

PB-ISOTOPIC DATING OF METEORITES USING ^{202}Pb - ^{205}Pb DOUBLE-SPIKE: COMPARISON WITH OTHER HIGH-RESOLUTION CHRONOMETERS. Y. Amelin¹, M. Wadhwa², and G. Lugmair³, ¹Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario K1A 0E8, Canada, ²Dept. of Geology, The Field Museum, 1400 S. Lake Shore Dr., Chicago, IL 60605, USA and The Chicago Center for Cosmochemistry, 5640 S. Ellis Ave., Chicago, IL 60637, ³Scripps Inst. of Oceanography, University of Calif. San Diego, La Jolla, CA 92093, USA.

Introduction: 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, and for linking the dates obtained from extinct radionuclide chronometers to the absolute time scale. Precision of ^{207}Pb - ^{206}Pb dating of meteorites is about ± 0.5 -1.0 My in most modern studies. Further improvement in precision requires better constraints on the instrumental mass fractionation [1]. This can be achieved by using MC-ICPMS, with normalization to isotopic composition of another element (e.g., thallium), or with sample-standard bracketing. Alternatively, fractionation can be measured by using Pb-isotopic spike containing two enriched isotopes (double spike, DS) - an approach applicable to both MC-ICPMS and TIMS. The MC-ICPMS can produce very precise Pb-isotopic data for meteoritic samples that yield 3-5 ng or more of radiogenic Pb per analysis, for example for large samples of angrites [2]. Most meteorites, however, have very low content of radiogenic Pb (about 1-10 ppb after removal of common Pb by acid washing) and require analysis of small samples: individual chondrules, fragments of CAIs, and mineral separates from small achondrite specimens. The amount of Pb per analysis for these materials is below 0.5-1.0 ng, and in many cases is less than 0.1 ng. Precise analysis of these amounts of Pb requires a technique which has the highest possible sensitivity, such as TIMS with a high efficiency emitter [3], along with monitoring of fractionation.

^{202}Pb - ^{205}Pb DS measurements: ^{204}Pb - ^{207}Pb double-spike has been used for high-precision isotopic analyses of large amounts of Pb from terrestrial rocks for over 30 years. This spike is, however, poorly suited for analysis of sub-nanogram amounts of radiogenic Pb, because the necessary splitting of samples for spiking introduces additional errors due to non-uniformity of blank, and makes sample utilization less efficient. In addition, the Pb isotopic composition of the unspiked aliquot is extremely sensitive to potential accidental contamination with ^{204}Pb - ^{207}Pb spike. A double spike made of artificial isotopes ^{202}Pb and ^{205}Pb [4] is free from these problems.

A ^{202}Pb - ^{205}Pb mixed spike has been prepared and calibrated at the Geological Survey of Canada from high-purity spikes ^{202}Pb provided by W. Todt [4] and

^{205}Pb provided by G.J. Wasserburg [5]. The $^{202}\text{Pb}/^{205}\text{Pb}$ ratio of 1.020032 was calibrated against $^{208}\text{Pb}/^{206}\text{Pb} = 2.1677$ in the SRM-981 standard. All Pb isotopes between 202 and 208 were measured in a static multicollector mode on the GSC Triton TI mass spectrometer. Pb was separated by double-pass through columns containing 50 μl of anionite AG50W x8, and loaded with dilute Merck silicic acid [3]. Multiple measurements of the total procedural blank averaged 2 pg. Pb was measured in semi-automatic mode, with increase of temperature of 15°C after each block of 15 8-second integrations. Pb isotopic measurements gave a total ion yield (the ratio of the number of detected ions of a certain isotope, ^{205}Pb in this case, to the number of atoms of the same isotope added to the sample) between 0.5-7.0 percent, with the median value of 2.6 percent. A few analyses that gave total ion yields below 0.5 percent showed anomalous emission behavior indicating a problem with chemical separation, and were discarded. The ion beam of BaPO_2^+ was monitored on the mass 201, and a correction was applied to ^{202}Pb and ^{204}Pb . The BaPO_2^+ interference correction on ^{202}Pb and ^{204}Pb remains insignificant until Pb is nearly exhausted and the 201/202 ratio exceeds 1. Inaccuracy in Pb isotopic ratios corrected for mass-dependent fractionation using DS can be caused by decoupled fractionation of even- and odd-mass isotopes [6]. This effect was monitored in all samples by checking the uniformity of normalized $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ ratios over the temperature range of analysis. We have not observed a typical pattern of odd-even mass fractionation, as seen in large (100 ng) loads of Pb [6], in any of the meteorite samples studied here.

Pb-isotopic results: We have measured Pb isotopic ratios using the ^{202}Pb - ^{205}Pb DS in acid-washed fragments of Efremovka CAI E60, acid-washed pyroxene fractions from eucrites Asuka 881394 and Ibitira, and phosphate fractions and single grains from primitive achondrite Acapulco. Pb-Pb isochron dates for these materials, obtained with DS, are presented in Table 1 together with the results obtained previously with conventional TIMS analyses with external fractionation correction (a data processing error in our previous data set for Asuka 881394 [7] has been corrected). Isochron regressions for DS data from E60 and Ibitira could not be calculated because of very

small spread of $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. Using DS has increased precision of the isochron dates. The biggest improvement is achieved for the sample with the most radiogenic Pb (CAI E60), where the error magnification in the y-axis projection of the isochron error envelope is minimal.

Discussion: The new high-precision Pb-isotope data allow us to re-examine the relationships between the timescales based on the ^{207}Pb - ^{206}Pb , ^{53}Mn - ^{53}Cr , and ^{26}Al - ^{26}Mg isotopic systems. Table 2 provides a summary of all samples for which high-precision Pb-isotope, ^{53}Mn - ^{53}Cr and/or ^{26}Al - ^{26}Mg data are available.

As can be seen in Table 2, there is concordance between the ^{207}Pb - ^{206}Pb and ^{53}Mn - ^{53}Cr ages for Ibitira and Acapulco. An upper limit on the $^{26}\text{Al}/^{27}\text{Al}$ ratio inferred for Ibitira is also consistent with the relatively young ages obtained from the other two chronometers. However, in the cases of the Asuka 881394 eucrite and the Sahara 99555 angrite, there is discordance between the ^{207}Pb - ^{206}Pb ages, on the one hand, and the ^{53}Mn - ^{53}Cr and ^{26}Al - ^{26}Mg ages, on the other. This might have been caused by a difference in the closure temperatures for Pb, Cr, and Mg diffusion in their host minerals combined with slow cooling of these samples, or by differential resetting of isotopic systems by a process other than volume diffusion, e.g. shock metamorphism. Alternatively, the discordance might have been caused by heterogeneous distribution of ^{26}Al and ^{53}Mn in the protoplanetary disk. The latter possibility can be considered if the discordance cannot be explained by any secondary processes.

The possibility that the apparent age discordance is caused by slow cooling can be tested by comparing the

cooling rates determined from isotopic dates (assuming homogeneous distribution of ^{26}Al and ^{53}Mn) and experimental diffusion data to the cooling rates determined independently using other approaches (e.g., mineral compositions). Given the coarse-grained, granulitic texture of Asuka 881394 [8], it is possible that it had a cooling rate that was slow enough (i.e., ≤ 50 - $100^\circ/\text{My}$) to account for the discordance between its old ^{207}Pb - ^{206}Pb age and the significantly younger ^{53}Mn - ^{53}Cr and ^{26}Al - ^{26}Mg ages. However, textural and mineralogical indicators in Sahara 99555 suggest that it cooled at a rate of ~ 50 - $100^\circ/\text{hr}$ [9]. Given this rapid cooling rate, the reason for the age discordance in this angrite is unclear since it appears unlikely that a difference in closure temperatures of the different isotope systems could account for it.

Acknowledgements: We are grateful to the NIPR for allocating a sample of Asuka 881394 for this study. We thank Nicole Foley, Julie Peressini and Tom Pestaj for helping to prepare mineral separates.

References: [1] Amelin Y. (2005) *MPS*, in press. [2] Baker J. et al. (2005) *Nature* 436, 1127-1131. [3] Gerstenberger H. and Haase G. (1997) *Chem. Geol.* 136, 309-312. [4] Todt W. et al. (1996) *Geophysical Monographs* 95, 429-437. [5] Wasserburg G.J. et al. (1977) *EPSL* 35, 294-316. [6] Amelin Y. et al. (2005) *GCA* 69, A215. [7] Wadhwa M. et al. (2005) *LPS XXXVI*, Abstract #2126. [8] Nyquist L. E. et al. (2003) *EPSL* 214, 11-25. [9] Mikouchi T. et al. (2000) *LPS XXXI*, Abstract #1970. [10] Amelin Y. et al. (2002) *Science* 297, 1678-1683. [11] Amelin Y. (2005) *Science* 310, 839-841. [12] Lugmair G. W. and Galer S. J. G. (1992) *GCA* 56, 1673-1694. [13] Nyquist L. E. et al. (2003) *LPS XXXIV*, Abstract #1388. [14] Glavin D. P. et al. (2004) *MPS* 39, 693-700. [15] Lugmair G. W. and Shukolyukov A. (1998) *GCA* 62, 2863-2886. [16] Zipfel J. et al. (1996) *MPS* 31, A160. [17] Spivak-Birndorf L. et al. (2005) *MPS* 40, A145. [18] Wadhwa M. et al. (2004) *LPSC XXXV*, Abstract #1843. [18] Ludwig K. R. (2003), *Berkeley Geochronology Center Special Publ.* 4, 71 pp.

Table 1. Summary of ^{207}Pb - ^{206}Pb isochron dates

Material	External normalization	Ref.	Double-spike	EN+DS data regressed together	N	Highest measured $^{206}\text{Pb}/^{204}\text{Pb}$
Asuka 881394	4566.50±0.85	[7]; this work	4566.46±0.36	4566.52±0.33	15	681
Efremovka CAI E60	4567.4 ±1.1	[10]	(no regression)	4567.11±0.16	19	2260
Ibitira	4557.03±0.82	This work	(no regression)	4557.44±0.55	9	756
Acapulco phosphates	4556.5 ±1.3	[11]	4556.5 ±1.0	4556.52±0.78	16	187

Table 2. Comparison of ages based on the ^{207}Pb - ^{206}Pb , ^{53}Mn - ^{53}Cr and ^{26}Al - ^{26}Mg chronometers.

Meteorite	^{207}Pb - ^{206}Pb age (Ma)	Ref.	^{53}Mn - ^{53}Cr age (Ma)	Ref.	Al-Mg age (Ma)	Ref.
Efremovka CAI E-60	4567.11±0.16	[10]; this work			≡ 4567.11±0.16	[10]; this work
Asuka 881394	4566.52±0.33	[7]; this work	4563.85+0.67/-0.69	[7]	4563.43±0.16	[7]
Sahara 99555	4566.15±0.25	[2]*	4562.91+0.60/-0.61	[13,14]	4562.43±0.17	[17]; unpubl.
LEW 86010	4557.84±0.52	[12]	≡ 4557.84±0.52	[12]		
Ibitira	4557.44±0.55	This work	4557+2/-4	[15]	<4560.7	[18]
Acapulco	4556.52±0.78	[11]	4555.0+1.1/-1.3	[16]		

For a given sample, ages that are concordant are indicated in green, while those that are discordant are indicated in red. Also, shown in black bolded letters are the ^{207}Pb - ^{206}Pb ages for samples that serve as anchors for the ^{53}Mn - ^{53}Cr (i.e., LEW 86010) and ^{26}Al - ^{26}Mg (i.e., Efremovka E60 CAI) systems. Errors in the ^{53}Mn - ^{53}Cr and ^{26}Al - ^{26}Mg ages include the errors in the $^{53}\text{Mn}/^{55}\text{Mn}$ and $^{26}\text{Al}/^{27}\text{Al}$ ratios, respectively, and the uncertainties in the ^{207}Pb - ^{206}Pb ages of their respective anchors.

* ^{207}Pb - ^{206}Pb age was calculated from the data of [2] using the IsoPlot Ex program [18].