CAUSES OF POSSIBLE BIAS IN ^{207}Pb-^{206}Pb AGES OF METEORITES. Y. Amelin[1] and L. A. Neymark[2], [1]Planetary Science Institute and Research School of Earth Sciences, The Australian National University, Canberra ACT 0200, Australia (yuri.amelin@anu.edu.au), [2]U.S. Geological Survey, DFC Box 25046, MS 963, Denver, CO 80225, USA (lneymark@usgs.gov).

Introduction: Pb-isotopic and extinct nuclide dates of meteorites recently reached an unprecedented precision of ±0.1-0.2 Ma [1-4]. If these dates are as accurate as they are precise, it should be possible to construct a consistent time scale of the early Solar System with the ~0.2 Ma time resolution. The agreement between the absolute and relative timescale is, indeed, improved [5], but the discrepancies of 1-2 Ma in time intervals, measured with ^{207}Pb-^{206}Pb, ^{26}Al-^{26}Mg, ^{53}Mn-^{53}Cr and ^{182}Hf-^{182}W chronometers [6, 7], between precisely dated meteorites such as angrites, eucrite Asuka 881394, and Allende and Efremovka CAIs [1-13], remain unexplained.

Systematic errors in both Pb-isotopic and extinct nuclide dates may be well beyond their analytical precisions, and, therefore, could be responsible for the time scales discrepancies. These systematic errors must be quantified to enable building a consistent time scale. Here we examine possible causes of bias in Pb-isotopic dates, including recently suggested possibilities such as an unknown abundance of ^{234}U at the time of meteorite formation [14] and fractionation of Pb isotopes during leaching [15]. In the meteorite age range of 4500-4570 Ma, the age difference of 1 Ma corresponds to the difference of 0.069% in the ^{207}Pb*/^{206}Pb* ratio. Thus we have to consider possible processes that can cause <0.1% shifts in ^{207}Pb*/^{206}Pb*.

Analytical artifacts: The uncertainty of external fractionation correction in conventional TIMS can be responsible for ^{207}Pb/^{206}Pb age errors of 0.5-1.0 Ma. Fractionation correction in modern MC-ICPMS and DS-TIMS is less uncertain and the ^{207}Pb/^{206}Pb ratio is measured with reproducibility of 0.01-0.02% or better. [16, 17, and references therein]. Maximum biases in the ^{207}Pb/^{206}Pb ratio, caused by the presence of isobaric interference from $BaPO_2^+$ and from mass-independent fractionation are < 0.005-0.01% [17]. All these factors can possibly cause systematic shifts in the MC-ICPMS and DS-TIMS ^{207}Pb*/^{206}Pb* dates of ~0.1-0.3 Ma, similar to the precision of the dates, but are too small to explain the 1-2 Ma time scale discrepancies.

Matrix effects on fractionation, in both TIMS and MC-ICPMS, are effectively eliminated by using double spike. Sample - standard bracketing and Tl normalization, which are also used for fractionation correction in isotopic analyses of meteoritic Pb by MC-ICPMS [1, 14], are not completely immune to matrix-related biases. It is essential to study the possible matrix-related biases at ≤0.01% levels of precision, and to use double spike MC-ICPMS whenever possible.

Multiple components of non-radiogenic Pb: Besides the radiogenic Pb accumulated in closed system, meteorites contain initial Pb (identical or close in isotopic composition to the primordial Pb), Pb added to the meteorite in terrestrial environments (most likely, similar to average modern crustal Pb), and possibly other components of terrestrial and extraterrestrial origins. Using initial Pb isotopic composition for model age calculation of a meteorite that contains modern terrestrial Pb produces biased ^{207}Pb*/^{206}Pb* model dates. The presence of multiple non-radiogenic Pb components distorts Pb-Pb isochron relationships and can make isochron dates imprecise and/or inaccurate.

The magnitude of the model date bias depends on the ^{206}Pb/^{204}Pb ratio, and for materials with blank-corrected ^{206}Pb/^{204}Pb>5000, achieved in some of the modern studies (e.g. [2]), is <0.2 Ma [18]. In the age determinations based on Pb isotopic analyses with ^{206}Pb/^{204}Pb<100 (e.g. [14]), the presence of multiple non-radiogenic Pb components can severely bias the ^{207}Pb*/^{206}Pb* model and isochron dates.

The presence of "aborted high-μ Pb": Along with primordial Pb and modern common Pb, volatile-depleted meteorites, such as angrites and eucrites, can contain radiogenic Pb accumulated in the parent body for a few million years before formation of their parental rocks. Alternatively, such Pb with very high ^{207}Pb/^{206}Pb ratio can be re-distributed in the parent body by a thermal metamorphism or an impact and embedded into minerals, or deposited in grain boundaries. The presence of such Pb in significant quantities could destroy ^{207}Pb/^{206}Pb-^{204}Pb/^{206}Pb isochron relationships and bias the model dates as it was observed for the pyroxene fractions from the angrite Sahara 99555 [18]. The preservation of isochron relationships for the whole rock fractions in this angrite suggests that the high-^{207}Pb/^{206}Pb radiogenic component was re-distributed at a mineral grain scale several million years after the meteorite crystallization. This source of uncertainty is probably unimportant for angrites AdoR, LEW 86010, and D'Orbigny [2], eucrite Asuka 881394 [10, 11], and Efremovka CAI E60 [11], all of which show good ^{207}Pb/^{206}Pb-^{204}Pb/^{206}Pb isochron relationships for pyroxene and/or whole rock. The absence of the radiogenic component re-distribution should be verified by analysis of various minerals from the same meteorite.

The presence of "freshly" synthesized ^{234}U: It was suggested that the unknown abundance of ^{234}U at the time of meteorite formation is a major uncertainty of the ^{207}Pb-^{206}Pb chronometer [14].

The estimated yields of ^{234}U, ^{230}Th and ^{231}Pa (three relatively long-lived daughters in the U decay series) in the r-process in a core-collapse supernova are similar to the yield of ^{232}Th, and are higher than the yields of ^{235}U and ^{238}U [19]. The estimated yields of actinides obtained with a wide range of r-process model conditions [20] (that study, unfortunately, includes only nuclides with half-lives of 1 Ma or longer) vary by a factor of 2 to 50 among the models for each nuclide. Therefore, it is reasonable to assume that the r-process yields of ^{234}U, ^{230}Th and ^{231}Pa [19] are accurate within two orders of magnitude.

The excess ^{234}U decays with time so that the produced in r-process $^{234}U_{ex}/^{238}U$ ratio of 2.61 (from the yields estimated by [19]) declines to 1.54×10^{-1}, 5.38×10^{-4}, 1.88×10^{-6}, and 1.35×10^{-12} in 1, 3, 5, and 10 million years, respectively, after the termination of the r-process. The possible presence of ^{206}Pb from "freshly" synthesized ^{234}U thus critically depends on the time interval between the termination of the r-process and accretion of the protoplanetary disk (the interval of free decay). From the upper limit on the $^{247}Cm/^{235}U$ ratio in meteorites of $8\text{-}10\times10^{-5}$ [21, 22], the minimum interval of free decay for actinides is estimated at 200-230 Ma, during which the $^{234}U_{ex}/^{238}U$ ratio becomes undistinguishable from zero. Therefore, the presence of excess ^{234}U is irrelevant, unless an independent evidence is found that there is a stellar process that produces ^{234}U but does not produce ^{247}Cm, and that actinides synthesized in this process were rapidly injected into the accreting protoplanetary disk.

Fractionation of Pb isotopes during leaching: Laboratory acid leaching to eliminate surface contamination is a common routine in ^{207}Pb-^{206}Pb dating of meteorites. For atoms that reside in the crystal lattice, isotopic fractionation during this acid leaching of minerals is unlikely. However, multiple α-decays on the way from U to radiogenic Pb produce α-recoil tracks, and radiogenic Pb atoms reside in these tracks. During leaching, the acid attacks α-recoil tracks that are exposed to the surface of the crystal, whereas the tracks inside the crystal of an acid-insoluble mineral are shielded. The probability that the recoil tracks are exposed at the surface can be calculated from the relative size of the crystal and the track [23]. If the average sizes of recoil tracks containing radiogenic ^{206}Pb and ^{207}Pb differ, then the isotope enclosed in larger tracks would be more easily extractable and the extent of fractionation would be greater for smaller crystals.

The decay chains of ^{235}U and ^{238}U differ by the number of α-decays (7 and 8, respectively), the average recoil range (37.7 and 35.1 nm), and the total recoil energy (773 and 786 keV) [24, 25]. The sizes of tracks (defined as the maximum distance between the consecutive positions taken in by the recoiling nucleus), modeled using a Monte Carlo method [24], vary broadly for both decay chains [25]. The average sizes of tracks, produced by complete decay series, are ~115 nm for ^{235}U, and ~110 nm for ^{238}U [25]. Although the difference of the average track sizes is less than 5%, it is sufficient to produce a measurable difference between the fraction of extractable ^{206}Pb* and ^{207}Pb* and to shift the $^{207}Pb^*/^{206}Pb^*$ ratio in small crystals. For the crystal (approximated as a sphere) with the radius of one μm, about 8% of tracks are exposed, and the fractionation between ^{207}Pb* and ^{206}Pb remaining in the crystal is as large as 0.4%. For a crystal with the radius of 30 μm, about 0.28% of tracks are exposed, and the fractionation between ^{207}Pb* and ^{206}Pb* remaining in the crystal is 0.013%.

It should be noted that this simple model involves major uncertainties. First, the track size evaluation [25] was done for phlogopite in the age interval of 0.1-1.0 Ma, and may be different for other minerals of older age. Second, the "tracks in a sphere" model assumes a fixed track size, whereas the sizes of tracks created by multiple α-decays are widely variable. When these uncertainties are resolved, the model outcome could change radically.

Of the possible causes of bias in ^{207}Pb-^{206}Pb ages of meteorites considered here, substantial isotopic fractionation that may be induced by acid leaching is one of the least understood. This effect may be important for both precise meteorite chronology and "terrestrial" U-Pb dating, and requires detailed experimental and theoretical evaluation.

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