A users guide to Neoproterozoic geochronology

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Chapter summary

Radio-isotopic dating techniques provide temporal constraints for Neoproterozoic stratigraphy. Here we review the different types of materials (rocks and minerals) that can be (and have been) used to yield geochronological constraints on [Neoproterozoic] sedimentary successions, as well as review the different analytical methodologies employed. The uncertainties associated with a date are often ignored but are crucial when attempting to synthesise all existing data that are of variable quality. In this contribution we outline the major sources of uncertainty, their magnitude and the assumptions that often underpin them.

1. Introduction

Key to understanding the nature and causes of Neoproterozoic climate fluctuations and links with biological evolution is our ability to precisely correlate and sequence disparate stratigraphic sections. Relative ages of events can be established within single sections or by regional correlation using litho-, chemo- and/or biostratigraphy. However, relative chronologies do not allow testing of the synchroneity of events, the validity of correlations or determining rates of change/duration of events. At present, the major limitation to our understanding of the Neoproterozoic Earth System is the dearth of high-precision, high-accuracy, radio-isotopic dates. However, the increase in geochronological constraints over the past five years demonstrates that progress is being made.

This chapter outlines the radio-isotopic dating techniques used for the dating of [Neoproterozoic] sedimentary rocks. It is aimed at the many geologists, climate modellers, palaeobiologists and geophysicists, who use Neoproterozoic geochronology, especially those less familiar with the process of obtaining a date from a rock. We provide an outline of the strengths, weaknesses and limitations of the different techniques as well as critical evaluation of the assumptions that underpin the accuracy and precision of the calculated dates and uncertainties. There is an emphasis on U-Pb (zircon) geochronology that reflects it's prevalence in the current published literature. We have also tried to place an emphasis on the 'isochron geochronometers' (Re-Os, Lu-Hf and Pb-Pb) applied directly to sedimentary rocks as they are proving to be critical in the direct dating of sedimentary using that are devoid of extrusive igneous rocks. Although the K-Ar and $^{40}Ar/^{39}Ar$ are mainstays of Phanerozoic timescale calibration, there are few examples where they have been applied to Neoproterozoic strata. This is most likely due to the susceptibility of K bearing minerals to alteration and argon loss.

2. Dateable rocks and minerals

Traditionally the absolute age of sedimentary successions are determined via radio-isotopic dating of uranium and potassium bearing minerals (zircon and sanidine) from volcanic rocks via U-Pb and K-Ar/^{40}Ar-^{39}Ar techniques. These minerals crystallise at (or close to) the time of the magmatic eruption and therefore the age of the mineral is

assumed to approximate the depositional age of the volcanic rock. It is also possible to apply radio-isotopic dating to certain sedimentary deposits (chemical precipitates and organic residues) providing they have an elevated parent/daughter ratio and that any initial daughter nuclide can be accounted for (see section 3.2).

2.1 Dating accessory minerals from volcanic rocks

Zircon ($ZrSiO_4$) is a common accessory mineral in volcanic rocks ranging from lavas to air-fall tuffs and is a nearly ubiquitous component of most clastic sedimentary rocks. The most common volcanic rocks in fossil-bearing sequences are air-fall layers deposited in marine settings that range in thickness from a millimeter to many meters. In most of these rocks the primary volcanic material has been altered, probably soon after deposition, to clay minerals in a process that has little effect on zircon. The refractory and durable nature of zircon over a wide range of geological conditions means that it is likely for zircon to remain a robust indicator of magmatic events even through subsequent metamorphism. What makes zircon ideal for U-Pb dating is that because U has a similar charge and ionic radius to Zr it substitutes readily into the zircon crystal structure (in modest amounts, typically in the 10's to hundreds of ppm range) whereas Pb has a different charge and larger ionic radius leading to its effective disclusion from the crystal lattice. Therefore at t_0 there is effectively no Pb present in the crystal (although mineral and fluid inclusions may contain both common and radiogenic Pb). An additional factor that makes zircon such a robust chronometer is its high closure temperature (>900°C), the temperature below the zircons are effectively sealed and U and Pb do not undergo thermally activated volume diffusion. This means that zircons preserve their primary ages even in volcanic rocks contained in amphibolite facies metasedimentary successions (e.g., Hoffmann et al., 2004).

The refractory and durable nature of zircon means that it is often recycled through crustal processes of erosions, metamorphism and magmatism, which combined with its high closure temperature means that it is possible to inherit older zircon in newly formed igneous rocks. This commonly occurs as older cores surrounded by a rim of younger, magmatic zircon. Such grains pose an analytical challenge in that the different domains need to be analysed separately, which is best achieved using either microbeam techniques (see section 4.2) that employ ion beams and lasers to micro-

sample different domains within a single zircon crystal or micro sampling of single grains followed by conventional analysis.

A further complication arises when one considers that the crystallization history of a magma is not always an instantaneous event and that in certain circumstances (such as large volume silicic eruptions) zircons may crystallize several tens of thousands of years prior to eruption and/or over a protracted interval. Furthermore, in long-lived magmatic systems it is possible that older material is cannibalized and that zircons in an air fall tuff may record a continuum of dates from eruption up to several million years before. In such situations high-precision single grain analyses are required in order to deconvolve the complexity within a population and to assign an age to the sample.

It is also possible to date other accessory phases from volcanic ahs beds such as monazite and titanites, however these are much less common in their occurrence than zircon. Monazite [(LREE)PO_4] is typical of peraluminous magmas and metamphic rocks, however it also rarely found in volcanic ash beds (reference). Monazite has a similarly high closure temperature (>900°C) to zircon and in addition to incorporating uranium into its crystal lattice will incorporate ThO_2 at the percent level making it ideally suited to Th-Pb dating. Titanite (sphene) ($CaTiSiO_5$) is a common accessory phases in metamorphic rocks, and somewhat less common in plutonic and volcanic rocks. The advantage of titanite is that it has a moderate closure temperature (ca. 650°C) that means it does not accumulate Pb until it cools below that temperature. In the case of volcanic rocks equates to the eruption event and therefore pre-eruptive residence of titanite is not a limiting factor for its use in dating volcanic eruptions. Unfortunately, titanite also incorporates some Pb into its crystal structure resulting in moderate initial common Pb that limits the precision of titanite U/Pb dates.

2.2 Dating chemical precipitates and organic residues

It is becoming increasingly apparent that chemically precipitated rocks and organic residues from sedimentary rocks can serve as chronometers using the isochron approach and calculated dates are interpreted to approximate the time of sedimentation and/or early diagenesis. The most commonly applied chronometers in Neoproterozoic rocks include carbonates, phosphates and organic-rich shales, as they contain high concentrations of the various parent nuclides (Re, U and Lu etc.).

2.2.1 U-Pb dating of carbonates

At the time of formation, carbonates can incorporate uranium into their crystal lattice, typically with several parts per million (ppm) concentration (although in some cases this can be many tens of ppm), as well as (initial) Pb with concentrations typically in the ppb range, and therefore have the potential for U-Pb dating. Carbonates form in a variety of terrestrial and marine environments however Neoproterozoic successions targeted for U-Pb dating are invariably marine. Fluid mediated recrystallisation of carbonates is a common processes during burial and metamorphism and very few (if any) Neoproterozoic carbonates are pristine. Whilst fluids are unlikely to cause isotopic fractionation the variable solubility of Pb and U means that it is common for the two to become uncoupled, in which case the U-Pb systematics are somewhat unreliable and the Pb-Pb system is relied upon for age information. Several studies have generated Pb-Pb isochrons from Neoproterozoic successions with varying success and most studies finding significant evidence for disturbance of the Pb-Pb systematics during subsequent burial/metamorphic events (Babinski et al., 1999; Babinski et al., 2007). Recent studies have been successfully employing combined textural and Sr isotope analyses of the carbonates as an independent proxy for disturbance during fluid flow events (Babinski et al., 2007).

2.2.2 Re-Os dating of organic-rich sediments

Both Re and Os become concentrated within anoxic sediments by redox reactions close to the sediment-water interface and are known to be incorporated in the organic matter of organic rich shales (Creaser et al., 2002). Furthermore, both Re and Os are apparently hydrogenous in nature and following deposition they can act as a closed system allowing for their exploitation for geochronology. In the past 5 years the Re-Os geochronometer has been applied been applied to several organic rich Neoproterozoic stratigraphic intervals (Kendall et al., 2006; Kendall et al., 2004; Schaefer and Burgess, 2003). Studies of the greenschist facies Old Fort Point Formation (Kendall et al., 2004) suggests that Re-Os systematics can remain coherent during low grade metamorphism.

2.2.3 U-Pb and Lu-Hf dating of phosphates

Phosphates are known for their enrichment (relative to the fluid from which they precipitate) in rare earth elements (REE), thorium and uranium thus allowing for

potential use as geochronometer through exploitation of the Lu-Hf, Th-Pb and U-Pb decay schemes. Few studies have yet to exploit the Lu-Hf and U-Pb system for the dating of sedimentary phosphates. Barfod et al (Barfod et al., 2002) presented a combined U-Pb and Lu-Hf isochron study of the Douhantuo phosphorites obtaining a Lu-Hf 'isochrons' at ca. 600 Ma (uncertainties of 26 to 81 Ma and MSWDs from 2.0 to 25) and a Pb-Pb isochron of 599.3 ± 4.2 Ma (n = 5, MSWD = 2.9). These dates are consistent with U-Pb zircon dates from the top and bottom of the Doushantuo formation (Condon et al., 2005), however all 'isochrons' recorded excess scatter. This scatter was attributed to the presence of detrital clays that were not fully eliminated despite sample pre-treatment to remove clay fractions.

In addition to dating 'bulk' phosphates, both monazite and xenotime (YPO_4) are known to form during early diagenesis (Evans et al., 2002; Rasmussen, 2005). Both minerals have highly favourable U/Pb systematics and are robust phases however their form within the sediments makes them difficult to analyse. Xenotime occurs as syntaxial overgrowths on zircons but due to their small size (a few 10's of μm), and textural complexity, an *in-situ* isotopic technique with a spatial resolution of <10 μm is required to successfully date xenotime; to date, this has only been achieved by ion microprobe. In addition, precipitation of xenotime also occurs during fluid and thermal events adding a further layer of complication if the timing of sedimentation is the target. In contrast to xenotime, diagenetic monazite tends to occur as nodules (up to 2mm diameter) in shales. Studies of Palaeozoic diagenetic monazites nodules have demonstrated that the Pb-Pb and Th-Pb systems are robust however the U-Pb has been perturbed indicating U remobilization (Evans et al., 2002). Neither (diagenetic) monazite or xenotime U-Pb geochronology have (yet) been successfully have been successfully applied to the dating of a Neoproterozoic sedimentary succession.

The 'isochron geochronometers' are invaluable for obtaining age information from sedimentary successions devoid of volcanic material that can be dated by the U-Pb zircon method. Despite the large uncertainties intrinsic to the dating of these types of materials, techniques such as the Pb-Pb isochron method are providing critical in providing age information for stratigraphic intervals that are devoid of volcanic units for U-Pb (zircon) dating (Babinski et al., 2007; Barfod et al., 2002). Uncertainties on Re-Os isochron dates are now yielding uncertainties comparable to U-Pb (zircon) microbeam dates. Issues relating to the isochron geochronometers are centred around

the lack an independent check on open-system behaviour. Quite often the MSWD and agreement with existing constraints are used to assess accuracy, if ages are younger than a minimum age constraint then the isochron date must reflect a fluid event. For the Pb-Pb method applied to carbonates, the evaluation of the Sr isotopes may serve as a good proxy for disturbance (or lack thereof).

2.3 Maximum and minimum age constraints

Not all sedimentary successions are amenable to direct dating via radio-isotopic methods. In the absence of zircon bearing volcanic rocks, or chemical sediments for isochron dating, another approach is to obtain maximum age constraints by the dating of detrital zircons. Detrital zircons in clastic rocks can range from being considerably older than the estimated age of the sedimentary rock they are contained within (often many hundreds of millions of years older) to close to the age of sedimentation and in this case can provide valuable constraints (Bingen et al., 2005). Minimum age constraints can be provided by overlying strata (which may contain age-diagnostic fossils) and/or cross-cutting igneous intrusions. If a radio-isotopic date provides the age control then the issues outlined in this chapter will apply. When the radio-isotopic constraint is somewhat temporally distant from the presumed age of the sediment there is a tendency to ignore the age uncertainties but this can sometimes be misleading (see section 5 for further discussion).

3. Radio-isotopic geochronometers

A relatively small number of radioactive decay systems are suitable for dating Neoproterozoic rocks due to their long half-lives and are listed in table 1. All of these systems are based upon the radioactive decay of a parent nuclide to a stable daughter nuclide. Exploiting these decay systems for the purposes of determining the age of a mineral or rock is dependent upon (1) the decay constant of the parent nuclide must be accurately and precisely determined; (2) closed system behaviour, which can be simply stated to mean there has been no loss or gain of parent or daughter nuclide since formation (or ‘closure’) of the material, and (3) the initial daughter nuclide, if present, can be precisely and accurately accounted for. In this section we outline the basic principles of the various radio-isotopic geochronometers, differentiating the U-

Pb system applied to U-bearing accessory minerals from the isochron geochronometers (Re-Os, Lu-Hf, Pb-Pb etc.) applied to chemical precipitates and organic residues.

Radioactive Parent Nuclide	Radiogenic Daughter Nuclide	Half life (yrs)
^{238}U	^{206}Pb	4.468×10^{9}
^{235}U	^{207}Pb	7.038×10^{8}
^{187}Re	^{187}Os	4.16×10^{10}
^{176}Lu	^{176}Hf	3.71×10^{10}
^{87}Rb	^{86}Sr	4.944×10^{10}
^{40}K	^{40}Ar, ^{40}Ca	1.25×10^{9}

Table 1. Radiometric decay systems used in geochronology.

3.1 Uranium-Lead

U-Pb geochronology is often regarded as the gold standard of geochronology because unlike all other chronometers it exploits two independent decay schemes, ^{235}U to ^{207}Pb and ^{238}U to ^{206}Pb and ^{238}U and ^{235}U decay constants are relatively precise (Jaffey et al., 1971). Two separate dates for a zircon based on each individual decay schemes may be calculated and visualised using the concordia diagram (Fig. 1). On a conventional (Wetherill) concordia diagram the X and Y axis are the $^{207}Pb/^{235}U$ and $^{206}Pb/^{238}U$ ratios respectively, and the concordia curve represents the simultaneous solution of the decay equations for a given age. A third ^{207}Pb-^{206}Pb date can be determined from only Pb isotopic measurements through knowing both the ^{235}U and ^{238}U decay constants and the present day $^{235}U/^{238}U$ ratio which is assumed invariant at ca. 137.88. Calculation of the U/Pb dates requires determination of the Pb*/U ratio (Pb* denotes radiogenic Pb) and the corresponding decay U constant. See Fig. 1 for age equations.

The advantage of two independent chronometers in the same mineral is that it is possible to detect small amounts of open system behaviour such as Pb loss or the inheritance of older material. This is a major factor in our ability to make reliable, high-precision age determinations as we can evaluate whether a number of analyses represents a time of mineral growth. The different half lives of ^{238}U and ^{235}U, ca. 4.5

and ca. 0.7 Ga respectively, combined with their varying abundances in nature, means that much smaller amounts of ^{207}Pb are produced per increment of time in the Neoproterozoic. Although all three dates can be calculated from most published analyses, the relative precisions are related to the analytical technique employed (see section 5 for further discussion of age uncertainties). The U-Pb method is most-often applied to U-bearing accessory minerals such as zircon found in igneous rocks but it has also been applied to both carbonates and phosphorites using Pb-Pb isochrones where the initial Pb contribution is significant.

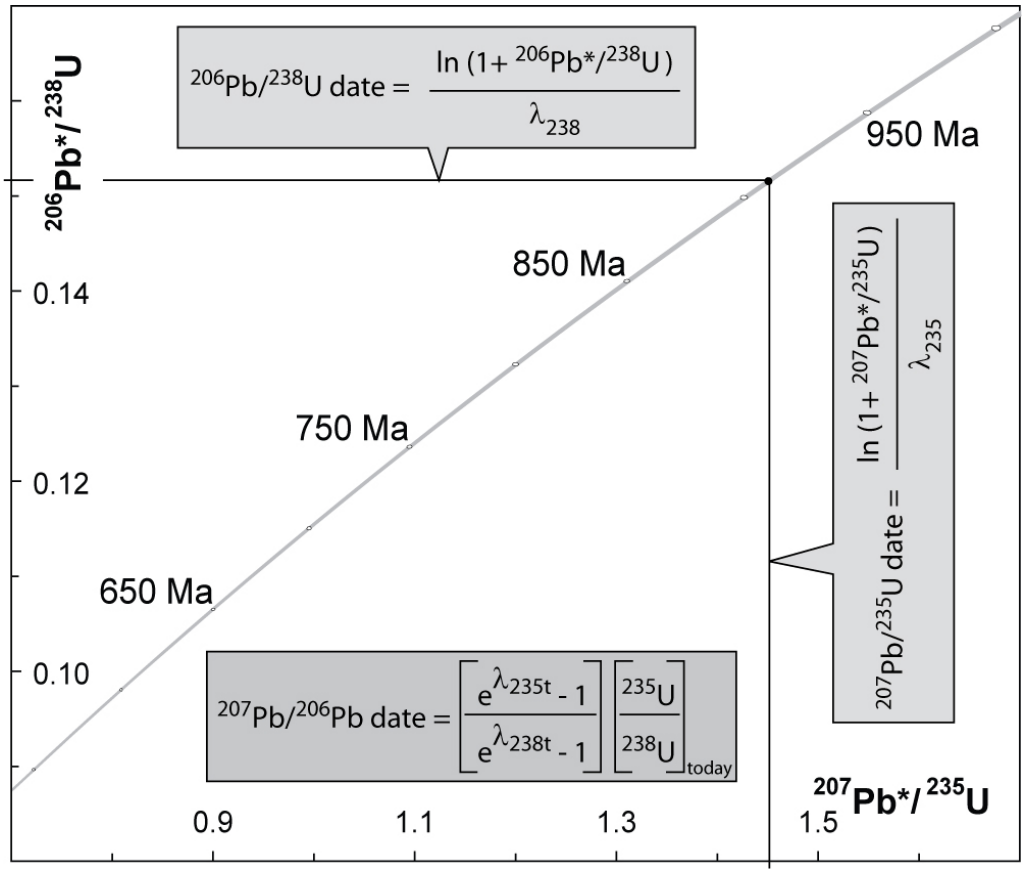

Figure 1. U-Pb (Wetherill) concordia diagram for the age range 542 to 1000 Ma. The grey band represents the concordia cure plotted to reflect the uncertainties in the ^{235}U and ^{238}U decay constants. Unfilled ellipses are plotted at 50 Myr intervals. λ = decay constant.

Assuming that zircon crystallization and deposition of an ash are approximately simultaneous, is it correct to assume that the calculated radio-isotopic dates be assumed to accurately date the time of zircon crytallisation or stated another way, has the zircon remained a closed system? It has been known for several decades that zircons often show evidence for post-crystallisation Pb-loss. This has the effect of

lowering the U/Pb ratios and the derived dates (see Fig. 2). In order to minimise/eliminate the effects of post-crystallisation Pb-loss it is possible to subject zircons to pre-treatment techniques in order to physically remove the domains that have suffered Pb-loss thus increasing the probability of closed system behaviour. The first approach was to physically abrade away the exterior portions of the zircons (Krogh, 1982a), based on the observation that the outer portions were richest in U and thus susceptible to radiation damage and Pb-loss. At the same time Krogh (Krogh, 1982b) also suggested the selection of the most non-magnetic zircons as they corresponded to lowest U contents and had least amount of Pb-loss. These approaches were widely applied until the development of a new technique described as 'chemical abrasion' (Mattinson, 2005). This technique involves annealing zircon grains at 800-900 °C followed by partial dissolution. This method effectively "mines out" the higher U parts of the zircon that have been damaged by radiation and are thus susceptible to fast-pathway diffusion of Pb from the zircon crystal. This method seems to offer the promise of total elimination of open system behaviour in most zircon. Microbeam techniques (see section 4.1.2) have not typically employed pre-treatment techniques as they assume that Pb-loss is restricted to the exterior portions of grains which they attempt to avoid during the in-situ analyses.

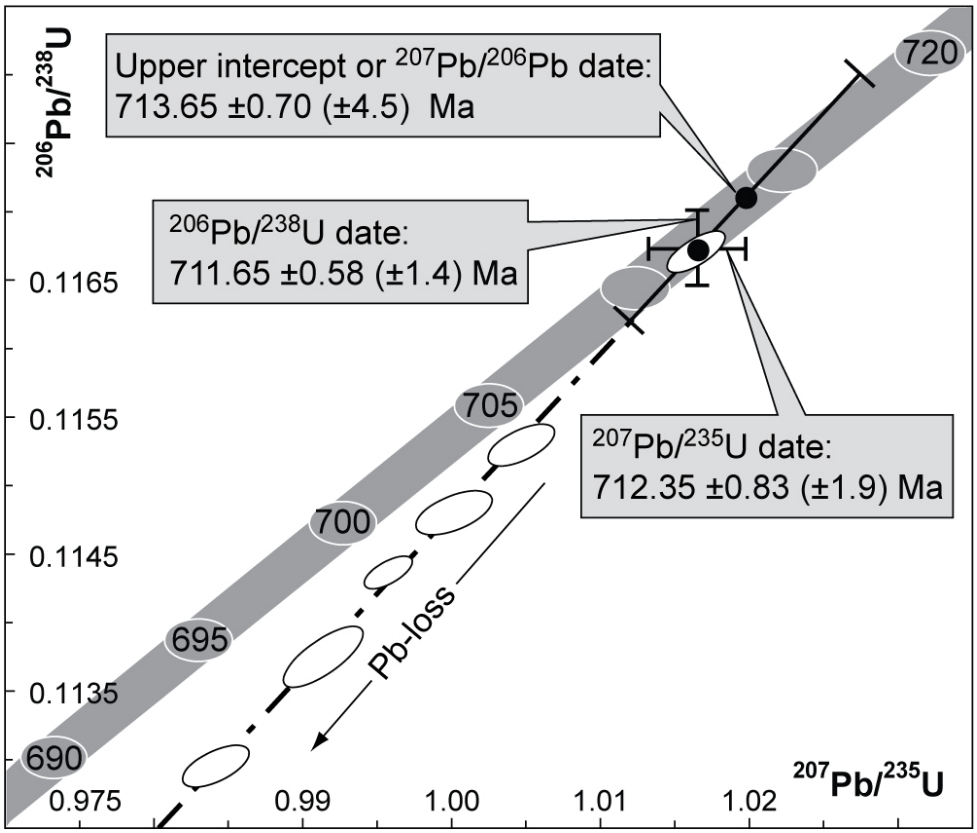

Figure. 2. Schematic U-Pb concordia diagram illustrating the $^{206}Pb/^{238}U$, $^{207}Pb/^{235}U$ and $^{207}Pb/^{206}Pb$ dates can be calculated. The data presented is a subset of analyses from sample WM54 (Bowring et al., 2007). Uncertainties are the 2σ internal uncertainties those in parenthesis are the 2σ internal plus the systematic decay constant uncertainties; 0.11% for ^{238}U and 0.14% for ^{235}U (Jaffey et al., 1971). The grey band is the concordia line plotted to reflect the uncertainties in the U decay constants. Error ellipses (white) are plotted with 2σ internal uncertainties, black error bars represent 2σ internal plus the systematic decay constant uncertainties.

3.2 'Isochron goechronometers' (Re-Os, Lu-Hf, Pb-Pb etc.).

The isochron method involves the analyses of multiple cogenetic samples (minerals or sub-samples of a rock from a stratigraphic interval) and is used when an initial amount of daughter atoms may be present and there is the possibility of a range in Parent/daughter. This is the situation for the Re-Os, Lu-Hf and U-Pb chronometers applied to carbonates, phosphates and organic-rich shales which tend to incorporate an both parent and daughter isotopes at the time of their formation. Ideally, the isochron approach allows determination of both an age and an initial isotopic composition of the daughter element that can be used to identify its source (i.e., mantle vs crust) and track changes in seawater chemistry.

For multiple, cogenetic samples to preserve the time of system closure, samples must begin with (1) a homogenous initial daughter isotopic composition, and (2) a spread in parent/daughter ratio such that over time different samples with a range in parent/daughter will fall on a straight line whose slope is equal to $e^{\lambda t} - 1$ (Fig. 3). A typical isochron is plotted P/D_{ref} on the X axis and D^*/D_{ref} on the Y axis, where P is the number of parent atoms in sample, D_{ref} is the number of atoms of a stable reference isotope of the daughter element and D* is the total number of radiogenic daughter atoms plus initial atoms of the same isotope (amount of daughter atoms due to decay = $D^* - D_0$) (Fig. 3). At the time of sample formation (t_0) all samples should plot on a horizontal line, however as the parent decays over time (t_1, t_2, etc.) each sample will evolve along a slope of -1 and samples with higher initial parent/daughter ratio (P/D_{ref}) will be displaced the most (Fig. 3) such that the isochron rotates to a positive slope. Assuming closed system behaviour since the formation of the sample, a linear regression through the points allows calculation of the slope and y-intercept from which the age and the initial isotopic composition of the daughter can be determined (Fig. 3).

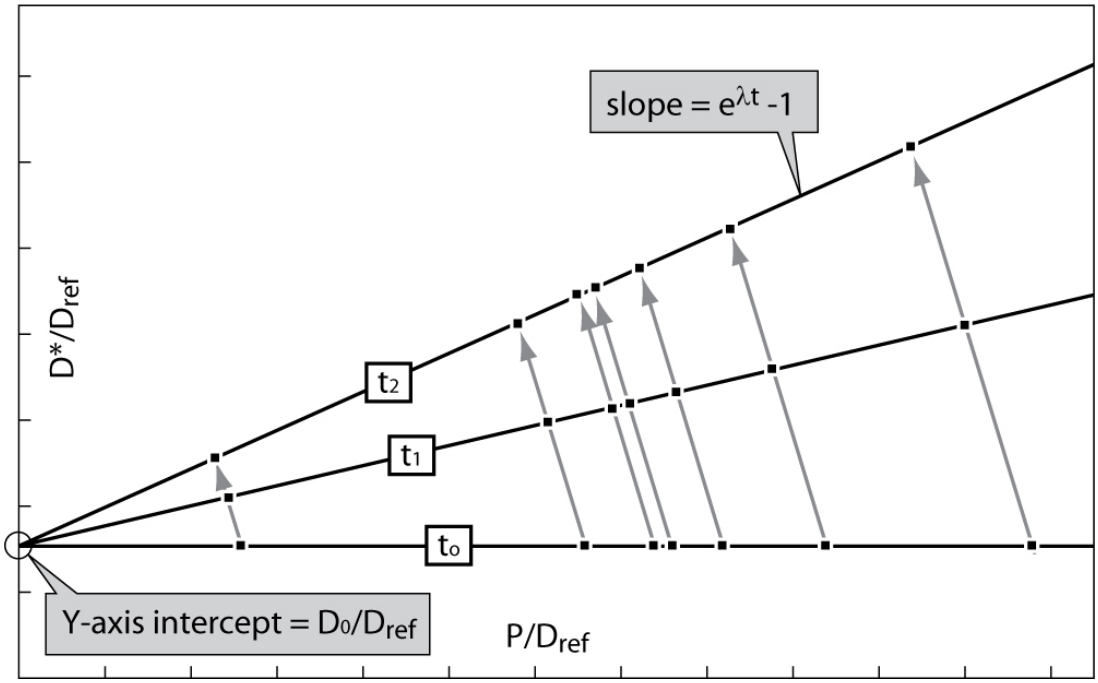

Figure 3. Schematic isochron diagram illustrating (1) the situation at t_0 where different samples from the same stratigraphic interval record a spread in parent(P)/daughter(D_{ref}) ratios but a constant initial daughter isotopic composition. D_0 is the initial amount of the daughter isotope and D* is the radiogenic daughter isotope (from decay and initial) such that the daughter produced solely from decay (since t_0) = D^*-D_0.

4. Analytical methodolgies

The majority of age constraints for Neoproterozoic strata are derived from U-Pb zircon dates therefore most of this section is concerned with U-Pb analytical methodologies. The analytical methodologies used for the 'isochron geochronometers' are somewhat similar to ID-TIMS U-Pb method however the differences are discussed below.

4.1 U-Pb methodologies

There are two main approaches to U-Pb zircon geochronology: in-situ 'microbeam' techniques and isotope dilution thermal ionization mass spectrometry (ID-TIMS). The major difference is that in ID-TIMS geochronology, zircon is dissolved and the U and Pb separated from the other elements prior to analysis whereas in microbeam techniques the zircon is analyzed by a laser or ion beam in a sectioned and polished epoxy mount or thin section.

4.1.2 U-Pb ID-TIMS

ID-TIMS analyses of zircon (either as multi-grain fractions, single grains or grain fragments) involves dissolution of the zircon in the presence of tracer isotopes called isotope dilution. For U-Pb ID-TIMS analyses the most common tracers are ^{205}Pb and ^{235}U. ^{205}Pb is an artificial tracer that does not occur in nature whereas ^{235}U is natural however its abundance to ^{238}U is assumed to be constant with ^{235}U/^{238}U = 137.88 therefore it can be used to determine the number of moles of ^{238}U and ^{235}U. Following dissolution the sample undergoes chemical purification using anion exchange chemistry that allows separation of the Zr and REEs from the Pb and U, and Pb and U from one another.

Following purification Pb and U are analysed separately by thermal ionisation mass spectrometry where the sample isotopes (^{204}Pb, ^{206}Pb, ^{238}U, etc) can be ratio-ed against the tracer isotope (^{205}Pb, ^{235}U) and the number of atoms of each naturally occurring isotope in the sample can be determined. Because the ratio of tracer isotopes to isotopes in the rock or mineral are established before any processing, inefficient separation of U and Pb and typically low ionisation efficiency of U and Pb do not affect the ratios and ultimately the age. After corrections for mass fractionation, the minor contribution of common Pb and U from the reagents, the tracer and labware, the sample ^{206}Pb/^{207}Pb, ^{206}Pb/^{238}U and ^{207}Pb/^{235}U ratios can be determined and ^{206}Pb/^{207}Pb, ^{206}Pb/^{238}U and ^{207}Pb/^{235}U dates calculated.

Optimisation of this technique means that it is now possible to date zircons with <10 pg radiogenic Pb and obtain precision <0.1% on the U/Pb ratio for single grain analyses. However, it is a very time consuming technique, each single U/Pb analyses takes several hours of mass-spectrometry, making it difficult to develop high-*n* datasets.

4.1.3 U-Pb Microbeam techniques

U-Pb geochronology by microbeam techniques has revolutionized geochronology over the past two decades. The two major techniques are Secondary Ion Mass Spectrometry (SIMS), typified by the SHRIMP (Sensitive High Resolution Ion Microprobe), and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). Both of these techniques (collectively termed 'microbeam' techniques) offer high-spatial resolution analyses using either a focused ion beam to sputter a

volume of zircon (SIMS) or a laser that is used to vaporise a volume of zircon (LA-ICP-MS). Microbeam techniques allow in-situ analysis of very small volumes and thus high-spatial resolution; a typical volume of zircon analyzed by an ion-probe is cylindrical, 20-30 microns in diameter and several microns deep, with somewhat larger volumes for LA-ICPMS (Kosler and Sylvester, 2003). In addition the analyses can be done relatively rapidly (many 10's analyses per day for LA-ICPMS and SIMS). Furthermore, these techniques allow analysis of remaining mineral for other isotopes/elements of interest (Hf, O, REE's) can be made on the same zircon grains in close proximity to the volume analyzed for geochronology.

Fundamental to the microbeam U-Pb zircon methods is use of a primary standard against which the U/Pb ratio of the unknown zircon is calibrated. For SIMS techniques this calibration involves the analyses of standard zircon to develop a calibration curve for a known U/Pb ratio (which is determined via ID-TIMS analyses) and against which analyses of unknown zircons can be compared. This is achieved through analytical sessions where a standard zircon is repeatedly analysed interspersed with analyses of unknown zircons (this is termed sample-standard bracketing). For LA-ICPMS the approach is somewhat similar manner in that sample-standard bracketing is employed in order to determine the interelemental fractionation which is then applied to the unknown zircons. In both SIMS and LA-ICPMS techniques the $^{207}Pb/^{206}Pb$ ratio is a direct measurement, for SIMS mass-dependent fractionation appears to be minimal and the measured ratio is commonly used whereas in LA-ICPMS analyses mass dependent fractionation is quantifiable and is corrected for either using sample-standard bracketing and/or using a solution with known $^{205}Tl/^{203}Tl$ ratio to correct for mass bias on Pb isotopic ratios. For further details of microbeam techniques see Ireland and Williams (Ireland and Williams, 2003) for a review of SIMS U-Pb geochronology and Kosler and Sylvester (Kosler and Sylvester, 2003) for a review of LA-ICPMS geochronology.

The benefit of the high spatial resolution provided by microbeam techniques is a tradeoff in that the precision of individual spot analyses using LA-ICPMS and SIMS is lower than ID-TIMS by approximately an order of magnitude (Ireland and Williams, 2003; Kosler and Sylvester, 2003). In-situ techniques are without question essential tools for characterizing complex (zoned) zircons from volcanic and

metamorphic rocks and for characterizing detrital populations which in some cases can provide robust estimates of the minimum age of a sequence.

4.2 Isochron techniques

Isochron techniques involve analysis of multiple samples assumed to be the same age, have a spread in parent/daughter ratio, and have remained closed systems. In order to ensure the samples are the same age and have the same initial isotopic composition it is preferable to sample laterally from the same unit (e.g., (Kendall et al., 2004)), minimizing thickness and to avoid integration of samples from a stratigraphic thickness. In some cases, such as working with core samples, this is not always possible (Kendall et al., 2006). This could be a complicating factor if there is temporal variation in the initial isotopic composition of the daughter element, and/or represents a significant amount of time, especially in condensed sections.

Sample dissolution and purification are similar to the procedures for U-Pb ID-TIMS. Prior to isotope ratio mass spectrometry samples undergo dissolution and chemical purification. For multi-element systems (such as Re-Os, U-Pb and Lu-Hf) isotopic tracers are added prior to dissolution for the isotope dilution (see above) whereas for single element systems (such as Pb-Pb), direct measurements of the isotope ratios are made. The isotopic composition is determined via thermal ionization mass-spectrometry although it is also possible to use solution mode ICPMS for most elements.

The accuracy and precision of isochron techniques is largely controlled by the quality of the rock or mineral itself, primarily a spread in initial parent/daughter ratio, and closed system behaviour. For precipitates such as carbonates and phosphates there is often no significant detrital input however this is not the case for organic rich shales targeted for Re-Os. Because the organic rich shales contain detrital material there is potential that significant concentrations of Os from multiple sources can occur. This has been demonstrated in several studies (Creaser et al., 2002; Kendall et al., 2004) however it is possible to limit the detrital Os contribution by selective dissolution of the organic component using CrO_3-H_2SO_4 dissolution approach. Kendall et al (Kendall et al., 2004) compared two dissolution methods (aqua regia vs. CrO_3-H_2SO_4 dissolution) on greenschist facies organic rich shale from the Old Fort Point Formation in Western Canada. Both dissolution techniques were used on the same

powders, however the aqua regia method yielded scattered data and a resulting "isochron" regression with an MSWD of 65 and a large "age" uncertainty (9%) in comparison to the CrO_3-H_2SO_4 dissolution method which yielded an isochron with much less scatter (MSWD = 1.2) and a relatively low uncertainty (0.8% 2σ) (Kendall et al., 2004).

5. Sources and types of uncertainty

Without an accurate estimation of uncertainty, the radio-isotopic age of a given rock or mineral is of limited value. For example, suppose a date of 618 Ma is reported for a detrital zircon from a unit that underlies a Marinoan-type glacial deposit? If the date is relatively precise (and accurate), say ± 2 Myr, then it could be inferred that the onset of glacial sediment accumulation post-dates deposition of the detrital material at 618 ± 2 Ma. On the other hand, if the 618 Ma date has an uncertainty of 100 Myr then the detrital mineral could be as old as 718 Ma or young as 518 Ma, making it of limited use. Consider the case where the 618 Ma is the $^{206}Pb/^{238}U$ date with an uncertainty of 10 Myr but the $^{207}Pb/^{206}Pb$ date is 650 ± 400 Ma. Although the two dates overlap the concordia curve (and are therefore technically concordant), the lack of precision on the $^{207}Pb/^{206}Pb$ date renders it impossible to assess open-system behaviour (such as Pb-loss or inheritance) within the limits imposed by the precision of the $^{207}Pb/^{206}Pb$ date and thus the accuracy of the $^{206}Pb/^{238}U$ date is unknown. This later example might at first seem extreme but data of this type exist in the published literature and are often cited. For example, Ireland et al (Ireland et al., 1998) published an extensive dataset of SHRIMP U-Pb zircon dates on detrital zircons from the Kanmantoo Group in Australia (it should be noted that it was not the intention of this study to constrain the timing of sediment accumulation). The units sampled included the Marino Arkose where fifty detrital zircons were analysed, the majority of which were >1 Ga (n =48). Two grains yielded $^{206}Pb/^{238}U$ dates of 649 ± 17 and 655 ± 17 which many researchers use to indicate that the Marino Arkose is ca. 650 Ma (or younger) (Halverson et al., 2005; Peterson et al., 2005; Zhou et al., 2004). The $^{207}Pb/^{206}Pb$ dates associated with these two analyses are 470 ± 440 Ma and 666 ± 307 Ma respectively. Statistically it is possible that the two zircons are ca. 650 Ma, but the probability is quite low and it is not legitimate to assume the $^{206}Pb/^{238}U$ date is an accurate estimate of the age of the zircons without considering both the $^{206}Pb/^{238}U$ and

$^{206}Pb/^{207}Pb$ uncertainties. In practical terms these two detrital zircon dates provide no significant constraint.

It is necessary for anyone who uses geochronological data to understand the various sources of error and when one must consider the total uncertainty of a given date as opposed to it's constituent parts. Although the uncertainty of each date contains an internal/random component in the total uncertainty, there are also components that are systematic (such as those related to the decay constants). In some circumstances these can be ignored offering a potential increase in resolving power. In this section we review the different sources of uncertainties and the assumptions that underlie the often quoted (or not) errors. For more detailed treatment of uncertainties in geochronology the following articles are recommended: Ireland and Williams (Ireland and Williams, 2003); Stern and Amelin (Stern and Amelin, 2003), Schmitz and Schoene (Schmitz and Schoene, 2007), and various papers by Ludwig (Ludwig, 1980, 1991, 1998, 2003).

5.1 Random/internal uncertainties

Random/internal uncertainties can be considered as those relating to the measurement of isotopic ratios of the sample, standards and blank and are used in the derivation of the radiogenic ratios. Most of these sources of random uncertainty relate to the mass-spectrometry and our ability to measure isotopic ratios with precision and accuracy. Factors such as the electronic noise of detectors place a theoretical limit on the precision which can be achieved by detecting a certain number of ions over a finite period of time. However for almost all geochronologic applications other factors such as correction for mass dependent fractionation that occurs during sample ionisation, and correction for common and/or initial parent and daughter nuclide dominate the analytical uncertainty budget. It is possible to reduce the uncertainty in the mass dependent fractionation via 'double-spiking', where two tracer isotopes of the same element (^{202}Pb-^{205}Pb, or ^{233}U-^{235}U for example) are used for real time mass fractionation correction.

The analytical uncertainties associated with U-Pb ID-TIMS dates have decreased substantially over the past decade. This is due in large part to a reduction in the common Pb levels introduced in the laboratory, as the isotopic composition of this common Pb is imprecisely determined (due to it's variability), therefore the reduction

in common Pb levels reduces the uncertainty associated with the common Pb correction. The nature of SIMS and LA-ICPMS (in 'dry' mode) analyses means that common Pb levels are intrinsically low.

5.1.1 Microbeam U/Pb standardisation

Microbeam U-Pb dating of zircons is a relative analytical technique where dates are calculated relative to a standard zircon of known age. Microbeam U-Pb data are acquired in analytical sessions where the unknown zircons are analysed in conjunction with the standard zircon of known age. The raw measured U/Pb ratio of the standard varies or "drifts" during an analytical session due to slight changes in instrument parameters. Therefore there is an uncertainty associated with the Pb/U standardisation that has to be considered. This uncertainty is on the order to 1% (Stern and Amelin, 2003), however the accuracy of its quantification is dependent upon the number and frequency with which the standard is analysed.

There are differences of opinion on how the uncertainty related to the U/Pb standardisation is factored into the total uncertainty of a date. Some groups consider that the 'standardisation' value is constant for a given session and therefore the uncertainty is systematic and needs only be considered when comparing data collected in different analytical sessions (if this is correct then the session Pb/U uncertainty can be simply added to the weighted mean uncertainty in a manner analogous to the ID-TIMS tracer calibration uncertainty). Conversely, other groups consider that the reproducibility of the standard is a reflection of the external reproducibility of all analyses and that this uncertainty should be incorporated into the uncertainty of each individual analyses of an unknown zircon (Ireland and Williams, 2003; Stern and Amelin, 2003). This results in a reduction in the MSWD and has implications for the identification of outliers (Ireland and Williams, 2003). Information regarding the approach taken to the standardisation uncertainty is often recorded in the footnotes to the data table or in the data repository but can be crucial when trying to precisely sequence rocks or calculate durations of events.

Typical internal (2σ) uncertainties for ID-TIMS $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$ dates are ca. 0.5-0.2% and ca. 0.1-0.05 % respectively, and for microbeam techniques internal (2σ) uncertainties on $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{238}U$ dates are ca. 3-5% and ca. 1-2% respectively.

5.2 Systematic/external uncertainties

Systematic uncertainties are those related to the uncertainty in absolute value of various constant parameters used in the calculation of either an isotopic ratio or in the calculation of the date itself.

5.2.1 Decay constants

One source of systematic uncertainty that affects all radio-isotopic dates are those related to the uncertainty in the decay constants (Table 1). Three approaches have been taken to determine the decay constants (the probability that a given atom will decay per unit of time) of the long-lived radionuclide; (1) direct counting; (2) ingrowth and (3) geological comparison. Direct counting involves the detection of alpha, beta or gamma activity relative to the total number of radioactive atoms. Ingrowth relies upon the quantification of a decay product that is accumulated from a quantity of high-purity parent nuclide over a well-defined period of time. Geologic comparison involves the analyses of cogeneitc materials with multiple chronometers, knowing that each chronometer should yield an equivalent date. This approach has the potential for relative intercalibration of the decay constants but accurate intercalibration requires that at least one decay constant is accurate and known with some precision. This is usually assumed to be the ^{238}U and ^{235}U due to the precision with which the decay constants have been determined (Jaffey et al., 1971) and the internal check provided by closed system zircon analyses (Mattinson, 2000; Schoene et al., 2006).

The counting experiments of Jaffey et al (1971) determined the ^{238}U and ^{235}U decay constants with uncertainties of 0.11% and 0.14% respectively. These values have been adopted for use in geochronology (Steiger and Jager, 1977). The ^{187}Re and ^{176}Lu decay constants have been determined by both direct counting experiment and through geologic comparison with the U-Pb system and uncertainties are estimated at ca. 0.4 to 0.5% (Scherer et al., 2001; Selby et al., 2007).

The incorporation of decay constant uncertainties are becoming increasingly important as both the internal precision of dates is reduced and multiple geochronometers are being used to investigate the same time intervals. The decay constant uncertainties for isochron dates are typically <20% of the total uncertainty budget, in contrast the uncertainties in the U decay constants are often >50% of the

total uncertainty budget of U/Pb ID-TIMS dates (Fig. 2). The situation for the ID-TIMS U/Pb community is that they are now often generating $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ dates that do not overlap within analytical precision and the U decay constant uncertainties have to be considered (Begemann et al., 2001; Ludwig, 2000). As the 'user' often uses these date interchangeably we are now seeing $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ age uncertainties as ± X/Y/Z and ± X/Z respectively, where X is the analytical/internal uncertainty, Y is the analytical uncertainty plus the systematic tracer calibration uncertainty and Z is the total uncertainty including X, Y and the decay constant uncertainties. This permits use of the data with the level of uncertainty that is appropriate to the problem being addressed.

5.2.2 Age of primary standards for microbeam U/Pb dating

As discussed above, U-Pb microbeam techniques rely upon measurement of the U/Pb ratio relative to standard minerals of known age. The U/Pb dates of these minerals are determined via ID-TIMS analyses with typical total uncertainties of 0.1 to 0.3% which should be propagated into the total uncertainty of the final U/Pb microbeam date. Since the systematic uncertainty related to the age of the primary standard is about an order of magnitude less than the random errors related to the dating of the unknown mineral and often not considered.

Intra- and inter-crystal homogeneity is a fundamental requirement of a zircon standard for microbeam U/Pb geochronology as the U/Pb ratio of the standard is considered invariant. Isotopic homogeneity is assessed by multiple ID-TIMS analyses on single crystals and/or crystal fragments (Black et al., 2003; Schmitz et al., 2003) and assess variability on a microgram scale, however microbeam techniques require standards that are homogeneous on the sub-micron scale. At present zircons standards are either chips of megacrysts (e.g., SL13 and 91500) or multi-crystal mineral separates from plutonic rocks (e.g., Temora). In general the zircon standards are relatively homogenous (at the level that can be detected by either microgram ID-TIMS analyses or nanogram SIMS analyses) however there has been issues with at least one of the megacryst standards (SL13) which is heterogeneous at the micron-scale (Ireland and Williams, 2003). The fact that all zircon standards are natural means they are not ideal as they are likely to be affected by zonation and/or Pb-loss and/or other (matrix related) differences which may occur below the level of quantification.

5.2.3 Calibrating tracers for isotope-dilution

For isotopic analyses that use the addition of isotopic tracers (isotope dilution), the accuracy of the tracer calibration (isotopic composition and concentrations) has a major control on the accuracy of the derived dates for a mineral or rock. Calibration of tracers is performed through admixing the tracer with another solution of known isotopic composition and, importantly, known purity. High-purity metals or salts (see (Selby et al., 2007), for details of a Re-Os tracer; Condon et al., in prep, for details of a U/Pb tracer calibration) are used as the basis the gravimetric reference solutions against which the concentration of the tracer isotope can be determined, therefore the purity of the metal or salt, and the accuracy of the weighing prior to dissolution, controls the precision and accuracy of the calibration. This total uncertainty is typically estimated at ca. 0.1%. For multi-element tracers the elemental (i.e., U/Pb) ratio is fixed therefore the uncertainty in the tracer calibration is systematic and can be ignored for the practical purposes of age determinations generated using the same tracer. This is particularly useful when attempting to determine the relative time difference between samples such as determining sediment accumulation rates (Bowring et al., 2007), or assessing synchroneity of events (Condon et al., 2005). At present it is typical that each isotope laboratory has their own tracer therefore the tracer uncertainty has to be considered when comparing dates with other labs and other techniques. Recently the U/Pb ID-TIMS community has made an effort to eliminate this inter-laboratory uncertainty through the development and calibration of a large amount of ^{205}Pb-^{233}U-^{235}U tracer for community use under the auspices of the EARTHTIME Initiative (Condon et al., in prep).

5.3 Calculating an age from multiple dates

A significant proportion of age constraints for Neoproterozoic strata are U-Pb dates on zircons from extrusive (volcanic) or intrusive igneous rocks. The final reported date and associated uncertainty are commonly *weighted mean* dates derived from a number (*n*) of individual dates on different zircons (or zircon sub-domains), and commonly calculated using the algorithms in the Isoplot software (Ludwig, 1991). This is the case for data acquired using both ID-TIMS and microbeam techniques. The weighted mean is favoured as it weights each individual an analyses (such as a single SIMS spot or single grain ID-TIMS analyses) according to its precision so analyses with a low uncertainty (high weight) contribute more to the weighted mean

than do elements with a high uncertainty (low weight). Importantly, the use of a weighted mean algorithm (or other averaging) is underpinned by the expectation of a single population with normally distributed errors. If the errors on the individual analyses are approximately equal (as is typical for microbeam U/Pb data) then the weighted mean uncertainty is proportional to $1/\sqrt{n}$, therefore high-*n* datasets can be used to reduce the overall age uncertainty for data collected on a single population with normally distributed errors. If the uncertainties on the individual analyses are variable (as is common in ID-TIMS U/Pb data with a range of Pb^*/Pb_c ratios) then the weighted mean uncertainty is controlled by the few most precise analyses, however the high-*n* dataset is critical for assessing the spread of dates from a given sample.

A common measure of the "coherence" of a data set is a statistical parameter called the MSWD (mean square of the weighted deviates; (York, 1966, 1967). A value of approximately 1 indicates that the scatter in the data can be explained by analytical uncertainties alone, values much less than 1 indicates that analytical uncertainties have been overestimated, and values greater than 1 can indicate either that the uncertainties have been underestimated or that another source of scatter, often called "geological" scatter is present. Although not often explicitly stated, an MSWD of 1 does not necessarily mean there is a single age population. Rather, it indicates that if real age variation is present, it cannot be resolved within the precision of the individual analyses.

5.4 Uncertainties as a result of geologic complexity

Uncertainty as a result of geologic complexity is the most difficult to quantify. The most common cause of excess scatter is open system behaviour resulted from either inheritance of older zircon or Pb loss. For U-Pb zircon analyses reduced errors on single analyses often exposes fine-scale variability that may reflect protracted growth of zircon crystals in a magma chamber or the effects of very subtle open system behaviour thus that high-precision analyses do not always transform into reduced uncertainties in calculated weighted mean dates.

5.4.1 Complex U-Pb zircon systematics

In the past decade errors associated with ID-TIMS analyses have dropped by almost an order of magnitude and while this is good it also exposes complexity at the <0.1 % level sometimes resulting in scatter and higher values of MSWD. It is now common

for the geochronologist to be faced with a population of zircon analyses that do not form a coherent cluster (MSWD = 1) and the crucial question is how to interpret the data to arrive at a depositional age. The advent of CA-TIMS pre-treatment for the elimination of Pb-loss has been extremely important as it gives one confidence that in many cases Pb-loss need not be considered as a cause of excess scatter. Furthermore, for Neoproterozoic rocks, the concordia curve has a shallow enough slope, and the $^{207}Pb/^{235}U$ dates measured precisely enough to be able to evaluate discordance at the per mil level, however this is not the case for microbeam U/Pb dates.

As outlined above, microbeam U/Pb dates on volcanic rocks rely upon the averaging of a relatively high-*n* dataset (10-20) of relatively imprecise (ca. 2 to 4%) U/Pb determinations to get a weighted mean date with precision ca. 1%. Underpinning these lower uncertainties is the assumption of a single population with normally distributed errors. However, it is the low precision of each analysis combined with variability of the standard analyses that bracket unknowns that often precludes the detection of subtle amounts of Pb loss or inheritance. Stated another way, if the amount of Pb-loss or inheritance is less than the precision of a single spot analyses then it cannot be detected via normal statistical proxies (such as the MSWD) therefore the assumption of a normal distribution maybe be invalid (see Fig. 4). If Pb-loss is the main source of open-system behaviour, this will have the effect of lowering the $^{206}Pb/^{238}U$ date on some analyses as well as the weighted mean $^{206}Pb/^{238}U$ date (Fig. 4). The inability to detect small amounts of Pb loss in small volumes of zircon analyzed by microbeam techniques represents a significant limitation for their application to high precision geochronology (Bowring et al., 2006).

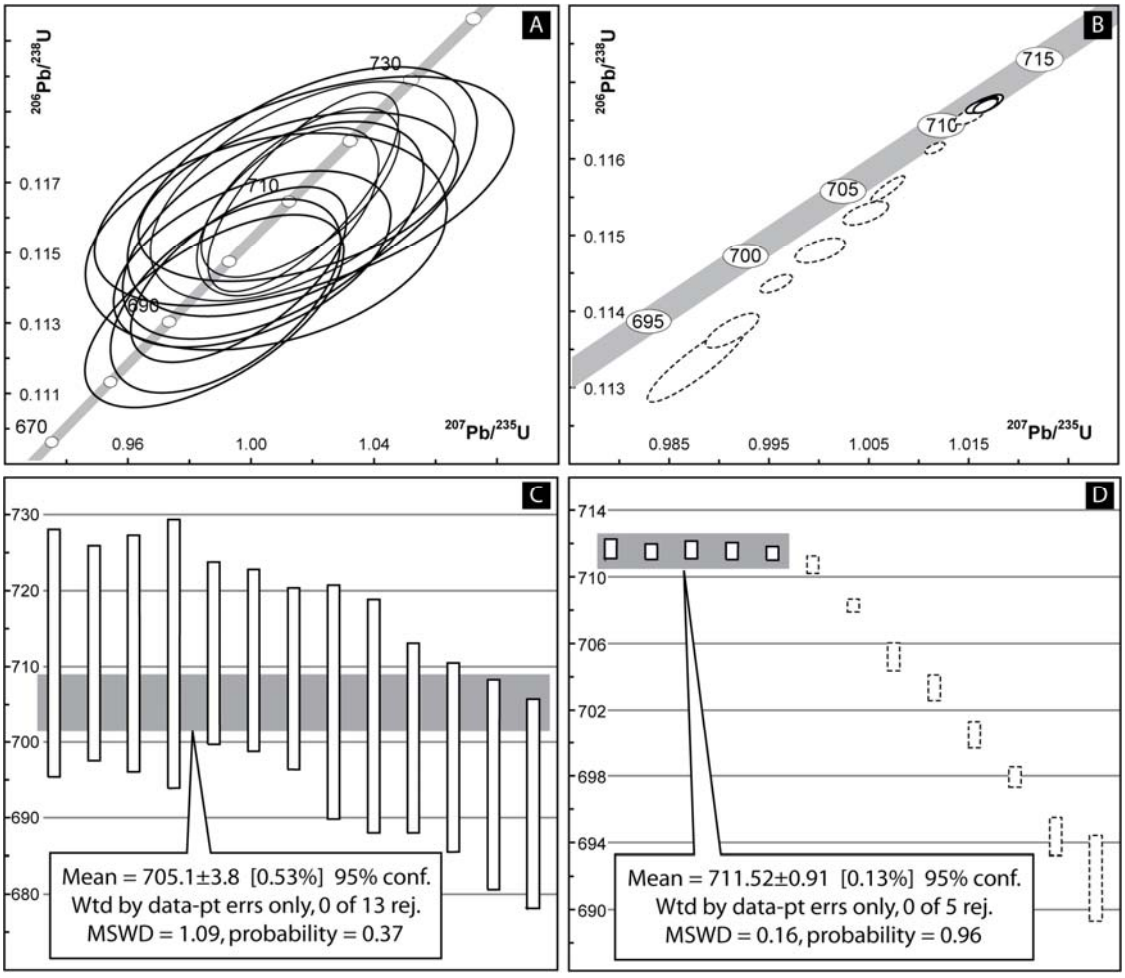

Figure 4. U-Pb concordia and weighted mean $^{206}Pb/^{238}U$ plots for a somewhat synthetic dataset. Plotted are U/Pb ratios (A and B) and $^{206}Pb/^{238}U$ dates (C and D). A and C are analyses with typical 2σ 'microbeam' (1.5 to 2.5% for $^{206}Pb/^{238}U$ and 2.4 to 5.5% for the $^{207}Pb/^{235}U$ ratio) the uncertainties whereas B and D are the exact same analyses with typical ID-TIMS uncertainties (0.06 to 0.16% for $^{206}Pb/^{238}U$ and 0.09 to 0.22% for the $^{207}Pb/^{235}U$ ratio). Weighted mean ID-TIMS $^{206}Pb/^{238}U$ date include a 0.1% uncertainty in the U/Pb of the tracer. All error ellipses and error boxes are plotted at 2σ level.

In-situ techniques are without question essential tools for characterizing complex zircons from volcanic and metamorphic rocks and for sifting through detrital populations to characterise source areas and in some cases provide robust estimates of the minimum age of a sequence. Ideally, microbeam techniques would be used to rapidly characterise a population of zircons by analyzing a small volume of many zircons, which could then be followed by conventional high-precision geochronology of selected grains.

5.4.1 Non-simple Isochrons

As outlined above, a limitation of the 'isochron geochronometers' is the lack of an independent check for 'open-system' behaviour, unlike the dual decay scheme of the U-Pb system. Most studies employ a combination of bracketing age constraints and/or a statistical measure of coherence (MSWD or uncertainty) to assess whether the system has been perturbed, however precision and amount of scatter cannot be used as a proxy for closed system behaviour. For example, organic rich sediments from the Aralka Formation, Australia, have been analysed for Re-Os geochronology using both the aqua regia and CrO_3-H_2SO_4 dissolution methods. Schaffer and Burgess (Schaefer and Burgess, 2003) used the aqua regia dissolution method and obtained a 3 point isochron (samples integrated over 1.6 m stratigraphic thickness) of 592 ± 14 Ma (MSWD << 1). An expanded dataset collected over 10m stratigraphic thickness yielded a 9 point regression and an age of 623 ± 18 Ma (MSWD = 5.2). Subsequent Re-Os analyses (on samples from a 2 m interval within the 10m interval sampled by Schaffer and Burgess., 2003) using the CrO_3-H_2SO_4 dissolution method yielded a 10 point isochron with an age of 657.2 ± 5.4 Ma (2σ internal uncertainties, MSWD = 1.2) (Kendall et al., 2006). This difference is attributed to either a sampling and/or analytical artefact related to sample digestion (Kendall et al., 2006).

It is clear from the Alralka case study that care must be taken when using coherence of a dataset as means to assess the accuracy, especially with isochrones based upon low-*n* datasets. The bottom line is that a suite of samples with the same initial ratio and a range of parent daughter ratios that evolve in a closed system yield an isochron but if a suite of samples define a statistically significant linear array one cannot necessarily infer closed system behaviour as simple mixing of two reservoirs can yield linear arrays.

6. Conclusions

(a) *There are a number of radio-isotopic dating techniques that can be employed to constrain the age of a sedimentary succession.* These include U-Pb dating of minerals from volcanic rocks which date the eruption, to Re-Os or U-Pb 'isochron' dating of organic-rich sediments or carbonates. The suitability of a given technique is governed by the geological material. Most Neoproterozoic age constraints are based upon U-Pb

zircon dates from extrusive igneous rocks, this dataset is augmented by a growing number of Re-Os, Pb-Pb and Lu-Hf isochron dates.

Each of the radio-isotopic systems have different strengths and weaknesses, maily relating to the specific type of material needed for analyses and its presence in the stratigraphic section of interest. U-Pb (zircon) dating is considered the premier geochronometer however it is of limited use in successions devoid of zircon bearing volcanics. Realising the goal of a robust and highly-resolved temporal framework for the Neoproterozoic will require exploitation of all these different methodologies.

(b) *All dates are underpinned by a series of assumptions and include a component of interpretation.* Radio-isotopic dates such as U-Pb (zircon) dates from volcanic rocks and isochron dates from sediments are based upon datasets that comprise a number of separate analyses. In the case of U-Pb (zircon) dates from volcanic rocks, the final product is usually a weighted mean $^{206}Pb/^{238}U$ date in which a number (up to ca. 15) of single $^{206}Pb/^{238}U$ dates (either single grain or single spot analyses) are weighted (based upon their associated uncertainty) and a mean calculated. Underpinning this mean date, and its lower uncertainty (about 2 to 4 times lower than the uncertainty on a single analyses), is the assumption of a single population with normally distributed errors. Isochron dates are similarly based upon the linear regression through a number of data points that are assumed to be cogenetic, have a common initial daughter isotopic composition, and that the materials analysed have acted as a 'closed system' since their formation.

(c) *The uncertainty of the date is no less significant than the date itself.* The total uncertainty of a radio-isotopic date comprises random, or internal, and systematic components. The random/internal uncertainties are related to the measurement of the isotopic ratios and the corrections applied. Systematic uncertainties are those related to the uncertainty in absolute value of various constant parameters used in the calculation of either an isotopic ratio or in the calculation of the date itself. Analytical uncertainties should reflect the ability to reproduce a given isotopic ratio and represent the minimum uncertainty that should be considered. For microbeam U/Pb dates the standard calibration is best considered as a non-systematic uncertainty and should be incorporated into each individual U/Pb date uncertainty (Ireland and Williams, 2003). If comparing dates generated using different techniques or using different calibration materials (such as mineral standards for microbeam dates of

isotopic tracer for ID-TIMS) then the systematic uncertainties related to these calibrations must be considered. An additional systematic uncertainty is that related to the decay constants used in the age calculation. These uncertainties have been determined experimentally or assessed via geological comparison with another decay scheme. There is considerable variation in the published literature regarding the treatment of the constituent parts of the total uncertainty budget. In some cases, such as using ID-TIMS $^{206}Pb/^{238}U$ dates generated using a single isotopic tracer solution, certain components can be ignored (in this case tracer calibration uncertainty and ^{238}U decay constant uncertainty). This can be useful when attempting to determine sediment accumulation rates or assess the synchroneity of events.

Although there is a desire for a date with the lowest possible uncertainty, the high-precision is most beneficial when considered in the context of the single analyses. It is the precision of the single analyses that controls our ability to assess the occurrence of 'open-system' behaviour and thus the accuracy of the final date. Although the coherence of a dataset is often used as a proxy for closed-system behaviour, the coherence is limited by the precision of the individual analyses.

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6. References Cited.

Babinski, M., Van Schmus, W.R., and Chemale, F., 1999, Pb-Pb dating and Pb isotope geochemistry of Neoproterozoic carbonate rocks from the Sao Francisco basin, Brazil: implications for the mobility of Ph isotopes during tectonism and metamorphism: Chemical Geology, v. 160, p. 175-199.

Babinski, M., Vieira, L.C., and Trindade, R.I.F., 2007, Direct dating of the Sete Lagoas cap carbonate (Bambui Group, Brazil) and implications for the Neoproterozoic glacial events: Terra Nova, v. 19, p. 401-406.

Barfod, G.H., Albarede, F., Knoll, A.H., Xiao, S.H., Telouk, P., Frei, R., and Baker, J., 2002, New Lu-Hf and Pb-Pb age constraints on the earliest animal fossils: Earth and Planetary Science Letters, v. 201, p. 203-212.

Begemann, F., Ludwig, K.R., Lugmair, G.W., Min, K., Nyquist, L.E., Patchett, P.J., Renne, P.R., Shih, C.Y., Villa, I.M., and Walker, R.J., 2001, Call for an improved set of decay constants for geochronological use: Geochimica Et Cosmochimica Acta, v. 65, p. 111-121.

Bingen, B., Griffin, W.L., Torsvik, T.H., and Saeed, A., 2005, Timing of Late Neoproterozoic glaciation on Baltica constrained by detrital zircon geochronology in the Hedmark Group, south-east Norway: Terra Nova, v. 17, p. 250-258.

Black, L.P., Kamo, S.L., Allen, C.M., Aleinikoff, J.N., Davis, D.W., Korsch, R.J., and Foudoulis, C., 2003, TEMORA 1: a new zircon standard for Phanerozoic U-Pb geochronology: Chemical Geology, v. 200, p. 155-170.

Bowring, S.A., Grotzinger, J.P., Condon, D.J., Ramezani, J., Newall, M., and Allen, P.A., 2007, Geochronologic constraints of the chronostratigraphic framework of the Neoproterozoic Huqf Supergroup, Sultanate of Oman: American Journal of Science, v. 307, p. 1097-1145.

Bowring, S.A., Schoene, B., Crowley, J.L., Ramezani, J., and Condon, D.J., 2006, High-precision U-Pb zircon geochronology and the stratigraphic record: progress and promise: The Paleontological Society Papers, v. 12, p. 25-46.

Condon, D., Zhu, M.Y., Bowring, S., Wang, W., Yang, A.H., and Jin, Y.G., 2005, U-Pb ages from the neoproterozoic Doushantuo Formation, China: Science, v. 308, p. 95-98.

Creaser, R.A., Sannigrahi, P., Chacko, T., and Selby, D., 2002, Further evaluation of the Re-Os geochronometer in organic-rich sedimentary rocks: A test of hydrocarbon maturation effects in the Exshaw Formation, Western Canada Sedimentary Basin: Geochimica Et Cosmochimica Acta, v. 66, p. 3441-3452.

Evans, J.A., Zalasiewicz, J.A., Fletcher, I., Rasmussen, B., and Pearce, N.J.G., 2002, Dating diagenetic monazite in mudrocks: constraining the oil window?: Journal of the Geological Society, v. 159, p. 619-622.

Halverson, G.P., Hoffman, P.F., Schrag, D.P., Maloof, A.C., and Rice, A.H.N., 2005, Toward a Neoproterozoic composite carbon-isotope record: Geological Society Of America Bulletin, v. 117, p. 1181-1207.

Ireland, T.R., Flottmann, T., Fanning, C.M., Gibson, G.M., and Preiss, W.V., 1998, Development of the early Paleozoic Pacific margin of Gondwana from detrital-zircon ages across the Delamerian orogen: Geology, v. 26, p. 243-246.

Ireland, T.R., and Williams, I.S., 2003, Considerations in Zircon Geochronology by SIMS: Reviews in Mineralogy and Geochemistry, v. 53, p. 215-241.

Jaffey, A.H., Flynn, K.F., Glendenin, L.E., Bentley, W.C., and Essling, A.M., 1971, Precision measurement of half-lives and specific of 235U and 238U.: Physics Reviews, v. C4, p. 1889-1906.

Kendall, B., Creaser, R.A., and Selby, D., 2006, Re-Os geochronology of postglacial black shales in Australia: Constraints on the timing of "Sturtian" glaciation: Geology, v. 34, p. 729-732.

Kendall, B.S., Creaser, R.A., Ross, G.M., and Selby, D., 2004, Constraints on the timing of Marinoan "Snowball Earth" glaciation by Re-187-Os-187 dating of a Neoproterozoic, post-glacial black shale in Western Canada: Earth And Planetary Science Letters, v. 222, p. 729-740.

Kosler, J., and Sylvester, P.J., 2003, Present trends and the future of zircon in geochronology: Laser ablation ICPMS: Zircon, v. 53, p. 243-275.

Krogh, T.E., 1982a, Improved accuracy of U-Pb zircon ages by the creation of more concordant zircon systems using an air abrasion technique: Geochimica Et Cosmochimica Acta, v. 46, p. 637-649.

—, 1982b, Improved Accuracy of U-Pb Zircon Dating by Selection of More Concordant Fractions Using a High-Gradient Magnetic Separation Technique: Geochimica Et Cosmochimica Acta, v. 46, p. 631-635.

Ludwig, K.R., 1980, Calculation of Uncertainties of U-Pb Isotope Data: Earth and Planetary Science Letters, v. 46, p. 212-220.

—, 1991, Isoplot - a plotting and regression program for radiogenic isotope data: USGS Open File Report, p. 91-445.

—, 1998, On the treatment of concordant uranium-lead ages: Geochimica Et Cosmochimica Acta, v. 62, p. 665-676.

—, 2000, Decay constant errors in U-Pb concordia-intercept ages: Chemical Geology, v. 166, p. 315-318.

—, 2003, Mathematical-Statistical Treatment of Data and Errors for 230Th/U Geochronology: Reviews in Mineralogy and Geochemistry, v. 52, p. 631-656.

Mattinson, J.M., 2000, Revising the "gold standard" - the Uranium decay constants of Jaffey et al., 1971.: EOS, AGU Fall meeting Supplement Abstact V61A-02.

—, 2005, Zircon U-Pb chemical abrasion ("CA-TIMS") method: Combined annealing and multi-step partial dissolution analysis for improved precision and accuracy of zircon ages: Chemical Geology, v. 220, p. 47-66.

Peterson, K.J., McPeek, M.A., and Evans, D.A.D., 2005, Tempo and mode of early animal evolution: inferences from rocks, Hox, and molecular clocks: Paleobiology, v. 31, p. 36-55.

Rasmussen, B., 2005, Radiometric dating of sedimentary rocks: the application of diagenetic xenotime geochronology: Earth-Science Reviews, v. 68, p. 197.

Schaefer, B.F., and Burgess, J.M., 2003, Re-Os isotoic age constraints on deposition in the Neoproterozoic Amadeus Basin: implications for the 'Snowball Earth': Journal of the Geological Society, v. 160, p. 825-828.

Scherer, E., Munker, C., and Mezger, K., 2001, Calibration of the lutetium-hafnium clock: Science, v. 293, p. 683-687.

Schmitz, M.D., Bowring, S.A., and Ireland, T.R., 2003, Evaluation of Duluth Complex anorthositic series (AS3) zircon as a U-Pb geochronological standard: New high-precision isotope dilution thermal ionization mass spectrometry results: Geochimica Et Cosmochimica Acta, v. 67, p. 3665-3672.

Schmitz, M.D., and Schoene, B., 2007, Derivation of isotope ratios, errors, and error correlations for U-Pb geochronology using Pb-205-U-235-(U-233)-spiked isotope dilution thermal ionization mass spectrometric data: Geochemistry Geophysics Geosystems, v. 8, p. -.

Schoene, B., Crowley, J.L., Condon, D.J., Schmitz, M.D., and Bowring, S.A., 2006, Reassessing the uranium decay constants for geochronology using ID-TIMS U-Pb data: Geochimica Et Cosmochimica Acta, v. 70, p. 426-445.

Selby, D., Creaser, R.A., Stein, H.J., Markey, R.J., and Hannah, J.L., 2007, Assessment of the Re-187 decay constant by cross calibration of Re-Os molybdenite and U-Pb zircon chronometers in magmatic ore systems: Geochimica Et Cosmochimica Acta, v. 71, p. 1999-2013.

Steiger, R.H., and Jager, E., 1977, Subcommission on Geochronology - Convention on Use of Decay Constants in Geochronology and Cosmochronology: Earth and Planetary Science Letters, v. 36, p. 359-362.

Stern, R.A., and Amelin, Y., 2003, Assessment of errors in SIMS zircon U-Pb geochronology using a natural zircon standard and NIST SRM 610 glass: Chemical Geology, v. 197, p. 111-142.

York, D., 1966, Least Squares fitting of a straight line: Canadian Journal of Physics, v. 44, p. 1079-1086.

—, 1967, The best isochron: Earth and Planetary Science Letters, v. 2, p. 479-482.

Zhou, C., Tucker, R., Xiao, S., Peng, Z., Yuan, X., and Chen, Z., 2004, New constraints on the ages of Neoproterozoic glaciations in south China: Geology, v. 32, p. 437-440.