



## The prospect of high-precision Pb isotopic dating of meteorites

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**Abstract**—The radiogenic  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio is the only extant nuclide chronometer with sufficient time resolution for studies of the solar nebula accretion and early asteroidal differentiation and metamorphism. Pb isotopic dates can be used to link the dates obtained from extinct nuclide chronometers to the absolute time scale. The factors that control precision and accuracy of Pb isotopic dates of meteorites: instrumental mass fractionation in isotopic analysis, mass spectrometer sensitivity, removal of common Pb, multi-stage evolution of U-Pb systems, disturbances caused by diffusion, alteration, and shock metamorphism, and uncertainties in decay constants and the natural ratio of the U isotopes are reviewed. The precision of Pb isotopic dates of meteorites attained with currently available techniques and methodology is  $\pm 0.5$ – $1.0$  Myr in favorable cases. The accuracy of time interval measurements is approximately the same. The most serious limitation on precision and accuracy of Pb isotopic dates is placed by the presence of common Pb of uncertain and/or variable isotopic composition. Improvement in precision and accuracy of Pb isotopic dates would be possible through combined advancement of techniques of isotopic analysis (most importantly, better control over instrumental mass fractionation) and more effective techniques for the removal of common Pb, together with a better understanding of the effects of thermal metamorphism, shock metamorphism, and aqueous alteration on the U-Pb system in meteorites.

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### INTRODUCTION

The U-Pb method and its derivative Pb-Pb method occupy a special place in the family of isotope chronometers used for dating meteorites. Since the pioneering work of Patterson (1955, 1956), the Pb-Pb method has been used for dating bulk chondrites and achondrites, CAIs, chondrules, and individual minerals in meteorites. The precision of Pb-Pb dates rarely exceeded 5–10 Myr in the early days of cosmochemistry studies, but it improved with advancements in analytical techniques and with using a more selective approach to meteorites (analyzing individual chondrules, CAIs, and minerals instead of bulk meteorites). In more recent studies, a precision of about 0.5–1.0 Myr is achieved. This level of precision allows using the Pb-Pb method for dating processes that spanned only a few million years: formation of the first solids from the solar nebula, and accretion, differentiation and metamorphism of asteroids. During the same time, the techniques and methodology of terrestrial U-Pb geochronology have been greatly advanced (see recent reviews by Davis et al. 2003; Parrish and Noble 2003; Ireland and Williams 2003). These new methods and concepts can be applied to cosmochemistry to improve the

precision of the ages of meteorites and to get better constrained age interpretations. In this paper, I shall discuss some of the key issues of U-Pb geochronology and consider their relevance to Pb isotopic dating of meteorites. I shall also discuss the weaknesses in the present techniques and methodology of Pb isotopic dating and possible ways of overcoming them, and a few general issues in geochronology relevant to the dating of meteorites. This paper is complementary to the chapter by Kita et al. (2005), which shows the present status of isotope cosmochemistry with application to the processes in the protoplanetary disk in a broader way.

### Terminology

In this paper, the terms “date” and “age” are used as suggested by Faure (1986). The “age” is the time between a geological (or any other natural) event and the present. The “date” is the time calculated from the ratio of a radioactive isotope and its daughter isotope using the law of radioactive decay. The time values calculated from a linear regression in the isochron diagram, or from analysis of a single rock or mineral, are called “isochron date” and “model date.”

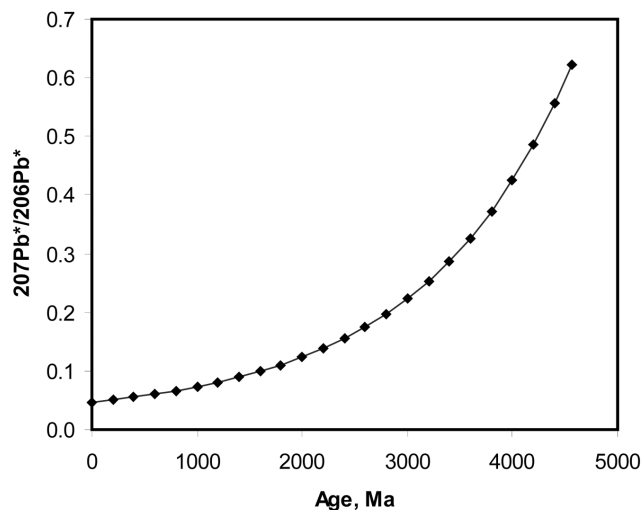


Fig. 1. Variation of the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratio with the age.

respectively. If there is sufficient proof that the conditions of the isochron approach and/or model (single-point) approach are satisfied, then the date may be interpreted as the age. This usage of the terms “date” and “age” differs from the current practice, where the term “age” is commonly used in both meanings. However, the common use of the term “age” is both confusing and harmful to science, because it creates a false impression that any measure of time calculated from the isotopic relationships has a geological significance.

#### $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ : A Unique Isotopic Chronometer

The U-Pb dating method (Faure 1986; Dickin 1995) includes two isotopes of uranium which decay into two different isotopes of lead at different rates:  $^{238}\text{U}$  decays to  $^{206}\text{Pb}$  with the half-life of  $4.468 \times 10^9$  yr, and  $^{235}\text{U}$  decays to  $^{207}\text{Pb}$  with the half-life of  $0.704 \times 10^9$  yr. This dual decay scheme can be used in two different ways. The most common way is to directly compare the two schemes by plotting the  $^{238}\text{U}/^{206}\text{Pb}^*$  (the asterisk denotes radiogenic Pb) against the  $^{235}\text{U}/^{207}\text{Pb}^*$  dates and check the position of the analytical point relative to the concordia line (a locus of identical  $^{238}\text{U}/^{206}\text{Pb}^*$  and  $^{235}\text{U}/^{207}\text{Pb}^*$  dates). Interpretation of U-Pb data using the concordia diagram tests whether the studied mineral remained closed to exchange of U and/or Pb with its surrounding. In certain cases, it is possible to determine the accurate timing of mineral formation and transformation (for example, an episodic loss of radiogenic Pb related to metamorphism), or the timing of two episodes of mineral growth.

An alternative use of the dual decay scheme is to calculate the date from the ratio of radiogenic isotopes  $^{207}\text{Pb}^*$  and  $^{206}\text{Pb}^*$  alone, without using U/Pb ratios. The  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  method is unique among isotopic chronometers in several ways. First, since the date is determined from the ratio of isotopes of one element, it is insensitive to recent fractionation between parent and daughter elements caused

by natural processes (e.g., recent impact or terrestrial weathering) or induced by laboratory treatment, e.g., cleaning or partial dissolution. Extraction of radiogenic Pb with varying  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  has been observed by Corfu (2000) in partial dissolution of zircon, but this selective extraction is related to ancient radiation damage and subsequent annealing, whereas U concentrations in meteorites are too low to cause detectable radiation damage and related selective leaching of radiogenic isotopes. The risk of obtaining inaccurate isochron dates due to recent parent/daughter elemental fractionation exists in all isotopic dating methods and compromises, or even prohibits, the use of mineral leaching or partial dissolution to increase the spread of the parent/daughter ratios and hence improve precision of the isotopic date. In contrast, the same partial dissolution methods are very unlikely to cause fractionation of radiogenic  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratios. Second, the rates of decay of the two uranium isotopes used in  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  dating are very different:  $^{235}\text{U}$  decays approximately six times faster than  $^{238}\text{U}$ . Uranium-235 has the shortest half-life of all extant nuclides used in isotopic dating and actually approaches extinction: only one  $^{235}\text{U}$  atom is left out of 90 that were present in solar system material 4560 Myr ago. High abundance of  $^{235}\text{U}$  and hence high  $^{235}\text{U}/^{238}\text{U}$  ratio in the early solar system together with fast decay of  $^{235}\text{U}$  resulted in rapid growth of  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ . Because of the difference in the rate of decay between  $^{235}\text{U}$  and  $^{238}\text{U}$ , the change of the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratio over time in the closed system is strongly non-linear (Fig. 1). As a result, the precision of the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  date for a given uncertainty of the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratio increases with the age of the object (Fig. 2). The  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratio with a relative error of 0.05% (a typical analytical uncertainty attainable for relatively large amounts of radiogenic Pb using external instrumental mass fractionation correction—upper curve in Fig. 2) yields a  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  date with an absolute error of 0.72 Myr for 4560 Ma old material. This precision approaches the precision of state-of-the-art extinct nuclide dating techniques. De-magnification of the errors in  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  dates due to the fast growth of radiogenic  $^{207}\text{Pb}$  is illustrated in Fig. 3.

An additional factor that facilitates high precision of  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  dating is that the error of the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratio is free of uncertainties involved in the determination of elemental ratios (e.g., calibration of spikes for isotope dilution and elemental fractionation in ion microprobe and ICP-MS analyses), which limit the precision of other dating methods. The precision and accuracy of parent/daughter ratio determination by isotope dilution for some isotopic systems, for example Sm-Nd and Lu-Hf, can be almost as high as the precision of  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratio measured with TIMS with external instrumental mass fractionation correction. However, the error de-magnification involved in converting a  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratio to a  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  date is a unique feature of the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  method.

Because of its high time resolution, the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  is the only “absolute” dating method suitable for studies of the

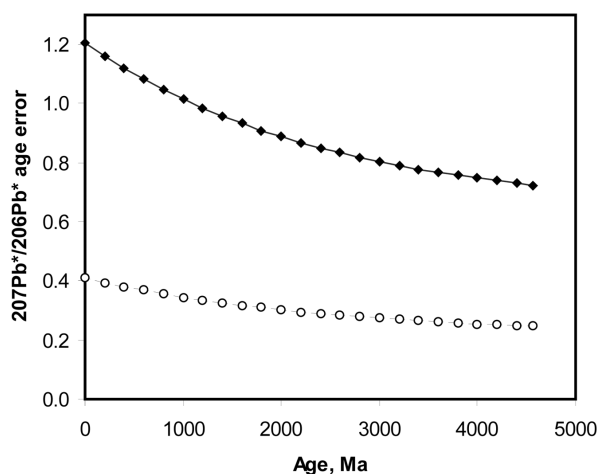


Fig. 2. Absolute error of the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  age (Ma) as a function of age assuming constant relative error in the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratio. Upper curve (solid with black diamonds) corresponds to a 0.05% error in  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratio (a typical analytical uncertainty attainable for relatively large amounts of radiogenic Pb using external mass discrimination correction). Lower curve (dashed with open circles) corresponds to a 0.017% error in  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratio (an estimated three-fold improvement in precision of Pb isotopic analysis by using double isotope dilution).

solar nebula accretion. This is also the only method used for linking the dates obtained from extinct nuclide chronometers to the absolute time scale.

### THE FACTORS THAT AFFECT THE PRECISION OF Pb ISOTOPIC DATES

The error of a  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  isotopic date is proportional to the error of the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratio, which in turn depends on the error of the measured  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio (controlled mostly by counting statistics and analytical parameters of the mass spectrometer), uncertainty in correcting instrumental mass fractionation, and uncertainties related to subtraction of the analytical blank and common Pb (here all Pb other than in-situ accumulated radiogenic Pb is referred to as common Pb), plus spike subtraction if the sample is spiked. The relative contributions of these sources of error depend on the size of the sample, the concentrations of radiogenic Pb and common Pb, and uncertainty of instrumental mass fractionation. It is important to identify and deal with the biggest source of uncertainty first: for example, improving analytical precision and better control over instrumental mass fractionation will not significantly improve the precision and accuracy of the age of a mineral that contains abundant common Pb with unknown isotopic composition.

#### Analytical Limitations

##### Instrumental Mass Fractionation

Measured Pb isotopic ratios are altered by isotopic fractionation in mass spectrometer sources. The systematic

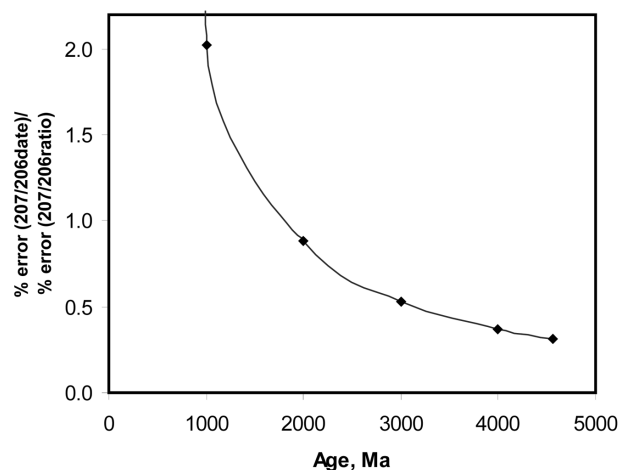


Fig. 3. The ratio of relative errors in the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  date and the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratio plotted against the age. For materials younger than 1816 Ma, the relative errors in  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  dates are larger than the relative errors in  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratios; the relationship for the older materials is the opposite. Error magnification is most favorable for very old materials: for a 4560 Ma mineral or rock the relative error of the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  date is 3.2 times smaller than the error of the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratio. The Pb isotope method is therefore uniquely suited for dating very old minerals.

error can be as large as 0.1–0.2% per atomic mass unit (amu) in thermal ionization mass spectrometry (TIMS) and about 1–2% per amu or larger in multicollector inductively coupled plasma mass spectrometry (MC-ICPMS). The uncertainty in the correction of instrumental mass fractionation is the main limitation on precision and accuracy in analyses of relatively large Pb samples (>50–100 pg) with low content of common Pb. Since only one natural Pb isotope ( $^{204}\text{Pb}$ ) is free from radiogenic addition, the internal normalization based on assuming constant ratios of natural non-radiogenic isotopes cannot be used for Pb and other methods of instrumental mass fractionation correction are sought.

There are several alternative ways of correcting instrumental mass fractionation in TIMS, the method almost exclusively used for Pb isotopic analysis in meteorites until now. The conventional approach (applying a fractionation factor determined from analysis of a standard to the analyses of geological samples) has a limited precision of about 0.03–0.08% per amu and involves an uncertainty related to the presence of incompletely separated major elements, which can shift the instrumental mass fractionation (Woodhead et al. 1995, Woodhead and Hergt 1997). The reproducibility of mass fractionation can be improved by using the “zero-time correction” method (Kuritani and Nakamura 2002). Using a double (or triple) spike is considered the most accurate and precise way of correcting instrumental mass fractionation in Pb isotope analysis (e.g., Hamelin et al. 1985; Woodhead and Hergt 1997; Galer 1999; Thirlwall 2000; Kuritani and Nakamura 2003). However, the double spike procedures developed so far are optimized for analysis of large amounts (>>  $10^{-9}$  g) of common Pb, involve spiking with  $^{204}\text{Pb}$  and

$^{207}\text{Pb}$  (which are unacceptable for radiogenic Pb analysis because of extremely high sensitivity to memory and cross-contamination), and require the splitting of samples for double spiking. These procedures in their present form are not suitable for analysis of sub-picomole quantities of radiogenic Pb. A double-spiking procedure using  $^{202}\text{Pb}$ - $^{205}\text{Pb}$  (Todt et al. 1996) does not introduce undesirable enriched isotopes and does not require aliquotting, and the cost of a high-purity  $^{202}\text{Pb}$ - $^{205}\text{Pb}$  spike is not prohibitive for small samples (although the availability of these isotopes is limited). This procedure has to be optimized for analysis of radiogenic Pb in order to achieve the best possible precision of Pb isotopic dating of meteorites.

Instrumental mass fractionation correction in Pb isotopic measurements by MC-ICPMS is achieved most commonly by normalization to the ratio  $^{205}\text{Tl}/^{203}\text{Tl}$  (Hirata 1996) in thallium added to the Pb fraction (assuming that the fractionation factors of Pb and Tl are identical or proportional, see Albarede et al. [2004] for a detailed discussion). This normalization can be used to correct additional fractionation related to the sample matrix (Woodhead 2002), but the correlation between Pb and Tl fractionation can be disturbed by anomalous fractionation of Tl, which depends on oxidation and speciation, during membrane desolvation (Kamenov et al. 2004). The precision of Tl-corrected Pb isotopic ratios varies between 0.01–0.05% per amu in different studies, depending on the consistency between Tl and Pb fractionation achieved in each study. Double isotope dilution with a  $^{204}\text{Pb}$ - $^{207}\text{Pb}$  spike has also been used and gave a precision of about 0.01% per amu or better (Thirlwall 2002; Baker et al. 2004), but the problems with memory, which are generally much greater in MC-ICPMS compared to TIMS, make the  $^{204}\text{Pb}$ - $^{207}\text{Pb}$  double spike unsuitable for measurements of small amounts of radiogenic Pb, as required for dating meteorites. No attempts at using the  $^{202}\text{Pb}$ - $^{205}\text{Pb}$  spike in plasma ionization Pb isotope analyses have been reported so far.

### *Sensitivity*

Analytical sensitivity is important because the content of U in chondrites is low at about 10 ppb. Chondrules, CAIs and most of their minerals have similar or only slightly higher U concentrations (Amelin et al. 2003). As a result, the amount of radiogenic Pb produced in situ is low (~10 ppb of radiogenic  $^{206}\text{Pb}$  in a 4560 Ma meteorite). An individual, relatively large, chondrule from a typical chondrite, with a weight of 1–10 mg, contains as little as ~10–100 picograms of radiogenic  $^{206}\text{Pb}$ . The amount of radiogenic Pb is further reduced by a factor of 2 to 5 by acid leaching necessary for removing common Pb. This low content of Pb makes precise isotope analysis very sensitive to analytical blank and requires high instrument sensitivity. Nevertheless, low electrometer noise and improved baseline stability of modern mass spectrometers, high ionization efficiency achieved with

the best available emitters (total ion yield up to ~10%, Gerstenberger and Haase 1997), and low procedure blanks of about 1–2 picograms make precise analyses of samples containing about 20 pg or more of radiogenic  $^{206}\text{Pb}$  possible. In some cases (e.g., dating of small chondrules), it may be necessary to combine several chondrules for each analysis in order to obtain a sufficient amount of Pb.

Based on an evaluation of the factors considered above (instrumental mass fractionation correction, sensitivity, and memory), the TIMS method using a  $^{202}\text{Pb}$ - $^{205}\text{Pb}$  mixed spike appears to hold the most promise for improving high-precision analysis of Pb in meteorites. The MC-ICPMS analysis with double spike may be a viable alternative for meteorites that contain sufficient amount of radiogenic Pb.

### *Precision Limits and Sample Size*

The minimum amount of sample required for the best precision analyses can be estimated from counting statistics and the analytical parameters of the best existing methods. The theoretical limit on precision is set by the number of ions that are registered by collectors, which in turn depends on the sample size (number of atoms of the analyzed element), ion yield (a product of ionization efficiency and mass spectrometer transmission), and atomic abundances of the studied isotopes (e.g., Birck 2001). Assuming a 10% ion yield and 100% recovery of Pb from the sample, we should be able to obtain a  $2\sigma$  relative precision of 0.01% for the  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio, and hence a precision of  $^{207}\text{Pb}/^{206}\text{Pb}$  of 0.15 Myr, from a sample with  $3 \times 10^{-12}$  g of radiogenic Pb (electrometer noise and other instrument-specific sources of error are ignored). This amount of radiogenic Pb is contained in  $3 \times 10^{-4}$  g of unleached chondrule material, and a 3–5 times larger amount would be required if most radiogenic Pb is removed during acid leaching in sample preparation. It follows from this estimate that it may be very difficult or impossible to obtain high-precision Pb isotopic ages from portions (fragments or individual minerals) of a typical chondrule weighing  $10^{-3}$  g or less, even with the best analytical technique. If the highest possible precision is required, it may be necessary to combine several chondrules for each analysis.

The sample sizes are additionally constrained by the limitations of the detector systems of the mass spectrometers. Currently available ion counting detectors are prone to deadtime, linearity, and gain stability problems and have relatively low upper limit for the ion beam, in most cases  $2$ – $3 \times 10^6$  cps and in some cases lower. Because of these limitations, ion counting detectors are not suitable for measurement requiring a relative precision of better than 0.03–0.05%. This precision limit is similar to the uncertainty of the instrumental mass fractionation of Pb in TIMS. As a result, ion counting detectors can be used with a minimum loss of precision in conventional Pb isotopic measurements with external fractionation correction, but the more precise double-spike measurements require the use of Faraday cups.

## THE FACTORS THAT AFFECT THE ACCURACY OF Pb ISOTOPIC DATES

### Complete Removal of Common Pb

The importance of complete removal of common Pb for precise and accurate Pb isotopic dating cannot be overestimated. Of all the findings in U-Pb geochronology of the last 20–30 years, perhaps the most significant is the observation that only minerals that contain uranium but negligible common Pb (high  $^{238}\text{U}/^{204}\text{Pb}$  ratios) are suitable for obtaining precise and interpretable dates. Uranium-bearing minerals with negligible common Pb, such as zircon, monazite, and baddeleyite in terrestrial rocks (Heaman and Parrish 1991; Hanchar and Hoskin 2003) and Ca phosphates and pyroxenes in meteorites (Lugmair and Galer 1992; Göpel et al. 1994; Amelin et al. 2003) are the minerals of choice for dating.

There are two reasons why a negligible level of common Pb is important. First, it eliminates the major, non-analytical uncertainty in  $^{207}\text{Pb}/^{206}\text{Pb}$  age calculations. It is usually assumed that initial common Pb in meteorites corresponds to the most primitive Pb isotopic composition known in the solar system (primordial Pb), as measured in a troilite inclusion from the Canyon Diablo iron meteorite (CDT Pb) (Tatsumoto et al. 1973). Because the solar  $^{238}\text{U}/^{204}\text{Pb}$  ratio is low ( $\sim 0.1$ ), it is expected that with solar U/Pb ratios the Pb isotopic composition would not have changed significantly in the first 10 million years. However, there are other components of common Pb in addition to primordial Pb, including one or more Pb components mobilized and redistributed by metamorphism, alteration and impacts in the parent body, and one or more components added to the meteorite in terrestrial environments (Unruh 1982; Tera and Carlson 1999; Amelin et al. 2005). These common Pb components can be distributed unevenly among chondrules, CAIs, and matrix and their constituent minerals. Therefore, the common Pb isotopic composition can vary even within a meteorite. The presence of two or more common Pb components can produce inaccuracy in the isochron dates (Tera and Carlson 1999; Amelin et al. 2005).

The common Pb isotopic composition in a particular part of a meteorite is generally unknown, therefore model dates calculated using an assumed common Pb isotopic composition can contain a systematic error of an uncertain magnitude. The effect of the common Pb correction on the accuracy of model dates decreases as the ratio of radiogenic Pb to common Pb increases (Fig. 4). The precision and accuracy of Pb-Pb isochron dates is also improved if we use highly radiogenic Pb because the effect of the presence of multiple common Pb components is minimized (Amelin et al. 2005).

The second reason why low common Pb is important is that it is much easier to recognize the patterns of multi-stage evolution in systems containing only radiogenic Pb than in

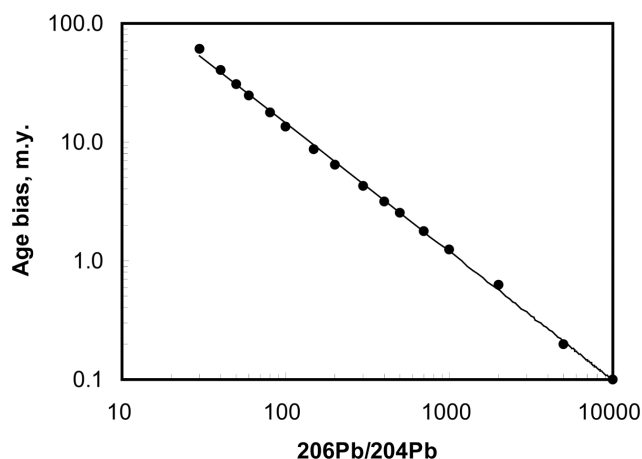


Fig. 4. Systematic error in  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  model date caused by using inaccurate common Pb isotopic composition, plotted against  $^{206}\text{Pb}/^{204}\text{Pb}$  (the measure of the ratio of radiogenic Pb to common Pb). In this model, each simulated analytical point is based on a mixture of radiogenic Pb corresponding to the age of 4566 Ma ( $^{207}\text{Pb}^*/^{206}\text{Pb}^* = 0.62447$ ) and average modern terrestrial crustal Pb (Stacey and Kramers 1975). The model date calculations assume, however, that the initial Pb is primordial Pb (Tatsumoto et al. 1973). All model dates are too young, and the systematic error increases with the proportion of common Pb in the mixture (with decreasing  $^{206}\text{Pb}/^{204}\text{Pb}$ ). For a simulated sample with  $^{206}\text{Pb}/^{204}\text{Pb} = 2000$ , the systematic error is 0.62 Myr, similar to the age uncertainty introduced by analytical error; for a sample with  $^{206}\text{Pb}/^{204}\text{Pb} = 200$ , the systematic error increases to 6.5 Myr—a longer time interval than the presently estimated lifespan of the solar nebula.

systems containing a mixture of radiogenic Pb and common Pb. The role of common Pb in detecting multi-stage evolution is discussed below.

Achieving a low level of common Pb in analyses involves two steps. The first is choosing minerals that do not incorporate common Pb due to their structural properties and conditions of formation. The second is removing adhering phases rich in common Pb (e.g., chondrite matrix) by a combination of air abrasion, ultrasonic agitation, and acid leaching. Since these cleaning procedures affect only the surface of a mineral or an aggregate (e.g., chondrule) and the immediate sub-surface layer, it may be necessary to pulverize a chondrule to expose internal surfaces for effective removal of common Pb present in the chondrule minerals.

### The Effects of Possible Multi-Stage Evolution

Two-stage or three-stage evolution of the U-Pb isotopic system can produce linear arrays in Pb-Pb isochron coordinates (Gale and Mussett 1973). If these arrays are interpreted as single-stage (conventional) isochrons, then dates with large systematic errors may be obtained. The potential for re-distribution of Pb during chondrite metamorphism, which leads to anomalously old  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  dates, has been discussed by Tera and Carlson (1999) and Amelin et al. (2005). It is important to note that anomalously

old  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  dates can only be observed if a mineral has gained ancient radiogenic Pb. Minerals (e.g., zircon) that do not accommodate Pb during their growth typically do not gain Pb during secondary processes, unless their lattice is damaged by radiation or another process. The possible multi-stage evolution for these minerals is therefore reduced to ancient Pb loss, which leads to lower  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  apparent dates. For a set of mineral grains (or chondrules, CAIs, etc.) that experienced ancient Pb-loss during the same secondary process, the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  apparent date would vary with the fraction of radiogenic Pb lost. Variation in  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  is therefore an indicator of multi-stage evolution. The consistency of  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ , on the other hand, strongly suggests single-stage evolution, because there are many factors (e.g., grain size, mineral composition, fracturing) that lead to variations in metamorphic or alteration-related Pb loss, and there is no known secondary process that would cause the exact same amount of secondary Pb loss in a set of samples.

Some cases of multi-stage evolution, for example, multiple events of U/Pb fractionation that immediately followed formation of the mineral, or a recent Pb loss event, do not change the consistency of  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratios. Although such cases technically represent multi-stage evolution, the U-Pb system is adequately described by a single-stage model.

There is still the hypothetical possibility that the studied mineral could gain radiogenic Pb released from other minerals. Thus the best choice for accurate Pb isotopic dating are minerals or mineral aggregates (CAIs, chondrules) with very high  $^{238}\text{U}/^{204}\text{Pb}$  extracted from a host with much lower  $^{238}\text{U}/^{204}\text{Pb}$ . Any mobile radiogenic Pb in such cases would be mixed with sufficient amounts of common Pb to be detected by elevated  $^{204}\text{Pb}$  content. This demonstrates once again the importance of using only minerals with negligible common Pb for Pb-Pb dating. In Pb-Pb dating of chondrules and CAIs, the condition of much higher  $^{238}\text{U}/^{204}\text{Pb}$  in the studied mineral aggregate than its surrounding is usually satisfied. This is not always the case for achondrites (e.g., eucrites and angrites), which can have fairly high  $^{238}\text{U}/^{204}\text{Pb}$  in the whole rock (e.g., Tera et al. 1997). In studies of such meteorites it is important to identify and analyze all minerals that carry uranium and radiogenic Pb.

The variability of  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  can serve as a gauge for possible multi-stage evolution only if we have a set of high-precision analyses of highly radiogenic Pb from each studied meteorite component (a CAI, a chondrule population, etc.). Distinguishing between single-stage and multi-stage systems from single analysis does not seem to be possible.

### Pb-Pb versus U-Pb

Unfortunately, CAIs and chondrules are not as resistant to acid attack as zircon. Intensive acid leaching, which is

necessary for common Pb reduction, is likely to disturb the ratio of U to radiogenic Pb in these materials, making the accurate determination of  $^{238}\text{U}/^{206}\text{Pb}^*$  and  $^{235}\text{U}/^{207}\text{Pb}^*$  dates difficult or impossible (Tera et al. 1997; Amelin and Krot 2005). The capability of the U-Pb system to reveal open-system behavior and the possibility of calculating both ages in a two-stage model are therefore lost. As discussed above, the dates based on the ratio of radiogenic Pb isotopes are not affected by leaching.

### The Uncertainty in Decay Constants

The uncertainties in the decay constants of uranium isotopes is an additional factor that can significantly contribute to the total error of  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  dates (Ludwig 2000). The decay-constant-related component in the total error of a  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  date, which can be calculated by using Equation 3 of Ludwig (2000), is about 9.3 Myr for a 4560 Ma old material if one assumes the decay constant uncertainties of Jaffey et al. (1971). If Pb isotopic dates are compared to the dates obtained with another long-lived nuclide chronometer, then the decay constant errors should obviously be included for both isotopic chronometers. In the determination of age intervals with the Pb-Pb method within a relatively short period of the early solar system evolution (~4570–4400 Ma), the errors of decay constants almost completely cancel and should be excluded from the uncertainty of age intervals. However, decay constant errors must be considered in all other interpretations.

The known values of the decay constants of other radioactive nuclides used in geochronology are burdened with even larger relative errors than those for  $^{235}\text{U}$  and  $^{238}\text{U}$  (Begemann et al. 2001). These uncertainties, about one per cent or larger for extant isotopes like  $^{40}\text{K}$ ,  $^{87}\text{Rb}$ , and  $^{147}\text{Sm}$ , as well as uncertainties in the branching ratio for the nuclides that experience branched decay ( $^{40}\text{K}$ ,  $^{138}\text{La}$ ) are directly propagated into the errors of the dates and present a serious difficulty for comparing results obtained with different methods. For example, the uncertainty in the decay constant of  $^{40}\text{K}$  makes comparison between cooling rates of asteroids determined with the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  method (Amelin et al. 2005) and with  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  method (e.g., Trierloff et al. 2003) very difficult or even impossible.

The decay constant errors are usually considered a less significant source of error in extinct nuclide chronometry (e.g., Russell et al. 2005), and are rarely taken into account. However, with improvement in precision of dating, the contribution of decay constant errors to the total uncertainty of an extinct nuclide date may become a significant portion of the total error. The relative uncertainties in the decay constants of extinct isotopes are propagated into the measured time intervals and have to be taken into account in all comparisons between time scales based on different nuclides. In comparing “absolute” ages reconstructed by “mapping”

two (or more) extinct nuclide chronometers onto an absolute time scale the decay constant errors must be considered for both extinct nuclides. In addition, if these extinct nuclide chronometers utilize different  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  dates as their primary anchors to the absolute time scale, e.g., the date for pyroxene from the angrite Lewis Cliff (LEW) 86010 (Lugmair and Galer 1992) for  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  and the date for Ca phosphate from Acapulco (Göpel et al. 1992) for  $^{129}\text{I}$ - $^{129}\text{Xe}$ , then the uncertainties of these reference  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  dates must be included in the total errors of reconstructed “absolute” dates and time intervals. The decay constant errors of uranium isotopes are, however, not included because they cancel out almost completely for the relatively short time intervals as discussed above.

It is particularly difficult to account for decay constant errors if one attempts to combine the reconstructed “absolute” errors from different extinct nuclide chronometers in order to improve the precision of a date. Error propagation for such averaging involves other sources of error besides the decay constant uncertainty and can give an incorrect result if some of the contributing errors or their correlations are overlooked or poorly known. I suggest that averaging reconstructed “absolute” errors from different extinct nuclide chronometers should be avoided.

A word of caution must be added here about the uncritical use of decay constants and their uncertainties determined by  $\gamma$ -counting. The present situation with the decay constant of  $^{176}\text{Lu}$  illustrates the problem. Numerous  $\gamma$ -counting determinations of the  $^{176}\text{Lu}$  half-life published after 1980 (summarized by Begemann et al. [2001], as well as the newer studies by Grinyer et al. [2003] and Nir-El and Haquin [2003]) show a scatter of over 12% in the apparent decay constant values, well outside the internal errors reported in each study of about 1% or lower. This indicates that major unresolved analytical problems still exist for  $\gamma$ -counting techniques in many laboratories involved in half-life determinations. The half-lives of most nuclides used in extinct nuclide chronometry were determined in only one or two modern, relatively precise,  $\gamma$ -counting studies for each nuclide using similar techniques as those used in  $^{176}\text{Lu}$  half-life determinations. It is possible that the decay constants of some of these short-lived nuclides contain systematic errors that greatly exceed the quoted random errors but remain undetected because of the lack of comparison. Therefore, new determinations of decay constants using the best available  $\gamma$ -counting techniques as well as radiogenic isotope ingrowth experiments are therefore needed.

### The Uncertainty in the $^{238}\text{U}/^{235}\text{U}$ Ratio

The currently used formalism of U-Pb dating is based on the assumption that the  $^{238}\text{U}/^{235}\text{U}$  ratio is uniform in the solar system. If the ratio of the U isotopes is variable, for example, as a result of the presence of  $^{247}\text{Cm}$  in the early solar system,

then these variations have to be accounted for in the calculation of Pb isotopic dates. The variations of  $^{238}\text{U}/^{235}\text{U}$  are directly propagated into  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  ratios. A recent high-precision search for  $^{238}\text{U}/^{235}\text{U}$  anomalies in a wide range of chondrites, achondrites, and terrestrial rocks (Stirling et al. 2005) has shown that this ratio is constant within  $\pm 0.02\%$ . The maximum error in  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  dates of meteorites due to this uncertainty in  $^{238}\text{U}/^{235}\text{U}$  is  $\sim 0.3$  Myr, smaller than the best precision of  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  dates achieved so far.

### Ages Derived from Imperfect Isochrons

Isochron models used in isotopic dating assume that the samples included in an isochron regression formed simultaneously, with a parent element of uniform isotopic composition, and remained closed to subsequent migration of parent and daughter isotopes. In natural systems these conditions are only approximately satisfied. Possible inaccuracy in isochron regressions for imperfect systems need to be studied using modeling with realistic simulation of variations in the age and initial ratios. Models of Pb-Pb isochrons for systems with variable initial Pb isotopic composition have been discussed by Amelin et al. (2005). A possible inaccuracy of a Pb-Pb isochron date for a heterogeneous set of chondrules has been modeled (Amelin and Krot 2005) by applying a distribution of  $^{26}\text{Al}$ - $^{26}\text{Mg}$  ages for Allende chondrules (Bizzarro et al. 2004) to a simulated Pb-Pb isochron data set with or without random scatter caused by analytical uncertainties. Modeling a Pb-Pb isochron for a set of chondrules with variable ages, as suggested for Allende chondrules by  $^{26}\text{Al}$ - $^{26}\text{Mg}$  data, shows that the Pb-Pb isochron date remains accurate, even if less precise, if there is no correlation between  $^{206}\text{Pb}/^{204}\text{Pb}$  and the age for individual chondrules. The isochron date may be inaccurate if  $^{206}\text{Pb}/^{204}\text{Pb}$  and the age are correlated.

### Diffusion and Other Mechanisms of Resetting

Isotopic clocks in meteorites can be modified and even completely reset by the processes that occurred after formation of their parent bodies: thermal metamorphism that caused volume diffusion and recrystallization, aqueous alteration, and shock metamorphism caused by asteroidal collisions. All these processes may be important for isotopic resetting of the U-Pb system. Quantitative assessment of the role of thermal metamorphism, aqueous alteration, and shock metamorphism will be possible when experimental data about redistribution of Pb, U, and other elements of interest to cosmochronology in these processes are available.

An extensive set of experimental data for thermal diffusion of Pb and U in minerals is now available for the interpretation of Pb isotopic dates in terms of diffusion models. Some of these data, as well as the rates of diffusion in other systems relevant to dating meteorites, are summarized

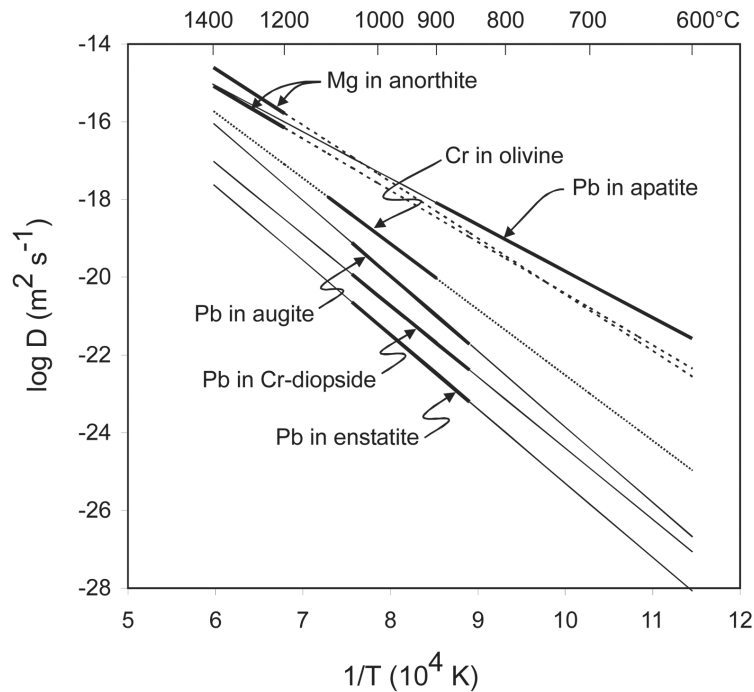


Fig. 5. An Arrhenius plot showing a summary of experimental diffusion data relevant to cosmochronology. The sources of data: Pb in apatite—Cherniak et al. (1991), Pb in pyroxenes—Cherniak (2001), Mg in anorthite—LaTourrette and Wasserburg (1998), Cr in olivine—Ito et al. (2004). The two rates of diffusion of Mg in anorthite correspond to different crystallographic directions. Data in the temperature intervals in which the diffusion experiments were performed are shown with thick lines; thin, dotted, and dashed lines show extrapolated diffusion coefficients assuming that the diffusion parameters (activation energy and pre-exponential factor) remain unchanged over the entire range of temperature (linear extrapolation in an Arrhenius plot).

in Fig. 5. These experimental data can be applied to the interpretation of isotopic dates for meteorites derived from slowly cooled asteroids using either the classical model of Dodson (1973) or the model of Ganguly and Tirone (1999), which extends Dodson's formulation to include cases with arbitrarily small amounts of diffusion. Since similar experimental data sets for aqueous alteration and shock metamorphism (necessary for comprehensive evaluation of resetting of isotopic chronometers in meteorites) have not been obtained yet, the following discussion is limited to thermal diffusion.

There is a long history of using experimental data for diffusion in the interpretation of isotopic dates in metamorphic terrains. In contrast, using diffusion data in cosmochronology is in its infancy and in some cases lacks necessary rigor. It would therefore be useful to discuss some basic concepts and methodology of applying experimental diffusion data to the interpretation of isotopic dates.

Before applying experimental diffusion data to geochronology, we need to answer several questions. The first question is whether it is possible and likely that the isotopic systems were reset not by diffusion but by another process. The alternative mechanisms that can reset isotopic clocks in meteorites and their minerals are aqueous alteration and shock metamorphism. The second question is how the parent and daughter isotopes are distributed between minerals.

Without knowing the host minerals of the parent and daughter isotopes, we would not be able to use diffusion data, because the rates of diffusion of the same elements can vary by several orders of magnitude between co-existing minerals in a chondrule or a CAI. The third concern is the geometry of minerals which we consider in a diffusion model. Mineral geometry may be relatively straightforward for an equigranular rock, such as an igneous or metamorphic rock or some achondrites (although the structures of achondrites are complicated by exsolution in many cases), but the structural complexity of chondrules makes evaluation of diffusion patterns particularly difficult. If an entire chondrule is being analyzed, then the degree of diffusion-related resetting of the isotopic date depends on how fast the radiogenic isotopes, e.g.,  $^{206}\text{Pb}^*$  and  $^{207}\text{Pb}^*$  for pyroxene and  $^{26}\text{Mg}^*$  for feldspar, migrate from the minerals to the surface of the chondrule. The total effect of diffusion in such a case depends on the rates of diffusion in the minerals that comprise the chondrule, their grain sizes, the chondrule texture, and the efficiency of migration along the grain boundaries. A detailed study of these parameters has not been performed yet.

An important uncertainty involved in using experimental diffusion data derives from the necessary extrapolation of diffusion parameters (activation energy of diffusion expressed by the slope of a line in the Arrhenius plot and pre-exponential factor expressed by the vertical position of the



line with a given slope) from the temperature range of diffusion experiments to the usually much lower temperature range of the studied metamorphism. This uncertainty does not exist if annealing experiments are performed at temperatures similar to the potential metamorphic temperature range. However, annealing of a mineral with a slow diffusion rate for an experimentally reasonable length of time would produce a diffusion profile with negligible depth. In order to obtain a measurable depth of a diffusion profile, researchers are forced to anneal minerals at a temperature much higher than the metamorphic temperatures. The problem is most severe if the diffusion in a mineral is slow and the depth resolution of a technique used to study concentration profile is relatively low. Among the results shown in Fig. 5, the data for Mg diffusion in anorthite are most affected by the extrapolation uncertainty because these data were obtained in a limited range of very high temperatures. When we compare two minerals and/or two isotopic systems with similar rates of diffusion, e.g., Mg in anorthite and Pb in apatite, we should consider uncertainties in diffusion coefficients to see whether the difference is significant.

#### WHAT IS THE MEANING OF AN “AGE OF A METEORITE”?

Just like any “date of a rock,” a “date of a meteorite” is not an “age” unless the rock or the meteorite under consideration were formed instantaneously and remained undisturbed since their formation. In less ideal (and more common) cases we can only discuss an age of a mineral or, even more specifically, the time when migration of certain elements, e.g., U and Pb, ceased in that mineral. The “ages” of different minerals or mineral aggregates in the same meteorite can vary significantly, even if they were determined using the same dating method (e.g., Amelin et al. 2005). It is particularly important to consider the minerals used in age determinations in linking relative dates to the absolute time scale. For example, some of the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  dates of chondritic Ca phosphates (metamorphic minerals!) reported by Göpel et al. (1994) are sometimes referred to as the formation ages of their host meteorites—this is unacceptable.

For chondrites, in particular, whole-rock dates obtained using the  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  or other methods are likely to be meaningless because they provide at best an average time of numerous processes that span an unknown and potentially rather long period including: formation of CAIs, chondrules, matrix and metal, accretion, and metamorphism and/or alteration. It is also very difficult to apply an accurate correction for initial Pb to a whole rock analysis and to assure the absence of U and Pb migration in the geological past. Isotopic dating of minerals with high parent/daughter ratios and known rates of migration of parent and daughter elements can yield much more precise and interpretable dates.

#### COMMENTS ABOUT THE RELIABILITY OF $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ AGES OF CHONDRITES

An isotopic date derived from isotopic ratio measurements is loaded with analytical uncertainty, but does not include the uncertainties related to the imperfect state of isotopic systems: the presence of multiple common Pb components, migration of U and Pb, and, in the case of isochron dating, formation of the studied objects (chondrules, etc.) at different times. These types of uncertainty in isotopic dates can be collectively referred to as “geochemical errors.” We can use the criteria discussed above to evaluate how large the geochemical errors of published Pb isotopic ages of chondrites may be, and, hence, how reliable these ages are.

Whole rock data are burdened with the largest geochemical errors. The presence of multiple common Pb components and ancient and recent migration of U and Pb cause scattering of analytical points for multiple fragments from the same meteorite (e.g., Abranches et al. 1980; Gale et al. 1980) and result in low precision of an isochron date. Model dates based on high-precision Pb isotopic analyses of individual fragments of chondrites appear precise, but their accuracy is compromised by the same factors that cause scattering of Pb-Pb whole rock isochrons. Additional uncertainty is introduced by a potentially inaccurate choice of the initial Pb isotopic composition for the model date calculation. An apparently high precision of whole-rock Pb isotope model dates for chondrites is therefore fictitious and misleading. These dates should never be quoted as geologically meaningful ages.

The dates based on analyses of minerals or mineral aggregates (chondrules, CAIs) with highly radiogenic Pb, extracted from meteorites with moderate or low  $^{238}\text{U}/^{204}\text{Pb}$  ratios, are much more likely to be accurate. Lead isotopic dates of phosphates can be interpreted using the concept of volume diffusion and experimental data for Pb diffusion in apatite (Ca phosphates in chondrites comprise two minerals, apatite and merrillite, but since the concentration of U in apatite is much higher than in merrillite (e.g., Crozaz et al. 1989), and compositions and structures of these minerals are rather similar, the experimental diffusion data for apatite should be representative for the bulk Ca-phosphate fractions). Isochron regression of multiple phosphate analyses eliminates uncertainties related to common Pb subtraction and provides a test for possible multi-stage history. These problems are, however, minor for phosphate model dates based on individual Pb isotopic analyses if the Pb isotopic composition is sufficiently radiogenic ( $^{206}\text{Pb}/^{204}\text{Pb}$  is higher than ~400–500). The consistency of the isochron date and model dates have been demonstrated for phosphates from the H5 chondrite Richardton (Amelin et al. 2005).

The reliability and interpretation of Pb isotope analyses of chondrules and CAIs are similar to those of chondritic

phosphates, if the Pb isotopic compositions are similarly radiogenic. The dates of chondrules from equilibrated chondrites probably reflect cessation of Pb diffusion in pyroxene—the main host mineral of U in chondrules (Amelin et al. 2005). In unequilibrated chondrites, which experienced only mild thermal metamorphism insufficient for isotopic resetting and were not strongly affected by aqueous alteration and shock metamorphism, the Pb-Pb dates correspond to the time of chondrule and CAI formation.

The main factor that currently hampers precise Pb isotopic dating of chondrites is the difficulty of common Pb removal. The reasons why the same leaching procedure that can effectively remove common Pb from chondrules in some chondrites but not others remains unclear. This is the subject of ongoing investigation. The other limiting factor is the lack of understanding of the effects of aqueous alteration and shock metamorphism on U-Pb and other isotopic chronometers. An additional problem is the dispersion of formation ages of chondrules within one meteorite, and its impact on Pb-Pb isochron dating. All these factors deserve systematic study.

## CONCLUSIONS

Currently used techniques and methodologies of Pb isotopic dating of meteorites allow precision of the dates of 0.5–1.0 Myr, and potentially similar accuracy of time interval measurements. Absolute  $^{207}\text{Pb}^*/^{206}\text{Pb}^*$  dates are burdened with an additional uncertainty of about 9 Myr from decay constant errors of the U isotopes, but this uncertainty cancels out when we calculate time intervals. Further improvement in precision and accuracy of Pb isotopic dates for meteorites would require analytical advancements (better control over instrumental mass fractionation, enhanced mass spectrometer sensitivity, lower blanks), more efficient methods for separating meteorite materials containing common Pb from chondrules and CAIs containing U and radiogenic Pb, and a better understanding of the response of the U-Pb systems in various meteoritic minerals to thermal metamorphism, shock metamorphism, and aqueous alteration. All these developments are important for the progress towards the ultimate limit on precision based on the number of atoms of radiogenic Pb isotopes present in chondrules, CAIs, and meteorite minerals.

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