in the inner part of the disk where the bulk O-isotopic composition equaled that of the proto-Sun (Hashizume and Chaussidon, 2005). Refractory inclusions probably formed in <0.3 m.y. at high ambient temperatures (1300 K) when the proto-Sun was accreting rapidly and were then distributed across the disk with refractory dust by bipolar outflows or nebula turbulence (Shu et al., 1996; Cuzzi et al., 2003; Wood, 2004). Chondrules and most matrix silicates formed under more oxidizing conditions at lower ambient temperatures when the proto-Sun was accreting more slowly. Chondrule melts were stabilized by higher total pressures or high dust/gas ratios. Chondrule formation involved melting, evaporation, condensation, and accretion of solid, partly melted, and wholly melted materials.

Chondrules and matrix grains formed after the nebula gas was depleted in 16O, probably as a result of evaporation of meter-sized icy bodies that were enriched in 17O and 18O due to self-shielding during UV photodissociation of CO in the protosolar molecular cloud or in the disk (Clayton, 2002; Lyons and Young, 2004; Yurimoto and Kuramoto, 2004; Krot et al., 2005). Chondrules may have formed soon after CAIs (Bizzarro et al., 2004), but most chondrules appear to have formed 1–3 m.y. after CAI formation (see Kita et al., 2005). Given the unique chemical and isotopic properties of the chondrules in many different groups and the evidence that CAIs and presolar grains were spread throughout the inner solar nebula, it seems likely that chondrules in a single group accreted soon after they formed, i.e., <0.3 m.y.

Accretion timescales in the nebula increased with increasing distance from the Sun as the surface density of solids decreased and the orbital periods increased. As a result, we might expect that the chemical compositions of the chondrules would correlate simply with the heliocentric distance at which they formed. However, chondrules cannot be simply arranged into a single chemical sequence because their concentrations of volatile, refractory, and siderophile elements are not simply correlated. The simplest explanation for the chemical complexity of chondrites is that many accreted close to the snow-line and the tar-line where the density of solids showed major step increases with increasing heliocentric distance. Thus, two (or perhaps three) accretion fronts may have advanced across the belt from opposite directions, requiring us to disentangle time and distance to reconstruct the primordial chemical zoning patterns of planetesimals in the inner disk.

Additional clues to the accretion locations of the chondrites have been derived from a wide variety of chondrite properties (e.g., Rubin and Wasson, 1995). The concentrations of water and volatiles in chondrites increase through the E-O-C sequence, supporting the view that this represents a sequence of increasing heliocentric distance. In addition, the concentration of chondrules probably decreased with increasing distance as the C-rich, volatile-rich carbonaceous chondrites like CIIs and Tagish Lake have fewer chondrules than enstatite and ordinary chondrites (Table 1). Wasson (1988) argued that E chondrites formed <1 AU from the Sun based on chondritic and planetary properties. Evidence for an inner nebula origin (although at >1 AU) comes from the correlation of 53Cr/52Cr with heliocentric distance, which places E chondrites between Earth and Mars (Lugmair and Shukolyukov, 1998; Shukolyukov and Lugmair, 1999).

2.3. Accretion Models

Planetary accretion is typically split into three distinct epochs. The first epoch comprised accretion of dust from a gas-rich disk. Turbulence and gas drag transported gas dust and solid bodies smaller than 1 km over large radial distances (e.g., Chambers, 2006), within 10^5 yr from T_0. The second epoch consisted of accretion of planetesimals from dust-sized particles. That these planetesimals were homogeneous is attributed to homogeneity in both Mg isotopes (Norman et al., 2004; Zhu et al., 2001), and this occurred on a 10^4–10^6-yr timeframe. The third epoch involved
accretion of planet-sized bodies from planetesimals and requires on the order of $10^7$ yr for completion. These three epochs of growth define the accretion process, and here we include only a brief discussion of the third epoch, with an emphasis on the width of feeding zones in the nebula during this stage, and the possibility that two stages of this epoch be distinguished — an early to mid stage and a late stage.

Early models for accretion of the terrestrial planets included narrow feeding zones for materials that ended up being incorporated into planets (e.g., Safronov, 1969; Lewis, 1972; Wetherill, 1980). Zones as narrow as 0.1 AU were considered to be sources for individual bodies, such as Earth and the Moon. This scenario has held true for the midstages of planet formation when eccentricities and inclinations are low (e.g., Canup and Agnor, 2000). For example, planetesimals that accreted inside 2 AU probably differed from the planetesimals that accreted in the asteroid belt as a result of both spatial and temporal variations. The inner planetesimals would presumably have had lower water and matrix abundances, as a result of differences in location, and higher $^{26}$Al concentrations as a result of more rapid accretion closer to the proto-Sun. Dynamical modeling by Bottke et al. (2005) suggests that the differentiated meteorite parent asteroids themselves may be derived from planetesimals that accreted inside 2 AU and were then scattered into the belt by planetary embryos. Thus the parent asteroids of the differentiated meteorites may give us the best clues to the nature of the innermost planetesimals. Enstatite chondrites remain a likely component of the 1–2-AU region, although their accretion time is not constrained by precise chondrule formation ages.

More recent models of the later stages of accretion have shown that the feeding zones widen substantially (Wetherill, 1994). In fact, the results of terrestrial planet simulations in which the starting embryos are “tagged” show that there is extensive mixing of material ending up in the surviving planets, between 0.5 and 3.5 AU (e.g., Chambers and Wetherill, 1998; Chambers, 2001). In light of these findings, discussions of “feeding zones” must explicitly define a timeframe since the extent of mixing apparently increases with age.

3. KEY ISOTOPIC AND ELEMENTAL TOOLS

The question of whether samples of the “building blocks” of Earth and other planets still exist as meteorites and comets is addressed by examining specific elemental and isotopic properties of the Earth, Mars, Venus, Mercury, comets, and meteorites. The ratios of Mg/Si and Al/Si and the isotopic compositions of O, H, Cr, Os, and noble gases are particularly useful.

3.1. Major Elements in Earth, Moon, Mars, Venus, and Meteorites

Magnesium/silicon vs. Al/Si ratios for a variety of solar system objects illustrate that these ratios vary significantly (Fig. 6). Primitive meteorites have distinct major-element compositions, and their Mg/Si values tend to be higher than those of Earth and its Moon. The Earth fractionation line, which defines the range of Mg/Si ratios found in Earth, Moon, and their potential parent asteroids, is shown in Fig. 6. The line is defined by terrestrial peridotites and picritic glasses, and it separates the Mg/Si values of differentiated meteorites from those of chondritic materials.

![Fig. 6. The major-element composition of primitive material in the inner solar system is not of uniform composition, but defines an unexplained trend. Mg/Si vs. Al/Si ratios in chondritic, terrestrial, lunar, martian, and venusian materials (Jagoutz et al., 1979; Taylor, 1992; Dreibus et al., 1998; Kargel et al., 1993; Basaltic Volcanism Study Project, 1981). Abbreviations are: E = enstatite chondrites; H, L = ordinary chondrites; CI, CM, CO, and CV = carbonaceous chondrites. Small open circles are terrestrial peridotite samples; terrestrial fractionation line is defined by peridotites, komatites, and basalts. The letters R, J, and P refer to estimates of the bulk silicate Earth composition by Ringwood (1979), Jagoutz et al. (1979), and Palme and Nickel (1986), respectively. Solid circles are lunar picritic glasses and large open circles are MORB (Basaltic Volcanism Study Project, 1981). Martian fractionation line is defined by Chassigny, shergottites, and martian soils and rocks from the Viking and Pathfinder mission (Dreibus et al., 1998). Venusian samples are analyses obtained from the Vega and Venera missions (Kargel et al., 1993).](image-url)
compositions and define a line with a positive slope, sometimes called the “cosmochemical trend” (Jagoutz et al., 1979). The origin of this trend is not well understood but undoubtedly results from condensation processes, differences in modal mineralogy (CAI, chondrules, metal), etc. The bulk Mg/Si and Al/Si ratios for differentiated objects such as Earth and Mars must be inferred from samples available at their surfaces. These ratios can be fractionated by the addition or subtraction of phases in mantle differentiation, such as Mg perovskite, garnet, pyroxene, and olivine (Jones, 1996; Agee and Walker, 1993). Also, Si in the core can lead to elevated Mg/Si ratios (e.g., Malavergne et al., 2004; Gessmann et al., 2001; Kilburn and Wood, 1997).

3.2. Oxygen Isotopes in Earth, Moon, Mars, and Meteorites

Various meteorite groups preserve unique O-isotopic compositions (Fig. 7a). Some meteorite groups define a slope of 1:2, which corresponds to control by mass-dependent fractionation processes. However, other bodies and groups define a slope of 1:1. The origin of the 1:1 slopes is debated and has been attributed to either 16O additions to the nebula (e.g., Clayton, 1993), or to photochemical reactions involving CO in the solar nebula (e.g., Clayton, 2002). Part of the uncertainty is due to lack of consensus on the position of the solar value on such a diagram, and this is the primary scientific goal of the Genesis mission (e.g., Burnett et al., 2003). Despite the large range of values recorded in meteorites, it appears that distinct O reservoirs are preserved over relatively small annuli of heliocentric distance, such as Earth, Mars, and the HED parent body (Fig. 7b). This makes O isotopes a very useful tool for tracing provenance. However, we still have no constraints on the O-isotopic composition of the inner solar system (Venus and Mercury).

3.3. Initial Osmium-187/Osmium-188 Ratio in Primitive Upper Mantles of Earth, Mars, and Meteorites

Highly siderophile elements (Re, Au, and the platinum group elements) can provide information about the conditions and/or timing of core formation and metal-silicate segregation since they are stripped almost entirely into metallic Fe. Rhenium and Os are two HSEs that are linked by beta decay, 187Re = 187Os + β. The concentrations of highly siderophile elements and ratios of Os isotopes have been used to argue for the late addition of chondritic material to the mantle of Earth, after the main stage of core formation had ended (e.g., Chou, 1978; Morgan et al., 1981). This is because the large differences in partition coefficients (both metal/silicate and solid silicate/liquid silicate) for various HSEs indicate that fractionation of these elemental ratios is otherwise easy (e.g., Righter et al., 2000). Although this idea initially seems rigorous, the latest results (Fig. 8) show...
that none of the chondrite groups match the \(^{187}\text{Os}/^{188}\text{Os}\) isotopic, Ru/Ir, or Pd/Ir ratios of Earth’s primitive upper mantle. Carbonaceous chondrites, the only abundant water-bearing meteorites, have a significantly lower \(^{187}\text{Os}/^{188}\text{Os}\) ratio of 0.1265 than Earth’s primitive upper mantle (PUM).

3.4. Deuterium/Hydrogen Ratios in Earth, Mars, Meteorites, and Comets

A fundamental question is whether planets accreted “wet” or “dry,” i.e., did their building blocks contain water, or was water delivered from exogenous sources after the planets formed. Meteorites, comets, and the interstellar medium define a large range of D/H ratios, and therefore the origin of planetary water can be investigated by examining D/H ratios in various planetary materials (Fig. 9) (Geiss and Reeves, 1972; Owen and Bar-Nun, 2000). Although D/H ratios may have varied substantially with heliocentric distance in the early solar system, partial to complete homogenization was likely on the timescale of \(10^6\) yr (Robert et al., 2000). As a result a range of D/H ratios could have been preserved in ancient materials, all of which could later be supplies for planet making.

3.5. Chromium-Isotopic Ratios in Earth, Moon, Mars, and Meteorites

Manganese-53 decays to \(^{53}\text{Cr}\) with a half-life of 3.7 ± 0.4 m.y. Daughter \(^{53}\text{Cr}\) will be unmeasurable after 5–7 half-lives, or about 20 m.y. to 26 m.y. after nucleosynthesis of \(^{53}\text{Mn}\). Thus, variations in the \(^{53}\text{Cr}/^{52}\text{Cr}\)-isotopic ratio in solar system materials must be established early in solar system history and reflect initial heterogeneities in the Cr-isotopic

Fig. 8. \(^{187}\text{Os}/^{188}\text{Os}\), Ru/Ir, and Pd/Ir ratios in carbonaceous, ordinary, and enstatite chondrites, Tagish Lake, and Earth’s primitive upper mantle (PUM) (Meisel et al., 2001). Also shown is the primitive martian mantle with nonchondritic \(^{187}\text{Os}/^{188}\text{Os}\) (from Brandon et al., 2005).

Fig. 9. The D/H ratios in \(\text{H}_2\text{O}\) in three comets, meteorites, Earth (Vienna standard mean ocean water — VSMOW), protosolar \(\text{H}_2\text{O}\), and Mars (Owen and Bar-Nun, 2000; Lecluse and Robert, 1994; Deloule and Robert, 1995; Robert et al., 2000; Deloule et al., 1998; Robert, 2001). CC = carbonaceous chondrites, LL3-IW = interstellar water in Semarkona, LL3-PS = protostellar water in Semarkona.
ratio (as with O), variations in the Mn/Cr ratio, or some combination of the two (Fig. 10). One cautionary note is that $^{54}$Cr anomalies have been found in carbonaceous chondrites (Rotaru et al., 1992), and these must be considered carefully when discussing Cr isotopes in the context of potential building blocks.

### 3.6. Noble Gases

The traditional view and interpretation of noble gases is that the solar compositions measured in many planetary atmospheres is the result of planetary accretion and retention (with perhaps later degassing) of solar nebular gases. Meteorites exhibited a range of values, but they were rarely identified as solar (e.g., Pepin, 1991). However, measurements of solar noble gases in angrites (Busemann et al., 2004) and enstatite chondrites (Busemann et al., 2003) show that there might be a significant solar component preserved in meteorites (see also Wieler et al., 2006; Podosek, 2003). In addition, ices and outer solar system objects can potentially carry noble gases, and Owen and Bar-Nun (2000) discuss this possibility with respect to Earth and Mars (Fig. 11).

### 4. INFERRING PLANETARY BULK COMPOSITIONS FROM SURFACE ROCKS: “SEEING THROUGH” ACCRETION AND IGNEOUS DIFFERENTIATION

As noted in the introduction, chondritic meteorite groups are commonly considered as building blocks for terrestrial planets. Mixtures of ordinary and carbonaceous chondrites (e.g., Lodders and Fegley, 1998), or even enstatite chondrites (Javoy, 1995), have been proposed. However, Drake and Righter (2002) and Burbine and O’Brien (2004) have demonstrated the difficulty of making Earth from any extant meteorite type. Regardless of the nature of the building blocks of the terrestrial planets, it is unlikely that a large planet will retain the exact chemistry of its building blocks, because such materials can be readily transformed by variations in $f_{O_2}$, temperature, pressure, reaction with water or other volatile species, and also by magmatic or mantle fractionation. Furthermore, large planets might sequester differentiated materials deep in their mantles, making inference of bulk composition from surface rocks problematic (Boyet and Carlson, 2005).

#### 4.1. Oxygen Fugacity

Oxygen fugacity is an important parameter in terrestrial planets, as it controls the relative proportions of FeO and Fe$_2$O$_3$ and the stability of metallic Fe. On Earth, variations in $f_{O_2}$ can affect magmatic fractionation trends and largely control Fe enrichment or depletion trends in oceanic and continental basalt suites (e.g., Carmichael, et al., 1974). Similarly, a large range of $f_{O_2}$ is defined by meteoritic materials (Fig. 12) (Rubin et al., 1988), and variations in $f_{O_2}$ in meteoritic materials can change chemical features and phase equilibria dramatically.

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**Fig. 10.** Variation in Cr-isotopic composition with heliocentric distance. Ordinary chondrites plot with HED meteorites. After Lugmair and Shukolyukov (1998). $\varepsilon(53)$ is defined as $[(^{53}\text{Cr}/^{52}\text{Cr})_{\text{measured}}/(^{53}\text{Cr}/^{52}\text{Cr})_{\text{standard}} - 1] \times 10^4$ (Lugmair and Shukolyukov, 1998).

**Fig. 11.** $^{36}\text{Ar}/^{132}\text{Xe}$ vs. $^{84}\text{Kr}/^{132}\text{Xe}$ for Earth, Mars, chondrites, venusian atmosphere, shergottites, Chassigny, ices, and the Sun (after Owen and Bar-Nun, 2000).
Equilibrium between graphite, CO, and CO$_2$ buffers $f_{O2}$ as discussed by Sato (1978). At low pressures, such $f_{O2}$ are lower than the IW buffer, i.e., in an Fe-metal stability field. However, the volume change of this reaction is quite large, such that at higher pressures, the $f_{O2}$ defined by C-CO-CO$_2$ is higher than the stability field of Fe metal. In fact, olivine-pyroxene-graphite-gas equilibria in ureilites allow the equilibrium pressure to be defined, since ureilites contain graphite (e.g., Goodrich et al., 1987; Walker and Grove, 1993). At even higher pressures, C-CO-CO$_2$ define $f_{O2}$ within the range of the relatively oxidized terrestrial mantle (LaTourette and Holloway, 1994). Because graphite is possibly present during the early stages of terrestrial planet formation, this buffer may control $f_{O2}$ and thus have an effect on the bulk chemistry of chondritic materials involved with planet formation (Fig. 13).

The $f_{O2}$ range over which Fe metal becomes unstable is relatively narrow (Arculus et al., 1990). Reduction or oxidation of Fe metal in chondrite material can occur over 2 log $f_{O2}$ units, a range easily covered by pressure effects on the C-CO-CO$_2$ surface, or even produced by equilibria involving H$_2$-H$_2$O (see below). Such oxidation will affect not only the amount of Fe metal stable during the oxidation (or reduction), but will also affect the distribution of siderophile elements such as Ni, Co, and W. Equilibria such as these can control the mass of a planetary core, as well as its overall composition (e.g., O-, H- or C-bearing), due to equilibria such as Fe + CO$_2$ = FeO + CO.

Differences in $f_{O2}$ may also produce very different differentiated meteorites that are otherwise derived from similar bulk compositions. For example, it has been shown that partial melting of chondritic material at IW–1 can produce eucritic liquids, whereas melting of the same material at IW + 2 results in angritic liquids (Jurewicz et al., 1991).

Finally, increasing temperature also causes reduction. For example, in an FeO-bearing system at QFM, if $f_{O2}$ is held constant and temperature is increased, FeO will eventually be converted to Fe metal. Similarly, but at higher $f_{O2}$, Fe$_2$O$_3$ will eventually form Fe$_3$O$_4$. Equally, a Fe$_2$O$_3$-bearing silicate melt will eventually become a FeO-bearing silicate melt with heating at a constant $f_{O2}$ (Kress and Carmichael, 1991). This simple relation could possibly be related to the presence of larger metallic cores in the hotter inner part of the solar system (i.e., Mercury with large core) compared to the cooler, outer region (i.e., Mars with small core).

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4.2. Pressure and Temperature: Melting and Fractionation of Phases

Pressure can affect phase equilibria of planetary materials, the compositions of phases that have solid solution, and the physical properties of minerals and melts such as density. All these effects can have significant leverage on transforming planetary materials at high pressures.

One of the most important phenomena with respect to planet formation is the density crossover between minerals and melts at interior pressures. For example, plagioclase flotation on the Moon is a now-classical concept of differentiation. Less-dense plagioclase will float on a denser ultrabasic or peridotitic magma ocean, thus leading to the anorthositic lunar highlands with positive Eu anomalies (and a corresponding negative Eu anomaly in mantle-derived lunar basalts). This example has become a textbook lesson on how geophysics and geochemistry are linked, and also how surficial products can be quite different as a result of postaccretional processes (e.g., Warren, 2003). Similarly, olivine and garnet will become less dense than their coexisting silicate melt at specific pressures within planetary mantles (Fig. 14). Because these pressures are strongly dependent upon FeO content of both the liquid and mineral, it is not possible to generalize about any given mineral — the crossover points will be a function of composition, which is in turn a function of pressure, temperature, and \( f_{O_2} \), to the extent to which these three variables control composition.

Finally, a topic of continued and ongoing research is the effect of pressure on the composition of metallic liquids that form planetary cores. This topic was honed on Earth because it has been recognized for some time that the density of Earth’s outer core is about 10% lower than that expected for a pure FeNi alloy. The identity of the light element in the core remains uncertain, but the list of possibilities includes Si, S, C, H, P, or O (see recent review of this topic by Hillgren et al., 2000). Most of these elements will not have a large effect on the surficial composition of planetary materials. But there are two notable exceptions. First, if a significant (>2%) amount of Si were partitioned into Earth’s outer core, the Mg/Si ratio of the mantle would increase. This very mechanism has been called on to explain the superchondritic Mg/Si of the terrestrial upper mantle (Allegre et al., 1995; Gessmann et al., 2001; Wade and Wood, 2001). Second, if a significant amount of O was partitioned into the core of Earth (as FeO), the mantle FeO content would be lowered accordingly (Rubie et al., 2004; Ringwood, 1979).

4.3. Water

It has been known for nearly 40 years that water is very soluble in silicate melts, with as much as 15 wt% water entering a basaltic liquid in a system saturated with a pure \( H_2O \) fluid at 1.5 GPa (Hamilton et al., 1964). Water solubility as a function of pressure and temperature is well

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**Fig. 14.** Density crossovers for terrestrial peridotite liquid and olivine (top) (Agee, 1998); Apollo 14 black glass, olivine, and orthopyroxene (middle) (Circone and Agee, 1996); and synthetic martian mantle melt, diamond, and majoritic garnet (bottom) (Ohtani et al., 1995).
known now for a large range of natural liquids, and much research has focused on systems relevant to terrestrial magmatic systems (basalt, andesite, dacite, rhyolite), both in water-saturated and mixed speciation (e.g., CO₂-H₂O) conditions (e.g., Moore et al., 1995, 1998).

The effect of water on phase relations of magmatic systems is significant. The olivine phase field is expanded in basaltic systems by the addition of even a small amount of water (e.g., Kushiro, 1969), and plagioclase is generally suppressed by dissolution of water in basic magmas (Sisson and Grove, 1993). Large changes have been documented in more basic systems as well. The liquidus in the enstatite system is 600°C lower in the water-saturated system (Inoue, 1994) than it is in the anhydrous system (Gasparik, 1993). Similarly, the forsterite liquidus has a huge depression at water contents of 20 wt% compared to dry conditions (e.g., Abe et al., 2000). Experiments on hydrous peridotitic materials have shown not only a large reduction in liquidus and solidus temperatures (Inoue and Sawamoto, 1992; Kawamoto and Holloway, 1997), but also a change in the liquidus phases from olivine in a dry system, to orthopyroxene and garnet in a hydrous system (Inoue and Sawamoto, 1992). A direct comparison of the effect of 2 wt% water on the phase relations of the CaO-MgO-Al₂O₃-SiO₂ system up to 25 GPa shows that it will have a very large effect, reducing the solidus and liquidus by hundreds of degrees (Fig. 15).

Finally, water can react with Fe metal to form FeO (dissolved in solid or liquid silicate) or FeH (dissolved in metal). If water is available during accretion, metal-bearing materials could become oxidized

\[ \text{Fe} + \text{H}_2\text{O} = \text{FeO} + \text{H}_2 \]

thus changing the bulk composition of the silicate materials that will ultimately become part of the mantle. Alternatively, Fe-metal-bearing materials could react with water to form FeH (e.g., Okuchi, 1997; Abe et al., 2000)

\[ 4\text{Fe} + 2\text{H}_2\text{O} = 4\text{FeH} + \text{O}_2 \]

in which case the metallic core may contain some H as a light element.

With respect to the first reaction, an illustration of various kinds of water sources and how much would be required to raise the FeO content of a mantle is constructed in Fig. 16. It would require 3,000,000 Borrelly-sized com-
ets to oxidize Earth’s mantle by 1 wt% FeO. It would take 10 large (1000 km) KBOs to oxidize the mantle to 4 wt% FeO higher than its standard value. And finally, it would take one 0.1 Mwet planetesimal (e.g., Morbidelli et al., 2000) to oxidize the mantle of an Earth-sized planet to 6 wt% higher. Thus water, FeO, the Mg# of the mantle, and the size of a metallic core are all potentially linked in a planet that accretes wet.

4. Fractionation

Lava flows can be used as probes of a planet’s interior, assuming that they have not fractionated dramatically as they migrated to the surface. It turns out that FeO is not greatly fractionated during partial melting and modest fractional crystallization, although the Fe/Mg ratio varies dramatically because of Mg fractionation. Robinson and Taylor (2001) assembled experimental and observational data to show this quantitatively. For example, the average FeO concentration of terrestrial mid-ocean-ridge basalts (MORB) divided by the composition of the primitive terrestrial mantle is only 1.3. Thus, the FeO concentration of a lava is only about 30% higher than the concentration of its mantle source region. This led Robinson and Taylor (2001) to conclude that Mercury contained 2–3 wt% FeO in its interior.

Magmatic fractionation can also have a large effect on the surficial properties of planetary materials. For example, it is well known that Ni, Cr, Co, and Mg are all very compatible in olivine and pyroxene or spinel during fractional crystallization of a basaltic liquid. As a result, a basaltic liquid that has undergone extensive fractional crystallization will have much higher concentrations of incompatible elements such as Sm and Th, and lower Ni and MgO than a primary mantle melt. Thorium and Sm concentration data from orbital gamma-ray spectroscopy should thus be interpreted in this context, and attempts should be made to be correlate such concentrations with MgO to assess whether high values are due to inherent planetary properties or simply to fractionation.

In summary, C-H-O fluids (and specifically $f_{O_2}$ and $f_{H_2O}$), pressure, temperature, and fractionation all affect the potential building blocks for planets and must be well understood in order to assess from what materials a planet has been constructed.

5. TERRESTRIAL PLANETS: MADE FROM EXTANT MATERIALS?

5.1. Earth

5.1.1. Composed of known materials? The composition of Earth’s primitive upper mantle (PUM — the Earth’s mantle immediately after core formation) is distinct from that of any kind of extant meteorite, barely overlapping CV3s (Fig. 6). The higher Mg/Si ratio of Earth’s mantle relative to chondrites led Hewins and Herzberg (1996) to suggest that Earth formed from Mg-rich type I chondrules, which are depleted in moderately volatile elements. Chondrites rich in such chondrules with only minor matrix provide a plausible precursor material, especially as olivine-rich type I chondrules in Semarkona tend to be ~0.5 m.y. older than pyroxene-rich chondrules (Kita et al., 2005).

However, as has been shown in the previous section, it is unlikely that such low-pressure and low-temperature (relative to Earth’s interior during differentiation) building blocks would survive the many changes in $T$, $P$, $f_{O_2}$, and volatile contents to be recognizable at the end of accretion.

A variety of other studies have proposed that Earth is made of extant meteorites. For example, Wänke (1981), O’Neill (1991), and Newsom and Sims (1991) all argue that Earth is made from a mixture of enstatite chondrites and carbonaceous chondrites (component A, reduced, and component B, oxidized). Then a chondritic late veneer is added (<1%) that accounts for the HSE in the primitive mantle. However, Earth’s PUM has a significantly higher $^{187}$Os/$^{188}$Os ratio than carbonaceous chondrites, effectively ruling them out as the source of the “late veneer” (Fig. 8). The PUM $^{187}$Os/$^{188}$Os ratio overlaps anhydrous ordinary chondrites and is distinctly higher than anhydrous enstatite chondrites. In summary, these models cannot be reconciled with the Os-isotopic data, and also can only be satisfied if the late veneer is a reduced (enstatite or ordinary) meteorite, which is the opposite of the originally proposed oxidized veneer (Chou, 1978).

Palme and O’Neill (2004) argue that Earth has many similarities to carbonaceous chondrites, such as refractory lithophile elements and volatile-element depletions. Simi-
larly, Allegre et al. (2001) demonstrate that volatile-element depletions in Earth could be controlled by a range of carbonaceous chondrites from CI (highly refractory), to CM (moderately refractory), to CV-like (volatile). Carbonaceous chondrites could also provide water for Earth of the right D/H ratio. The D/H ratio of Vienna standard mean ocean water (VSMOW) on Earth is $150 \times 10^{-6}$, similar to the average for carbonaceous chondrites ($150 \times 10^{-6}$). However, either of these ideas is inconsistent with terrestrial O-isotopic data, Os-isotopic data, and noble gas data, which are distinctly dissimilar to carbonaceous chondrites (Table 2).

Earth’s noble gases, specifically $^{84}$Kr/$^{130}$Xe ratios in Earth’s atmosphere, are distinct from both CI carbonaceous chondrites and enstatite chondrites. These differences may have arisen from some secondary process. Not surprisingly, then, the best explanations for noble gas concentrations and origins in Earth involve two-stage models where the first stage is hydrodynamic escape of a primary hydrogen-rich, isotopically solar atmosphere, followed by degassing of Kr, Ar, and Ne from deep within the planet. Subsequently, it appears unlikely that Earth’s Kr/Xe or other noble gas ratios are derived from carbonaceous chondrites (e.g., Pepin, 1991). Pepin’s (1991) modeling of noble gases coupled with C and N compounds resulted in the conclusion that a late accretional veneer similar in composition to enstatite chondrites could satisfy the C, N, and noble gas in surficial reservoirs. More recent modeling of N and Ne abundances in the terrestrial mantle by Owen and Bar-Nun (2000) suggest that icy planetesimals may have contributed some of terrestrial volatiles, including the light N component that has been difficult to explain. On the other hand, the extent to which solar components could have been supplied by meteoritic building blocks has recently received attention, but a full discussion of this possibility is beyond the scope of this paper (Wieler et al., 2006; Becker et al., 2003).

Motivated by O-isotopic and bulk compositional data, Javoy (1995) argued for an enstatite chondrite bulk Earth composition. This hypothesis satisfies the O-isotopic constraints, and is consistent with Os-isotopic data for the terrestrial mantle. However, there are a number of problems with this approach — E chondrites contain more Fe than is observed in Earth’s core. Oxidation of this Fe to FeO would result in a lower mantle with a higher FeO content than the upper mantle. This is not consistent with the bulk of geochemical constraints for the upper and lower mantle.

Finally, attempts have been made to explain the source of Earth’s water through known materials (some nonmeteoritic), such as comets (e.g., Delsemme, 1997). There are caveats to using cometary D/H ratios to limit the delivery of cometary water to Earth. First, we do not know that Oort cloud comets Halley, Hale-Bopp, and Hyakutake are representative of all comets. Certainly they are unlikely to be representative of Kuiper belt objects, the source of Jupiter-family comets, as Oort cloud comets formed in the region of the giant planets and were ejected while Kuiper belt objects have always resided beyond the orbit of Neptune. Second, D/H measurements are not made of the solid nucleus, but of gases emitted during sublimation. Differential diffusion and sublimation of HDO and H$_2$O may make such measurements unrepresentative of the bulk comet, as the D/H ratio would be expected to rise in diffusion and sublimation, as has been confirmed in preliminary laboratory experiments (Weirich et al., 2004). Intriguing experiments on mixtures of water ice and TiO$_2$ grains by Moores et al. (2005) suggest that D/H ratios could be lowered in sublimates. Lower bulk D/H ratios would increase the allowable amount of cometary water. Third, the D/H ratio of organics and hydrated silicates in comets is unknown, although that situation may be rectified by analysis of samples returned by the Stardust mission. Note, however, that D/H ratios up to 50x VSMOW have been measured in some chondritic porous interplanetary dust particles (CP-IDPs) that may have cometary origins (Messenger, 2000), and higher aggregate D/H ratios of comets would decrease the allowable cometary contribution to Earth’s water.

5.1.2. Composed of known, but transformed, materials?

There are several models that explicitly evaluate the possibility that Earth accreted from known materials, but were then transformed at higher temperature and pressure conditions. For example, Ringwood (1979) argued that Earth’s mantle has a low FeO content due to dissolution of FeO (or O) into the core at high pressures. Although this has shown to be true to a limited extent, it is difficult to partition enough O into the core the explain Earth’s composition by starting with a known chondritic material (e.g., Rubie et al., 2004).

Several suggestions have been made to explain the elevated Mg/Si and Al/Si ratios in Earth’s PUM relative to undifferentiated meteorites. The most prominent of these include (1) sequestering Si in the core of Earth, raising the Mg/Si and Al/Si ratios in the silicate mantle (Wańke, 1981, Allegre et al., 1995); (2) appealing to the possibility that the lower mantle of Earth has a different composition from the upper mantle, i.e., PUM is not representative of the bulk mantle (Anderson, 1989; Javoy, 1995); or (3) flotation or sinking of olivine or perovskite, respectively (e.g., Agee and Walker, 1988; McFarlane et al., 1994).

While Si can be extracted into metallic cores under very reducing conditions, it is difficult to partition enough Si into core metal at deep mantle conditions, or those at the base of a high-pressure/high-temperature terrestrial magma ocean, to account for the light element in the core, or the super-

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
Object & $^{84}$Kr/$^{130}$Xe Ratio \\
\hline
Solar system & $0.7 \times 10^{-2}$ \\
CI carbonaceous chondrites & $5.1 \times 10^{-2}$ \\
Enstatite chondrites & (5–23) \\
Earth atmosphere & $1.2 \times 10^{-2}$ \\
\hline
\end{tabular}
\caption{Ratios of $^{84}$Kr/$^{130}$Xe in various solar system objects (Pepin, 1991); note that extant meteorites have $^{84}$Kr/$^{130}$Xe ratios that are very different from Earth’s atmosphere.}
\end{table}
chondritic Mg/Si ratio. At conditions of a deep mid-mantle magma ocean, the metal/silicate partition coefficient for Si is approximately $10^{-3} - 10^{-2}$ (Wade and Wood, 2001). Partitioning under very reducing conditions is also inconsistent with the primitive upper mantle abundances of first transition series elements such as V, Cr, and Mn, as they would be depleted far below observed abundances if conditions were sufficiently reducing to allow Si to dissolve in Earth’s core (Drake et al., 1989). Only for metal-silicate equilibria at much higher pressures and temperatures, 50 GPa and 3000 K, would the abundances of Si, V, Mn, and Cr be satisfied (Wade and Wood, 2005; Chabot and Agee, 2003), but other elements such as Mo, W, and P have not yet been adequately evaluated at these conditions.

The question of whether the composition of the lower mantle is different from the upper mantle is more complicated. If the lower mantle, constituting 68% by volume of the mantle, has a different bulk composition than PUM, then arguments about the bulk composition of the silicate Earth based on PUM are flawed. While we have no direct samples of the lower mantle, geophysical measurements provide indirect clues to its composition (e.g., Stixrude et al., 1992). Although there is no firm consensus, Bina (2004) concludes that high-pressure mineral physics constraints, including elasticity and thermal conductivity data, are most consistent with the lower and upper mantle having the same composition (see also discussion in Drake and Righter, 2002). Furthermore, Boyet and Carlson (2005) argue on the basis of $^{146}$Sm-$^{142}$Nd systematics that most of Earth’s mantle has the composition of the MORB source.

Agee and Walker (1988, 1993) proposed making Earth from CV3 chondrites and then floating olivine or removing perovskite into the upper or lower mantle, respectively. Olivine flotation (Fo$_{90}$) occurs at pressures of approximately 8.0 GPa, and has been proposed as a mechanism for giving the upper mantle of Earth a superchondritic Mg/Si ratio (Agee and Walker, 1993). It has also been proposed as a possibility in the early martian mantle (Righter and Drake, 1996). Although olivine flotation is most likely inconsistent with our knowledge of the Ni, Co, Ir, Pd, Re, and Os contents of the upper mantle (McFarlane and Drake, 1990; Righter, 2005), it remains an important concept and could undoubtedly be an important postaccretional process altering planetary surficial compositions.

5.1.3. Composed of unknown materials? Difficulties in explaining the bulk composition of Earth from either a known or transformed meteoritic material have led some to conclude that Earth may have accreted from materials that no longer exist and are unrepresented in the collections (e.g., Drake, 1984; Drake and Righter, 2002). A cursory examination of the O-isotopic composition of meteorites indicates that only the enstatite meteorites (chondrites and achenoids) share a common O reservoir with Earth and the Moon (Fig. 7). This link is strengthened by similarities of Cr isotopes. There appears to be a systematic variation in the $^{53}$Cr/$^{52}$Cr ratio, usually expressed in units of $\varepsilon^{53}$Cr or simply $\varepsilon(53)$ with heliocentric distance (Fig. 10), unlike any other isotopic system such as O (Lugmair and Shukolyukov, 1998). Earth is by definition at $\varepsilon(53) = 0$. The identical value for the Moon implies a close connection in terrestrial and lunar origin, a conclusion supported by O-isotope studies of Wiechert et al. (2001). There is a linear trend of increasing $\varepsilon(53)$ through Mars to the asteroid belt. Such systematic variation, unseen in any other isotopic system, most probably reflects a primordial gradient in the Mn/Cr ratio, with more volatile Mn increasing in composition with distance from the Sun. Birck et al. (1999) argue that the solar system started with homogenous $^{53}$Mn and $^{53}$Cr, with differences in $\varepsilon(53)$ reflecting the timing and relative volatility of Mn and Cr during isolation from the solar nebula. A correlation with other volatile-refractory parent-daughter pairs would support this alternative view. It is possible that Earth accreted from a larger reservoir of material that no longer exists.

Extensive computational modeling by Burbine and O’Brien (2004) has also demonstrated that there is no known combination of building blocks that can explain Earth’s bulk composition if PUM is representative of the bulk silicate Earth and Si has not been sequestered in the core or added to the upper mantle. Additionally, Zolensky (1998) and Zolensky et al. (2006) have shown that the flux of material to Earth’s surface changes over time such that material accreting to Earth today may not be entirely representative of that available in the early solar system. Thus Earth could be made from material no longer extant, i.e., it has all been swept up by Earth (and the Moon-forming impactor — see section 5.2).

5.1.4. Moon. We have no direct samples of the lunar mantle, but our detailed models of its bulk composition are based on basaltic samples from the Apollo, Luna, and meteorite collections (e.g., Fig. 6), as well as geophysical data. The distinguishing features of the Moon are its small metallic core (<2 mass%), high mantle FeO content relative to Earth and low total Fe content, and volatile-element depletion. Some of the aspects of the Moon’s composition can be easily explained by an impact origin, such as its small metallic core.

The Moon is very similar to Earth in a number of compositional ways (e.g., Jones and Palme, 2000). Since impact modeling predicts that Earth’s Moon formed in a giant impact and the Moon is largely derived from the impactor (Cameron, 2000; Canup and Asphaug, 2001), it is remarkable that the O- and Cr-isotopic compositions of Earth and the Moon are so similar (Δ$^{17}$O for the Moon is <15% of the Mars value). This could imply that at least two large bodies, proto-Earth and the impactor, had identical O- and Cr-isotopic compositions (Wiechert et al., 2001; Lugmair and Shukolyukov, 1998). If the Moon is made from the mantle of a differentiated impactor, either both Earth and the impactor formed in the same region of space, or both Earth and the Moon were chemically and isotopically homogenized in the impact event(s). Alternatively, Earth and the Moon were isotopically equilibrated during the impact (Pahlevan and Stevenson, 2005).

There has been very limited work on Os-isotopic compositions of lunar materials, because the concentrations of Re and Os in pristine materials are so low that the measure-
ments are very difficult. Analyses of dunite 72415 (Walker et al., 2004) yield results indicating that the Re/Os ratio of the lunar mantle and its corresponding $^{187}\text{Os}/^{188}\text{Os}$ ratio are most likely superchondritic. This is, however, in contrast to measurements by Birck and Allegre (1994) on two lunar basalts showing nearly chondritic present-day $^{187}\text{Os}/^{188}\text{Os}$ ratios. A near-chondritic lunar mantle source is not favored or ruled out by this limited dataset, and resolution requires additional measurements.

The volatile content of the Moon is low (e.g., Taylor et al., 1995; Humayun and Clayton, 1995), making a discussion of its D/H and noble gas composition difficult. However, this highlights the issue of the Moon’s volatile element depletion — its origin is not well understood and remains one of the largest outstanding questions in lunar science.

In summary, the Moon may have been derived from the mantle of the proto-Earth, from a differentiated protoplanet [Theia (Halliday and Porcelli, 2001)] of unknown origin and composition, or a mixture of the two (Canup and Asphaug, 2001). Because of this uncertainty, compositional information provided by the Moon must be interpreted carefully.

5.2. Mars

5.2.1. Composed of known materials? In terms of major elements, Mars is different from Earth in that the array of martian meteorites and Mars Pathfinder analyses fall beneath carbonaceous chondrites and the solar value. Bulk martian Mg/Si and Al/Si ratios may plausibly be near the H and L chondrites (Fig. 6). Later processes acting on these bulk compositions, such as melting and fractionation, may have produced a linear array for martian materials, similar to that for Earth (e.g., McSween, 2002; Dreibus et al., 1998). Interestingly, most Mars Spirit and Opportunity rocks do not plot on these “primitive” trends, but plot on trends expected if fractionation of aluminous phases (feldspar, clays) was involved. This similarity to a known meteorite group, however, precludes the need to call upon secondary processes, such as Si in the core or garnet or perovskite fractionation, for the martian mantle. Mars is distinct from the Earth-Moon system and from all chondrite and achondrite fractionation, for the martian mantle. Mars is distinct from the Earth (e.g., Birck and Allegre, 1998). A solution to this problem may come from studies with lower FeO compositions that also satisfy density and moment-of-inertia data for Mars (e.g., Bertka and Fei, 1998a,b). Bertka and Fei (1998a,b) show that the moment-of-inertia data for Mars (Pathfinder) are inconsistent with a CI chondritic martian bulk composition, as proposed by Wänke and Dreibus (1988). Even attempts to fit the data with endmember core compositions such as FeH, Fe$_2$O$_3$, FeS, and Fe$_3$C result in mantle Fe/Si ratios that are unlike CI — Mg-Fe-Si and chondrite types. A detailed analysis using this same approach for bulk compositions that are ordinary-chondrite-rich has not yet been done.

The Cr-isotopic composition of Mars is clearly higher from that of Earth, probably reflecting a higher Mn/Cr ratio in the material accreted at 1.5 AU. Higher Mn is consistent with the higher volatile-element content of Mars compared to Earth. This difference, along with the differences in O isotopes and major-element abundances, highlights the argument that the terrestrial planets had narrow feeding zones for the majority of their growth.

Martian volatiles could also have come from a known source. The average D/H for Mars (there is considerable spread and there is no extant water ocean) is about $300 \times 10^{-6}$, similar to the value for comets — $300 \times 10^{-6}$ (Fig. 9). It is possible that the D/H ratio on Mars has been raised from its original value by differential loss of H, as is suggested by the elevated D/H ratio in the martian atmosphere (Fig. 9). However, Mars has been outgassed less than Earth because its smaller mass would lead to more rapid loss of heat. Thus, the lower martian mineral and rock D/H ratios are most likely representative of the solid undegassed planet (Fig. 9). An alternative interpretation (Owen and Bar-Nun, 2000) notes that the lack of exchange between the martian lithosphere and hydrosphere allows for the possibility that the D/H ratio of the unsampled martian interior could be very different from rocks, minerals, and atmosphere. Sampled rocks, minerals, and atmosphere could reflect addition of unrecycled cometary material.

The noble gas distributions on Mars are generally similar to those on Earth and can be explained by a two-stage model that involves early escape of a H-rich solar atmosphere, followed by degassing of Kr, Ar, and Ne from the interior (Pepin, 1991; Becker et al., 2003). As for Earth, the extent to which solar components could have been supplied by meteoritic building blocks has recently received attention and a full discussion of this possibility is beyond the scope of this paper (see Wieler et al., 2006). However, as opposed
to Earth, Xe-isotopic data indicate that the degassed material from the interior could have been CI-chondrite like, with the additional possibility that radiogenic $^{129}$Xe was added by decay of extinct $^{129}$I in surficial and crustal processes (Musselwhite et al., 1991; Musselwhite and Drake, 2000).

In summary, there is a general consensus that Mars can be made from a mixture of existing meteorite types, with possible input from comets. Remaining issues are whether specific ordinary chondrite groups can provide the right amount of FeO for the mantle and still be consistent with the moment-of-inertia data and core mass.

3.5. Composed of known, but transformed, materials?

No specific models of this type have been proposed for Mars, most likely because so many of its properties can be explained without appealing to major transformations. For example, pressure at the base of the martian mantle is not high enough to stabilize perovskite, which is often called upon in terrestrial models for promoting mantle differentiation. In addition, the water content of Mars is unlikely to be high enough to have had a major effect on Fe-FeO equilibria. And the $f_{O_2}$ of martian materials exhibit a lower range than those for Earth, thus suggesting $f_{O_2}$ changes have been less important in defining the bulk composition.

3.5.2. Composed of unknown materials?

Measurements of Os isotopes on martian meteorites show that the $^{187}$Os/$^{188}$Os of the primitive martian upper mantle (PMUM) is 0.132 ($\pm 0.001$), outside the range of any known chondritic value [highest known is 0.1305 (Brandon et al., 2005)]. As a result, the martian mantle is nonchondritic in its HSE content, which is also reflected in the concentrations of HSEs in martian meteorites (e.g., Kong et al., 1999; Warren, 1999; Jones et al., 2002). If Mars received a late accretional veneer as some have argued for Earth, it may have been provided by a chondrite group that is not currently represented in our meteorite collection.

5.3. Asteroid 4 Vesta

The howardite-eucrite-diogenite (HED) clan of differentiated meteorites is thought to be from asteroid 4 Vesta (e.g., McCord et al., 1970; Drake, 2002). They provide the opportunity to learn more about the bulk composition of a large, differentiated asteroid. Dreibus and Wänke (1980) proposed a MgO-rich bulk composition based on geochemical modeling of a mixture of eucrite and diogenite materials. Attempts to determine how large a metallic core could have produced the significant siderophile-element depletions in eucrites (e.g., Newsom and Drake, 1982) resulted in estimates of core mass of approximately 30–50%. Coupling of core formation with basaltic eucrite liquid formation led Righter and Drake (1997b) and Ruzicka et al. (1997) to propose that Vesta has a 15–20 mass% core. In particular, Righter and Drake (1997b) chose the modeling results of Boesenberg and Delaney (1997) to constrain bulk compositions. This combined approach led to a complete model for the origin of HED meteorites by differentiation of a mixture of CM and L chondrites that satisfied O isotopes, Fe/Mn, and siderophile and lithophile trace-element data (Righter and Drake, 1997b).

5.4. Mercury

Not much is known empirically about the bulk chemical composition of Mercury. Because we have no samples of Mercury, we have no constraints on its O-, Os-, or Cr-isotopic compositions. We emphasize the three compositional features that are reasonably well determined: a large metallic core, a low FeO content in the mercurian crust, and the presence of at least a little Na. This skimpy list gives us surprisingly useful information.

The mean density of Mercury is 5.43 ± 0.01 g/cm$^3$ (Anderson et al., 1987), and has been interpreted to indicate a large metallic FeNi core making up ~70% of the planet’s mass and ~40% of its volume (assuming a silicate density of about 3 g/cm$^3$). If this is correct, Mercury has a very high Fe/Si ratio. However, as Goettel (1988) points out, we have no direct evidence that the core is composed of Fe and Ni only. If the core is made of pure FeS, it would make up an even larger percentage of the planet.

A variety of spectral observations using Earth-based telescopes show that the surface of Mercury is low in FeO + TiO$_2$ (Vilas, 1988; Sprague et al., 1994; Jeanloz et al., 1995). Robinson and Lucey (1997) recalibrated the Mariner 10 data for Mercury and concluded that there were compositional heterogeneities in the crust, although all of it is low in FeO. All these constraints suggest that the crust and perhaps mantle of Mercury contain a very low FeO content, near 3 wt%.

We have no knowledge of noble gases or D/H ratios for Mercury, but there is some information about volatiles from a tenuous atmosphere that contains Na and K (Potter and Morgan, 1985, 1986). These elements are derived from the surface by a variety of loss mechanisms, apparently dominated by sputtering (e.g., Killen and Ip, 1999). Although it is not possible to determine the Na and K abundances on the surface from their abundances in the atmosphere, their presence shows that some Na and K must be present, which is important in assessing the volatile inventory of the planet. Similarly, Sprague et al. (1995) suggested on the basis of midinfrared spectral observations that the surface of Mercury is relatively rich in Fe sulfides. They also suggest that the radar anomalies in polar regions, which are generally attributed to cometary water ice (Slade et al., 1992; Harmon and Slade, 1992), might be caused by deposits of elemental S in cold traps.

We do not know anything about the differentiation history of Mercury, ignorance that currently limits our understanding of its interior. Did Mercury have a magma ocean? Or did its ancient crust form by serial magmatism early in its history? It is thus difficult to ascertain whether Mercury is made of known building blocks. We hope that data from
NASA’s MESSENGER and ESA’s BepiColumbo missions will help to answer these questions.

5.6. Venus

As with Mercury, because we have no samples of Venus, we have no constraints on its O-, Os-, or Cr-isotopic composition. However, we do have data for Venus from the Soviet -landed spacecraft Veneras 13 and 14 and Vega 2. While we have no direct sample of the Venus mantle, Venus crustal basalts fall on the trend of lunar picritic glasses and terrestrial MORB, suggesting that Venus may have the same bulk Mg, Al, and Si abundances as Earth (Fig. 6).

The D/H ratio of the Venus atmosphere has been measured by spacecraft and is about 100× that of Earth’s atmosphere, but cannot represent the original venusian D/H ratio because of significant differential loss of H relative to D (e.g., Hunten and Donahue, 1976; Donahue et al., 1982). The Venus greenhouse vaporized water, and solar UV at the top of the atmosphere dissociated the water. Hydrogen is lost preferentially to D by Jeans escape to space (Hunten and Donahue, 1976).

The venusian atmosphere is much richer in noble gases than Earth’s, by as much as a factor of 70 for 40Ar (Pepin, 1991). In addition, Xe/Kr-, Ar/Kr-, and Ne-isotopic ratios all have a solar-like signature, albeit with larger error bars, suggesting that Venus retained a slightly fractionated version of a primary solar atmosphere. The much-lower-than-solar Ne and N abundances may indicate that icy planetesimals may have played an important role in providing venusian volatiles, as they may have for Earth as well. Furthermore, coupling of noble gas with C and N data indicates that the inventories of these elements are consistent with the addition of enstatite-chondrite-like material (Pepin, 1991), late in the hydrodynamic escape period.

6. CONCLUSIONS AND UNRESOLVED ISSUES REGARDING THE ACCRETION OF THE TERRESTRIAL PLANETS

A major deficiency in our understanding of the relationships between meteorites and planets is our inadequate understanding of the elemental and isotopic compositions of Venus, Mercury, and the Sun, as well as the inventory of volatiles available to planets during and after accretion. It is likely that some of these uncertainties will be resolved in the near future, by recent and upcoming missions such as Genesis, MESSENGER, Stardust, and BepiColumbo. Several issues, however, such as O-, Os-, and Cr-isotopic measurements, can only be resolved by sample return, and thus will have to await future mission planning.

6.1. Compositional Uncertainties in Venus, Mercury, and the Sun


As shown in Fig. 6, the major elements Mg, Al, and Si appear to be robust discriminators among different differentiated and undifferentiated planetary objects, provided the most “primitive” samples from differentiated objects are used in the comparison and major reservoirs are not sequestered in the interiors of differentiated planets. Primitive objects preserve their original bulk compositions and the most “primitive” samples of differentiated objects define trends with negative slopes that include their bulk compositions, i.e., they are either mantle samples or high-degree melts of the mantle. The reason is that Mg is compatible (remains behind in silicate melts during melting) while Al is incompatible (is extracted into magmas during melting).

Measurements of the moment of inertia, topography, and gravity field of Mercury by future missions will be able to place strong constraints on the size of the core and the thickness of the crust (e.g., Spohn et al., 2001).

Basaltic rocks from Venus also fall on an aluminous fractionation line in the Mg/Si vs. Al/Si diagram (Fig. 6), based on analyses by Venera and Vega spacecraft summarized in Kargel et al. (1993), and overlap the terrestrial MORB and lunar picritic glass data. This similarity to Earth is also seen in U/Th ratios (Fig. 11 of Kargel et al., 1993), as expected of two refractory elements. More importantly, Venus data fall on the terrestrial lines or fields in volatile element/refractory element diagrams such as K/Th, K/U, and MnO/FeO (Figs. 12–14 respectively of Kargel et al., 1993). Venus even falls in the terrestrial fields for FeO/MgO and Al2O3/MgO, although these fields have more overlap with other terrestrial planetary bodies. It seems reasonable to conclude that Venus is Earth-like within analytical error for major and minor elements, perhaps suggesting mixing between 1 AU and 0.72 AU. It is unknown whether Mercury differs from Earth solely in degree of reduction and mass of the core, or formed from profoundly different material.


As noted earlier, only with sample return will the O-isotopic compositions of Venus and Mercury be known with adequate precision. There is an intriguing possibility that we may soon know the O-isotopic composition of the Sun, however, as a result of the Genesis mission, which collected solar wind. Currently there are two conflicting predictions of the isotopic composition of the Sun. Clayton (2002) and Yurimoto and Kuramoto (2004) predict that the Sun should be rich in 16O, near the 18O-rich end of the CAI line in Fig. 7, based on considerations of photodissociation, and self-shielding in molecular clouds can yield to 16O enrichment in the CO gas. In contrast, Ireland et al. (2005) argues that the Sun is 16O-poor, based on measurements of lunar metal grains exposed to the solar wind. Samples returned by the Genesis mission should resolve this disagreement. If Venus and Mercury share the same O-isotopic reservoir as Earth and Moon (and by inference the same Mg, Al, and Si composition), the implication would be that the solar system inward of 1 AU was well-mixed, but remained heterogeneous outward from 1 AU. Such a result would provide significant constraints on the thermal history of the inner solar system.


It is unknown if Venus and Mercury fall on the
extrapolated trend indicated by the dashed line, or whether the solar system inside 1 AU is well mixed, with Venus and Mercury plotting at ε(53) = 0. Clearly sample return missions to Venus and Mercury would reveal much about the chemical and isotopic structure, and hence mixing processes, in the inner solar system.

6.2. Volatile-Element Inventories

Some bodies in the inner solar system are volatile-element-depleted (e.g., the Moon, 4 Vesta, Mercury), and it is not clear if this is due to the materials from which they accreted, or to subsequent modification of those compositions [e.g., loss of lunar volatiles (e.g., Becker et al., 2003)] due to a process such as impact events (e.g., Genda and Abe, 2005). These two endmember ideas have formed the basis of evaluations for the Moon.

On the other hand, those planets that have retained volatiles to a certain degree (e.g., Mars, Earth, Venus) could have acquired volatiles from a number of sources and by a number of processes. Many of the potential sources of volatiles are not well characterized, such as Jupiter-family comets, asteroids, and Kuiper belt objects, and better characterization by future spacecraft (and sample return) missions would be hugely beneficial. Further work on the processes affecting volatile retention in planets, such as impacts (e.g., Pierazzo and Melosh, 2001) and deep mantle storage (e.g., Abe et al., 2000; Williams and Hemley, 2001), will aid our understanding of the ability of small and large planetesimals to acquire and store volatiles over geologic time.

It is clear that integration of all geochemical data will not be simple, and is an enticing challenge around the corner.

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