

cosmochemistry Cosmochemistry is concerned with experimental, observational, and theoretical studies of the chemical, isotopic, and mineralogical composition of extraterrestrial materials such as cometary dust particles (e.g., the *Giotto* mission to comet P/Halley), interplanetary dust particles (known as IDPs) collected using high-flying aircraft), lunar samples, and meteorites. The seminal work by Harold Urey, Hans Suess, and Harrison Brown on the chemical processes involved in the origin and evolution of the Solar System and the abundances of the elements led to the emergence of cosmochemistry as a separate sub-discipline in the late 1940s.

Historically, two major areas in cosmochemistry research have been: (1) the determination of the solar-system abundances of the elements, and (2) the chemical behaviour of the elements in a solar composition (i.e. hydrogen-rich) environment. These two topics are interwoven because the observed elemental abundances in primitive meteorites (chondrites) are generally correlated with the volatility of the elements, or their compounds, in material of solar composition.

Before proceeding some commonly used terms need to be defined. Chondrites are stony meteorites that contain small, melted beads known as chondrules and finer-grained material known as matrix. Some chondrites also contain calcium, aluminium-rich inclusions (CAIs), which are dominated by calcium, aluminium, and titanium-bearing refractory oxides and silicates. Observational studies indicate that the chondrules, mineral fragments, inclusions, and matrix in chondrites formed in the solar nebula and have been little altered since that time by planetary processes (e.g., aqueous alteration, igneous differentiation). The chondrites are divided into three groups; carbonaceous, ordinary, and enstatite chondrites, on the basis of their major element composition and mineralogy. These three major classes are further subdivided into different petrographic types. The most primitive chondrites, in the sense of most closely reproducing the elemental abundances in the photosphere of the Sun, are the CI (or C1) carbonaceous chondrites.

Solar abundances of the elements

Figure 1 shows the relative abundances of the 20 most abundant elements in the Sun and solar nebula. These abundances are primarily derived from chemical analyses of chondrites and astronomical observations of the elemental abundances in the Sun. To a very good approximation, the abundances of most elements in the CI carbonaceous chondrites and in the Sun are identical. The few exceptions to this generalization are: light elements such as lithium, which are destroyed by thermonuclear reactions in the Sun; atmophile elements such

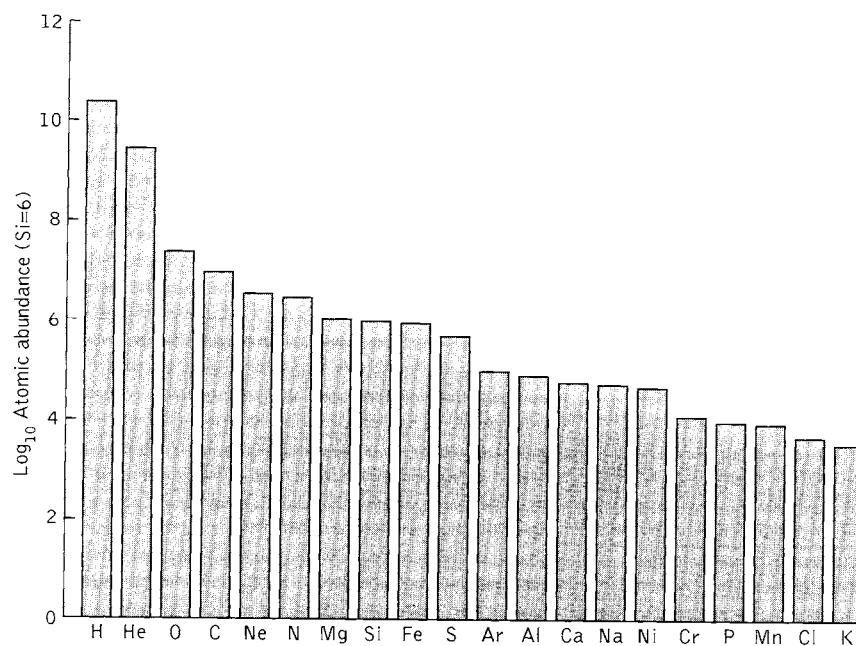


Fig. 1. The relative abundances of the 20 most abundant elements in solar composition material according to Anders and Grevesse (1989), *Geochimica et Cosmochimica Acta*, 53, 197–214. The abundances are normalized to Si = 10^6 atoms.

as hydrogen, oxygen, carbon, nitrogen, and the noble gases, which are incompletely condensed in meteorites; and some rare elements such as mercury, germanium, lead, and tungsten, which are difficult to analyse in the Sun or in meteorites. To a lesser extent there is also a good correspondence between elemental abundances in the Sun and in all chondrites. This close relationship has led cosmochemists to believe that chondrites are relatively unaltered samples of material that condensed in the solar nebula. Over 30 years of meteorite studies and chemical equilibrium modelling of nebular chemistry demonstrate that evidence of nebular chemical reactions is preserved, with varying degrees of alteration by subsequent processes such as thermal metamorphism and aqueous alteration, in chondritic meteorites.

Cosmochemical behaviour of the elements

Chemical analyses of chondrites and interplanetary dust particles, and thermochemical equilibrium calculations of chemistry in hydrogen-rich solar material, show that the elemental fractionations in chondrites and IDPs are primarily the result of volatility controlled processes such as gas \rightarrow solid condensation and solid \rightarrow gas evaporation in the solar nebula. The occurrence of some characteristic mineral morphologies, such as enstatite (MgSiO_3) whiskers with screw dislocations, in some IDPs shows that gas \rightarrow solid condensation was directly responsible for growing some minerals.

Cosmochemists therefore classify the elements according to their chemical behaviour in hydrogen-rich solar material. Refractory elements are the first elements to condense from solar composition gas. Both lithophiles (preferentially found in oxides or silicates, or both) and siderophiles (preferentially found in metals) with low vapour pressures, or that form compounds with low vapour pressures, fall into this category. The condensation of iron metal alloy and magnesian silicates (MgSiO_3 , enstatite, and Mg_2SiO_4 , forsterite) divides the refractory elements from the moderately volatile elements. In turn, troilite (FeS) condensation divides the moderately and highly volatile elements. Finally, water-ice condensation separates the highly volatile elements (e.g., lead, indium, bismuth, and thallium) from the atmophile elements (hydrogen, carbon, nitrogen, and the noble gases). Table 1 summarizes the major condensation reactions in solar composition material.

Refractory lithophiles include the alkaline earths (e.g. calcium and magnesium) the lanthanides (rare earth elements, or REE), the actinides, aluminium, and elements in groups 3b (scandium, yttrium), 4b (titanium, zirconium, and hafnium), and 5b (vanadium, niobium, and tantalum) of the periodic table. The refractory siderophiles are the platinum-group metals (except palladium), molybdenum, tungsten, and rhenium. As shown in Table 1, the refractory lithophiles and siderophiles constitute about 1 per cent by mass of the total condensable material (rock + ices) in the solar nebula. Exten-

Table 1. Condensation sequence for the 20 most abundant elements in the solar nebula (10^{-4} bar total pressure)

Reaction	Temperature (K)	Fraction condensed (mass %)
Ca, Al oxides, and silicates condense	1670–1530	1.1
Fe alloy condenses	1337	9.1
Forsterite (Mg_2SiO_4) condenses	1340	20.4
Schreibersite (Fe_3P) forms	1151	20.5
Alkali feldspar ($\text{Na, K} \text{AlSi}_3\text{O}_8$) forms	1000–970	20.9
Sodalite [$\text{Na}_4(\text{AlSiO}_4)_3\text{Cl}$] forms	863	20.9
Troilite (FeS) forms	719	23.4
Magnetite (Fe_3O_4) forms	400	24.0
Hydrated silicates (talc, serpentine) form (?)	~280	—
H_2O ice condenses	180	50.9
Ar, Kr, and Xe clathrate hydrates condense	74–50	51.5
CO and N_2 ices condense	~20	100.0

sive studies of the chemical composition of stony meteorites show that these refractory elements behave as a group in most meteorites: that is, their abundances in different types of meteorites are either enriched or depleted by about the same factor. Large enrichments, which are 20 times solar elemental abundances on average, of the refractory lithophile and siderophile elements are found in CAIs in the Allende meteorite and other carbonaceous chondrites. The CAIs have a mineralogy dominated by minerals rich in calcium, aluminium, and titanium such as hibonite, $\text{CaAl}_{12}\text{O}_{19}$, melilite, a solid-solution of gehlenite, $\text{Ca}_2\text{Al}_2\text{SiO}_7$, and åkermanite, $\text{Ca}_2\text{MgSi}_2\text{O}_7$, spinel, MgAl_2O_4 , and perovskite, CaTiO_3 .

Table 1 gives the 50 per cent condensation temperatures for metallic iron alloy and forsterite (Mg_2SiO_4). Metallic iron and magnesian silicates account for most of the rocky material in solar composition matter. The large excess of molecular hydrogen (H_2) in solar gas leads to extremely low oxygen fugacities and the FeO content of the magnesian silicates is insignificant until low temperatures of about 400–600 K. At these temperatures olivine and pyroxene solid solutions containing ~20 mole per cent of fayalite (Fe_2SiO_4) and ferrosilite (FeSiO_3) are predicted to form and any remaining iron metal is predicted to form magnetite at a pressure-independent temperature of about 400 K. However, slow solid-state diffusion at 400–600 K may inhibit solid–solid reactions such as the formation of FeO-rich silicates over the estimated 10^5 – 10^7 year lifetime of the solar nebula.

The moderately volatile elements have condensation temperatures intermediate between those of the major elements iron, magnesium, and silicon and troilite, FeS. The elements in this group are geochemically diverse and include sodium,

potassium, rubidium, chromium, manganese, copper, silver, gold, zinc, boron, gallium, phosphorus, arsenic, antimony, sulphur, selenium, tellurium, fluorine, and chlorine. The highly volatile elements condense at temperatures below 719 K, where troilite forms. These elements include mercury, bromine, cadmium, indium, thallium, lead, and bismuth. The condensation chemistry of many of the moderately and highly volatile elements is not well known because of uncertainties in the relevant thermodynamic data.

As Fig. 1 shows, hydrogen is the most abundant element and H_2 is therefore the most abundant gas in material of solar composition. At sufficiently high temperatures, dissociation to atomic H occurs. However, the phase boundary where abundances of H_2 and H are equal is at lower pressures and higher temperatures than those expected in the solar nebula. H_2 remains in the gas until temperatures of about 5 K, where it will condense out as solid hydrogen. It is unlikely that temperatures as low as this were ever reached in the solar nebula.

About 0.1 per cent of all hydrogen condenses out as water-ice at temperatures of 150–250 K, depending on the total pressure. Hydrated silicates such as serpentine and talc are also predicted to form by reactions between anhydrous silicate grains and water vapour in the nebular gas at temperatures below 300 K at 10^{-4} bar. However, although they are thermodynamically favourable, these reactions probably did not occur in the solar nebula because the vapour phase hydration of rock in a near-vacuum is a very slow process. Theoretical studies of hydration kinetics in the solar nebula and petrographic studies of water-bearing chondrites both suggest that the production of hydrated minerals occurred on the meteorite parent bodies. It is thus very likely that water-ice is the first H-bearing condensate to form.

Carbon chemistry is significantly more complex. To a good first approximation, carbon monoxide (CO) is the dominant carbon gas at high temperatures and low pressures and methane (CH_4) is the dominant carbon gas at low temperatures and high pressures in solar composition material. The two gases are converted by the net thermochemical reaction: $\text{CO}(\text{g}) + 3\text{H}_2(\text{g}) = \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$. (The symbol g denotes the gaseous state). Increasing the H_2 pressure (essentially the total pressure in solar material) or decreasing the temperature drives this reaction to the right and yields more CH_4 . The CO– CH_4 boundary is in the region of 600 K at 10^{-4} bar total pressure. CO is more abundant at higher temperatures, and CH_4 is more abundant at lower temperatures.

As first noted by Urey and later quantified by Lewis and Prinn, the kinetics of the CO→ CH_4 conversion may be so slow under the pressure and temperature conditions expected in the solar nebula that CO cannot be converted to CH_4 within the lifetime of the nebula. An exception to this occurs in the giant protoplanetary subnebulae, which are higher-density environments that are predicted to exist around Jupiter and the other gas giant planets during their formation. The CO→ CH_4 conversion is predicted to take place in these environments.

At low temperatures in the outer solar nebula and the giant protoplanetary subnebulae, CO and CH₄ may react with water-ice to form the clathrate hydrates CO·6H₂O(s) and CH₄·6H₂O(s) (The symbol s denotes the solid state.) (Clathrates are solids in which one chemical component is enclosed in the structure of another, as if in a cage.) The formation of these clathrate hydrates requires sufficiently rapid diffusion of CO or CH₄ through the water-ice crystal lattice. Theoretical models, which use experimentally determined activation energies for clathrate formation, predict that CH₄ clathrate hydrate can form in the giant protoplanetary subnebulae but that CO clathrate hydrate cannot form in the lower-density environment of the outer solar nebula.

The most important features of nitrogen chemistry are that N₂ is the major nitrogen gas at high temperatures and low pressures while NH₃ is the major nitrogen gas at low temperatures and high pressures. The two species are converted by the reaction N₂ + 3H₂ = 2NH₃, which is analogous to the reaction which converts CO and CH₄. Reduction of N₂ to NH₃ is also predicted to be kinetically inhibited in the solar nebula and to be both thermodynamically favoured and kinetically facile in the giant protoplanetary subnebulae. This is true even when the possible catalytic effects of grains of metallic iron are taken into account. Thus, N₂ is predicted to be the dominant nitrogen gas throughout the solar nebula, and NH₃ is predicted to be the dominant nitrogen gas throughout the giant protoplanetary subnebulae.

At low temperatures in the outer solar nebula, N₂·6H₂O(s) becomes thermodynamically stable, but its formation is probably inhibited by two factors. One is the limited availability of water-ice, which may already be totally consumed by reactions to form other hydrates and clathrates. The other is the expected kinetic inhibition of clathrate hydrate formation in the outer solar nebula. In this case, N₂, like CO, will not condense until temperatures of about 20 K (at 10⁻¹ bar pressure) are reached, where the solid ices form. On the other hand, NH₃·H₂O formation is predicted in the giant protoplanetary subnebulae, because it is both thermodynamically favoured and kinetically facile.

The noble gases helium, neon, argon, krypton, and xenon display fairly simple chemistry in material of solar composition. All are present in the gas as the monatomic elements and argon, krypton, and xenon undergo condensation to either ices or clathrate hydrates at sufficiently low temperatures. Condensation of the pure ices will occur at slightly lower temperatures than condensation of the clathrate hydrates. The formation of these species, like the clathrates of CO and N₂, may, however, be kinetically inhibited. Temperatures of about 20 K (at 10⁻⁴ bar pressure) are required for the quantitative condensation of argon, krypton, and xenon as pure ices. Neither helium nor neon will condense out of the gas because temperatures of 5 K or below are required for this to happen.

BRUCE FEGLEY

Further reading

- Kerridge, J. F. and Matthews, M. S. (eds) (1988) *Meteorites and the early Solar System*. University of Arizona Press, Tucson.
- Lewis, J. S. and Prinn, R. G. (1984) *Planets and their atmospheres: origin and evolution*. Academic Press, New York.
- Weaver, H. A. and Danly, L. (eds) (1989) *The formation and evolution of planetary systems*. Cambridge University Press.

cratons The term *craton* has been used for many years for the broad central parts of continents that are affected only by *epirogenic* movements. These areas thus contrast with mobile eugeosynclinal, *orogenic* regions. Cratons are essentially rather stable, continental, shield areas that have a basement of Precambrian rocks. They make up the cores of present-day continents in both North and South America, Australia, Russia, Fennoscandia, and Africa, where there are several cratons separated by more mobile belts. Within them *intracratonic basins* may develop that are characterized by very slow subsidence.

The nature of sedimentation is particularly important, both on the cratons and within their basins. The absence of faulting and of any rapid vertical uplift leads to a shortage of sediment. At the same time the very slow subsidence of the basins means that very little accommodation space is generated in which the sediments can collect. Instead of being swallowed up, as in a typical rift valley, the sediments are spread widely over the basin or anywhere that is slightly lower than the uplifted area.

Many of these basins develop as lakes, known as 'sag' lakes to contrast them with lakes that form in rift valleys. Lake Chad in North Africa is a typical example. It is very shallow, just a few metres deep, yet, over very short periods of time it can extend and contract its margin by hundreds of kilometres as rainfall fluctuates. Lake Eyre in Australia and the Great Lakes of North America are other examples. All these lakes are characterized by a lack of sediment from the surrounding rivers.

A major feature of ancient cratons is the presence of extensive 'sheet' sandstones of great textural and compositional maturity, some of which yield almost pure orthoquartzites. These orthoquartzites cover very large areas of cratons: the Nubian Sandstones of North Africa, the Roraima Sandstone of Brazil and Venezuela, the sandstones of North Norway around the Baltic Shield, and the extensive late Precambrian and Cambro-Ordovician Sandstones of north-central USA.

One feature of such sandstones is that their depositional environments are not easy to establish. Even the most experienced sedimentologists have difficulty in deciding whether they have been formed in braided rivers, as shoreface-beaches, or as shelf sand bars, especially when fossils are absent or sparse, as in the Precambrian.

A second, but equally important, feature of cratons, is the existence of unconformities that can also be traced over vast