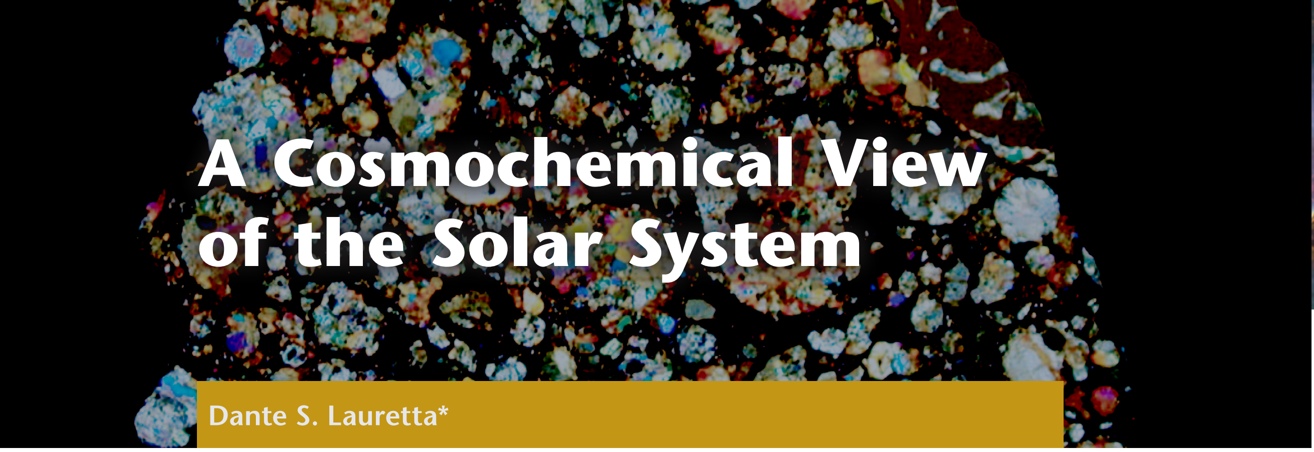

A Cosmochemical View of the Solar System

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1811-5209/11/0007-0011$2.50 DOI: 10.2113/gselements.7.1.11

This NASA Hubble Space Telescope image shows a small portion of one of the largest observable star-forming regions in the Galaxy, the Carina Nebula, located 7500 light-years away in the southern constellation Carina. It captures the chaotic activity atop a three-light-year-tall pillar of gas and dust that is being eaten away by the UV light from nearby massive stars. The pillar is also being assaulted from within, as infant stars buried inside it fire off jets of gas that can be seen streaming from towering peaks. The image celebrates the 20th anniversary of Hubble's launch and deployment into an orbit around Earth. Credit: NASA, ESA, and M. Livio and the Hubble 20th Anniversary Team (STScI)

Cosmochemistry is the study of extraterrestrial materials aimed at understanding the nature of Solar System bodies, including the planets, their natural satellites, and small bodies. An important goal is to increase our understanding of the chemical origin of the Solar System and the processes by which its planets and small bodies have evolved to their present states. Research in cosmochemistry covers an enormous range of disciplines and techniques, including mineralogy, petrology, major and trace element chemistry, isotope compositions, radiometric ages, magnetism, and radiation-exposure effects. These studies provide a wealth of data about the processes of stellar evolution, planetary-system formation, alteration in asteroidal and cometary interiors, and the accretion history of the Earth, including the origin of Earth's volatile and organic materials.

Keywords: cosmochemistry, meteorites, solar abundances, condensation, chondrites, isotopes, nucleosynthesis, asteroids, comets

ELEMENT PRODUCTION AND STELLAR EVOLUTION

The basic chemical structure of the Solar System is a result of the chemistry of just a handful of major elements. Combined, just five elements (in order of abundance, Fe, O, Mg, Si, and Ni) make up 95% of the mass of the Earth and the other terrestrial planets (McDonough and Sun 1995). Thus a planet composed of an Fe–Ni metallic core surrounded by a Mg-silicate mantle is a perfectly acceptable first-order model for planet Earth. The addition of nine other elements (Ca, Al, S, Cr, Na, Mn, P, Ti, and Co) brings the total to over 99.9% of the mass of our planet. The story of how our planet, and ourselves, came to be, however, is often unraveled by studying the details of the remaining 0.1%.

The bulk elemental abundances in the Solar System reflect the astrophysical evolution of the Universe (Fig. 1). Almost 99.9% of the Solar System is composed of hydrogen (H) and helium (He). These elements, along with trace amounts of Li, Be, and B, are remnants from the Big Bang (Copi et al. 1995). Hydrogen and helium were the feedstock for the first stars, which were massive and ran through their evolution in a few million years. It was not until the formation of these stars that carbon and the heavier elements came into existence.

Hydrogen burning is the principal energy source in main sequence stars. This process fuses four H nuclei together to make ^{4}He. In solar-mass stars, H burning proceeds via proton–proton chain reactions. In stars of somewhat higher mass, core temperatures are greater and the burning proceeds by the CNO cycle, in which the net reaction is catalyzed by isotopes of C, N, and O. Side reactions in H burning generate rare but important isotopes, including ^{14}N, ^{17}O, and the short-lived radioisotope ^{26}Al.

After a star has consumed the H in its core, it contracts and heats, resulting in the onset of He burning. This process produces ^{12}C in the "triple-α process," in which three ^{4}He nuclei collide simultaneously. In addition, ^{16}O is produced during He burning when ^{12}C nuclei capture alpha particles (which are simply ^{4}He nuclei). Neutrons are also liberated during He burning, resulting in "s-process" neutron-capture nucleosynthesis (Gallino et al. 1998). Helium burning is the last stage in the life of stars below eight solar masses. At the end of this stage, strong stellar winds blow off the stellar envelope, delivering gas and dust back to the interstellar medium (ISM), creating a planetary nebula (which, by the way, has nothing to do with planets). Once the envelope of the star is completely lost, a white dwarf star is left behind. Accretion of material given off by a companion star can result in explosive H burning on the surface of the white dwarf, forming a nova. If enough mass is accreted, C and O may burn explosively and completely disrupt the star, forming a type-Ia supernova.

In stars greater than eight solar masses, C burning occurs, producing an excited nucleus of ^{24}Mg by fusion of two ^{12}C nuclei. This nucleus decays into ^{20}Ne and an α particle, ^{23}Na and a proton, or ^{24}Mg and a gamma ray. The ^{20}Ne is the next nuclear fuel in the star's life. In this stage, ^{20}Ne nuclei disintegrate into ^{16}O nuclei and α particles. Other ^{20}Ne nuclei may capture these α particles to produce ^{24}Mg. Ne burning is thus the major producer of ^{24}Mg.

As Ne burning ends, the star contracts and heats until O burning is initiated. This process produces an excited nucleus of ^{32}S. This nucleus decays into ^{28}Si and an α particle, or ^{31}P and a proton, or relaxes down to ^{32}S through gamma ray emission. Thus, ^{28}Si and ^{32}S are the principal products of O burning. As the star contracts further, Si burning occurs. In this process, some of the nuclei disintegrate into lighter nuclei, neutrons, protons, and α particles. The remaining nuclei capture these light particles to produce a range of isotopes, including ^{40}Ca, ^{56}Fe (the

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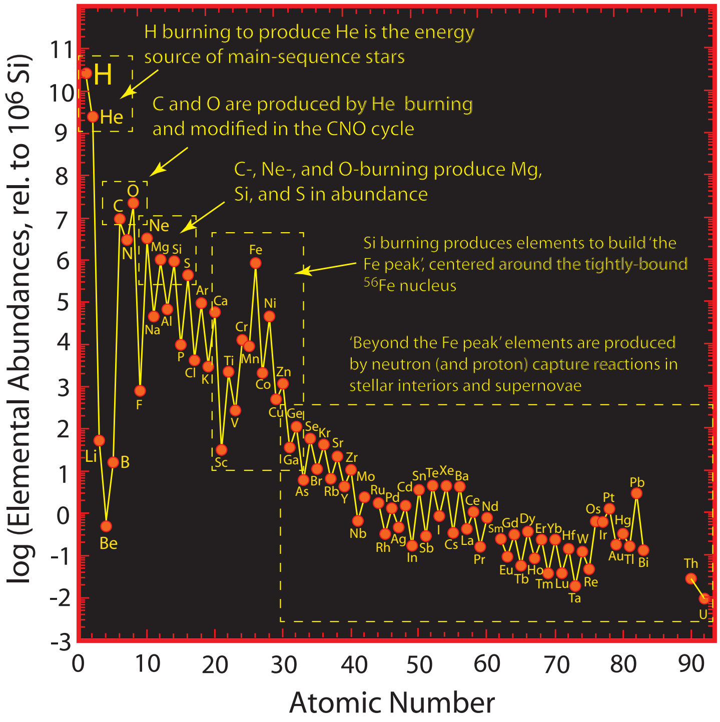

FIGURE 1 Solar System elemental abundances as a function of atomic number. The bulk elemental abundances are the result of nucleosynthetic reactions during different stages of stellar evolution.

primary product), and the short-lived radioisotope ^{60}Fe. These massive stars end their lives in gigantic explosions as type-II supernovae, expelling these newly synthesized elements into the ISM. Ejection of neutron-rich matter from these supernovae results in r-process neutron-capture nucleosynthesis, in which elements heavier than Fe are created (Arnould et al. 2007; Schatz 2010).

When the Solar System formed, it incorporated material from many of these stellar sources, including supernovae, late-stage stars, and novae. The evidence for this diversity is recorded in presolar grains, which preserve detailed chemical signatures of the end stages of stellar evolution and processes in the ISM. In their article in this issue, Ann Nguyen and Scott Messenger (2011) provide an overview of the study of presolar materials, which record the detailed history of the end of stellar evolution and the beginning of Solar System formation.

The starting material for the Solar System was mixed extremely well, such that the system as a whole has a nearly uniform elemental and isotopic composition. In addition to H and He, the primary products of stellar nucleosynthesis are C, N, O, Ne, Na, Mg, Al, Si, S, Ar, Ca, and Fe. These elements account for 99.5% of the matter in the ISM that is not H and He. With the exception of the noble gases, they form the chemical basis of the bodies of our Solar System and all planetary systems. C/O ratios determine the ultimate chemistry of planetary systems, with C-rich systems dominated by graphite and carbides (Bond et al. 2010). O-rich systems, like our Solar System, are dominated by silicates and oxides.

CHEMICAL PROCESSES IN THE SOLAR NEBULA

The transition from the ISM to a protoplanetary system happens within a few million years. The process begins when a dense cloud core in a giant molecular cloud starts to collapse gravitationally. Initially, the mass infall rate is large. Due to the angular momentum of the original cloud, much of the material collapses into a disk (the solar nebula) that orbits the center of mass. The mass accretion rate decreases over time and the system reaches a relatively quiescent state, known as the T Tauri phase, which is the phase prior to becoming a main sequence star. For the next ten million years, different processes (solar wind interactions, photo evaporation, etc.) erode the protoplanetary disk. It is during this brief time period that the major chemical structure of a planetary system is established.

Stable isotopes in planetary materials record this complex history of gas-phase photochemistry and multicomponent mixing (MacPherson et al. 2008). The stable isotope ratios of O in the Solar System appear to be anomalous compared to our galactic neighbors, providing evidence for the injection of freshly nucleosynthesized material into the early Solar System. Gas-phase chemical processes left distinctive isotopic signatures in the residual solids from this era. In particular, the selective photodissociation of the CO molecule isotopomers (the prime carriers of both C and O) produced the distinctive, mass-independent O isotope fractionation that characterizes all primitive materials from the early Solar System. Unlike well-known mass-dependent isotopic fractionation, the amount of separation in this process does not scale in proportion with the difference in the masses of the isotopes. Mass-independent fractionation thus resulted in ^{16}O-rich solids and ^{16}O-poor ices without altering the ^{18}O/^{17}O ratio. Mixing and reactions between these components produced the unique oxygen isotope anatomy of Solar System bodies, providing a convenient way to classify and discriminate among extraterrestrial objects of different origins. In their article in this issue, Doug Rumble and colleagues (2011) discuss the wide variety of stable isotope systems that are studied to understand chemical processes in the early Solar System.

In our Solar System, the surviving products of chemical and physical processes in the solar nebula were incorporated into the asteroids, comets, and planets (Lauretta and McSween 2006). Primitive meteorites that originate from small asteroids and comets preserve much information about the original composition of the Solar System. The most primitive unequilibrated chondritic meteorites escaped significant processing and preserve many signatures of their formation and processing within the solar nebula (Scott 2007). See Scott 2011 this issue for an overview on meteorites.

Chemically, the most primitive meteorites are the CI chondrites. Their elemental abundances agree very well with that of the Sun (determined by spectroscopic observations of the solar photosphere) except for the volatile elements H, C, N, and O, the noble gases, and Li (Fig. 2; Anders and Grevesse 1989). Combining data from the CI chondrites and the Sun provides an accurate estimate of the bulk composition of the Solar System and, by inference, the solar nebula. This data set provides a starting point for understanding the initial chemistry and chemical evolution of the Solar System.

Condensation calculations are a fundamental tool for understanding solar nebula chemistry (Ebel 2006). *Condensation calculation* is a generic term for a model describing the equilibrium distribution of the elements between coexisting phases (solids, liquid, vapor) in a closed chemical system with vapor present. Such chemical equilibrium calculations describe the identity and chemical composition of each chemical phase in the assemblage toward which a given closed system of elements will evolve, to minimize the chemical potential energy of the entire system. Amazingly, this simple, first-order model goes a long way to describing the bulk composition of meteorites and even that of the Earth and Mars.

A useful cosmochemical tool is the 50% condensation temperature (T_{50}) (Lodders 2003). This theoretical value describes the temperature at which any given element is equally partitioned between solid and gas species in a canonical nebular system (typically defined as solar abundances at 10^{-4} bars total pressure). The cosmochemical classification of the elements is based on their relative volatilities, quantified in their T_{50} value. Elements with the highest T_{50} values (e.g. Ca, Al, and Ti) are called highly refractory. As the T_{50} values decrease, elements are classified as moderately refractory (e.g. Si, Mg, and Fe), moderately volatile (e.g. K and Na), volatile (e.g. S), or highly volatile (e.g. Hg and Tl). These designations are often combined with Goldschmidt's (1954) geochemical classification of lithophile, siderophile, chalcophile, and atmophile elements, such that, for example, W is considered a highly refractory siderophile element and Zn a moderately volatile lithophile element.

This concept of equilibrium condensation goes a long way towards explaining the major mineralogy of chondritic meteorites. The first predicted condensates are Ca–Al-rich phases. The oldest Solar System solids are Ca–Al-rich inclusions (CAIs). Major condensates are olivine, pyroxene, and metal. These phases make up over 90% of the mass of chondritic meteorites. Sulfur condensation represents the incorporation of the most volatile major element. Sulfur abundances vary widely across all classes of primitive meteorites, thus recording variable temperatures of formation and accretion. Compared to the CI chondrites, all meteorite types are depleted in volatile elements. The magnitude of this depletion is a smooth function of T_{50}, as demonstrated in a representative meteorite class, the CV chondrites (Fig. 3). These trends provide convincing evidence that key drivers of elemental fractionation in the early Solar System were volatility-controlled processes.

Condensation calculations act as a guide for the chemical evolution of the solar nebula. However, studies of meteorites and astronomical observations of star-forming regions demonstrate that the chemical evolution of planetary systems is much more complicated (Apai and Lauretta 2010). The history of the early Solar System is preserved in the small bodies (asteroids and comets) that are the survivors of planetary accretion and giant-planet migration (Gomes et al. 2005). They record a wide range of environments, yet all show striking similarities. The line separating asteroids and comets used to be clearly defined in astronomical terms, but has become increasingly blurred as samples of these bodies are returned to Earth and studied in the laboratory. In this issue, Mathieu Gounelle (2011) reviews the history of asteroid and comet studies and discusses recent results that suggest these two classes of objects are much more similar than previously thought.

Differences in elemental abundances among different asteroidal and cometary materials reflect variations in the environment where they formed. Meteorites and cometary samples record a wide range of oxidation states from the early Solar System. The chemistry of Fe is a prime tool for discriminating between these chemical states. Iron exists as metal and in silicates, oxides, sulfides, carbonates, sulfates, carbides, and more. Any model of the early Solar System is challenged to explain this vast range of chemical environments, while maintaining roughly solar elemental abundances of refractory siderophile and lithophile elements. It is likely that the bulk oxidation of asteroids and comets is established as an average of its accretionary constituents.

The major components (50–80 vol%) of most chondrites are ~1 mm diameter igneous spheres, called chondrules (Fig. 4). Chondrule fragments have also been found in the

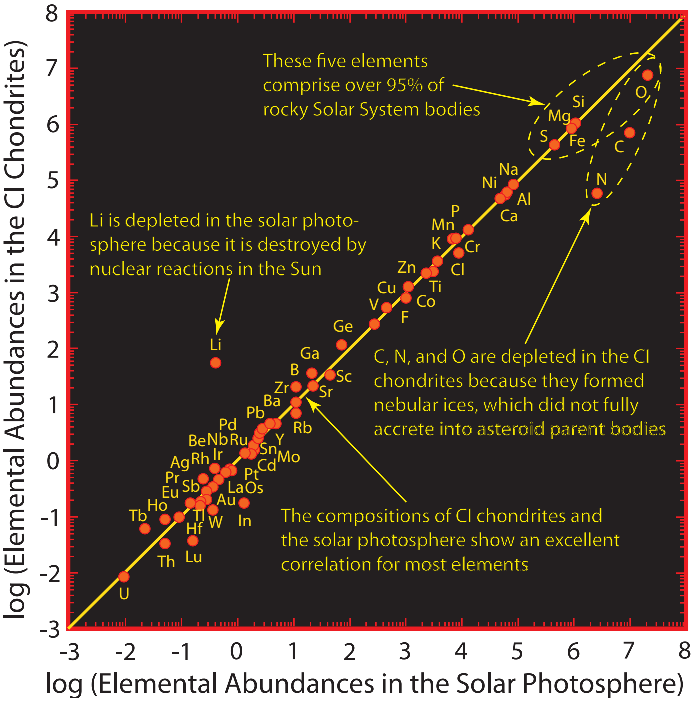

Figure 2 Elemental abundances in CI chondrites compared to abundances in the solar photosphere. For comparison purposes, the abundance of Si is set at 10^6 Si. The bulk compositions of the CI chondrites and the solar photosphere show an amazing correlation, with a few key exceptions. Combined, these data sets provide our best estimate for bulk solar elemental abundances. H and the noble gases are not shown.

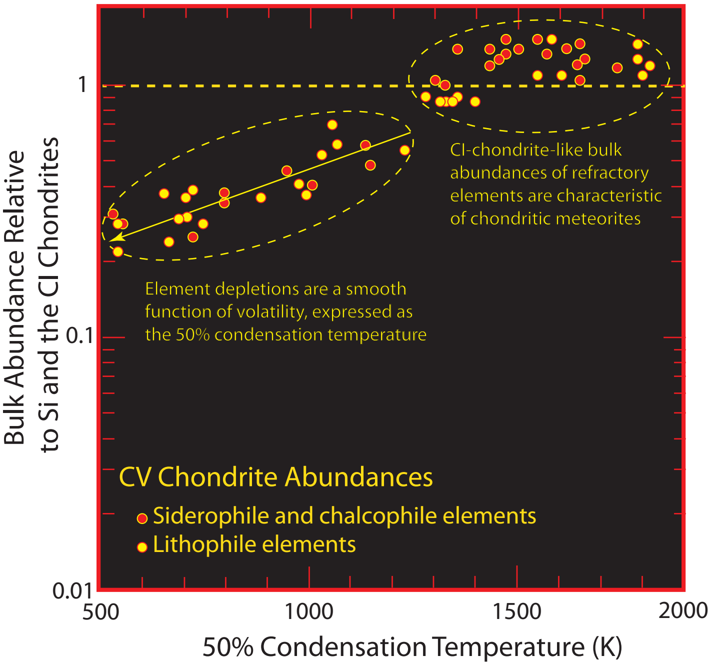

Figure 3 Elemental abundances of CV chondrites compared to average CI chondrites as a function of 50% condensation temperature. CV chondritic meteorites are characterized by bulk depletions in volatile elements, relative to the CI chondrites. These depletions are smooth functions of the 50% condensation temperature in a canonical solar nebula model. The dashed line at the abscissa value of 1 corresponds to values equal to the average CI chondrite composition.

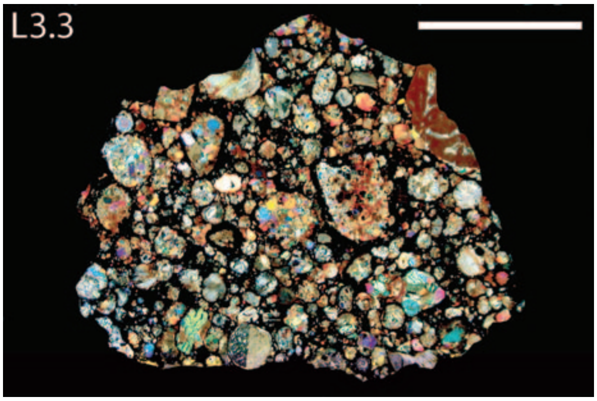

FIGURE 4 A primitive type-3 ordinary chondrite (L3) illustrates the diversity of chondrule textures and morphologies. Scale bar = 0.5 cm. PHOTO FROM LAURETTA AND KILLGORE 2005

Stardust samples from comet Wild 2 (Nakamura et al. 2008). The shapes, textures, and mineral compositions of these chondrules are consistent with crystallization of a molten droplet that was floating freely in space in the presence of a gas. Chondrites are primitive samples of the early Solar System. By extension, chondrule formation was thought to represent the earliest igneous processes. However, recent radiometric dating of magmatic iron meteorites suggests that their parent bodies may have formed and completed differentiation prior to the first generation of chondrule formation. Nevertheless it is still widely accepted that chondrule formation is a critical step in planet formation. This process thus proceeds by dust-particle (up to a few microns) agglomeration, followed by flash heating and melting, forming millimeter-to-centimeter-sized igneous particles. These chondrules are then somehow size sorted and concentrated to form planetesimals along with dust that either escaped heating or recondensed during post-chondrule-formation cooling.

Farther out in the solar nebula, water ice became stable. Because H and O represent the first and third most abundant elements in the Solar System, respectively, water ice was the most abundant condensed solid. Despite this, many researchers in cosmochemistry fail to consider water ice as a "planet-building material" in the same way as silicates and metals. This bias is due in large part to the fact that we do not have samples of icy material to study in the laboratory. The radial distance along the nebular midplane at which water ice condenses is referred to as the snowline. It was thought that this snowline existed beyond five astronomical units (AU; one AU is the mean distance between the Sun and the Earth), and that ice provided the critical mass needed to accrete the giant protoplanetary core of Jupiter. However, recent observations of water ice on asteroid surfaces in the main asteroid belt (Campins et al. 2010; Rivkin and Emery 2010) as well as the discovery of the "main-belt comets" (Hsieh and Jewitt 2006) suggest that the snowline may have reached as far inward as two AU. This finding confirms the information from meteorite studies that many asteroidal bodies accreted water ice (and perhaps other ices, such as methane, ammonia, or carbon dioxide) along with silicate and metallic material.

PROCESSES IN ASTEROID AND COMET INTERIORS

Several carbonaceous chondrite groups record intense hydrothermal alteration that lasted for up to 15 million years. This process was likely initiated by radioactive decay of short-lived radioisotopes such as ^{26}Al and ^{60}Fe, which melted ice particles and provided the necessary energy for alteration reactions. Aqueous alteration of chondritic materials resulted in the formation of a variety of secondary phases, including hydrous minerals such as serpentines and clays, and also carbonates, sulfates, oxides, sulfides, halides, and oxyhydroxides. In addition, alteration modified the stable isotope compositions of the bulk meteorites and their individual components. Though the parent bodies of these chondrites themselves could not have supplied water and other volatiles to the terrestrial planets, there were likely thousands of other such bodies, which have long since been removed from the asteroid belt.

Carbon, though a major element in the Solar System, is a minor or trace element in most planetary materials. Despite its low abundance, it is of prime importance as the central element of life, and its chemistry has received much attention in cosmochemical investigations. In her article in this issue, Zita Martins (2011) discusses the latest results in organic cosmochemistry and their implications for the origin of life on Earth. Asteroids and comets record the history of the primordial organic compounds that may have seeded early Earth with the precursors of life. Organic matter in many classes of meteorites consists almost exclusively of an insoluble kerogen-like material. However, the hydrothermally altered chondrites also contain numerous soluble organic compounds, many of key interest to studies on the origin of life. This organic material records a complex history, starting in the ISM, proceeding through solar nebula processes, and ending with alteration in planetesimal interiors.

While some planetesimals were altered by hydrothermal processes, some of those that accreted "dry" experienced thermal metamorphism. This metamorphism was also driven by the decay of short-lived radioisotopes. The least thermally altered chondrites have well-defined chondrules and a fine-grained, opaque matrix (FIG. 5A). Thermal metamorphism resulted in many changes, including textural integration and recrystallization, mineral equilibration, destruction of primary minerals, and growth of secondary minerals (FIG. 5B–D). Asteroids that experienced no partial melting retained their bulk chondritic abundances, and samples of these bodies that reach the Earth are still considered chondritic meteorites, even though most traces of chondrules have been erased. Other meteorites have been heated to the point of partial melting and are known as "primitive achondrites," meaning they have chondritic compositions but achondritic textures (FIG. 5E, F).

Planetesimals larger than ~50 km were able to retain the energy released by radioactive decay and, as a result, experienced intense heating leading to complete melting of all silicate and metallic material. These bodies separated into fully differentiated, layered worlds consisting of core, mantle, and crust. Meteorite collections include many of these achondrites, which are examples of the products of this transformation (FIG. 5G, H). The basaltic eucrites, magmatic iron meteorites, and pallasites all originated on asteroidal bodies that experienced extensive differentiation. While primitive chondrites may dominate the flux of material encountering Earth, the majority of distinct asteroids that have delivered meteorites to Earth are differentiated, indicating that differentiation was widespread in the inner Solar System.

THE PAST AND FUTURE OF PLANETARY ACCRETION

All the terrestrial planets and our own Moon experienced igneous differentiation. Isotope studies of meteorites provide fundamental data for determining how the terrestrial planets, including Earth, accreted. Recently there have been major advances in understanding the timing and

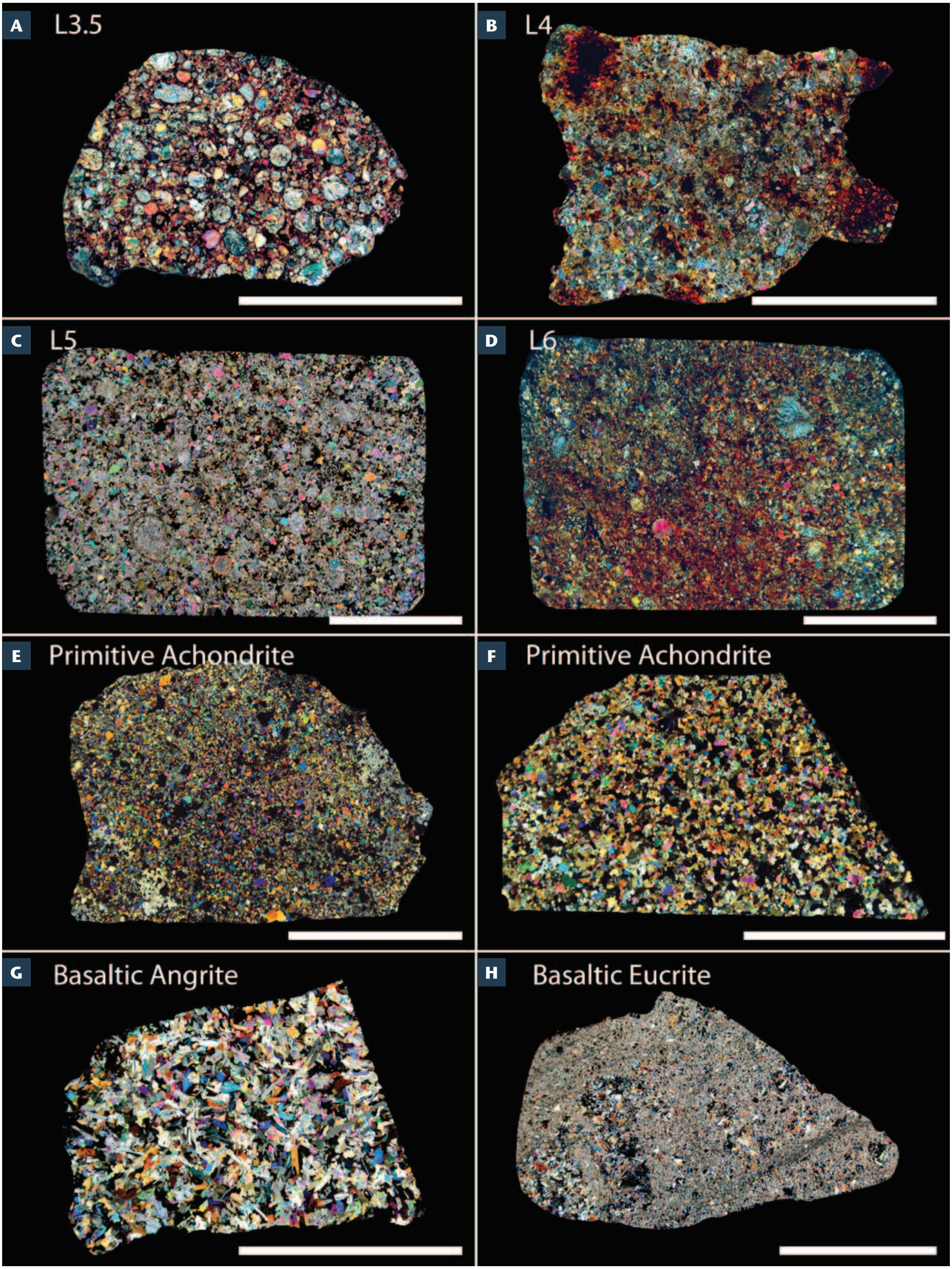

FIGURE 5 Textural variations among various meteorite types. This series of photomicrographs illustrates the effects of thermal metamorphism, melting, and recrystallization in chondritic (L) and achondritic meteorites. In all images, the scale bar equals 1 cm. PHOTOS FROM LAURETTA AND KILLGORE (2005)

nature of terrestrial planet accretion. These advances are largely the result of better definition of initial Solar System abundances of short-lived nuclides and their daughters, as determined from meteorites. Recent improvements to Hf–W chronology have led to major improvement in understanding the timing of core formation in a wide variety of planetary bodies, including the Earth, the Moon, and Mars. In this issue, Thorsten Kleine and John Rudge (2011) discuss the radiometric techniques that are used to construct a detailed timeline of planetary formation. What is most striking from these studies is the fact that major planet formation and differentiation all occurred within the first 50–100 million years of Solar System evolution.

In addition to unraveling the ancient history of our Solar System, cosmochemical studies also provide insight into processes that are currently active. In particular, the physical and chemical properties of meteorites help us understand how asteroids from the main belt continue to evolve into near-Earth objects (NEOs), and ultimately into meteorites or, in the case of larger bodies, Earth impactors. This process begins when a major collision occurs between two asteroids, leaving them shattered and ejecting many fragments on trajectories that will not return them to their parent. For small bodies (on the order of 1–10 km) a nongravitational force known as the "Yarkovsky effect" alters their orbits (Bottke et al. 2002). This effect is the result of an imbalance in the absorption and reemission of electromagnetic radiation. Basically, an asteroid receives most of its radiation at noon, local solar time. Because of its thermal inertia, this energy is reradiated back to space as thermal photons later in its afternoon. Since these thermal photons carry momentum, they impart a tiny force that leads to large, long-term effects in the orbits of small bodies. Thus, study of the way in which asteroidal material interacts with and is modified by solar radiation is important to understanding the orbital evolution of NEOs. This work is particularly important when trying to determine the impact probability of a potentially hazardous asteroid with the Earth (Milani et al. 2009).

THE OUTLOOK FOR COSMOCHEMISTRY

Cosmochemistry is a dynamic field with a bright future. It promises to be at the forefront of Solar System exploration, which is following a natural progression from flyby missions, to orbiters, to landers that perform in situ analyses, to missions that return samples to Earth for detailed analyses. The Stardust mission, which returned samples of comet Wild 2, and the Genesis mission, which returned samples of solar wind, have yielded unprecedented scientific returns. With many national space agencies developing future sample-return missions, we can look forward to samples from asteroids, comets, the Moon, and Mars over the coming decades. Some day we may even see samples returned from more challenging targets, such as Venus, Mercury, and the Galilean satellites. Only when humanity has acquired a complete geologic inventory of the Solar System will the entire history of our planetary system be understood. In the meantime nature continues to deliver new and amazing samples, each one of which reveals a heretofore-unknown chapter in the history of our Solar System. ▪

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