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Evaluation of Duluth Complex anorthositic series (AS3) zircon as a U-Pb geochronological standard: New high-precision isotope dilution thermal ionization mass spectrometry results

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Abstract—U-Pb zircon geochronology is increasingly called upon to achieve the resolution of absolute time at the 0.1% to 1% level for rocks of Phanerozoic to Hadean age. Doing so requires accurate calibration of the several methods (conventional isotope dilution thermal ionization mass spectrometry [ID-TIMS], Pb evaporation, high-resolution ion microprobe [e.g. SHRIMP], and laser ablation inductively coupled plasma mass spectrometry [LA-ICPMS]) currently in use, in numerous laboratories, for the analysis of U and Pb isotopes in accessory minerals. Toward this end, the geochronological community would benefit from the establishment, distribution and widespread analysis of one or more standard reference materials. Among the candidates is natural zircon from the Duluth Complex anorthositic series of the Midcontinent Rift system of North America. These zircons, first dated by conventional ID-TIMS at 1099.1 ± 0.5 Ma, have been subsequently adopted as a geochronological standard by a number of high resolution ion microprobe facilities. A new and independent analysis of the systematics of a large set of single zircons ($n = 27$) from the same mineral separate yields indistinguishable $^{207}\text{Pb}/^{206}\text{Pb}$, upper intercept, and U-Pb concordia dates for the AS3 zircons. The concordia date, based on a subset of 12 concordant and equivalent zircons, of 1099.1 ± 0.2 Ma (± 1.2 Ma considering systematic uncertainties in Pb/U tracer calibration and U decay constants) is indistinguishable from previously published results. We further document the absence of inherited Pb in the AS3 zircons, and discuss strategies for avoiding certain domains within the AS3 zircons exhibiting small amounts of radiation-induced, surface and fracture-correlated, recent Pb loss. Although the AS3 zircons do not represent the ideal (and elusive) homogeneous closed U-Pb system, we conclude that these and similar zircons from the Duluth Complex anorthositic series can provide a suitable geochronological reference standard for numerous U-Pb zircon analytical methods, given appropriate preparation guided by the results of this study. Our high-precision data set also serves as a useful confirmatory test of the currently accepted U decay constants. *Copyright © 2003 Elsevier Ltd*

1. INTRODUCTION

U-Pb zircon geochronology is firmly established as among the most precise and accurate means of resolving time throughout the geologic record. The available internal assessment of closed system behavior through the paired U-Pb chronometers, precisely measured U decay constants, high initial U/Pb ratios, and the geochemically robust and geologically common nature of zircon makes it a near ideal mineral for the radiometric measurement of time. The precision of concordant zircon U/Pb ages, for samples from a few millions years old to the age of the earth, can thus approach 0.1% by the ID-TIMS method, potentially accessing an intriguing array of problems regarding geologic histories, correlations, and rates of processes. However, excepting relative U/Pb zircon ages measured by identical methods in the same laboratory, systematic errors in mass spectrometry, tracer calibrations, and/or decay constants can introduce further, and perhaps larger, sources of uncertainty and bias into absolute U/Pb zircon ages.

Microanalytical techniques (e.g., SHRIMP, LA-ICPMS) can unravel the geologic histories of single zircon domains but

must rely on normalization to a standard zircon of known isotopic character. Current methodologies essentially limit U-Pb measurements to the 1% level and it is often unclear during any given analytical session whether the limitation is imposed from the technique or the geological behavior of the sample. In this regard, Pb loss and inheritance are undesirable attributes of a standard but U and Th heterogeneities can also cause difficulties in obtaining precise ion ratios. Ultimately, any source of uncertainty in the standard must be propagated onto the analyses of the unknowns whether they arise from the accumulated counting statistics, or from systematic effects contributing to uncertainty in the calibration. The minimization of geologic effects in the standard zircon would allow the assessment of instrumental artifacts, and in turn advance the analytical protocols used in microanalysis.

Recognizing the potential limitations of systematic error, Wiedenbeck et al. (1995) reported the results of a study of several large zircon crystals for possible use as standard materials for U/Pb and other isotopic and geochemical measurements. Of these zircons, only the 91500 (Kuehl Lake or Harvard Museum) zircon was found to have U/Pb systematics appropriate to its use as a standard material. Although used as a standard by some LA-ICPMS studies (Nesbitt et al., 1997; Horn et al., 2000), fragments of the zircon show an analytically resolvable scatter in $^{206}\text{Pb}/^{238}\text{U}$ ratios, and as a single large

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zircon, 91500 has obvious limitations for widespread and long-term usage as a standard material. The work of Paces and Miller (1993) in the ca. 1.1 Ga Midcontinent Rift of North America, indicated a source for another standard material in zircons from the anorthositic series of the Duluth Complex layered mafic intrusion. The abundance, moderate to high U and radiogenic Pb content, relative age, lack of inheritance, and apparent concordance of the measured dates suggested that the AS3 zircons could be a suitable geochronological standard for U-Pb isotopic analysis, and re-collections of the AS3 material were subsequently adopted as a standard in several ion microprobe laboratories (e.g., Muir et al., 1996; Reid et al., 1997; Bacon et al., 2000).

The present study set out to re-examine the isotopic systematics of the AS3 zircons for the purposes of confirming their age, understanding possible sources of geological uncertainty (i.e., inheritance or Pb loss), and identifying any potential systematic errors in high-precision U/Pb zircon ages obtained in different laboratories. Such systematic errors include the correct assessment of instrumental fractionation, laboratory blanks, sample-tracer equilibration, and the calibration of isotope dilution tracer solutions. By characterizing the AS3 zircon, we hoped to establish a material that could serve as a benchmark for U/Pb geochronological laboratories around the world.

The minimization of systematic errors in U/Pb accessory mineral geochronology is also desirable because of the "gold standard" that the U-Pb system provides for the relative geological intercalibration of other radionuclide decay rates that are more difficult to measure by counting or accumulation experiments. This intercalibration is, of course, incumbent upon the accuracy of measured U/Pb ages (hence the value of an interlaboratory standard), and the accuracy of the U decay constants. While the decay constants of ^{238}U and ^{235}U are the most precisely measured of the long-lived radionuclides, they are based on a single high-precision counting experiment. In complement to counting experiments, U-Pb isotopic measurements of geological samples which have remained closed systems since formation can also provide constraints on the U decay constants (Nier, 1939; Banks and Silver, 1966; Mattinson, 1973). In this vein, Schmitz and Bowring (2001) established a large U-Pb zircon data set from the Oligocene Fish Canyon Tuff (FCT) to evaluate the accuracy of the currently utilized uranium decay constants (Jaffey et al., 1971). While that data set was interpreted as confirming the accuracy of the current U decay constant values, it was recognized as being limited by assumptions regarding intermediate daughter product disequilibrium in the relatively young FCT zircons. The Proterozoic AS3 zircons provide a possible point of comparison free from disequilibrium effects.

2. ANALYTICAL PROCEDURES

Zircon grains were hand-picked from the same diamagnetic mineral separate of AS3 used by Paces and Miller (1993). Cathodoluminescence images of AS3 zircons showed diffuse, undulose variations with little internal contrast, thus the technique was not used to screen the samples. All zircons were air-abraded after the method of Krogh (1982), bathed in 4M HNO_3 at 50° C for 2 h, ultrasonicated for an additional 30 min, and then rinsed with high-purity water and acetone. After

photographing to estimate sample weights, single zircons were loaded into 300 μL Teflon PFA microcapsules, washed again in 150 μL 4 M HNO_3 at 50° C for 12 h, and rinsed with four capsule volumes of 4 M HNO_3 . Zircons were dissolved in 120 μL 29 M HF with a trace of 4 M HNO_3 at 220°C for 48 h with a mixed ^{205}Pb - ^{233}U - ^{235}U tracer (approximately 40–60 pg of ^{205}Pb , and 4–6 ng of ^{233}U and ^{235}U), dried to salts, and redissolved in 120 μL 6 M HCl at 180°C overnight. After conversion of the zircon solution to 3 M HCl, Pb and U were separated by anion exchange chromatography in 50 μL shrink Teflon FEP micro-columns, using methods modified from Krogh (1973).

Purified Pb and U were analyzed separately by conventional thermal-ionization mass spectrometry on the MIT VG Sector 54 multicollector mass spectrometer. Lead was loaded with 1 μL of a silica gel-phosphoric acid mixture (Gerstenberger and Haase, 1997) on previously out-gassed (4 A for 20 min) single Re filaments, and its isotopes measured either: (1) for ^{207}Pb ion beams $<10^{-10}$ mA, by peak-jumping all ion beams into an axial Daly-type photomultiplier detector in ion-counting mode; or (2) for ^{207}Pb ion beams $>10^{-10}$ mA, in a two-cycle, dynamic, four Faraday cup + axial Daly routine utilizing the ^{205}Pb beam to establish a real-time Daly detector gain measurement. Uranium was loaded with 1 μL dilute colloidal graphite and 1 μL 0.1 M H_3PO_4 on previously out-gassed single Re filaments, and its isotopes measured in static mode on three Faraday cups with an average ^{235}U ion beam of 5×10^{-10} mA.

Instrumental Pb isotopic fractionation was monitored throughout the course of the study by daily analysis of the NBS-981 common Pb standard, with an average of $0.12 \pm 0.04\%$ (2σ) per a.m.u. measured on Faraday cups; a small additional detector bias is incorporated into the fractionation correction of $0.15 \pm 0.04\%$ (2σ) per a.m.u. for single collector Daly analysis. Uranium fractionation was monitored and corrected using the double isotope spike. A total of 9 zircon procedural Pb blanks ranged from 1.1 to 2.9 pg during the course of the study; a mean of $2.0 \pm 50\%$ (2σ) was used to reduce all data. The U blank of $0.5 \pm 50\%$ (2σ) was also negligible relative to the amount of sample U. Error propagation for each analysis followed the algorithms of Ludwig (1980); analytical data are presented in Table 1.

3. RESULTS

Of the 30 dissolved zircon grains (Fig. 1), three sample runs were unsuccessful due to deficient or unstable Pb or U signals, likely resulting from partial sample loss or inefficient chemical separation. The remaining 27 successful analyses include 12 essentially concordant zircons ($<0.1\%$ discordant), and 15 grains exhibiting variable degrees of minor discordance, up to a maximum of 2% (Fig. 2). Certain systematic trends evident in this discordance are pertinent to the use of these zircons as standard materials. The AS3 zircon separate comprises a fairly uniform population of slightly amber-pink colored, flattened, vaguely prismatic to anhedral elongate grains and fragments, ranging up to 1 mm in longest dimension (Fig. 1A). In detail, a discernible spectrum in grain types is evident, ranging from smaller, nearly colorless, very flat crystals to larger, more strongly-colored, blocky grains. The first eight grains (z1-z8)

Table 1. U-Pb isotopic data for AS3 zircon.

Fraction ^a	Composition						Isotopic ratios								Dates (Ma)				
	Wt. (μg) ^b	[U] (ppm)	Th/U ^c	[Pb] (ppm)	Pb*/Pbc ^d	Pbc (pg) ^d	²⁰⁶ Pb/ ²⁰⁴ Pb ^e	²⁰⁸ Pb/ ²⁰⁶ Pb ^f	²⁰⁶ Pb/ ²³⁸ U ^f	% Err ^g	²⁰⁷ Pb/ ²³⁵ U ^f	% Err ^g	²⁰⁷ Pb/ ²⁰⁶ Pb ^f	% Err ^g	Corr. coef.	²⁰⁶ Pb/ ²³⁸ U ^h	²⁰⁷ Pb/ ²³⁵ U ^h	²⁰⁷ Pb/ ²⁰⁶ Pb ^h	Discordance (%)
z1,c,f	4.4	417	0.675	85	372	1.0	21710	0.205	0.18529	(.08)	1.9464	(.10)	0.076186	(.06)	0.796	1095.8	1097.2	1100.0 ± 1.2	0.41
z2,c,f	1.2	594	0.609	118	134	1.1	7971	0.188	0.18230	(.14)	1.9139	(.16)	0.076144	(.08)	0.872	1079.5	1085.9	1098.9 ± 1.6	1.92
z3,c,f	2.1	505	0.574	100	88.4	2.4	5244	0.176	0.18367	(.21)	1.9277	(.24)	0.076123	(.12)	0.873	1087.0	1090.7	1098.3 ± 2.3	1.12
z4,c,f	3.5	405	0.593	81	198	1.4	11808	0.180	0.18505	(.10)	1.9425	(.12)	0.076133	(.07)	0.830	1094.5	1095.9	1098.6 ± 1.4	0.40
z6,c,f	1.0	457	0.624	96	15.7	5.7	911	0.190	0.18518	(.36)	1.9451	(.38)	0.076177	(.11)	0.957	1095.2	1096.7	1099.7 ± 2.2	0.44
z8,c,f	2.5	444	0.591	89	93.4	2.3	5527	0.180	0.18523	(.16)	1.9451	(.18)	0.076158	(.09)	0.876	1095.5	1096.8	1099.2 ± 1.8	0.37
z9,a,b,k	58	455	0.764	95	599	9.2	32627	0.231	0.18591	(.09)	1.9513	(.10)	0.076124	(.04)	0.910	1099.2	1098.9	1098.3 ± 0.9	-0.09
z10,a,b,k	40	310	0.702	64	738	3.5	41681	0.213	0.18590	(.05)	1.9520	(.06)	0.076155	(.04)	0.771	1099.2	1099.1	1099.2 ± 0.8	0.00
z12,a,b,k	43	113	0.553	22	335	2.9	19769	0.170	0.18341	(.07)	1.9267	(.08)	0.076186	(.04)	0.848	1085.6	1090.4	1100.0 ± 0.9	1.42
z13,a,b,k	169	626	0.930	135	1906	12.0	99335	0.285	0.18387	(.15)	1.9304	(.15)	0.076144	(.04)	0.964	1088.1	1091.7	1098.9 ± 0.8	1.07
z14,a,b,k	27	283	0.647	58	488	3.1	28043	0.196	0.18556	(.05)	1.9483	(.07)	0.076148	(.04)	0.794	1097.3	1097.9	1099.0 ± 0.8	0.17
z15,a,b,k	20	477	0.558	95	508	3.7	29614	0.170	0.18467	(.05)	1.9384	(.07)	0.076130	(.04)	0.798	1092.4	1094.5	1098.5 ± 0.8	0.60
z16,a,b,k	43	216	0.714	45	287	6.7	15907	0.217	0.18539	(.05)	1.9472	(.07)	0.076176	(.04)	0.775	1096.4	1097.5	1099.7 ± 0.8	0.33
z17,a,b,k	28	237	0.693	49	295	4.6	16553	0.210	0.18589	(.07)	1.9519	(.08)	0.076158	(.04)	0.853	1099.0	1099.1	1099.3 ± 0.9	0.02
z18,a,b,k	48	276	0.663	56	907	3.0	52047	0.201	0.18591	(.06)	1.9520	(.07)	0.076151	(.04)	0.826	1099.2	1099.1	1099.0 ± 0.8	-0.02
z19,a,b,k	41	288	0.640	59	450	5.3	25472	0.194	0.18585	(.05)	1.9521	(.07)	0.076178	(.04)	0.786	1098.9	1099.2	1099.8 ± 0.8	0.09
z20,a,b,k	62	214	0.617	43	251	10.7	14132	0.188	0.18496	(.11)	1.9418	(.12)	0.076144	(.04)	0.930	1094.0	1095.6	1098.9 ± 0.9	0.49
z21,a,b	12	142	0.580	29	155	2.1	9238	0.176	0.18586	(.14)	1.9518	(.16)	0.076163	(.08)	0.880	1098.9	1099.1	1099.3 ± 1.5	0.04
z22,a,b	11	131	0.658	27	75.9	3.9	4323	0.202	0.18331	(.20)	1.9245	(.23)	0.076143	(.09)	0.913	1085.0	1089.6	1098.8 ± 1.8	1.37
z23,a,b	5.1	183	0.728	39	33.3	5.8	1861	0.220	0.18588	(.19)	1.9520	(.24)	0.076166	(.15)	0.781	1099.0	1099.1	1099.4 ± 3.0	0.04
z24,a,b	3.5	140	0.598	33	5.42	18.3	322	0.182	0.18523	(.34)	1.9453	(.42)	0.076167	(.23)	0.833	1095.5	1096.8	1099.4 ± 4.6	0.39
z25,a,b	21	345	0.687	72	75.1	20.0	4149	0.208	0.18592	(.14)	1.9522	(.15)	0.076156	(.05)	0.948	1099.2	1099.2	1099.2 ± 0.9	-0.01
z26,a,b	8.5	174	0.648	35	108	2.7	6260	0.200	0.18190	(.32)	1.9091	(.34)	0.076119	(.12)	0.939	1077.4	1084.3	1098.2 ± 2.3	2.06
z27,a,b	9.2	328	0.670	67	237	2.6	13650	0.203	0.18593	(.11)	1.9522	(.12)	0.076148	(.05)	0.897	1099.3	1099.2	1099.0 ± 1.1	-0.03
z28,a,b	18	248	2.263	70	224	5.6	9119	0.686	0.18590	(.10)	1.9530	(.11)	0.076195	(.06)	0.858	1099.1	1099.5	1100.2 ± 1.2	0.11
z29,a,b	8.1	233	0.674	48	321	1.2	18791	0.204	0.18585	(.09)	1.9519	(.12)	0.076174	(.09)	0.707	1098.8	1099.1	1099.7 ± 1.8	0.08
z30,a,b	12	286	0.654	59	54.2	12.8	3034	0.198	0.18591	(.07)	1.9524	(.09)	0.076165	(.05)	0.832	1099.2	1099.3	1099.4 ± 1.0	0.02

^a All fractions composed of single abraded zircon grains; descriptors: c = colorless, a = amber-colored, f = flat, b = blocky, k = cracked.

^b Sample weights were estimated to within 40% using measured grain dimensions and a nominal density of 4.5 g/cm³.

^c Th/U calculated from radiogenic ²⁰⁸Pb and the ²⁰⁷Pb/²⁰⁶Pb date of the sample, assuming concordance between U-Th-Pb systems.

^d Pb* and Pbc represent radiogenic Pb and common Pb, respectively.

^e Measured ratio corrected for fractionation and tracer contribution; Pb fractionation = 0.12 ± 0.04 (2σ) %/a.m.u. (Faraday cup) or 0.15 ± 0.04 %/a.m.u. (Daly) based on daily analysis of NBS-981.

^f Measured ratios corrected for fractionation, tracer, blank, and initial common Pb; nominal Pb blank = 2.0 pg ± 50% (2σ); nominal U blank = 0.5 pg ± 50% (2σ); measured laboratory blank composition (with propagated 2σ errors): ²⁰⁶Pb/²⁰⁴Pb = 19.10 ± 0.05, ²⁰⁷Pb/²⁰⁴Pb = 15.72 ± 0.05, ²⁰⁸Pb/²⁰⁴Pb = 38.65 ± 0.05 (2σ); initial common Pb composition (with propagated 2σ uncertainties) from the model of Stacey and Kramers (1975): ²⁰⁶Pb/²⁰⁴Pb = 16.88 ± 0.5, ²⁰⁷Pb/²⁰⁴Pb = 15.49 ± 0.1, ²⁰⁸Pb/²⁰⁴Pb = 36.57 ± 0.5.

^g Numbers in parentheses are the % errors reported at the 2σ confidence interval, propagated using the algorithms of Ludwig (1980).

^h Isotopic dates calculated using the decay constants of Jaffey et al. (1971); λ(²³⁵U) = 9.8485 × 10⁻¹⁰ yr⁻¹ and λ(²³⁸U) = 1.55125 × 10⁻¹⁰ yr⁻¹; error in ²⁰⁷Pb/²⁰⁶Pb date reported at the 2σ confidence interval.

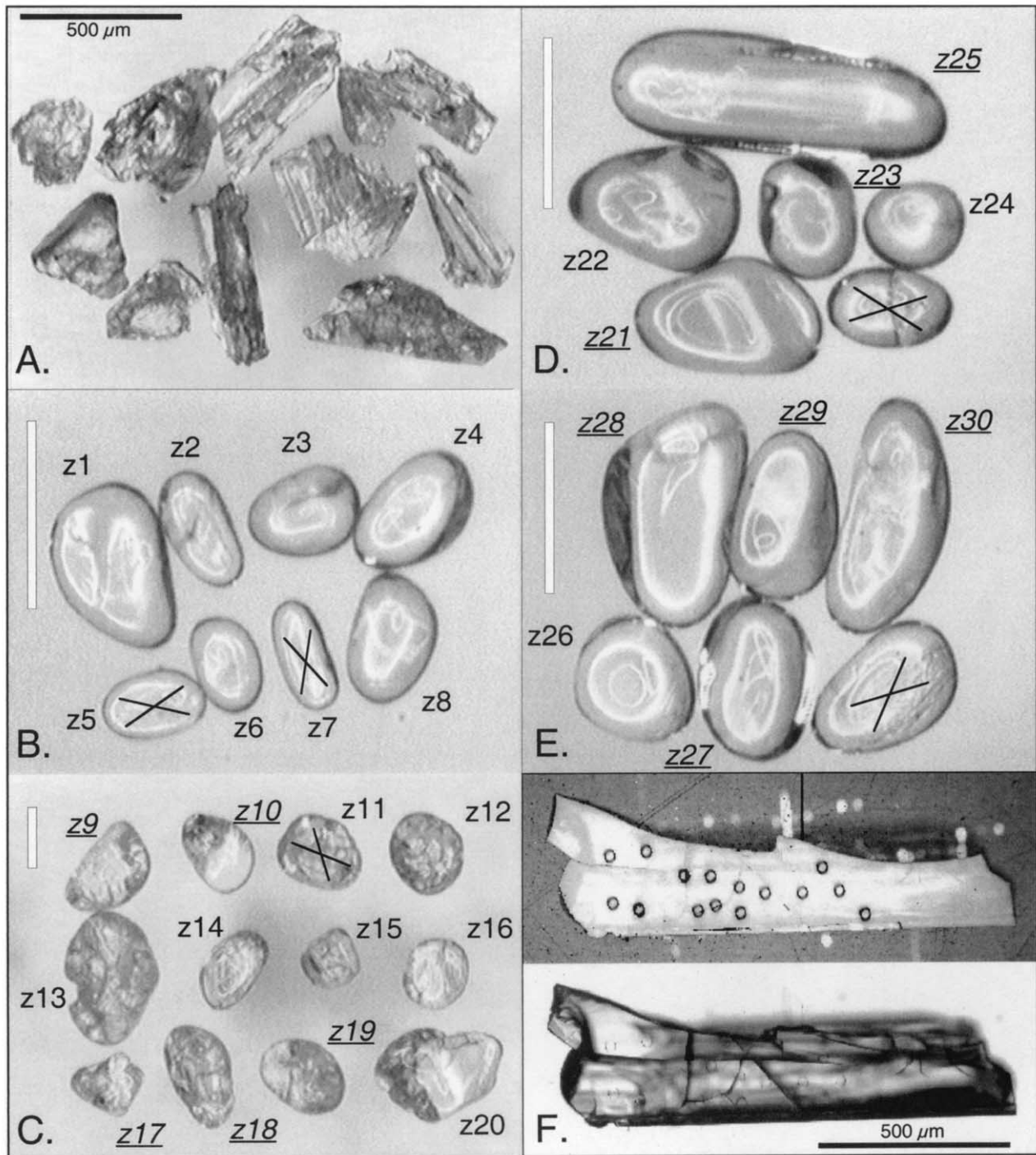


Fig. 1. Photographs of AS3 zircons. (A) Larger grains before abrasion. (B–E) All prepared grains subsequent to air-abrasion and acid-washing. Grains with crosses were not successfully analyzed; italicized and underlined labels correspond to grains with concordant U–Pb dates. Scale bars = 200 μm . (F) One AS3 standard zircon grain used by Muir et al. (1996) for SHRIMP analysis of mount Z1903. The upper image is taken in reflected light; lower image is transmitted light. Spots are approximately $20 \times 30 \mu\text{m}$. This grain has uniform U concentration ($280 \pm 30 \text{ pp}$; s.d.) and uniform Th/U (0.70 ± 0.02 ; s.d.). Of the 15 U–Pb analyses from this zircon, only one shows Pb loss (5%) despite several analyses being located on cracks. The remaining analyses give a calibrated age of $1099 \pm 5 \text{ Ma}$ ($2\sigma_m$) with an MSWD of 1.51. Cracking of this grain may have been produced during polishing and hence the cracks have not been a locus of Pb loss. This is not always the case and so cracks are generally avoided during spot selection.

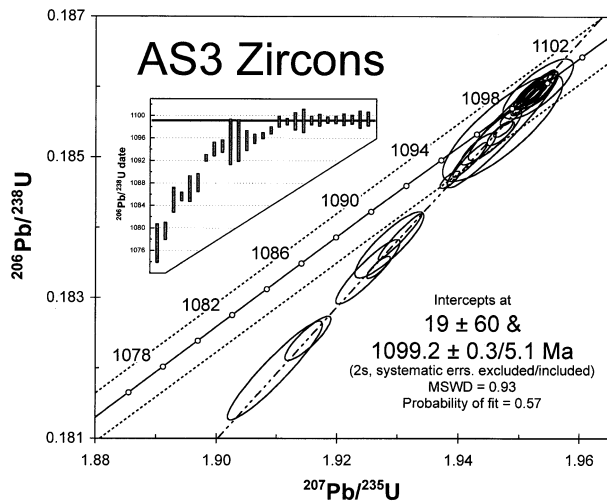


Fig. 2. U-Pb concordia diagram for all AS3 zircons, and plot of ranked $^{206}\text{Pb}/^{238}\text{U}$ date (inset). Error ellipses are plotted at 2σ (95% confidence interval). Error envelope on concordia curve (gray dotted lines) computed from the 2σ counting statistic errors of Jaffey et al. (1971).

prepared for analyses were exceptionally clear, crack-free, and relatively small grains taken from the colorless, flattened end of the spectrum (Fig. 1B). Although free of discernible flaws, and abraded to remove edges and most grain surfaces, all six of the analyzed grains exhibited discordance (Table 1, Fig. 2). The second group of grains (z9–z20) was picked as the largest of the more strongly-colored, blocky grains in the separate. During abrasion, these often cracked grains fragmented to varying degrees, losing from 30–50% by mass; these grains were not, however, abraded to smooth ellipsoids, and retained numerous internal fractures, as is evident in Figure 1C. Six of the 11 analyzed grains again exhibited discernible discordance, however five crystals yielded equivalent U-Pb and Pb-Pb dates ($<0.1\%$ discordance), clustering around the concordia curve. The final set of grains (z21–z30) was also picked from the more strongly colored, blockier end-member of the grain spectrum; however, these grains were slightly smaller than the former batch of such grains, and of higher quality with regard to internal flaws. These grains were heavily abraded to smooth crack-free ellipsoids as shown in Figures 1D, E, and seven of 10 grains yielded equivalent and concordant U-Pb dates.

As illustrated in Figure 2, all zircons fall on a discordia array with upper and lower intercepts of 1099.2 ± 0.3 Ma and 19 ± 60 Ma, respectively, with a high probability of fit (MSWD 0.93), using uncertainties propagated from measurement, fractionation, blank and initial common Pb subtraction errors, but excluding systematic tracer calibration or decay constant errors. The upper intercept date is indistinguishable from the weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ date of 1099.2 ± 0.2 Ma (MSWD 0.91) for all zircons. Twelve grains with equivalent isotopic ratios and U-Pb dates also yield a concordia age (Ludwig, 1998) of 1099.1 ± 0.2 Ga (MSWD = 0.50; Fig. 3). All of the zircon analyses have moderate to very high radiogenic to common Pb ratios, and thus are highly insensitive to the assumed partitioning of common Pb between laboratory blank and initial common Pb, or their isotopic compositions. For example, changing

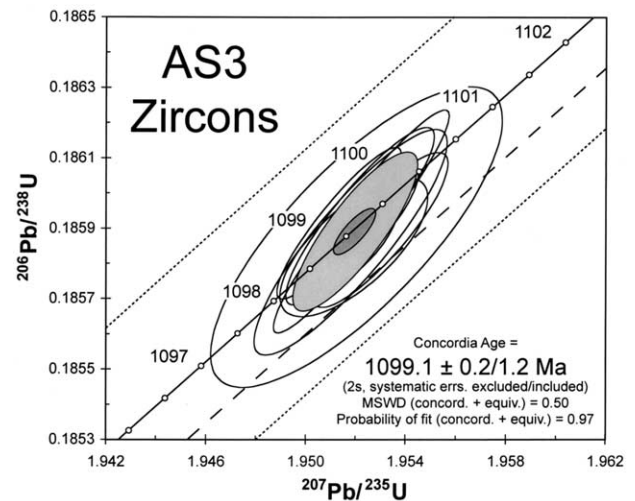


Fig. 3. U-Pb concordia diagram of the 12 concordant AS3 zircons analyzed in this study; the small dark-shaded ellipse represents the inverse-variance weighted mean of this population, while the larger light-shaded ellipse represents the error envelope taking into account systematic tracer calibration and U decay constant errors. The solid concordia curve with associated error envelope (dotted lines) is calculated from the U decay constants and associated 2σ statistical errors of Jaffey et al. (1971). The dashed line illustrates the concordia curve resulting from the modification to the ^{235}U decay constant proposed by Mattinson (2000).

the amount of the assumed laboratory blank by 100% shifts the concordia age by less than ± 0.04 Ma. The Stacey and Kramers (1975) model 1.1 Ga Pb isotopic composition used for initial common Pb correction is approximately the mean of two end-member estimates for the initial Pb of the Duluth Complex (Zartman and Wasserburg, 1969; Nicholson and Shirey, 1990); adopting either of the extreme values shifts the concordia age by only ± 0.06 Ma.

The reproducibility of the U/Pb and $^{207}\text{Pb}/^{206}\text{Pb}$ isotopic ratios indicates that efficient sample-spike equilibration was achieved by the dissolution method, and that between-sample variability in instrumental fractionation is well described by the assigned magnitude and uncertainty in mass bias. For comparison of these AS3 U-Pb zircon data to similar results from other laboratories, error contribution due to Pb/U tracer calibration uncertainties must be incorporated. The accuracy of the MIT tracer calibration against gravimetric standard solutions is estimated at $\leq 0.1\%$ (2σ); addition of this error to the weighted mean Pb/U ratios (in quadrature) results in an uncertainty in the concordia age for the AS3 zircon of ± 0.7 Ma. Similarly, to establish the absolute age of the AS3 zircons, the incorporation of decay constant uncertainty (as the 2σ counting errors of Jaffey et al., 1971) yields an ultimate uncertainty of ± 1.2 Ma in the concordia age.

4. DISCUSSION

4.1. Age, Concordancy, and Pb Loss

The U-Pb concordia age of 1099.1 ± 0.7 Ma for the AS3 zircon resulting from this study is in exact agreement with the 1099.1 ± 3.0 Ma age (including stated 0.6% tracer calibration

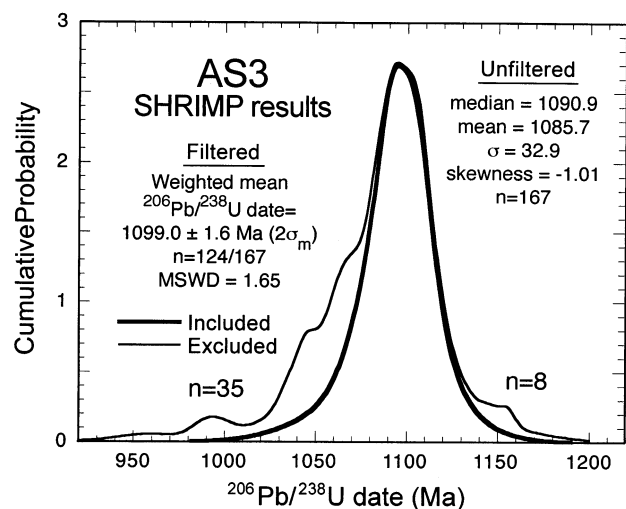


Fig. 4. Probability density functions of 167 analyses from 14 mounts containing AS3, carried out on SHRIMP I between May and August 1994. Approximately 75% of the data are included in the filtered, group-mean, near-gaussian density function (heavy line); the predominance of outliers (thin line) on the younger side of the unfiltered mean is ascribed to geological scatter (viz. Pb loss), while the occurrence of data on the high side is due to instrumental artifacts. Obviously the latter will be present on the younger side as well, however the asymmetry of the distribution is consistent with another source of deviation. These analyses accentuate the occurrence of low U-Pb ages ascribed to Pb loss because these were some of the first SHRIMP analyses of AS3 with it used as a U-Pb standard, before the development of protocols for visual recognition of the common loci of Pb loss. Analysis uncertainties are based on measurement errors alone; error augmentation from reproducibility within a single session would result in a higher degree of acceptance into the group mean, but mask the dispersion.

uncertainties) of Paces and Miller (1993). The agreement between these two measurements indicates that despite potential systematic error sources including instrumental fractionation, detector bias, laboratory contamination, sample-spike equilibration, and tracer calibration, geochronological reproducibility at the $\leq 0.1\%$ level is obtainable between different ID-TIMS U-Pb zircon laboratories.

In accordance with the study of Paces and Miller (1993), there is no indication of older crystal inheritance within the AS3 zircon population, and a significant fraction of analyzed crystals within the AS3 zircon population yielded concordant isotopic systematics. Unlike the data of Paces and Miller (1993), our larger data set on diverse grain types and qualities reveals domains within the AS3 zircons that have suffered minor amounts of Pb loss. Perhaps more importantly, the present data set constrains the timing of Pb loss in the AS3 zircons to a very late event in the history of the zircons, as the weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ date of variably discordant grains is indistinguishable from the upper intercept and Concordia dates. The near zero-age of Pb loss appears to be a consistent characteristic of zircons in both volcanic and plutonic rocks along the northern limb of the Midcontinent rift (Paces and Miller, 1993; Davis and Green, 1997). The invariance of the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio in the AS3 zircon thus makes it a suitable standard for techniques relying solely upon the Pb-Pb chro-

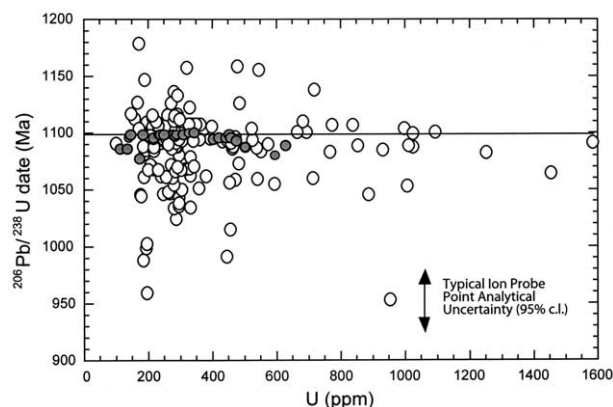


Fig. 5. $^{206}\text{Pb}/^{238}\text{U}$ date versus U concentration for AS3 ID-TIMS (shaded circles, enlarged $\sim 4\times$ beyond analytical errors for visibility) and SHRIMP ion probe (open circles) analyses. Seventy percent of the analyses lie between 150 and 350 ppm, and 80% have Th/U between 0.55 and 0.70. While a weak correlation between U content and discordance is apparent in the ID-TIMS data, there is no clear correlation in the SHRIMP data. Discordance is more commonly correlated with visible grain defects.

nometer. For use in calibrating U/Pb isotopic ratios, however, more information on the topology of Pb loss is desirable.

Pb loss has also been noted by SHRIMP zircon analysis. For example, Muir et al. (1996) used AS3 on 14 separate mounts for normalization of U-Pb ratios in zircon (cf. Fig. 1F). These data show a strong clustering about the mean with an asymmetric over-dispersion towards younger effective U/Pb ages for the standard (Fig. 4). Over-dispersion can be caused by underestimated instrumental error, but that error is likely to be normally distributed, and thus the asymmetry of the over-dispersion toward younger U/Pb ages is attributed to geological Pb loss in the standard zircons. Documenting the spatial scales of this Pb loss and its relationship to grain character and morphology is a necessary step toward avoiding those domains during future use of the AS3 zircons (or other zircons from the Duluth Complex anorthositic series) as a standard material.

In the zircons of this study, up to 2% Pb loss is correlated both with a specific slightly higher U content (400–600 ppm), high surface area-to-volume crystal type in the grain spectrum (e.g., z1-z8), as well as the presence of fractures in the larger, blockier, and more strongly colored grain types. Heavily abraded, crack-free, blocky, lower-U content (100–400 ppm) grains have the highest probability of concordant isotopic systematics. The aberrant SHRIMP analyses of Muir et al. (1996), exhibiting up to 10% Pb loss, are likewise commonly correlated with proximity to planar micro-fractures, however little correlation is observed with U content (Fig. 5). The lack of correlation between Pb loss and U content in the SHRIMP work suggests that the weak trend exhibited by the TIMS analyses may be more related to the high surface area-to-volume character of the smaller high-U grains. These observations would place the majority of Pb loss near the surface of grains (or at the surfaces of ancient grain fractures), which is consistent with the effectiveness of abrasion for reducing or eliminating Pb loss at the grain-scale. The higher degrees of Pb loss revealed at the

smaller spatial scale of SHRIMP sampling ($\leq 10\%$), relative to that found at the larger partial grain scale of our ID-TIMS work ($\leq 2\%$), also demands that zones of Pb loss are highly localized. Such localization is inconsistent with homogeneous Pb loss by volume diffusion, and rather supports transport along micro-scale fast-pathways associated with grain defects.

4.2. Interlaboratory Standard

The presence of any measurable Pb loss is an obvious departure from ideality for any U-Pb geochronological standard. On the other hand, decades of U-Pb zircon analysis illustrate the true rarity of absolutely homogeneous closed-systems at the grain scale. Thus we find that the isolation of consistently concordant domains from AS3 zircons merits their consideration as a standard material, with the caveat of proper preparation, in various capacities for the currently utilized analytical techniques. As a primary standard for the generation of Pb/U working curves in SHRIMP or LA-ICPMS analysis, avoiding the grain-surface and micro-fracture correlated Pb loss phenomena present in the AS3 (or other Duluth Complex anorthositic series) zircons through magnetic separation, sizing, and abrasion of crystals should be a feasible (and necessary) means of preselecting grains with concordant U-Pb systematics. Grain preselection would serve to minimize the geological dispersion in measured Pb/U ratios of the standard and thus the propagated uncertainty of the calculated U-Pb dates for samples (Claoué-Long et al., 1995). For applications of microanalytical and Pb-evaporation methods utilizing the Pb-Pb geochronometer, the precisely determined and apparently invariant $^{207}\text{Pb}/^{206}\text{Pb}$ ratio of the AS3 zircons makes them suitable for quantifying analytical isotopic discrimination and assessing external reproducibility. The AS3 zircons may also be carefully used as a secondary standard for evaluating systematic errors in high-precision ID-TIMS U-Pb zircon analysis. Again, we suggest this use only with the caveats of rigorous preparation of zircons following the lessons learned in this study, and the analysis of sufficient single grains to establish a confident plateau of statistically equivalent data. Ultimately the Duluth Complex anorthositic series zircons may serve as one benchmark for interlaboratory calibration of U-Pb zircon geochronometry at the $\leq 0.1\%$ precision level.

4.3. Decay Constants

Recent discussions regarding the accuracy and precision of presently accepted values for the decay constants of the long-lived radioisotopes (Renne et al., 1998; Begemann et al., 2001) have extended to the isotopes of uranium (Mattinson, 1994, 1997; Ludwig, 1998, 2000). Although the radioisotopes of uranium have the most precisely measured decay constants of the commonly used geochronological systems, questions regarding the precision and accuracy of these values have been raised (Mattinson, 1997; Begemann et al., 2001), and it has been suggested that evaluation of the U-decay constants may be made through analysis of geological materials (Mattinson, 1973, 2000). The AS3 zircon data set, which has internal errors minimized such that the uncertainty of the clustered group of analyses with equivalent Pb/U ratios is essentially reduced to the 0.1% systematic error of tracer calibration, provides a

potential point of evaluation. Under the single assumption that the data plateau represents the approach to closed system behavior, the correspondence of the point defined by the AS3 zircons with the presently defined concordia curve suggests the accuracy of the ratio of the Jaffey et al. (1971) decay constants to within 0.1%. Other high precision data sets of statistically equivalent zircons are needed to further evaluate the accuracy of the presently accepted decay constants. Obviously, the caveats to this evaluation include not only finding isotopically closed geological systems, but also the imprecision of isotope dilution tracer Pb/U calibrations. For example, while the proposed revision of the ^{235}U decay constant by Mattinson (2000) is apparently unnecessary for establishing concordancy of the AS3 zircon data, in fact, tracer calibration uncertainty significantly limits our ability to evaluate this suggestion. Minimizing the uncertainty in tracer calibration error significantly below 0.1%, and thus *improving* the U decay constant errors through analysis of geological materials, will be difficult to achieve.

As a final note, a number of authors have advocated or pursued refining the half-lives of other radioisotopes through "normalization" to those of the U isotopes (Renne et al., 1998; Begemann et al., 2001; Scherer et al., 2001; Amelin and Zaitsev, 2002), by establishing the age of the material in question using the U-Pb method. Successful application of this method requires establishing the accuracy and precision of the latter method. In this regard, the AS3 zircon may be of use for confirming the intercalibration of U-Pb isotopic methods in different laboratories.

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