Average Lifetime and Age Spectra of Detrital Grains: Toward a Unifying Theory of Sedimentary Particles

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ABSTRACT

The observed average lifetime of minerals, as estimated by the average survival time of dated detrital grains, correlates linearly with D_C estimated from dissolution rates of minerals but does not correlate with D_H estimated by mineral hardness. The best predictor of the observed average lifetime is the total durability, an estimator that combines D_C and D_H indices. The age spectra of grains (i.e., age frequency distributions of radiometrically dated detrital minerals) tend to be right skewed, as predicted by the exponential model used to describe the lifetime of mechanical parts (Weibull function) or the radioactive decay of atoms. Consistent with the model, the less durable grains produce age spectra that are more right skewed and leptokurtic and may yield more accurate estimates of depositional age, whereas the more durable grains often depart from the exponential model, and their age spectra primarily reflect long-term geological changes in the rate of grain production. The integration of geochronological dates and laboratory mineralogical data indicates that the basic statistical parameters of age spectra of dated grains can be estimated and modeled in a quantitative way. The average lifetimes of detrital grains can be quantified from intrinsic properties of minerals, and these quantitative estimates agree well with the qualitative predictions of the classic weathering sequence of Goldich.

Introduction

As shown in numerous radiometric analyses (Gehrels and Ross 1998; Gehrels et al. 1999; Stewart et al. 2001), detrital grains tend to vary greatly in age, even when restricted to one mineral type collected from a single rock sample. Typically, individually dated crystals reveal broad age-frequency distributions (or age spectra), and fossils (biogenic sedimentary grains), even when collected from seemingly contemporaneous assemblages, tend to vary notably in age (Flessa et al. 1993; Flessa and Kowalewski 1994). There is increasing evidence that such age mixing of fossils, referred to as time averaging, typifies the fossil record (Kidwell and Bosence 1991; Kidwell and Behrensmeyer 1993; Kowalewski 1996; Kidwell 1998; Behrensmeyer et al. 2000). An age spectrum of any grains can be thus thought of as a descriptive, quantifiable characteristic that can be universally applied to the sedimentary record.

Here, we use a literature compilation of more than 2000 single-crystal radiometric dates obtained for various minerals to develop a general quantitative model that can be applied to any sedimentary particles, from mollusk shells to detrital zircon crystals, to estimate the average lifetime (survival time) and age spectra of grains. Development of such a unifying model is important because detrital sedimentary particles (including fossils) dominate both currently forming sediments and ancient sedimentary rocks. Moreover, age spectra of grains are used in earth sciences to study many key patterns and processes including, among others, geochronology (Gehrels and Ross 1998; Gehrels et al. 1999; Stewart et al. 2001), orogen accretion and suspect terranes (Aalto et al. 1998; Adams and Kelley 1998; Gehrels and Ross 1998), unroofing and denudation rates (Corrigan and Crowley 1990*a*, 1990*b*; George and Hegarty 1995; Najman et al. 1997), provenance and depositional history of sedimentary rocks and basins (Boryta 1994; Najman et al. 1997; Adams and Kelley 1998), and time resolution in the fossil record (Flessa et al. 1993; Kowalewski 1996; Kidwell 1998).

The lifetime of any detrital grain is finite and

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may vary greatly among different mineral types (discussed subsequently). The average lifetime of detrital minerals is thus an important parameter that may not only influence the relative abundance of different mineral types in sedimentary rocks but is expected to affect the nature of age spectra of detrital grains. That is, age spectra are not merely a diary of the rate of detrital grain production and the subsequent geological history of rocks that contain those grains (uplift, erosional unroofing, and related processes) but instead are a biased record distorted by the decreasing probability of survival of increasingly older grains.

It is obvious that the average lifetime of grains of a given mineral type should be heavily influenced by the intrinsic durability of that mineral. This is somewhat analogous to the half-life of radioactive isotopes, which is determined by the intrinsic characteristics of parent-daughter isotope systems. Thus, there should be a basic unifying rule that describes average lifetimes ("half-lives") and age spectra of detrital minerals. This idea was expressed in a more formalized way more than 50 years ago by Goldich (1938), who showed that chemical weathering rates are inversely related to the crystallization sequence of silicate minerals from magmas, as expressed by Bowen's reaction series. Even though Goldich's weathering sequence represented a purely qualitative attempt restricted to silicates, it still remains one of the most basic paradigms of earth sciences, routinely described in freshman-level geology textbooks. One of the main aims of this study is to quantify Goldich's sequence.

There are more quantitative measurements of mineral destruction rates available, but there are still some concerns about their reliability and meaning. For example, there is a significant difference between the rate of weathering measured in watersheds and the rate predicted from laboratory studies (White and Brantley 1995). Thus, models of weathering rates based on watershed measurements (Sverdrup and Warfvinge 1993, 1995*a*, 1995*b*) are incongruent with those based on laboratory dissolution rates (Lasaga and Berner 1998). The estimates reported here provide a new way to assess the reliability of such approaches.

Two independent types of data are combined here to obtain a quantitative understanding of the principles governing the average lifetime (half-lives) of various types of mineral grains. First, advancements in laboratory dissolution rate measurements offer a separate set of estimators of expected durability for many major minerals. Second, the rapid progress in high-resolution geochronological techniques, suitable for the dating of a wide spectrum of detrital grains from carbonate shells to zircon crystals, provides a way to empirically estimate the observed average lifetimes of several key minerals; thus, a quantitative comparison of laboratory dissolution rates and observed survival times is now possible.

Methods

Laboratory Estimates of Mineral Grain Durability. The expected average lifetime of a mineral grain should be predictable from its durability. Two main processes destroy mineral grains: dissolution and abrasion. These two processes include not only abiotic (physicochemical) processes but also biotic agents of destruction; many organisms, from microbes to macroorganisms, can bioerode or alter both inorganic and organic solids (Bromley 1992; Banfield and Nealson 1997; Edinger 2001).

The chemical durability (D_C) of a detrital grain of a given mineral type can be estimated from its dissolution rate. We define chemical durability as $D_C = \log(1/r)$, where r is the dissolution rate. This simple relation is based on the observation that the time needed to dissolve a mineral grain of diameter d is $t = d/2rV_M$ (Jurinski and Rimstidt 2001) and therefore, $\log t = \log(1/r) + \log(d/2V_M)$. Both V_M and d are treated as constants. V_M is the molar volume of the mineral and, for the minerals considered here, varies over about one order of magnitude, between 20 and 200 cm^3/mol. The diameter of dated crystals also varies in a relatively narrow range as the individually dated grains are typically sand sized to silt sized. Thus, for detrital grains of comparable size and molar volume, the average lifetime when expressed as a logarithm of time should be linearly related to the D_C of the grain. Recent detailed measurements of dissolution rates provide quantitative estimates of r for many important minerals (fig. 1; tables 1, 2).

The mechanical durability (D_H) of a detrital grain is directly related to its hardness. In this analysis, the Mohs hardness (H_M) values (after Nickel and Nichols 1991) were converted to Vickers hardness (H_V) using the relationship $H_V = 6.5H_M^{2.7}$, based on a best fit to the data provided by Szymanski and Szymanski (1989, table 4.2.2). The hardness values of the minerals considered here are listed in tables 1 and 2. We define mechanical durability as $D_H = \log(H)$. This is based on the following derivation. Rounding of transported grains is evidence that abrasion removes material from them as they are transported. Archard's equation (Archard 1953), $V/A = kWx/H$, which expresses the volume of ma-

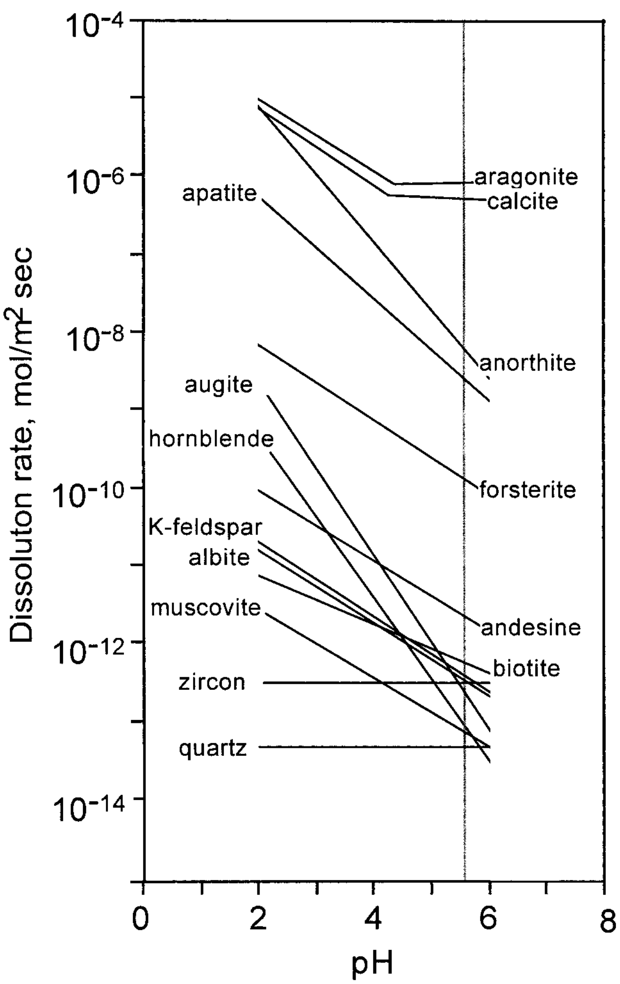

Figure 1. Dissolution rate of selected minerals as a function of pH (see tables 1 and 2 for data sources) plotted for the following minerals: aragonite, calcite, apatite (this rate is for hydroxyapatite and may significantly underestimate the dissolution rate for fluorapatite from igneous and metamorphic sources), muscovite, biotite, hornblende, augite, K-feldspar, anorthite, bytownite, andesine, oligioclase, albite, zircon (zircon dissolution rates reported for 87°C were extrapolated to 25°C using an activation energy of 70 kJ/mol [typical for silicate minerals], assuming that there is no dependence of the rate on pH), forsterite, and quartz (assuming there is no dependence of the rate of quartz dissolution on pH). The pH of soils, where most chemical weathering occurs, is highly variable. The value of 5.5 is assumed here as a reasonable average pH for soils in a humid, temperate-to-tropical climate where chemical weathering would be most rapid.

terial removed (V) per unit area of surface (A) as a function of an empirical constant (k), the applied force between the surfaces (W), the distance traveled (x), and the hardness (H), provides a simple way to quantify this effect. For a spherical particle ($V/A = d/6$), and assuming that the distance traveled (x) is proportional to the time of transport (t), Archard's equation can be recast as $t = (d/6k'W)H$ and $\log t = \log(H) + \log(d/6k'W)$. Consequently, for a spherical grain with any given diameter d, the average lifetime when expressed as a logarithm of time should be linearly related to the mechanical durability of a grain (D_H), defined as $D_H = \log(H)$. As in the case of D_C, we assume that the grain diameter is constant.

Whereas dissolution processes operate virtually continuously through the geological history of a sedimentary grain, abrasion of grains is limited to geologically rare and short periods of movement (Ager 1973), due to either lateral transport or agitation without any considerable net transport. Consequently, D_C should be a better predictor of average lifetime than D_H. However, abrasion increases dissolution rates (Petrovich 1981), and dissolution roughens and softens surfaces and thus increases abrasion and polishing (Craig and Vaughan 1994). This synergistic effect can be expressed by combining the two indicators into a measure of overall durability: $D_T = D_C + D_H$. The log-transformed average lifetime of detrital grains of comparable size should be linearly related to D_T.

Empirical (Radiometric) Estimates of Average Lifetimes of Detrital Grains. We compiled data from the geological literature (table 1) to estimate the average observed lifetime of detrital grains and the age spectra of samples of individually dated grains (a database with the raw data is available from *The Journal of Geology*'s Data Depository free of charge upon request). The database consists of 108 samples (with an average sample size of ca. 19 individually dated grains and a total of 2079 individually dated grains) representing eight types of grains: aragonite, calcite, apatite, biotite, muscovite, K-feldspar, hornblende, and zircon (table 1).

The age variation of detrital grains in a single sample represents an empirical measure of their average lifetime. If grains of a given mineral type are destroyed quickly and do not survive multiple rock cycles, they should be dominated by the youngest cohorts produced prior to the formation of the rock. In such cases, ages of dated grains should vary in a narrow age range, and few notably older specimens are likely to be sampled. If, on the other hand, grains are nearly immortal, they should be highly variable in age, even if collected from within a single bed.

Three different measures of dispersion were used initially to estimate the average lifetime of grains: the standard deviation of dates, the age range of

Table 1. Observed Average Lifetime of Grains and Durability Coefficients for Eight Minerals Represented in the Database of Radiometrically Dated Grains

Grain type[a]	No. of samples	Mean standard deviation (Ma)	Mean range (Ma)	Mean median age (Ma)	Mean no. of grains per sample	Observed average lifetime of grains[b]	Durability indices		
							D_H	D_C (reference)	D_T
Aragonite	13	.0004	.002	.0002	20.0	2.6	2.4	5.4 (Busenberg and Plummer 1986)	7.8
Calcite	4	.0005	.002	.0003	20.5	2.7	2.1	5.6 (Busenberg and Plummer 1986)	7.7
Apatite	18	10.8	48.6	9.4	29.9	7.0	2.7	8.5 (Thomann et al. 1990)	11.2
Hornblende	2	9.3	28.0	16.1	9.0	7.0	2.8	10.2 (Brantley and Chen 1995)	13.0
Biotite	5	26.7	85.7	56.4	10.2	7.4	2.1	12.2 (Nagy 1995)	14.3
Muscovite	26	94.3	312.0	121.9	11.6	8.0	2.1	13.0 (Nagy 1995)	15.1
K-feldspar	11	123.1	352.3	37.8	10.7	8.1	3.0	12.6 (Brantley and Chen 1995)	15.6
Zircon	29	372.6	1373.3	454.4	24.4	8.6	3.2	12.6 (Ewing et al. 1982)	15.8

Note. The observed average grain lifetime estimated as the logarithm of the mean standard deviation of samples of dated detrital grains of a given type. All data were obtained from the published literature. Durability indices were estimated from mineral properties. D_H is the logarithm of the Vickers hardness of each mineral. D_C is the logarithm of the inverse of the dissolution rate of the mineral at pH = 5.5 (fig. 1). $D_T = D_H + D_C$.

[a] The raw data on dated detrital grains were derived from the following sources. Aragonite: Flessa et al. 1993; Meldahl et al. 1997; Kowalewski et al. 1998. Calcite: Carroll 2001. Apatite: Corrigan and Crowley 1990*a*; George and Hagarty 1995; Sachsenhofer et al. 1998. Hornblende: Cohen et al. 1995. Biotite: Cohen et al. 1995; Adams and Kelley 1998. Muscovite: Copeland et al. 1990; Najman et al. 1997; Aalto et al. 1998; Adams and Kelley 1998; Tanner and Pringle 1999. K-feldspar: Copeland et al. 1990; Boryta 1994. Zircon: Bostock and van Breemen 1994; Gehrels and Ross 1998; Gehrels et al. 1999; Stewart et al. 2001. These and other data are in a database that is available from *The Journal of Geology*'s Data Depository free of charge upon request.

[b] Observed average lifetime of grains is estimated as $\log_{10}$ of the mean standard deviation of age spectra of a given mineral type. For example, the score of 7.0 indicates that average sample of detrital apatites (n = 18) has a standard deviation of ca. 10 m.yr.

Table 2. Predicted Average Lifetime of Common Mineral Types

Grain type	Observed average lifetime of grains[a]	Predicted average lifetime of grains[a]	Durability indices		
			D_H	D_C (reference)	D_T
Aragonite	2.6	3.13	2.4	5.4 (Busenberg and Plummmer 1986)	7.8
Calcite	2.7	3.06	2.1	5.6 (Busenberg and Plummmer 1986)	7.7
Apatite	7.0	5.48	2.7	8.5 (Thomann et al. 1990)	11.2
Biotite	7.4	7.63	2.1	12.2 (Nagy 1995)	14.3
Muscovite	8.0	8.18	2.1	13.0 (Nagy 1995)	15.1
K-feldspar	8.1	8.53	3.0	12.6 (Brantley and Chen 1995)	15.6
Hornblende	7.0	6.73	2.8	10.2 (Brantley and Chen 1995)	13.0
Zircon	8.6	8.66	3.2	12.6 (Ewing et al. 1982)	15.8
Augite	Unknown	8.46	2.9	12.6 (Brantley and Chen 1995)	15.5
Forsterite	Unknown	6.59	3.1	9.7 (Rosso and Rimstidt 2000)	12.8
Anorthite	Unknown	5.62	2.9	8.5 (Blum and Stillings 1995)	11.4
Bytownite	Unknown	7.49	2.9	11.2 (Blum and Stillings 1995)	14.1
Andesine	Unknown	7.83	2.8	11.8 (Blum and Stillings 1995)	14.6
Oligioclase	Unknown	8.46	3.0	12.5 (Blum and Stillings 1995)	15.5
Albite	Unknown	8.18	2.9	12.2 (Blum and Stillings 1995)	15.1
Quartz	Unknown	8.59	3.1	12.6 (Rimstidt and Barnes 1980)	15.7

Note. Predicted average lifetime of common mineral types is based on the regression equation for total durability D_T derived for minerals with the known observed lifetime (table 1; fig. 2). The chemical durability D_C is based on data presented in figure 1. The mechanical durability D_H is estimated from hardness data and $D_T = D_H + D_C$ (see text and table 1 for more details).
[a] See table 1, footnote b.

dates, and the median age (the difference between the median and minimum grain age in a sample). As expected, these three metrics are highly correlated ($r > 0.98$ in all cases) and yield consistent results (table 1). In addition to standard deviation, we also use two higher moments about the mean to estimate the age spectrum of a sample: skewness (i.e., the degree and direction of asymmetry in an age distribution) and kurtosis (i.e., the degree to which dated grains cluster around the mean of an age distribution).

It should be noted that the median age metric estimates the lifetime of grains as median age of grains relative to the age of the rock that contained it, as approximated by the youngest grain in the sample. This metric is thus somewhat analogous to the half-life of radioactive atoms and may be intuitively most appropriate. However, the half-life concept is not directly applicable because grain samples represent products of an open system, and the half-life may be measurable only if the rate of grain production is reasonably uniform through time. Moreover, the median age measure is highly volatile because the minimum age is a highly variable estimate, especially at small sample sizes. For this reason, we use standard deviation in our analysis. Out of the three metrics, standard deviation is the least sensitive to outliers and yields estimates that are within an order of magnitude of the estimates provided by median age.

Dispersion metrics do not need to be corrected for the geological age of a sample. For example, standard deviations of samples from rocks of different geological ages are fully comparable because the age dispersion of dated grains (and their standard deviation thereof) is independent of the mean (the average grain age). In other words, the age dispersion is not a function of the age of a deposit (although for long-lasting grains from very old rocks, which are not included in our analysis, the age of Earth might create a boundary condition). An increase in the geological age should be viewed as an additive transformation, which shifts a distribution toward higher values but does not affect its dispersion parameters. It is therefore appropriate to use standard deviation and not the coefficient of variation (see Kowalewski et al. 1998).

The proposed approach requires two important clarifications. First, ideally, empirical estimates of the average lifetime of grains should be all based on the same dating method. However, the scope of this study and limitations of current geochronological methods necessarily result in a data set composed of dates generated by several different dating techniques that are affected by different kinds of biases. For example, fission-track methods reset the clocks of grains buried below 100°C thermocline. Thus, apatite lifetimes may be underestimated relative to grains dated using the U-Pb method, where the original crystal age can often be estimated even for grains that have gone through multiple rock cycles. Moreover, the half-life of some radioactive elements is so short that it may constrain the potential age spectra obtained by radiometric dating. This problem is particularly severe for radiocarbon-dated grains: the limited temporal range of dating makes it impossible to produce age spectra with standard deviations higher than a few tens of thousands of years. Because the closure temperature and dating range both vary among techniques, spurious patterns can thus be generated by compiling disparate samples of dated grains. For this reason, the variation in dating techniques is explicitly considered in our analysis. Fortunately, the striking patterns obtained in this study cannot be attributed to variation in closure temperatures or the temporal ranges of dating techniques.

Second, by combining data from extremely diverse geological sources, we have inevitably introduced into the analysis variation that may obscure any relationships between the intrinsic durability of minerals and the observed average lifetime and age spectra of grains of those minerals. For example, data may combine samples from areas with a different geology of the source area and from regions affected by various exhumation rates. This undesirable heterogeneity makes our analysis extremely conservative: a meaningful statistical pattern can emerge only if intrinsic mineral durability plays an overriding role in controlling the average lifetime and age spectra of detrital grains.

In sum, this study aims to assess the extent to which the mineral durability controls average lifetimes and age spectra of detrital grains in a statistical sense: by pooling many samples from various tectonic-geomorphological settings and by averaging out geological heterogeneities. The results should be most applicable to overall tendencies observed in large sets of samples.

Results and Discussion

Average Lifetime of Detrital Grains. Comparison of the literature database with durability estimates shows that the observed lifetime of detrital grains does not display any significant correlation with the D_H, largely because of soft silicates (micas) with long observed average lifetimes (fig. 2*A*). However, the observed lifetime relates linearly to the D_C based on dissolution rates (fig. 2*B*). Even after carbonate grains are excluded (their inclusion results in a pronounced bimodality that might generate a spurious fit), the simple linear regression is close to significant despite a reduction in sample size (fig. 2*B*). When D_H and D_C are combined into a single metric (D_T), the regression fit improves and is highly significant, with carbonates both included and excluded (fig. 2*C*).

Despite many obvious limitations of the literature database—small sample sizes, a highly heterogeneous geological context of the data, differences in dating techniques and some variation in grain size (a parameter assumed constant in the analysis)—the basic predictions regarding average lifetime of grains are surprisingly well corroborated. As expected, D_H performs poorly as a lifetime predictor, whereas D_C and D_T show high and significant linear correlation with the observed average grain lifetime. The good fit obtained here suggests that the average lifetime of grains is a simple linear function of their intrinsic durability. The linear fit is not trivial because it indicates that the intrinsic characteristics of minerals, not the geological history (i.e., the rate of grain production), are the primary factor controlling the survival and age spectra of grains.

The observed correlation is also not a spurious artifact of differences in the closure temperatures of different isotopic systems used to date minerals included in this study. For example, the dated grains of the three most durable minerals ($D_T >$ 15; table 1) yielded the three highest estimates of the observed average lifetime (>8.0; table 1), despite the fact that these three minerals vary greatly in their closure temperatures: zircon (U/Pb, >750°C), muscovite (K/Ar, ca. 350°C), and K-feldspar (Ar/Ar, ca. 200°C). There is no significant correlation between the closure temperatures and observed average lifetimes of the studied minerals.

Similarly, the limited range of radiocarbon dating cannot be blamed for the very short average lifetimes observed for calcite and aragonite grains. Virtually all grains dated in the original studies (see references in table 1) were much younger than the range of radiocarbon dating; that is, the low standard deviations of age spectra are not imposed by limits of dating but truly reflect very short average lifetimes for those grains. In fact, none of the 2079 grains of various type included in this analysis were beyond the temporal limit of the methods used for dating; that is, these limits did not suppress average lifetime estimates for any of the analyzed grain type. Nevertheless, carbonate dates should be treated with particular caution because these grains (typically complete mollusk and brachiopod shells >10 mm in length) are much larger than other detrital grains used in this study. It is noteworthy, therefore, that the observed linear relationship is still very pronounced and significant even when carbonate grains are removed from the analysis (fig. 2*C*).

For all minerals, and regardless of which of the three dispersion metrics is used (table 1), the ob-

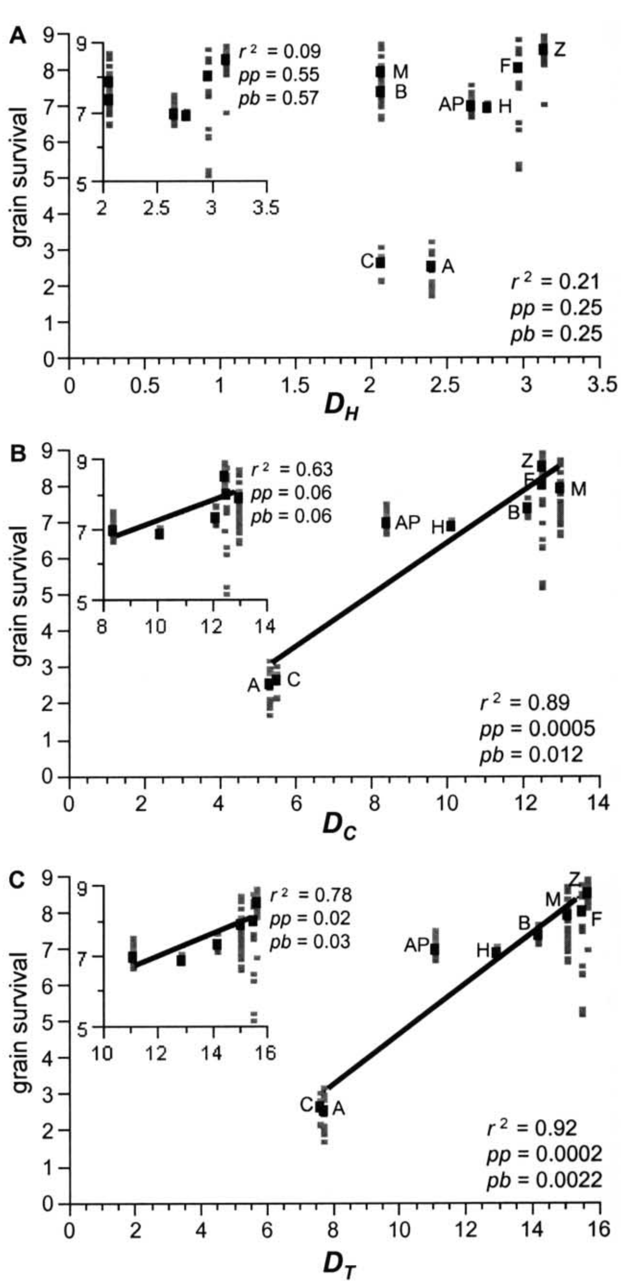

Figure 2. Observed average lifetime of eight types of detrital grains estimated as log-transformed standard deviation of grain age plotted against three estimates of grain durability (table 1): *A*, D_H = mechanical durability; *B*, D_C = chemical durability; and *C*, D_T = overall durability estimated as $D_H + D_C$. Gray symbols represent individual samples of dated grains and black symbols represent mean grain survival for a given type of grain (table 1). Grain type symbols: *A* = aragonite, *B* = biotite, *AP* = apatite, *C* = calcite, *F* = K-feldspar, *H* = hornblende, *M* = muscovite, *Z* = zircon. Inset plots exclude carbonate grains; r^2 = coefficient of determination for simple linear regression applied to the estimates of mean lifetime of a grain type; *pp* = significance of regression based on parametric regression (PROC REG; SAS Institute software); *pb* = significance of regression estimated by a 5000-iteration bootstrap simulation (IML; SAS Institute software), based on an approach described by Diaconis and Efron (1984).

served average lifetimes estimated in this study are as much as several orders of magnitude greater than those predicted from laboratory dissolution rates. Thus, our quantitative estimates support chemical weathering models that are based on field observations of watershed rates (Sverdrup and Warfvinge 1993, 1995*a*, 1995*b*).

As the quality and quantity of data increase, we should be able to improve our estimates of the slope of the relationship and predict the average lifetime of detrital grains with an increasing degree of certainty. For example, the notable departure of apatite from the predicted value (fig. 2*C*; table 2) suggests that the estimated value of D_C is too low (see table 1 and subsequent text). Also, with further refinements, the intercept should converge on zero because grains that lack any durability (e.g., marshmallow) are destroyed instantaneously, geologically speaking—indeed, the intercepts of the regression estimates for D_C and D_T are indistinguishable statistically from zero ($P > 0.05$ in both cases).

Structure of Age Spectra of Dated Grains. In addition to the average lifetime pattern, the literature database suggests that age spectra of samples of dated grains tend to be right skewed (fig. 3*A*): skewness > 0 in 79% of the samples, a proportion significantly higher than the 50 : 50 ratio ($P \ll 0.05$, the binomial test). This tendency is stronger for samples of the less durable grains (97% samples of carbonate and apatite grains are right skewed) than for samples of the more durable grains (70% samples of silicate grains are right skewed). The difference in proportion of right-skewed age spectra between the more durable and the less durable grains is highly significant ($P \ll 0.05$, the Fisher's Exact Test) and visually obvious when silicates and nonsilicates are compared on a cumulative plot (fig. 3*B*). Almost all left-skewed age spectra represent the two most chemically durable of the analyzed grain types: micas and zircon (figs. 3*A*, 4). Bivariate distribution of samples in terms of skewness and kurtosis (fig. 4) shows that the samples align along a second-order polynomial curve. The less durable nonsilicate grains cluster tightly around the second-order curve and plot in the right-skewed, leptokurtic sector of the graph. In contrast, more durable

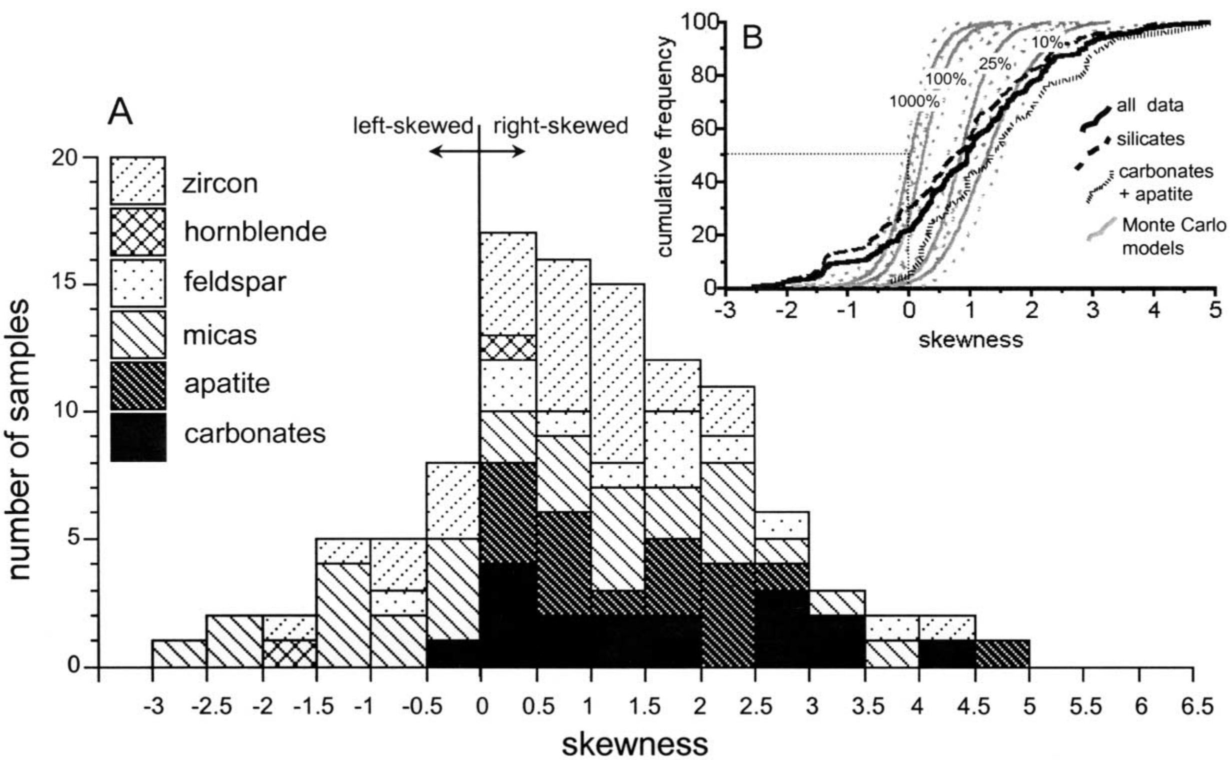

Figure 3. *A,* Shape-frequency distribution of age spectra of 108 samples of dated detrital grains. The shape of an age spectrum is estimated by the skewness of a sample of individually dated grains. Biotite and muscovite are grouped as micas, and aragonite and calcite are grouped as carbonates. *B*, Cumulative frequency curves plotted for all sampled minerals and plotted separately for samples of the more durable silicates and the less durable carbonate and apatite grains. Gray lines represent expected frequency curves for hypothetical grain types, with "half-lives" T representing 10%, 25%, 100%, and 1000% of t, the duration of the geological processes that affected the grains. Expected curves based on a Monte Carlo simulation (written using SAS Institute STAT procedures and IML language) for 100 time intervals t with a constant grain production (see text for details). A mean cumulative curve for a given half-life (*solid gray lines*) computed as the average curve for 100 sets of 108 random samples. The dashed gray lines envelop a total range of values for each set of 100 curves. Because the actual samples combine grains with different half-lives, the resulting cumulative curves (especially the curve for all grain types pooled together) span a much wider range of skewness values than do the simulated curves. The Monte Carlo curves shift to the left with increase in half-life (durability), mimicking the patterns observed when the more durable silicates are compared to the less durable nonsilicates. The shape and slope of curves is specific to a sample structure given by our data (note, e.g., that if very large sample sizes were simulated, all curves will converge onto vertical lines around their fiftieth percentile). For 1000% half-life, grains are virtually unaffected by exponential loss and the resulting cumulative curve has a fiftieth percentile approximating symmetrical distribution (*thin dashed lines*). The curve for 2% half-life is not shown here because it overlaps a 10% half-life curve. The range of curves represented in the simulation provides a comprehensive picture of possible cumulative structures (given the sampling scheme of the data) for samples of exponentially decaying grains.

silicates often depart notably from the curve and include numerous samples that are platykurtic and/or left skewed. The shape of the curve is an expected pattern that reflects a quadratic dependence between kurtosis (fourth-order moment about the mean) and skewness (third-order moment about the mean). The tight alignment of softer grains along a single line suggests that all samples of less durable grains are from the same type of distribution (most likely, density functions of exponential [Weibull] type; discussed subsequently).

The general tendency of age spectra toward a right-skewed shape is not surprising. Because the probability of destruction increases with time, old grains should become increasingly less abundant. In fact, if we assume that grain production is reasonably constant through geological time, the age spectra should follow right-skewed curves analo-

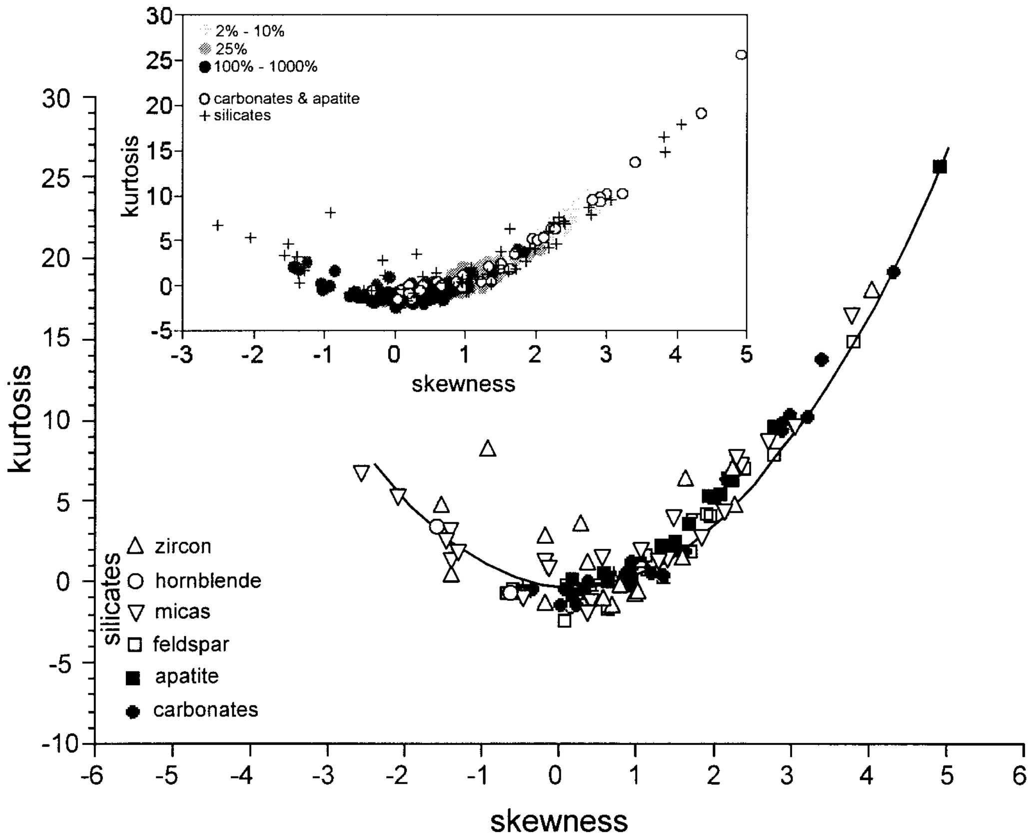

Figure 4. Skewness and kurtosis of age spectra of 108 samples of dated detrital grains. Biotite and muscovite are grouped as micas, and aragonite and calcite are grouped as carbonates. All samples align along a quadratic curve that centers around the 0, 0 point (note that the 0, 0 point represents *any* normal distribution). *Insert,* An example of the range of value represented by five sets of 108 samples derived from Monte Carlo simulations with half-lives varying from 2% to 1000% (see text and fig. 3*B* for details). Superimposed symbols differentiate the empirical data into silicate samples and the carbonate and apatite samples.

gous to those generated by exponential decay of radioactive elements (Titayeva 1994) or failure time of mechanical parts predicted by the Weibull function (Weibull 1951; Bhushan 1999). It is noteworthy that the radioactive decay function and the Weibull function are very closely related: the decay function is a special case of the two-parameter Weibull function with the shape parameter $\beta = 1$ and with the scale parameter α analogous to the radioactive decay constant λ.

To further evaluate the results, a Monte Carlo model based on the exponential function was performed for 100 time intervals, t (simulating duration of the geological processes that affected the grains), and half-lives, T, representing 2%, 10%, 25%, 100%, and 1000% of t. For example, for $T = 10\%$, the simulated grains have half-life representing one-tenth of the duration of geological processes (i.e., $t = 10$ intervals). For each of the five half-lives, a constant grain production through time was assumed and a large population (ca. 10 million) of grains was simulated with a probability of grain survival given by the exponential decay function $e^{-(0.693/T)t}$. A set of 108 samples with the sample structure replicating the actual structure of samples in the database was then drawn randomly multiple times (100 iterations) from the simulated population of grains and analyzed in terms of skewness and kurtosis.

The results of the Monte Carlo simulation (figs. 3*B*, 4 insert) indicate that the majority of samples (including all samples of the less durable nonsilicates) have the skewness and kurtosis values expected for exponentially decaying grains. The good fit to the exponential model observed for the less durable detrital grains is not surprising: The exponential nature of age distributions has been repeatedly demonstrated in recent case studies for aragonitic and calcitic shells using radiocarbon and amino acid methods (Flessa et al. 1993; Meldahl et al. 1997; Kowalewski et al. 1998; Carroll 2001). The fit obtained here suggests that either these grains are produced at a reasonably constant rate through time or, more likely, the exponential loss of those grains to geological processes masks completely any variations in their initial production rate.

The other prediction of the exponential model is that the right skewness and kurtosis of samples should decrease as the durability and average lifetime of grains increase. Soft grains that dissolve quickly and have average lifetimes (or half-lives using decay model analogy), T, representing only a small fraction of time (t) over which geological processes operated on those grains, are expected to produce highly leptokurtic and strongly right-skewed age spectra dominated by young grains with a thin tail of very few old grains. Conversely, durable grains with average lifetimes ("half-lives") notably exceeding t will be only slightly affected by removal of older age classes and thus will produce more platykurtic and less right-skewed distributions.

The Monte Carlo model illustrates this principle (figs. 3*B*, 4 insert). The differences observed among the simulation for different half-lives T parallel the direction of changes in skewness and kurtosis observed between the less durable nonsilicates and the more durable silicates in the actual data (figs. 3*B*, 4 insert). However, Monte Carlo models show that even when very durable grains are simulated (i.e., grains with half-lives 10 times longer than the simulated duration of the geological history; $T = 1000\%$), left-skewed distributions cannot be readily obtained for sets of samples matching the sample structure of the analyzed literature data. The departure of many samples of zircon and mica grains from the exponential model (fig. 4 insert) and the quadratic curve (fig. 4) reflects the fact that the rate of production of those grains was not constant through time. In other words, these grains are sufficiently durable and last so long that they can produce age spectra that record changes in the rate at which those grains were produced (and/or recycled) by geological processes. Indeed, strong multimodalities are frequently observed in age spectra of detrital zircon (Stewart et al. 2001) but rarely in the case of carbonate grains (Flessa et al. 1993; Meldahl et al. 1997; Kowalewski et al. 1998). It should be noted, however, that in the case of dated crystals of micas, the departures may also reflect a leakage of Ar in old or reheated grains.

The skewness and kurtosis patterns support the intuitive expectation that grains that are less durable should yield a better estimate of a stratigraphic age of a deposit. Samples of nondurable grains tend to have age spectra with a pronounced mode of young grains, which predate only slightly, in terms of the geological time, the time of the formation of a deposit that contains them (although this issue depends also on the intended resolution of dating: even soft carbonate fossils may yield inaccurate age estimates if high resolution is desired; e.g., Goodfriend 1989). Moreover, if only one or two grains are dated, their age is very likely to represent that mode and thus the approximate age of a deposit. Similarly, if a single date is based on multiple grains, such a date, averaging mostly grains from the mode, will also tend to approximate the actual age of a deposit. In contrast, durable grains may not provide as good a measure of depositional age, although the youngest grains can be and often are used to estimate the maximum depositional age of a sedimentary rock. However, durable grains may record more faithfully the variation in the rate of production of mineral grains through time; that is, our analysis offers a strong support for using zircon grains in orogen accretion and suspect terranes studies.

Implications and Conclusions

In qualitative terms, the lifetime of detrital grains has been understood for more than half a century. This study goes beyond a purely qualitative ranking by offering a first step toward an empirically derived quantitative scale for the predicted average lifetimes of major types of mineral grains. We can plot minerals on the diagram in a more rigorous way and consider any minerals, not just silicates from Bowen's reaction series. For various reasons discussed throughout this article, the presented quantitative scale (table 2; fig. 5) should be treated as a preliminary approximation. Thus, whereas the quantified weathering sequence summarized in figure 5 agrees quite well with our expectations based on Goldich's generalized model, there are clearly a few discrepancies that remain to be resolved. For example, rates of augite weathering are likely to be much faster than our model predicts, and the reported dissolution rate for this mineral should be reevaluated. On the other hand, we expect that apatite grains should weather more slowly. Not only is the observed average lifetime of apatite likely underestimated because of the low closure temperature of fission track dating, but the dissolution rate used to calculate D_C was derived for hydroxyapatite, and so it may seriously underestimate the D_C of the fluorapatite grains used in this study.

Ultimately, with future advances in rate measurements and dating techniques, the new ap-

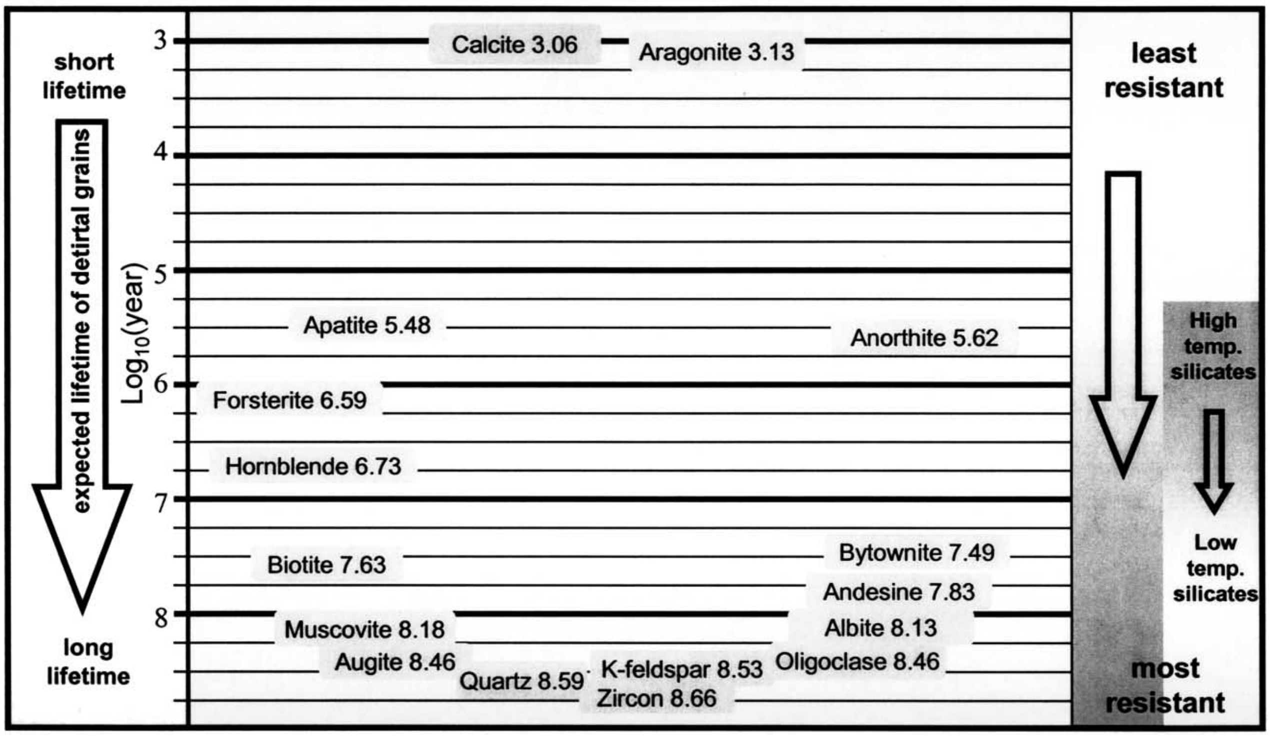

Figure 5. The quantitative refinement of the classic diagram of Goldich with the relative position of mineral grains based on their predicted average lifetime, indicated here for each mineral by a number placed to the right of that mineral's name (see table 2 for data). The silicate grains are arranged into two arrays largely mirroring the crystallization sequence of silicate minerals from magma as expressed by Bowen's reaction series. Nonsilicates are placed arbitrarily in respect to the *X*-axis of the diagram. Our results correlate remarkably well with Goldich's weathering sequence, suggesting that the laboratory dissolution rate measurements predict the correct weathering rates in a relative way. A lack of correlation observed in few cases (e.g., augite) suggests that some of the dissolution rate measurements may require substantial refinements.

proach described here should allow the formulation of a quantitative theory of detrital grains with diverse potential applications to the study of individual detrital grains and the sedimentary rocks that contain them. Despite the complexity of geological processes and the high spatiotemporal heterogeneity of the geological record, the average lifetime of detrital grains can be predicted from their intrinsic durability and their age spectra can be modeled using a simple exponential model.

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