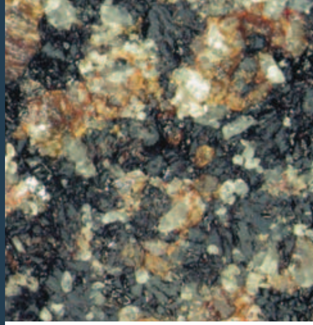

Dating the Oldest Rocks and Minerals in the Solar System

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Meteorites originating from asteroids are the oldest-known rocks in the Solar System, and many predate formation of the planets. Refractory inclusions in primitive chondrites are the oldest-known materials, and chondrules are generally a few million years younger. Igneous achondrites and iron meteorites also formed in the first five million years of the protoplanetary disk and escaped accretion into planets. Isotopic dates from these meteorites serve as time markers for the Solar System's earliest history. Because of the unique environments in the protoplanetary disk, dating the earliest meteorites has its own opportunities and challenges, different from those of terrestrial geochronology.

Keywords: Solar System, meteorites, protoplanetary disk, extinct radionuclides, U–Pb dating, isotopic dating

INTRODUCTION

Understanding the processes that transformed a cloud of interstellar gas into our Solar System, the only planetary system that is known to sustain life, is a key step in the quest for our origins. Due to recent discoveries of Earth-like exoplanets and the rapid accumulation of astronomical observations of young stellar objects, we have obtained, for the first time in history, an opportunity to place the formation of our Solar System in the context of an emerging general model of formation and evolution of planetary systems.

In his book *On the Origin of Species*, Charles Darwin referred to the formation of our Solar System as "so simple a beginning," but it is now realized that the beginning was not simple at all. Most stars are born in a sequence of complex processes in clusters within giant molecular clouds (Lada and Lada 2003). In such dynamic and short-lived environments, accreting protoplanetary disks do not evolve in isolation. Irradiation and influx of matter from nearby massive stars can change the structure and composition of the protoplanetary disk. The accretion of our Solar System is seen as an assembly of hot and cold domains, pristine dust and partially molten planetesimals that coexisted and interacted for a short period – less than 10 million years – some 4.5 billion years ago. Understanding the nature of the processes involved is impossible without accurate knowledge of their timing.

The key events of accretion and planetary growth can be sequenced with high precision and accuracy by means of U–Pb and extinct radionuclide dating of the oldest, best preserved meteorites and their components, combined with supporting information about metamorphism, aqueous alteration and shock history, necessary to validate the ages. In this paper, we discuss how the ages of the oldest solids are determined and how researchers are striving to improve understanding of the sequence of events that converted a dense clump in an interstellar molecular cloud into the planetary system we inhabit. Our review is complementary to the recent reviews of the early Solar System that are mainly concerned with the processes and application of the age data (Kleine and Rudge 2011) or with analytical techniques (Zinner et al. 2011).

COSMOCHRONOLOGY, COSMOCHEMISTRY AND STAR FORMATION

The early history of our Solar System cannot be observed directly. It is recorded in the early minerals and rocks that were removed from the final stages of accretion before formation of the planets. These primitive rocks are preserved in asteroids that experienced only moderate heating and in comets. Other asteroids that were extensively melted are thought to be the sources of igneous meteorites.

Cosmochronology is an application of the methods of isotopic dating to extraterrestrial rocks and minerals. A simplified view of the formation of the Solar System is shown in Figure 1. It is important to note that the astronomical and cosmochemical timescales use different reference "zero" points: ignition of the star in astronomy, which cannot be directly determined by means of isotopic dating, and formation of the first solid materials in cosmochemistry, which cannot be directly determined by means of astronomical observations. Finding a common reference point for the astronomical and cosmochemical timescales is one of the main goals in the development of a general theory of planetary system formation.

Stars and their planetary systems form in giant molecular clouds. In these environments, accretion disks are polluted by ejecta and stellar winds from nearby rapidly evolving massive stars. Freshly synthesized short-lived radionuclides are injected into the solar nebula during the first three stages of accretion (Fig. 1). The decline in the abundance of these radionuclides until extinction can be used for dating early Solar System processes (Kita et al. 2005). The method is similar to using the abundance of ^{14}C produced by the interaction of cosmic rays with the Earth's atmosphere for dating in archeology. In extinct radionuclide dating, it is

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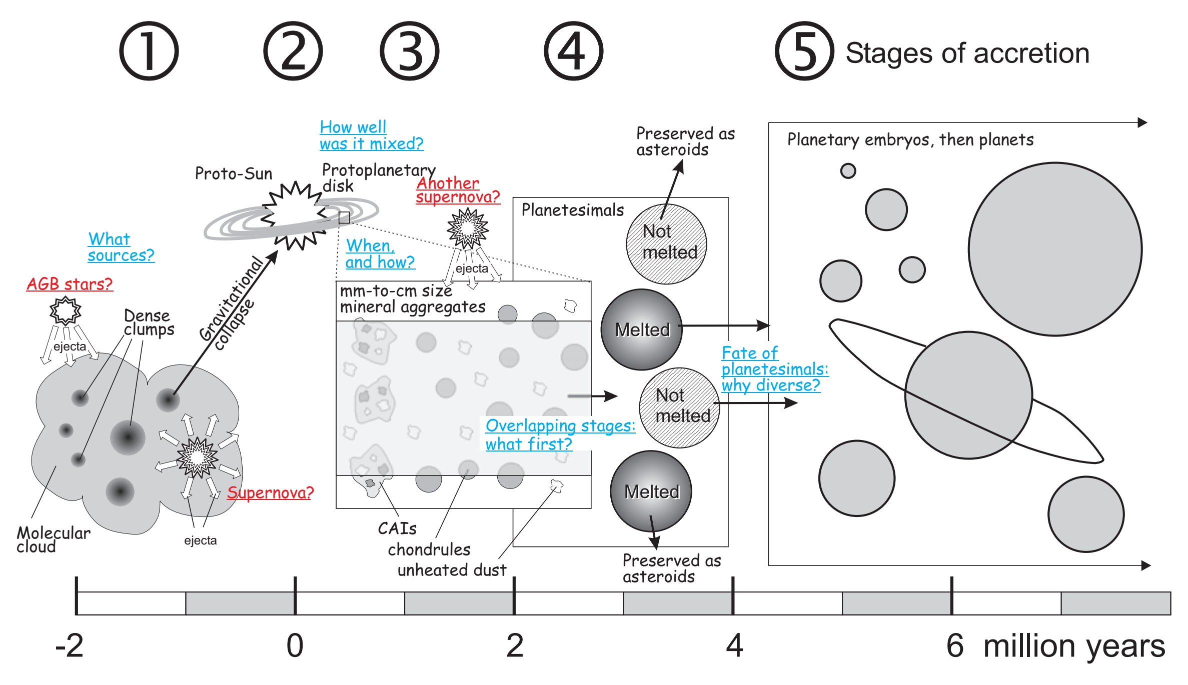

FIGURE 1 Five stages of formation and early evolution of the Solar System: (**1**) Formation of dense clumps in a giant molecular cloud. (**2**) The clumps collapse by gravitational force to form a protostar; conservation of angular momentum results in a protoplanetary disk. (**3**) The heating and rapid cooling of dust creates Ca–Al-rich refractory inclusions (CAIs) and droplets of silicate melt (chondrules). (**4**) Dust, CAIs and chondrules accrete into planetesimals. (**5**) Oligarchic growth into planetary embryos and planets. Possible external influences, such as radiation and ejecta from supernovae and/or asymptotic giant branch (AGB) or red giant stars, are shown in red. Outstanding questions with respect to Solar System formation are shown in blue.

assumed that the radionuclide was uniformly distributed in the solar nebula. The abundance of radionuclides is determined from the distribution of their decay products.

The short-lived radionuclides are produced by two dominant mechanisms: stellar nucleosynthesis followed by injection into the nascent Solar System, and spallation, where the breaking of larger nuclei produces radioactive nuclear fragments, which could have occurred within the Solar System. Identifying the production mechanisms is not straightforward. While ^{10}Be is produced only in spallation reactions and ^{60}Fe only by nucleosynthesis in massive stars, ^{53}Mn and ^{26}Al are produced by both stellar nucleosynthesis and irradiation (Huss et al. 2009). From U–Pb dating combined with extinct radionuclide abundances, we can determine at what stages of accretion freshly produced radionuclides were added to our Solar System.

COSMOCHRONOLOGY AND GEOCHRONOLOGY

Cosmochronology and geochronology share basic principles and many analytical techniques. Interaction and exchange of experience between the two research communities are mutually enriching. Because of unique environments in the protoplanetary disk that differ from those on the surfaces and in the interiors of the Earth and other planets, dating the earliest meteorites and their components has its own opportunities and challenges.

In “terrestrial” geochronology, the development of sophisticated ways of extracting simple, closed-system parts of crystals, and accurately analyzing them, proved much more productive than analyzing bulk mineral fractions and using elaborate models to interpret their isotopic systems. Sequencing early Solar System history requires a similar refinement in isotopic dating. Covering the great variety of processes that need dating requires many chronometers and analytical techniques. Most meteorites are ultramafic or mafic in composition, and minerals that concentrate radioactive parent elements and effectively exclude daughter elements, such as zircon for U–Pb, are only rarely found in meteorites. Concentrations of parent nuclides in meteorites and their minerals are usually very low, making the analyses demanding. Finally, meteorites are assorted random samples from an unknown, and possibly large, range of parent asteroids. Under these circumstances, the development of a coherent dating strategy is a great challenge for the small community of cosmochronologists.

WHAT ARE WE DATING?

Three central, and closely related, questions of cosmochronology are: Which processes are we dating? Which isotopic systems and techniques do we need to obtain those dates? And which meteorites do we need to analyze to get the dates of the processes we are interested in?

Which Processes?

Isotopic clocks measure the timing of the processes that fractionate parent and daughter elements. From this seemingly trivial notion, it follows that some processes can be directly dated, whereas others cannot.

The datable processes include melt crystallization (fractionation driven by crystal–melt partitioning), metamorphism (fractionation due to growth of new minerals in the solid state), metasomatism (fractionation driven by solubility in fluids), condensation and evaporation (volatility-induced fractionation), and metal–silicate separation (fractionation driven by the affinity of certain elements to Fe–Ni metal as opposed to silicate minerals, i.e. siderophile versus lithophile properties).

Parent–daughter-element fractionations by magmatic, metamorphic and metasomatic processes are well known and widely used in terrestrial geochronology, whereas fractionations by metal–silicate affinity and by volatility are unique to the early Solar System. Metal–silicate fractionation, such as in planetesimal core formation, influences the ^{107}Pd–^{107}Ag, ^{60}Fe–^{60}Ni and ^{182}Hf–^{182}W isotopic systems (Kleine and Rudge 2011). Differences in volatility are important for many parent–daughter pairs (Fig. 2). In solids that condense from a cooling gas, an isotope chronometer starts measuring time when both parent and daughter isotopes are retained in the solid phase. In several parent–daughter pairs – ^{26}Al–^{26}Mg, ^{41}Ca–^{41}K, ^{129}I–^{129}Xe, and U–Pb – parent elements are much more refractory than the decay products, and volatility-driven fractionation can be important for using these systems as chronometers. Calcium–aluminum-rich inclusions (CAIs), chondrules, and achondrites – and minerals that comprise them – experienced both volatility-driven and igneous fractionation. In some cases, it is possible to date these processes separately using different scales of sampling, for example, whole-rock versus microbeam analysis of minerals.

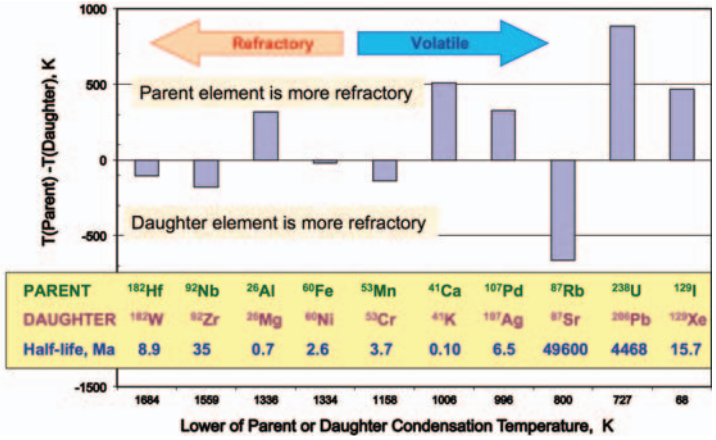

Figure 2 Isotope chronometers used in early Solar System studies arranged by volatility (the lower of the parent- or daughter-element condensation temperatures). The temperatures are equilibrium condensation temperatures for a gas of Solar System composition as given in Table 8 of Lodders (2003).

Several processes in the protoplanetary disk, most importantly accretion of solids into larger aggregates, planetesimal collisions and planetary accretion, do not cause chemical fractionation of elements and therefore cannot be dated directly. Their ages can only be bracketed or approximated using associated processes, such as the formation of new solids from shock melt.

Which Isotopic Systems?

Four isotopic systems have become the main contributors to modern early Solar System chronology: ^{207}Pb/^{206}Pb ^{26}Al–^{26}Mg, ^{53}Mn–^{53}Cr and ^{182}Hf–^{182}W. These isotopic systems feature in recent reviews of early Solar System chronology (Nyquist et al. 2009; Dauphas and Chaussidon 2011). Their wide applicability is based on their presence and fractionation in a variety of minerals and rocks, including both chondrites and achondrites. Several short-lived isotope chronometers, e.g. ^{92}Nb–^{92}Zr, ^{107}Pd–^{107}Ag and ^{41}Ca-^{41}K, are used when the parent nuclide is highly concentrated or when parent–daughter fractionation allows good temporal leverage. Other isotopic systems, including initial Sr, ^{129}I–^{129}Xe, U–Th–He and the systems based on the decay of ^{244}Pu, popular in the past, are now forgotten or used only rarely. The group of chronometers based on the decay of extant radionuclides – ^{87}Rb–^{87}Sr, ^{147}Sm–^{143}Nd, ^{40}Ar–^{39}Ar and ^{176}Lu–^{176}Hf – usually yield dates with ≥10 Ma uncertainties, which are insufficient for resolving processes in the protoplanetary disk but provide valuable information about possible late disturbances.

Which Meteorites?

Early studies of the most common and easily available meteorites, such as eucrites and equilibrated ordinary chondrites, helped to establish the main benchmarks of

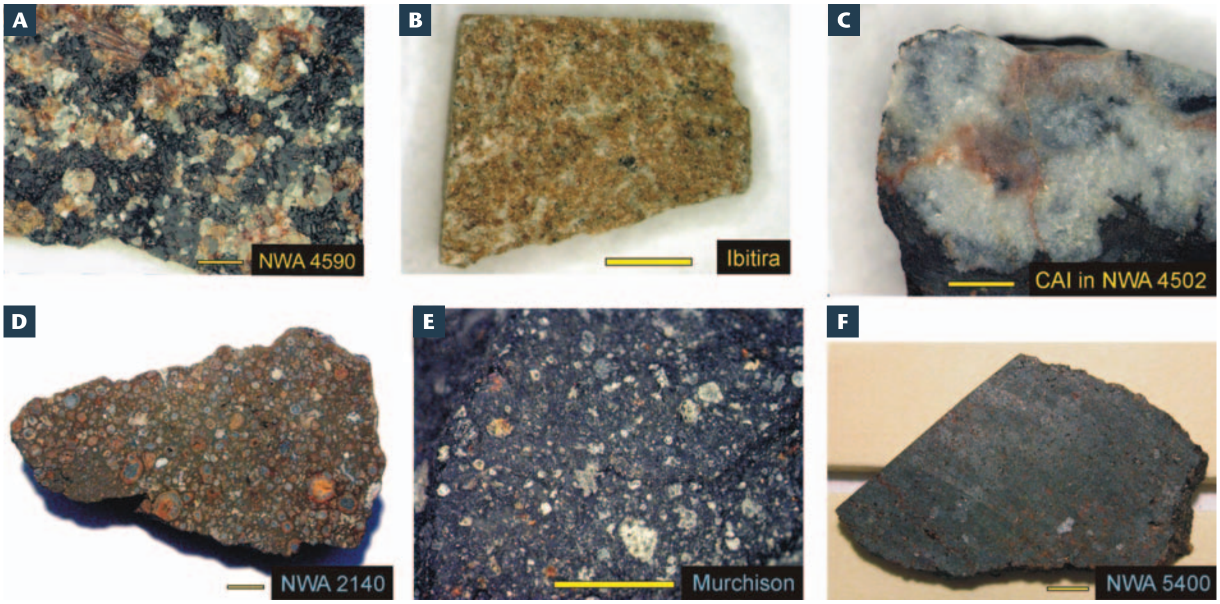

Figure 3 Some meteorites are better suited for age determinations than others. Angrites (**A**), eucrite-like achondrites (**B**) and large CAIs in CV chondrites (**C**) can be dated with U–Pb and one or more extinct radionuclide chronometers using both high-precision macroscopic [isotope dilution thermal ionization mass spectrometry (ID-TIMS) and multicollector inductively coupled plasma mass spectrometry (MC–ICP–MS)] and high-resolution microscopic [secondary ion mass spectrometry (SIMS) and laser ablation inductively coupled plasma mass spectrometry (LA–ICP–MS)] techniques. The ages of these meteorites serve as reference points ("golden spikes") in timescale construction. Dating chondrules (**D**) in various chondrites, small CAIs in chondrites other than CV chondrites (**E**) and ultramafic achondrites (**F**) is more difficult, and often requires in situ high-resolution analyses. The names of the meteorites are indicated. Scale bars are 2 mm long.

early Solar System evolution. Eventually it became clear that their geological history was very complex and eventful, and meteorites of other classes, although rare, are better suited for high-resolution dating of the stages of nebular condensation and accretion.

The modern chronology of Solar System formation is based primarily on the studies of three groups of materials (Fig. 3): (1) a relatively small number of exceptionally old and well-preserved igneous meteorites, such as angrites, anomalous eucrite-like meteorites and some unclassified basaltic achondrites (Wadhwa et al. 2009; Bouvier et al. 2011); (2) chondrules from well-preserved, unequilibrated ordinary and carbonaceous chondrites; and (3) CAIs and amoeboid olivine aggregates (AOAs) from chondrites. Establishing accurate age relationships between these groups of materials is among the most important goals of early Solar System chronology.

The principles of timescale construction using two chronometers, U–Pb and the extinct radionuclide system ^{26}Al–^{26}Mg, are illustrated in Figure 4. Direct comparison of different chronometric systems is not a trivial task. Two isotopic clocks in the same rock can read the timing of different events because of the differences in volatility, diffusion rate and chemical properties of parent and daughter elements. When we compare U–Pb and ^{26}Al–^{26}Mg ages of chondrules and chondrites, we have to consider that the parent elements may reside in different minerals. Chondrule mesostasis is the primary host of both Al and U, but the secondary host minerals are different: feldspar for Al, and Ca phosphates for U. The diffusion rates of the daughter isotopes (Pb and Mg) are also different and mineral dependent, so that in slowly cooled meteorites the U–Pb system in phosphates and the ^{26}Al–^{26}Mg system in feldspar could have closed at different times.

HOW WELL DO WE KNOW THE FOUNDATIONS?

It was thought, until recently, that the rates of decay of radionuclides used in cosmochronology were well known and that the isotopic ratios of elements are constant, apart from the accumulation of decay products and relatively minor mass-dependent fractionation. These tenets have been reexamined in several recent studies.

Half-Lives of Parent Radionuclides

In the last ten years, half-lives have been precisely redetermined for four isotopes used in early Solar System chronology: ^{182}Hf (Vockenhuber et al. 2004), ^{41}Ca (Jörg et al. 2012), ^{60}Fe (Rugel et al. 2009) and ^{146}Sm (Kinoshita et al. 2012). The first two papers confirm previously accepted values with greatly improved precision, whereas the latter two differ substantially from the currently used values. Obtaining reliable half-life values requires a combination of advanced decay counting, careful control of radiochemical purity, and accurate concentration determination with isotope dilution mass spectrometry. Many older half-life studies lack at least one of these components, and their results need confirmation.

Isotopic Composition of Uranium

The ^{238}U/^{235}U ratio, which was considered constant until recently, is now known to be variable and offset from the previously accepted value. Variations among the CAIs are most prominent (Brennecka et al. 2010), and it is currently unclear whether the ^{238}U/^{235}U ratio in bulk chondrites and achondrites is variable at a smaller scale and identical to the ^{238}U/^{235}U ratio in the Earth (Bouvier et al. 2011; Brennecka and Wadhwa 2012; Connelly et al. 2012). Revisions to the Pb isotope chronology of meteorites, with consideration of ^{238}U/^{235}U variability, are being undertaken by several

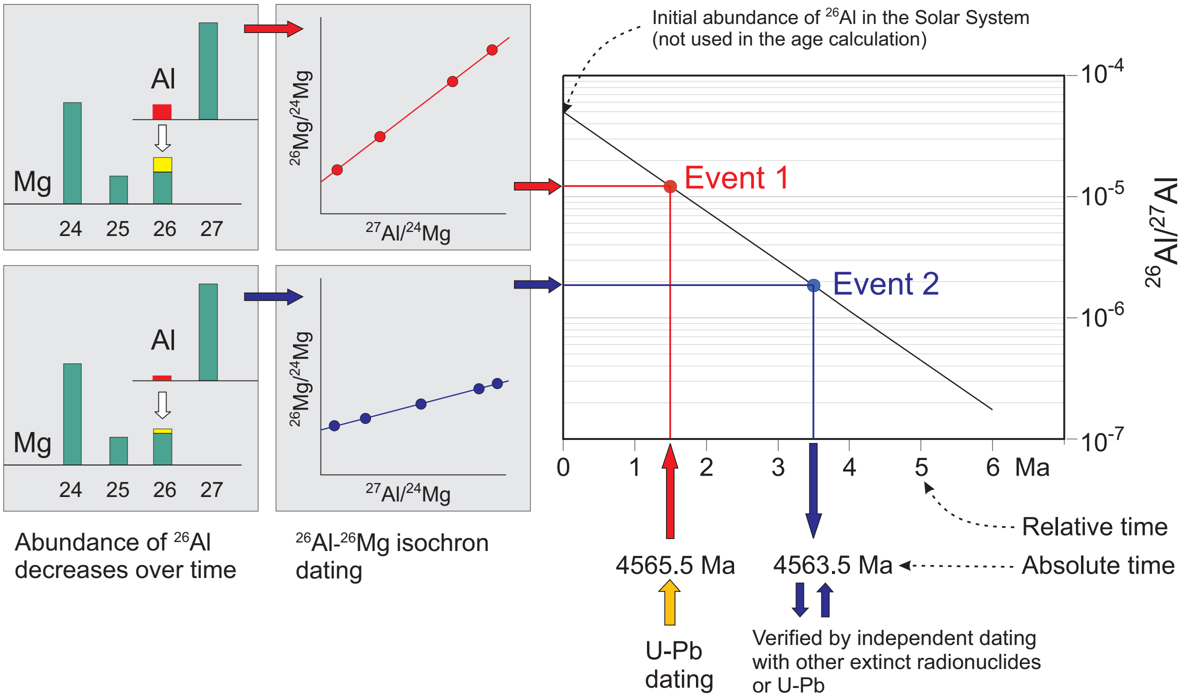

Figure 4 Linking extinct radionuclide chronometers to absolute time and construction of the timescale of Solar System formation using multiple chronometers. Most U–Pb and extinct radionuclide dates in modern cosmochemistry are based on isochrons (e.g. Kita et al. 2005), which usually give more accurate and reliable results than model dates. Extinct radionuclide (e.g. ^{26}Al–^{26}Mg) isochrons yield relative abundances of the parent radionuclide (e.g. ^{26}Al/^{27}Al) at the time of the system closure (e.g. crystallisation). Red and yellow bars show the quantity of radioactive ^{26}Al and radiogenic ^{26}Mg, respectively. From the difference in isochron slopes and known rate of decay of the radionuclide we can calculate the time interval between the events dated by these isochrons. If the absolute age of one of these events is known from U–Pb dating, then the time intervals based on ^{26}Al–^{26}Mg isochrons can be converted into absolute ages.

research groups. The U isotope ratios of many meteorites precisely dated with the $^{207}Pb/^{206}Pb$ method are still unknown, and their determination is one of the pressing tasks in the refinement of early Solar System chronometry.

THREE TALES OF METEORITE AGES

^{60}Fe–^{60}Ni: Not a Chronometer, and No Longer a Proof for Supernova?

^{60}Fe–^{60}Ni has recently been the most troubled of all cosmochronometers. The first TIMS work by Shukolyukov and Lugmair (1993) found that the $^{60}Fe/^{56}Fe$ abundance ratio in eucrites was below 10^{-8}. Ion microprobe analyses of chondrules (Tachibana et al. 2006) yielded much higher $^{60}Fe/^{56}Fe$ ratios, implying the need for an additional source of ^{60}Fe, such as a supernova, where this isotope was produced shortly before injection into the solar nebula. New MC–ICP–MS data for both differentiated meteorites and chondrites indicate an $^{60}Fe/^{56}Fe$ ratio around 10^{-8}, close to the original TIMS value (Regelous et al. 2008; Quitté et al. 2011). The high SIMS value appears to be an artefact of data reduction (Ogliore et al. 2011). As it stands now, the abundance of ^{60}Fe is consistent with the galactic background and no longer requires an input of material to the protosolar nebula from a nearby supernova.

Old Ages of Chondritic Carbonates: An Analytical Artefact Clarified

One of the long-standing inconsistencies in the timing of early Solar System events was the exceptionally old (close to the age of CAIs) ^{53}Mn–^{53}Cr age of secondary carbonates (calcite and dolomite) in chondrites (de Leuw et al. 2009). Taken at face value, these carbonate ages indicated that the accretion of the chondrite parent bodies was extremely early and fast, in contradiction to all the other evidence suggesting that accretion started relatively late and continued for several million years. The study by Fujiya et al. (2012) shows that extremely old ^{53}Mn–^{53}Cr ages are an artefact of inadequate standard-to-sample matching in the SIMS analyses in the earlier studies. New SIMS measurements with a matrix-matched standard for accurate Mn/Cr determination yield an age of 4563.4 +0.4/–0.5 Ma, much younger than the earlier estimated apparent ages between 4565 and 4569 Ma. The new result is consistent with late accretion of the chondrite parent bodies and suggests an onset of aqueous activity in the Solar System contemporaneous with early thermal metamorphism.

CAIs: How Old Is Old?

The progress in U–Pb dating of CAIs, recognized as the oldest macroscopic objects in the Solar System, provides an excellent illustration of the growth of scientific knowledge (Fig. 5). As analytical techniques progressed, the precision and consistency of CAI ages improved to less than 1 million years. Then the discovery of large $^{238}U/^{235}U$ variations in CAIs (Brennecka et al. 2010) added a previously unrecognized uncertainty to the age. An attempt to remedy the situation by applying an age correction based on an empirical $^{238}U/^{235}U$ versus Th/U correlation for other CAIs (Bouvier and Wadhwa 2010) made the CAI age data set discrepant. However, four $^{238}U/^{235}U$-corrected CAI dates reported recently (Amelin et al. 2010; Connelly et al. 2012) show excellent agreement, with a total range for the ages of only 0.2 million years – from 4567.18 ± 0.50 Ma to 4567.38 ± 0.31 Ma. This short age interval is also consistent with uniform $^{26}Al/^{27}Al$ values close to $5*10^{-5}$ in CAIs. Such rapid turnover of new ideas and interpretations in the wake of analytical innovation suggests we are on the way to a new paradigm for condensation in the protoplanetary disk.

CONCLUSION AND OUTLOOK

The road towards a unified timescale of Solar System formation is not straight. We know more about the behaviour of radionuclide chronometers in meteorites, possess better tools for isotope analyses and have accumulated much high-quality data. Some of these data are inconsistent with previous views on the formation of the Solar System and demand the development of new models. Recent findings remind us that the foundations of cosmochronology, and geochronology in general, require regular inspection, reinforcement and, if necessary, rebuilding, to make sure they are strong enough to sustain the growing body of knowledge.

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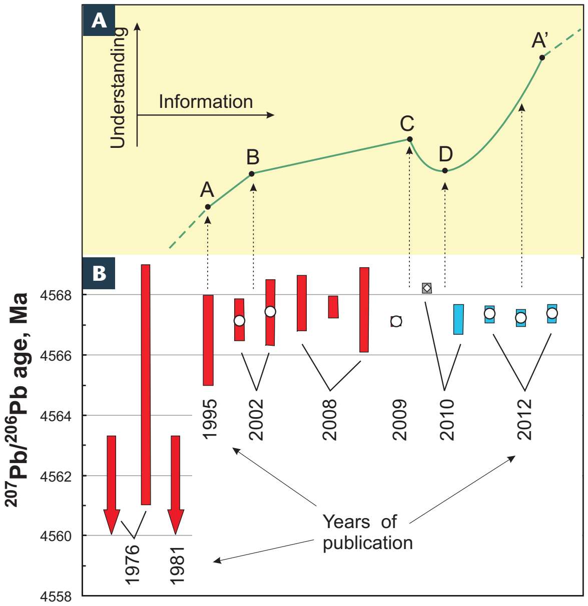

FIGURE 5 (**A**) Growth of scientific knowledge, and (**B**) Pb-isotope age determinations of CAIs through time. (**A**) Points in the knowledge growth curve. A: Paradigm established (the age of CAIs is known with a precision of +2/-1 Ma; Allègre et al. 1995). A–B: New observations confirm and refine the paradigm (further improvement in precision; Amelin et al. 2002). B–C: More facts consistent with the previous findings (more CAI dates consistent with the earlier results; Jacobsen et al. 2008, Connelly et al. 2008). C: First observations that contradict the paradigm; understanding plunges (demonstration of variable $^{238}U/^{235}U$ increases uncertainty in the age of CAIs; Brennecka et al. 2010). C–D: More facts, more controversies; understanding declines further (CAI ages disagreeing with the previous results are reported; Bouvier and Wadhwa 2010). D: It may be possible to reconcile the observations (first report of a CAI age corrected for measured $^{238}U/^{235}U$; Amelin et al. 2010). D–A': On the way to a new paradigm (three new, more precise $^{238}U/^{235}U$-corrected CAI ages from another meteorite; Connelly et al. 2012. All four $^{238}U/^{235}U$-corrected CAI ages reported to date are consistent).

(**B**) Error bars are 2σ. Symbols: red (earlier studies), calculated assuming $^{238}U/^{235}U = 137.88$; grey (Bouvier and Wadhwa 2010), calculated with $^{238}U/^{235}U$ inferred from the $^{238}U/^{235}U$ versus Th/U correlation of Brennecka et al. (2010); blue (new studies), calculated with measured $^{238}U/^{235}U$ and its uncertainty. Meteorites: bars with circles = Efremovka; bar with diamond = NWA 2364; bars without symbols = Allende

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