6 Historical Development of Zircon Geochronology

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Profit comes from what is there; usefulness, from what is not there. - Lao Tzu

INTRODUCTION

An exact knowledge of rock formation ages is perhaps the single most important tool needed for assembling the geologic record into a coherent history. Moreover, the age of Earth and the time scale of pre-human events are central to a civilization's sense of origin and purpose. Therefore, the quest for precise and reliable geochronometers has had a scientific and a cultural importance that few other enterprises can match.

Since the beginning of the last century it has been recognized that long-lived radioactive decay systems provide the only valid means of quantifying geologic time. The uranium-lead decay system has always played a central role for several reasons. Minerals that contain very high U concentrations, although rare, are well known and easily obtained. The half lives of the natural U isotopes ^{238}U and ^{235}U are long enough to span all of Earth's history but short enough that both parent and radiogenic daughter elements could be measured in such minerals even with the methods of a century ago. After the discovery that the U decay system is paired

$$^{238}\text{U} \rightarrow {}^{206}\text{Pb} + 8\,\alpha + 6\,\beta^- \;(T_{1/2} = 4468\text{ Myr})$$

$$^{235}\text{U} \rightarrow {}^{207}\text{Pb} + 7\,\alpha + 4\,\beta^- \;(T_{1/2} = 704\text{ Myr})$$

it was realized that two age determinations could be made on the same sample using the same two elements. If the system has been closed to mobility of parent or daughter these two ages should agree, thus furnishing an internal test on the accuracy of the age. Further, the chemical coupling of the decays allows the age of the radiogenic daughter to be determined solely from its isotopic composition without knowing the parent-daughter ratio, a more difficult and less reliable parameter to measure. The wide utilization of the U-Pb geochronometer would not have been possible without the mineral zircon ($ZrSiO_4$). Zircon normally contains U in concentrations well above its host rock average but discriminates strongly against the daughter element Pb during crystallization. Also, in many cases it is sufficiently robust to preserve its original U and accumulated radiogenic Pb contents even through remelting events. Although several other minerals have similar properties, zircon is the most widespread, being a common trace component of felsic rocks. Progress in U-Pb geochronology over the last 50 years has essentially involved the development of techniques for accurate determination of the U and Pb isotopic compositions of smaller and smaller quantities of zircon, culminating in our current ability to select and analyze those parts of single zircon grains that are concordant and record single or successive growth events. This chapter recounts the history of this development and reviews its impact on our understanding of Earth's past.

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PRELUDE

Geology began as a scientific discipline near the end of the 1700s, yet for the century following there was no reliable way to measure absolute geologic time. A detailed relative time scale was constructed based on the fossil record, but only for the Phanerozoic eon. Many geologists were content with the notion of an indefinitely long time span for Earth history, in accord with the uniformitarian concept put forth by Lyell in 1830. The need for more quantitative age estimates became acute, however, after the publication of Darwin's Origin of Species in 1859. Darwin proposed that evolution by natural selection required at least hundreds of millions of years and argued that the geological record of erosion furnished evidence of such time spans.

William Thompson (Lord Kelvin) was the first to try to set quantitative limits on geologic time. He used various physical approaches including estimating tidal deceleration of the Earth's rotation, the energy consumption required to keep the Sun burning and the cooling rate of the Earth. In 1862 he announced that the Earth could be no older than about 500 Myr. He subsequently reduced this estimate to 20-40 Myr based on new information on the melting temperatures and heat transport properties of rocks (Thompson 1899). No one knew of any process that could generate heat within the Earth, so for 40 years Kelvin's arguments posed a significant problem for Darwin's theory, as well as for the lengthy time estimates of geologists. The debate pitted scientific authority against geological observation in a similar way to the later debate between physicists and geologists over continental drift. Ironically, three years before Kelvin published his final paper on the subject, his arguments had already been invalidated by Becquerel's discovery of radioactivity. Nuclear processes furnished an energy source to keep the Earth warm and the Sun burning over a time span much longer than previously thought possible (Rutherford 1905a). It was quickly recognized that long-lived radioactive decay systems also have the potential to date geologic events.

Uranium was the first radioactive element to be discovered and to be exploited for geochronology (a term coined by Williams in 1893). The discovery of radium by the Curies in 1898, along with the work of Rutherford and Soddy (1902) and others, led to the realization that U disintegration produces a chain of shorter lived radioactive daughter elements including a 'radium' and an 'actinium' series. Rutherford and Soddy (1903) published the law of radioactive decay and Ramsay and Soddy (1903) demonstrated that helium was accumulating in substances that decay by α emission. Rutherford (1905b) was probably the first to suggest that this accumulation could be used to determine the formation age of rock.

Before the discovery of radioactivity, Hillebrand (1890) had analyzed uraninites at the U.S. Geological Survey and pointed out that they contain an excess of a non-reactive gas that he called nitrogen but which was actually He. His analyses also showed that uraninites consistently contain Pb. Following a suggestion by Rutherford, Boltwood (1907) used Hillebrand's analyses to support his contention that Pb is the stable end member of the U disintegration series. He showed that the Pb/U ratios in U-rich minerals are roughly constant in unaltered samples from the same area but higher in samples from areas that were thought to be older. When he failed to find excess Pb in analyses of thorite, however, he mistakenly concluded that the Th decay series produced no Pb. Boltwood calculated the decay constant of U using the estimated decay constant of Ra, its proportion relative to U in pitchblende and the assumption of secular equilibrium. His figure of 10^{-10}/year compares reasonably well with the actual value of 1.5×10^{-10}/year. He was thus able to determine approximate ages for his samples, which ranged from 410 Ma to 2200 Ma. These were the first radiometric age determinations on minerals. They conclusively resolved the debate about the terrestrial time scale in favor of Darwin. Thus, even at its most primitive stage, U-Pb geochronology was able to provide evidence essential to the acceptance of natural selection, arguably the single most important scientific discovery.

Rutherford's suggestions inspired John Strutt (Lord Rayleigh) to measure He in uraniferous substances (including shark's teeth and bones) to assess their dating potential. He was the first to attempt dating zircon (Strutt 1909). After experimenting with various methods of decomposition, he settled on fusing zircon with borax in a platinum crucible, the same method adopted 50 years later for early U-Pb isotopic studies. His oldest sample, based on the measured Th, U and He, was a Grenville-aged zircon from Renfrew County in southern Ontario, for which he calculated an age of about 600 Ma. The real age of the specimen was probably about 1100 Ma, but Strutt realized that, because of He loss, his ages were likely to be minimum estimates. He discussed the possibility of zircon in some rocks being inherited, but pointed out that such grains would have outgassed preexisting He at magmatic temperatures. Strutt remarked that zircon showed excellent potential for dating because of its chemical inertness. The U-He method was tried for several more decades but He leakage made it unreliable.

Attempts were made to date zircon using pleochroic haloes (Joly 1907), spheres of radiation damage that are visible in thin section around radioactive mineral inclusions in biotite. Without knowing the U content of the inclusions, however, it was impossible to arrive at better than order of magnitude age estimates. Arthur Holmes, a graduate student of Strutt at Imperial College, argued that the most reliable way to determine ages would be to measure Pb accumulation in high-U minerals (Holmes 1911). In this, the first real geochronology paper, Holmes listed the necessary criteria for an effective geochronometer. He re-evaluated Boltwood's data and presented new analyses of various minerals including zircon, which he again recommended because of its stability. Using the limited data available, Holmes constructed a Paleozoic to Precambrian time scale. Remarkably, considering the large errors in decay constants and isotopic compositions, the ages mostly fell within the presently accepted period boundaries. A few years later, Barrell (1917) presented a review of geochronology that included the earliest U-Pb dates.

Because normal zircon contains U in trace concentrations and occurs only in trace amounts in rocks, attempts to date it chemically were not pursued further for forty years. Instead, efforts concentrated on more radioactive minerals such as uraninite, thorite and monazite. Holmes remained a tireless promoter of the U-Pb method of dating. Largely through his efforts, by the late 1920s the Phanerozoic time scale was broadly delineated with absolute ages for the era boundaries accurate to within 20% or better (Holmes and Lawson 1927).

For fifty years, U-Pb ages were determined by chemical analyses of total U and Pb contents. The fact that elements can have different isotopes (different numbers of neutrons in their nuclei) was postulated independently by Soddy and Fajans in 1913. J.J. Thompson separated the isotopes of neon in an electric field the same year. The first thermal ionization magnetic mass spectrometer was constructed by Dempster (1918) who used an electrometer detector to observe ^{23}Na and ^{39}K ion beams. Aston (1929) used a photo-plate detector to make the first measurement of an isotopic ratio from radiogenic Pb. The sample had been extracted from a Norwegian broggerite (thorian-uraninite) specimen, converted to liquid lead tetramethyl at the Carnegie Institution of Washington (CIW), and shipped to Aston at Cambridge University. The experiment was in fact delayed a year because the first sample tube broke in transit. After analyzing a second sample, Aston noted that the relative proportions of the exposure lines for masses 206, 207 and 208 respectively were about 100 : 10.7±3 : 4.5±2. As he had previously determined that the dominant isotope in Pb ores is ^{208}Pb, he suggested that the ^{207}Pb from broggerite must contain a radiogenic component. Therefore ^{207}Pb must be the end product of decay of the 'actinium' series. In a companion paper, Rutherford (1929) deduced from Aston's data that the parent of this decay series must be ^{235}U. Using the Pb isotopic composition and a guess of about 1 Ga for the age of the broggerite, he estimated a value for the ^{235}U decay constant. Considering also the relative activities of the 'radium' (^{238}U) and 'actinium' (^{235}U) series he was able to calculate an isotopic abundance for ^{235}U, obtaining a value that was in error by only about a factor of 2. From this he suggested an upper limit on the Earth's age of 3.4 Ga, based on the assumptions that U production ceased when Earth separated from the Sun and that ^{235}U, with an odd number atomic weight, was unlikely to have been produced in greater abundance than the even numbered ^{238}U. No closer estimate of the Earth's age would be forthcoming until the mid-1950s. Although luck was a large factor in the accuracy of Rutherford's result, deducing the age of the Earth from such a thin shred of evidence stands as a brilliant feat of scientific imagination.

Aston's broggerite data were interpreted by Fenner and Piggot (1929), who had prepared the original Pb sample, to indicate an age of 900 Ma. Aston continued to analyze radiogenic Pb and the implications of his data for determining geologic ages were discussed by Grosse (1932), who furnished new estimates of the U isotopic composition and the ^{235}U decay constant, although these were still substantially in error. The ^{235}U isotope was finally detected by Dempster (1935). However the photographic method used was not sensitive enough to measure its relative abundance. Rose and Stranathan (1936) measured Pb isotopic compositions in various uraninites by intensity readings of hyper-fine structure lines from Pb optical emission, although this novel method was of limited usefulness since it required about 4 g of Pb. These authors were perhaps the first to suggest that, because the ^{207}Pb/^{206}Pb ratio is relatively insensitive to parent-daughter mobility, it could be used as a more robust age indicator than Pb/U.

The modern era of geochronology began in 1938 with Nier's development of quantitative mass spectrometry. He used a 180° instrument as had Dempster and Aston but with an electrometer vacuum tube detector, which was much more suitable for quantitative measurements than the photographic plate or older electrometer designs (Nier 1981). Nier was the first to determine the precise isotopic abundance of ^{235}U as well as that of ^{234}U (Nier 1939a). His initial values of 139±1% for ^{238}U/^{235}U and 17,000±10% for ^{238}U/^{234}U are within error of present day estimates. He used these data to calculate the first accurate decay constants for ^{235}U and ^{234}U. Nier also performed the first precise measurements of isotopic compositions of radiogenic Pb (Nier 1939b, 1941) and of common Pb (Nier 1938; Nier et al. 1941). The samples were converted into PbI vapor and ionized by electron bombardment. Analyses took "less than two days and less than six mg of lead are consumed in the process" (Nier 1939b, p. 155). Precisions on isotopic ratios were about 1% or better (Nier 1939a,b). A wide range of uraninites were investigated, as well as thorite and a cyrtolite (metamict zircon). Nier discussed the problem of correcting for common Pb and showed again how the most accurate ages could be calculated from the radiogenic ^{207}Pb/^{206}Pb ratio. He pointed out that his oldest ^{207}Pb/^{206}Pb age, 2200 Ma from a uraninite in Manitoba, was older than the then accepted age of the Earth. Nier's subsequent development of the 60° sector mass spectrometer, with lighter and cheaper magnets, made mass spectrometry accessible to many more laboratories and greatly aided the development of all forms of isotope work.

At the time of Nier's initial investigations, the oldest mineral considered to have been reliably dated gave 1750 Ma (Holmes 1937). Subsequently, by solving the growth curve equation for various Pb compositions, which Nier had measured on Pb ore deposits of different ages, Gerling (1942), Holmes (1946) and Houtermans (1946) independently calculated ages for the Earth in the range 3000-4000 Ma. As late as 1954, the oldest known mineral ages (from monazite) were only about 2600 Ma. The true breadth of the planetary time scale was finally established by Patterson (1956) from Pb isotopic analyses of meteorites. His measurement of 4550±70 Ma remains in agreement with current more precise estimates (Amelin et al. 2002).

ISOTOPIC DATING OF ZIRCON – 1955 TO 1973

After the outstanding success of Nier's initial studies World War II intervened. Work on uranium became focused on nuclear energy and there was little further activity in U-Pb geochronology for the next 15 years. A review of the U-Pb method by Kulp et al. (1954) listed only 28 published isotopic dates, most of which were from Nier's original papers. Only seven of these were considered to be accurate to within 5 per cent. The authors concluded optimistically, however, that "it would be wrong to conclude that the ultimate has been achieved" (Kulp et al. 1954, p. 364). They predicted that Pb measurements should approach the "phenomenal accuracy" of 2 percent in the near future.

Interest in dating zircon by the chemical Pb method was awakened by Larsen et al. (1952)

working at the United States Geological Survey. Larsen recommended zircon as a geochronometer because of its high (although trace) U content, resistance to alteration and the large difference in ionic radii between Zr^{+4} (0.84 Å) and Pb^{+2} (1.32 Å) in 8-fold coordination with O, which meant that zircon would probably contain no primary Pb. Because mass spectrometer methods required at least several milligrams of Pb for an analysis, isotopic dating of typical zircon would need to use on the order of 100 g from about a ton of rock. Larsen therefore preferred measuring the total Pb by atomic emission and the U by α counting (Pb-α method), which required much less than a gram of zircon. Detailed equations for calculating chemical Pb ages according to the proportion of U to Th had been worked out by Keevil (1939) and the U decay constants were more precisely measured by Fleming et al. (1952). The oldest sample dated by Larsen et al. was from Renfrew County, Ontario. This gave an age of 900 Ma, an improvement over the helium dating of zircon from the same area by Strutt (1908). The Pb-α method was popular during the 1950s and produced some important results (e.g., Webber et al. 1956). However, the zircon ages had a precision of only about 10%. Such results demonstrated that zircon might prove much more useful if methods could be found to precisely measure the parent and daughter isotopes on smaller amounts of sample.

Larsen's work attracted the interest of a group at the University of Chicago where graduate students Clair Patterson and George Tilton (Fig. 1) were determining U and Pb concentrations in meteorites under Harrison Brown. They had developed methods for measuring microgram and sub-microgram amounts of those elements by isotope dilution (ID). This involves mixing the sample with a known quantity of what is ideally a single non-radiogenic isotope of the element to be measured. This is called a spike and is usually prepared in a large isotope separator. Once sample and spike are mixed, the sample weight can be determined by measuring the ratio of its isotopes relative to the spike isotope, after subtracting off the proportion of spike isotope in the sample (Hayden et al. 1949). This work was possible because Brown's group had access to the advanced thermal ionization mass spectrometer (TIMS) laboratory of Mark Inghram in the physics department. The ID-TIMS method was especially important for Pb because it permitted accurate isotope analyses on microgram-size samples instead of the milligram amounts required in the PbI vapor method previously used by Nier.

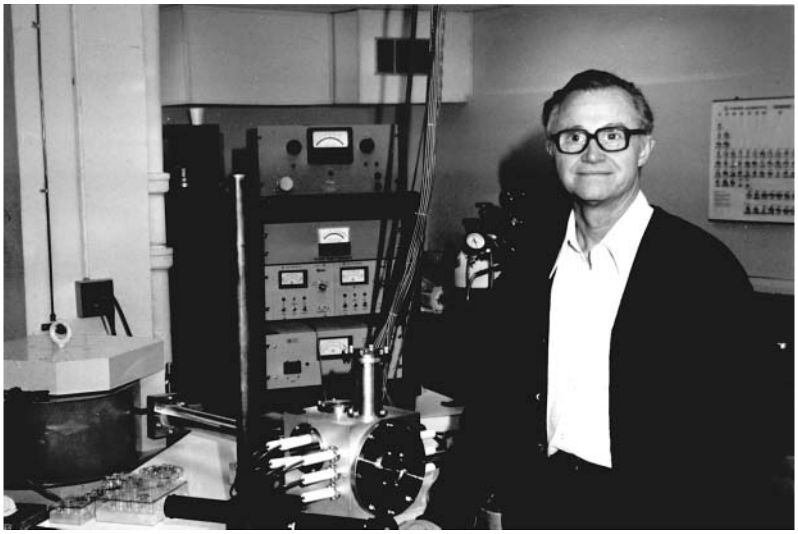

Figure 1. George Tilton in 1979 during a sabbatical return to the Carnegie Department of Terrestrial Magnetism.

On a trip to Washington, Brown met Larsen and recognized immediately that the methods already developed at Chicago would be a vast improvement over the alpha-lead method that Larsen had initiated. As a result, a group was formed with Larsen, Brown, Patterson, Tilton, and Inghram to measure a zircon age with corrections for the Pb isotope composition. Larsen provided the Chicago group with mineral separates from a granite in the Grenville province of southern Ontario. They analyzed a variety of minerals, but zircon and sphene (titanite) were the only ones in which Pb was sufficiently radiogenic to calculate a reliable age (Tilton et al. 1955). The two U-Pb ages for zircon (1030 Ma and 1060 Ma) were only slightly younger than the ^{207}Pb/^{206}Pb age of 1090 Ma, indicating that there had been little parent/daughter disturbance. These results agreed closely with previously measured ^{207}Pb/^{206}Pb ages (Nier 1939b, Nier et al. 1941) and chemical Pb ages (Ellsworth 1931) on uraninite samples from the area.

After graduating from Chicago, Tilton left to join the isotope group at the CIW, established by Thomas Aldrich and Gordon Davis. George Wetherill (another Chicago graduate) then arrived, followed by Stan Hart, Al Hofmann and Tom Krogh. The group set out to test the validity of age determinations by cross-comparing the systems U-Pb, Th-Pb, Rb-Sr and K-Ar. The work included extensive measurements on zircon of different ages from different areas (Tilton et al. 1957). Some of this work was used to determine better decay constants for ^{87}Rb (Aldrich et al. 1956) and ^{40}K (Wetherill et al. 1956), but the 1957 paper was also seminal for subsequent developments in the field of zircon geochronology. The authors pointed out that zircon often shows evidence of discordance (disagreement between the ^{206}Pb/^{238}U and ^{207}Pb/^{235}U ages), and discussed its possible causes. They noted that discordance tended to be greater in older samples and was associated with increased amounts of common Pb. They associated it with accumulated radiation damage, although an annealing experiment on metamict zircon showed that little Pb was lost during recrystallization. They concluded that zircon discordance was probably due to Pb loss caused by some post-crystallization geologic event. They also remarked on the presence of cores in zircons, which could potentially contribute an older inherited age component. Trying to understand and interpret discordance in zircon was to preoccupy U-Pb geochronologists over the next quarter century.

U-Pb isotopic data from zircon and other minerals became easier to assess following Wetherill's (1956a) introduction of the concordia diagram, in which the two daughter/parent isotope ratios (^{206}Pb/^{238}U and ^{207}Pb/^{235}U) are plotted against each other. The concordia is the locus of compositions for which the two U-Pb decay systems give the same age. This followed efforts to understand discordant but linearly correlated U-Pb data on monazites and uraninites from Canada and Africa (Ahrens 1955a,b; Wetherill 1956b). Assuming a simple two-stage history, the upper concordia intersection of a best-fit line through a data array should give the crystallization age of the zircon while the lower intersection should give the age of isotopic disturbance (Fig. 2). A variant of this diagram in which radiogenic ^{207}Pb/^{206}Pb is plotted versus ^{238}U /^{206}Pb was introduced by Tera and Wasserburg (1972). It has the advantage that the two variables are only weakly correlated.

Tilton (1960) noted that analyses of late Archean zircon from several different continents loosely defined a Pb loss line with a lower concordia intercept age of about 600 Ma, although there was little or no evidence for a geologic event of this age having affected the samples. He proposed that radiogenic Pb slowly diffuses out of zircon crystals over their entire history. Building on work by Wasserburg (1954) and Nicolaysen (1957), Tilton presented a mathematical model for this process where Pb loss was considered to result from intrinsic properties of zircon rather than environmental influences. Wasserburg (1963) and Wetherill (1963) derived more elaborate models in which the diffusion constant increases with the amount of radiation damage but these produced curves that were broadly similar to Tilton's. Since continuous diffusion produces a discordia that differs from a straight line only when Pb loss exceeds about 80% (Fig. 2), this mechanism of Pb loss was difficult to confirm, although as Tilton (1960) pointed out, the model predicted a unique Pb loss trajectory for a given age and could not apply in cases where the lower concordia age differed from that predicted by the model. Nevertheless, the continuous diffusion idea was very influential and de-

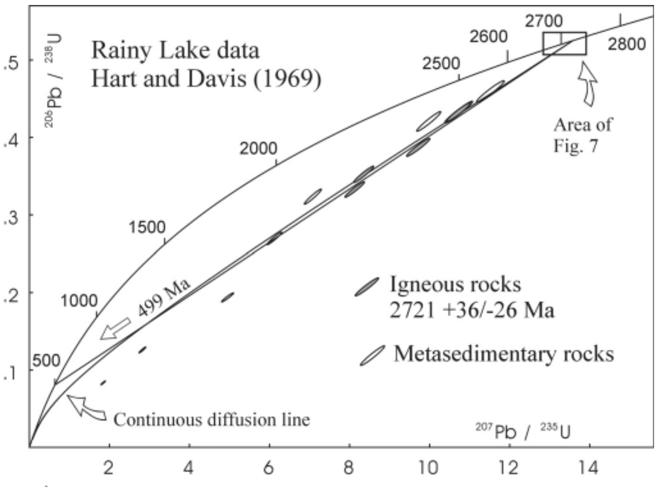

Figure 2. U-Pb concordia diagram showing episodic and continuous diffusion (Tilton 1960) Pb loss models fitted to moderately discordant zircon data from igneous rocks in the Rainy Lake area (Hart and Davis 1969). The concordia age is calculated using presently accepted U decay constants.

bates about the general validity of episodic versus continuous Pb loss models continued for over twenty years following Tilton's paper.

There were some cases in which discordance appeared clearly related to episodic Pb loss. Zircon data from gneisses in Minnesota defined a line with an upper concordia intercept age of about 3550 Ma, the oldest terrestrial age determined at that time, and a lower intercept age of 1850 Ma, which agreed with Rb-Sr and K-Ar biotite ages for metamorphism in the area (Catanzaro 1963). However, other studies of metamorphic resetting gave ambiguous results. Effects of contact metamorphism were tested by Gastil et al. (1967) using the Pb-α method and by Davis et al. (1968) with isotopic dating. In both cases significant Pb losses were observed, although the age of Pb loss could not be determined in the Pb-α study, and in the isotopic study resetting was accompanied by morphological changes in zircon, suggesting that the observed discordance may have resulted from mixing metamorphic overgrowths with older zircon. Aldrich et al. (1965) found no measurable effect on zircon that had been through amphibolite facies metamorphism, while Kuovo and Tilton (1966) found only minor thermal resetting of zircon from a xenolith in a granitoid pluton. Catanzaro and Kulp (1964) argued that discordance in zircon from the Beartooth, Little Belt and Santa Catalina Mountains was due to Pb loss caused, in some cases by metamorphism, in others by groundwater leaching. By analyzing zircon from weathered parts of the Archean gneiss dated by Catanzaro (1963), Stern et al. (1966) demonstrated that zircon could lose 50-85% of its radiogenic Pb even at ambient temperature. Such open system characteristics were evidently related to the metamict state of the zircon. For example, Pidgeon et al. (1966) showed that up to 85% of radiogenic Pb could be leached from metamict zircon in a hydrothermal salt solution with only minor loss of U whereas annealing greatly reduced Pb loss (Pidgeon et al. 1973). Shukolyukov (1964) suggested another radiation-related episodic Pb loss model in which Pb atoms are displaced into micro-fractures by alpha recoil, from which they can be leached. Goldich and Mudrey (1972) used this mechanism to explain how radiogenic Pb might be lost due to pressure release during regional uplift, possibly the cryptic event recorded by lower intercept ages.

The successes and frustrations in trying to date a variety of igneous and metasedimentary rocks using early methods were summarized by Hart et al. (1963). Despite uncertainty about the Pb loss mechanism it seemed clear that for many igneous rocks upper concordia intercept ages approximated crystallization ages. Silver and Deutsch (1963) carried out a detailed study of zircon from a Mesoproterozoic granite, demonstrating that U and Th concentrations varied considerably within and between grains from a single rock sample and that greater discordance correlated with higher radioactivity. They concluded that the primary cause of discordance was Pb loss, not U gain and that whether the loss was episodic or by continuous diffusion (although Silver was a strong advocate for episodic loss), it was promoted by radiation damage. Most importantly, they noted that cogenetic zircon fractions of different grain size and magnetic susceptibility can have variably discordant compositions which broadly define a discordance line. This paper was extremely influential over the next two decades because it provided a method for determining primary ages by generating arrays of variably discordant data that could be extrapolated to concordia. The accuracy of these ages was limited by the degree of concordance achieved, scatter about the discordance line and uncertainty about whether linear extrapolation was valid in many cases. Such considerations often produced errors of tens of million years for zircon crystallization even when it was possible to determine ^{207}Pb/^{206}Pb ages with precisions of a few million years.

Another problem with zircon dating is inheritance, although in favorable circumstances inheritance can also provide important age information on protoliths. Zircon is usually dated to determine the age of its host rock, but it is a leap of faith to assume that both are the same. If ages measured on concordant zircon fractions of different morphologies agree, this is normally taken as sufficient evidence that the zircon does date the rock. Producing a discordia with little or no scatter outside of experimental error is a less reliable indicator. Zircon fractions from some igneous rocks, however, yield scattered ages that are clearly older than the rock itself. This inheritance arises because zircon grains can survive episodes of partial melting with little or no effect on their U-Pb systems. The physical persistence of zircon through crustal melting events was demonstrated by Poldervaart and Eckelmann (1955) who documented core-overgrowth relationships in zircon crystals from anatectic granite. Some of the earliest accounts of inherited zircon ages are by Pasteels (1964) from a xenolith-bearing granite in the Swiss Alps and by Stern et al. (1965) who reported anomalously old zircon xenocrysts in a quartz diorite from the La Sal Mountains, Utah. Small amounts of inheritance were also noted by Grauert and Arnold (1968) in zircon from orthogneisses in the Swiss Alps. Older zircon cores were identified by Köppel and Grünenfelder (1971) and Gulson and Krogh (1973) in rocks from the Swiss Alps and by Pidgeon and Johnson (1974) and Pankhurst and Pidgeon (1976) in Scottish granites. In most of these cases the inherited component was fairly minor or it showed a roughly uniform average age that was much older than the age of igneous emplacement. Assuming a single age of inheritance and negligible post-igneous Pb loss, an emplacement age can be determined from the lower concordia intersection of the best fit line to the array of data, the upper intersection giving the age of the inherited component (Fig. 3). The linearity of these data from multigrain zircon fractions was taken as evidence that this simple model is valid. However, later single-grain dating on some of these samples showed that the averaging effect of large zircon fractions can preserve linearity even if there are diverse ages of inheritance, and concordia intersections may not be meaningful (Williams 1992).

Early researchers considered inheritance to be less of a problem than discordance, although Coppens et al. (1965) pointed out that analytical methods of the time, which required analysis of fractions containing 10^4-10^6 grains, would make inheritance difficult to avoid. This paper presented age results from single zircons using a method developed by Durand (1962) and Kosztolanyi (1965) for enhancing Pb ionization from zircon fixed to a filament with hydrofluoric and phosphoric acid. Coppens et al. (1965) observed that ^{207}Pb/^{206}Pb ages increased to a plateau and ^{204}Pb dropped to low levels as the temperature was increased, suggesting that Pb contaminants evaporated at lower temperature than radiogenic Pb in the crystal. This was a forerunner to the Kober evaporation method introduced two decades later (see below). At the time it was never strongly pursued, perhaps because the limited sensitivity of mass spectrometers made it difficult to determine Pb isotopic ratios to better than about 10%.

Interpreting ages of detrital zircon in sedimentary rocks was a problem of still greater complexity. In one of the earliest studies, bulk zircon fractions from North American beach sands (LeDent

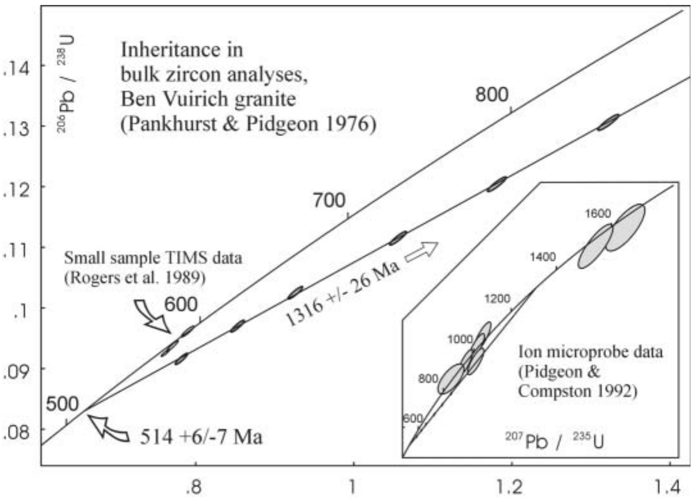

Figure 3. Inheritance mixing line based on data of Pankhurst and Pidgeon (1976) from the Ben Vuirich granite in Scotland. In a later ion microprobe study on single zircon grains (inset) these data were found to result from mixing concordant zircon xenocrysts, with ages ranging from 950 Ma to 1700 Ma, with 590±2 Ma zircon from the pluton (Rogers et al. 1989).

et al. 1964) and a Cambrian sandstone (Tatsumoto and Patterson 1964) were analyzed with the aim of determining the average age of rocks in the drainage basins and relating this to the growth rate of North American crust. There were few measurements and considerable uncertainties about the degree and time of Pb loss, but the authors found the data to be consistent with primary formation of the bulk of the North American continent between 3.0 Ga and 1.0 Ga. Pidgeon (1969), working at the Scottish Universities Reactor Centre, analyzed zircon from schist and quartzite from the Dalradian sequence in Ireland. This gave a quasi-linear array of discordant data with lower concordia intercepts of 400-500 Ma, which was the same age range that he found for granites in the region. Upper intercepts gave 1.3-1.6 Ga but Pidgeon pointed out the problem in distinguishing whether the linear array had been generated by partial Pb loss from a uniform aged source or was an artifact of mixing zircon populations with different ages.

The Swiss Federal Institute of Technology in Zürich (ETH) became an early center for zircon geochronology. Consequently, much work in the 1960s and 1970s was focused on some of the most complex rocks: polymetamorphosed gneisses from the Alpine fold belt. The survival of Precambrian zircon U-Pb ages through a later high-grade thermal event was first reported in early studies of paragneisses from the Swiss Alps (Pasteels 1964, Grünenfelder et al. 1964). More detailed work was carried out by Grauert and Arnold (1968), Pidgeon et al. (1970) and Köppel and Grünenfelder (1971) all of whom noted that highly discordant zircon data from different paragneisses formed distinct quasi-linear arrays with upper intercept ages in the range 1500-2500 Ma but similar lower intercept ages of about 440-500 Ma (Caledonian). This pattern was generally interpreted as due to severe Pb loss imposed upon a zircon population of roughly uniform age during metamorphism. However, Grauert et al. (1973) found that zircon from low-grade metasedimentary rocks in the Alps also give a quasi-linear array of data with similar intercept ages to the paragneisses, although with less discordance and more scatter. Allègre et al. (1974) attempted to interpret these data patterns with a generalized model involving multi-episodic and diffusive Pb loss. They pointed out that complex Pb loss histories could produce data arrays similar to those from the Alps but with meaningless concordia intercept ages. By assuming a cogenetic population with a 4-stage history and known ages of 30 Ma (Alpine) and 300 Ma (Hercynian) for the last two stages, they concluded that the original age of the Alpine zircon was late Archean or Paleoproterozoic and the major time of disturbance was 520-580 Ma (Cadomian rather than Caledonian). As emphasized by both Grauert and Pidgeon, data interpretation on bulk fractions would always be unclear because of uncertainty over the effects of averaging heterogeneous populations. This could only be resolved by improving analytical methods to the point where it was possible to date individual grains or parts of grains that represent single-growth episodes.

Zircon analysis during this period was extremely laborious, limiting the amount of age data that could be acquired. The basic procedures for sample extraction and purification had been worked out by Tilton and Patterson in the 1950s. Because of its chemical inertness, zircon was fused with borax in a Pt crucible, then dissolved with HCl. The solution was split into two aliquots. One was spiked with ^{208}Pb and ^{235}U for concentration determinations while the other was analyzed for Pb isotopic composition. This was necessary because zircon contains a substantial amount of radiogenic ^{208}Pb from the decay of ^{232}Th, which had to be subtracted from the composition of the spiked sample. Pb was separated from each aliquot either by multiple liquid-liquid extraction using dithizone (plus potassium cyanide and other chemicals) or with ion exchange columns. Pb-sulfide was precipitated by bubbling H_2S into the solution while U (and Th) bearing solutions were purified with ion exchange columns. The large amount of manipulation and the relatively primitive clean-lab conditions resulted in Pb blanks of about a microgram.

The method of loading Pb for TIMS as the oxide or sulfide developed by the Chicago group (Tilton et al. 1955) was the most important factor in making isotopic studies of zircon possible. However, such loads still required hundreds of milligrams of zircon so that only zircon-rich rocks could be dated and fractions normally had to contain thousands of grains. A more sensitive loading method was devised by Akishin et al. (1957) who used a mixture of silica and zirconium gel with phosphoric acid, but this was not used widely outside the USSR. The single-zircon method described by Coppens et al. (1965) and Kosztolanyi (1965), mentioned above, represented another early use of ionization activators. Cameron et al. (1969) found that by loading Pb with pure silica gel and phosphoric acid, stable signals could be produced with ion yields a thousand fold greater than by using PbS. Apparently, they electron probed mass spectrometer loads that produced unusually strong Pb signals, finding silica that had probably come from the quartz rod used to scratch the inside of the H_2S reaction vessel to promote PbS precipitation. This astute observation led to precise analysis of nanogram-size Pb samples with available mass spectrometers; this was an essential precursor to further improvements in U-Pb analytical methods. It also simplified the chemical extraction procedure, because Pb no longer had to be precipitated as a sulfide. Following its introduction, the high blanks of the dissolution and extraction procedures became the major barrier to reducing sample sizes. Overcoming this became the main focus of the next phase of development.

ADVANCES IN TECHNIQUE — 1973 TO 1982

The 1960s and early 1970s saw a paradigm shift in geologic thinking: the widespread acceptance of plate tectonics as a unifying theory of Earth history. K-Ar dating was used extensively to test and elaborate the theory, especially by tying the paleomagnetic record to an absolute time scale. Zircon had not yet achieved its potential as a precise geochronometer because of analytical difficulties and a lack of understanding of how to deal with discordance. However, major developments were imminent. The work of Tom Krogh (Fig. 4), who arrived at the CIW in 1965 just as George Tilton was leaving, would be pivotal.

Significant advances usually come about because of a pressing need to solve a particular geologic problem. Krogh had been attempting to resolve a closely spaced succession of magmatic and metamorphic events in the Grenville province of southern Ontario, an historical testing ground for U-Pb geochronology. Rb-Sr whole rock data had given inadequate precision and Rb-rich minerals were susceptible to metamorphic resetting. Zircon had the potential to record both precise primary and metamorphic ages precisely but multiple testing and experimentation would have involved a prohibitive amount of work. While on a visit to the CIW from South Africa, Tony Erlank introduced Krogh to a Teflon dissolution capsule for rock powders. Krogh refined the design and produced a capsule that could support the 220°C temperature needed to dissolve zircon in HF (Krogh 1973). He also introduced a method for separation of U and Pb in small anion exchange columns, based on his experience with Rb-Sr geochronology. Together, these techniques reduced Pb blanks by three orders of magnitude and made the dissolution and separation process much easier. Another important advance in blank reduction was the perfection of the two-bottle sub-boiling still by Jim Mattinson (1971), a concept explored earlier by Krogh. This furnished a cheap and effective method for producing reagents with picogram blanks.

Krogh's synthesis of ^{205}Pb spike using a cyclotron at Oak Ridge National Laboratories was another major step forward (Krogh and Davis 1975a). ^{205}Pb does not occur in nature because it has a half-life of only 30 Myr. Use of ^{205}Pb as a spike therefore allows isotopic compositions and concentrations to be determined on the same solution. Proton bombardment of a ^{206}Pb target produces ^{205}Bi and a minor amount of ^{206}Bi. ^{205}Bi, with a 15-day half-life, is intensely radioactive but can be chemically separated from Pb in a hot cell. However, the purification would have to occur in an environment surrounded by lead bricks and in a stream of unfiltered air, raising the possibility of contaminating the spike with common Pb. Even though the prospect of success was uncertain, Phil Abelson committed $5,000 to purchase the accelerator time. The irradiated ^{206}Pb-enriched target was dissolved and an initial separation of Bi was carried out by liquid-liquid extraction. Remaining Pb was then stripped from the Bi on an ion exchange column and the ^{205}Bi left to decay to ^{205}Pb (plus a few percent of ^{206}Pb from ^{206}Bi). A concern was whether the radiation would destroy the function of the ion exchange resin, which might also contaminate the spike. Fortunately, this was not the case (although the Teflon column became extremely brittle). ^{205}Pb is also produced when ^{204}Pb absorbs neutrons in a reactor. This process was exploited by Tatsumoto who had the product purified in an isotope separator, although it could not be made as free of common Pb as Krogh's spike without prohibitive ^{205}Pb loss.

More precise determinations of the ^{238}U and ^{235}U decay constants, carried out by Jaffey et al. (1971), were essential for exploiting the potential precision of the U-Pb method. Their values are still considered to be by far the most accurately determined geochronological decay constants.

The advances in dissolution and purification methods at CIW made low blank analyses available to many more laboratories. Ten samples could be chemically processed with a few hours of bench time, whereas each sample took a full day by the old method. This probably accounts for the

Figure 4. Tom Krogh in 1973 at the Carnegie Institution in Washington.

increase in the average output of zircon U-Pb geochronology papers from less than 10 per year in the decade before 1972 to over 50 per year in the decade after (Fig. 5). By the early 1980s the zircon U-Pb method had been used to determine primary ages for major periods of igneous activity in many areas. This growing database had an important impact on the Precambrian time scale and on the interpretation of results from other geochronometers. Many zircon ages from the Canadian shield, for example, were found to be older than ages obtained by the K-Ar and Rb-Sr methods (Stockwell 1982). Like the U-Pb system in zircon, K-Ar can produce precise ages because the Ar in K-bearing minerals is generally highly radiogenic. However, it was realized that Ar can be lost from minerals by subsolidus heating events. In these cases it records the time when the minerals passed through their blocking temperatures, which in metamorphosed terranes can be substantially later than when they crystallized. Use of the ^{40}Ar-^{39}Ar step heating method (Merrihue and Turner 1966), while revealing important information about the thermal history, only in part overcomes this resetting problem. The advantage of zircon ages is that they usually record primary igneous crystallization events.

A more subtle discrepancy was found between Rb-Sr whole rock and U-Pb zircon ages. It was recognized that Rb-Sr dating of minerals was subject to metamorphic resetting, but it was commonly assumed that whole rocks would remain closed systems. This seemed to be the case for granulites. Rb-Sr whole rock ages on the Amitsoq gneisses in West Greenland (3700-3750 Ma; Moorbath et al. 1972) approximately agreed with U-Pb zircon ages (3650±50 Ma; Baadsgaard 1973) and established the area as the oldest known segment of crust. However, Rb-Sr ages in rocks of lower metamorphic grade sometimes gave younger ages than zircon. As shown later, whole rocks can be open to fluid transport of Rb and Sr along micro-fractures, although they may remain closed in 'dry' metamorphic systems such as granulites (Heaman et al. 1986). During the 1970s the whole rock Rb-Sr method remained the most popular method for dating Precambrian rocks. As multi-collector mass spectrometers were introduced in the early 1980s, whole rock Sm-Nd dating, which probably does act as a closed system in most cases, also became popular. Because the radio-

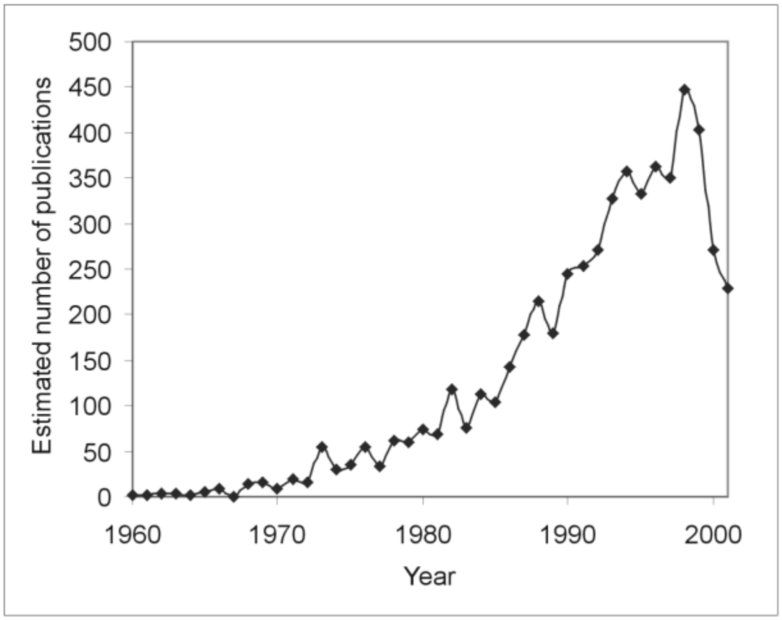

Figure 5. Publication rate of works with keywords "zircon" and "U-Pb" as recorded in the GEOREF database.

genic component is usually only a small proportion of the total Sr and Nd in rocks, however, determining an age requires construction of an isochron from analyses of several rocks with varying degrees of radiogenic enrichment. The result is commonly imprecise. Further, the differentiated sample suite necessary to generate an isochron might not be comagmatic, leading to ages that are not even accurate. This became evident in several studies after much debate (e.g., Claoué-Long et al. 1988; Cattell et al. 1984) and signaled the end of widespread use of isochron methods for dating metamorphosed rocks. Rb-Sr and Sm-Nd were supplanted as primary geochronometers by zircon U-Pb, although both decay systems are still very useful as petrogenetic tracers.

Attempts to use the full resolving power of the U-Pb system were frustrated by the limits that discordance imposed on precision and accuracy. Further, methods of data interpretation lacked rigor. Discordant arrays were often fitted by eye or using standard least-squares methods and concordia intercept errors were quoted without regard to whether the data actually defined a line. To regress isochron data, York (1969) had extended least-squares fitting to include error correlation. Ludwig (1980) adapted this method to U-Pb concordia data, while Davis (1982) incorporated Bayesian statistics in an even more sophisticated approach. To evaluate errors properly it was important to calculate a goodness-of-fit parameter such as the mean-square of weighted deviations (MSWD) or probability of fit. A poor fit usually indicates that the assumption of a simple two-stage model is invalid, either because of inheritance or multi-stage Pb loss. Also, as pointed out by Allègre et al. (1974), complex multi-stage episodes of Pb loss could result in quasi-linear data arrays with meaningless concordia intercept ages, but these would likely scatter outside of error in natural systems. Ludwig (1980) suggested dealing with the problem of poor fit by expanding the errors using Student's t, assuming a simple one-stage Pb loss model in which the excess dispersion about the line is random, such as might be caused by underestimating analytical errors. Davis (1982), on the other hand, expanded errors in proportion to discordance, assuming a random distribution of ages of Pb loss events. Both approaches are model-dependent and almost certainly over-simplistic when applied to natural zircons. A paradox in using the simple discordia model is that the apparent precision of intercept ages can be increased by analyzing the most altered samples. Such data increase the spread of discordance but are most likely to deviate from the linear model. The best, but more difficult, approach was to strive for concordance by analyzing pristine material.

The reduction in sample sizes allowed by the new analytical techniques permitted greater discrimination among zircon grains. The most cracked and altered grains could be eliminated to produce more concordant data. For many samples, however, especially from the Precambrian, it was still difficult to achieve data that were less than a few percent discordant, so much debate concerning age interpretation continued to revolve around Pb loss mechanisms. Grünenfelder (1963), working on a Hercynian granite, noted that some zircon had milky-white alteration zones with a cracked mosaic structure. Hand-picked concentrates of milky zircon contained higher U and water contents (measured by IR absorption) than associated clear zircon and gave a younger age. He suggested that the alteration was due to recrystallization of metamict zircon during the Alpine orogeny, which partially reset their U-Pb system. Gebauer and Grünenfelder (1976) elaborated on this interpretation in a study of zircon in metasedimentary rocks from southern France. Their samples ranged from chlorite to sillimanite metamorphic grade, but all of them gave quasi-linear data arrays with about the same degree of discordance. Rather than recording the age of Hercynean peak metamorphism (ca. 300 Ma), however, the lower intercepts were Caledonian (400-440 Ma). They proposed a model in which metamict crystal domains recrystallized and lost Pb during the low grade Caledonian metamorphism, then became annealed and resistant to further Pb loss during the later higher grade Hercynean event.

Grünenfelder's original observation supported a multi-phase mixing model for discordance that was later proposed by Steiger and Wasserburg (1966). These authors showed that zircon data from some Precambrian rocks, when plotted on a ^{208}Pb/^{232}Th versus ^{207}Pb/^{235}U diagram, formed linear arrays with negative lower intercept ages, but defined a normal discordia on a ^{206}Pb/^{238}U versus $^{207}Pb/^{235}U$ diagram. This was interpreted to result from mixing between a highly discordant phase with relatively high Th/U and a near-concordant phase. They reached a similar conclusion based on data from late Archean rocks with similar ages but different metamorphic histories (Steiger and Wasserburg 1969). They observed that discordant zircon data from many rocks seemed to reflect a mixing of non-metamict near-concordant phases and metamict phases that had lost much of their Pb by continuous diffusion or during low-grade events such as regional uplift.

Although high-uranium, radiation-damaged zircon was commonly found to be the most discordant, there were also cases of metamict zircon with slight or negligible discordance. Single-grain etching studies by Krogh and Davis (1974, 1975b) showed that polyphase radiation damaged zircon was susceptible to reaction with HF vapor, but undamaged zircon was not. This etching technique revealed amorphous altered domains that turned powdery-white and replaced damaged, high-U zones (Fig. 6). The altered zones contain several percent of Ca, Fe, Al (measured by electron microprobe) as well as H_2O. Krogh suggested that radiogenic Pb loss and gain of common Pb occurred when such radiation-damaged areas became altered. In his view, radiation damage does not itself cause Pb loss, although severely damaged areas can be leached, as was shown by Pidgeon et al. (1966). The main effect of radiation damage is to prepare the crystal for later alteration, which can occur by interaction with fluid at ambient temperature. The lower concordia intercepts might then represent an average age of multiple Pb loss events that affected individual zones as they accumulated sufficient damage to react with external fluid. Zircon in granitoid rocks often shows oscillatory zoning with inter-zone differences in U content of at least an order of magnitude (Fig. 6A). Holland and Gottfried (1955) documented the lattice expansion that accompanies radiation damage in high-U zones. This work grew out of attempts during the 1950s to date zircon by measuring its accumulated radiation damage (e.g., Kulp et al. 1952, Hurley and Fairbairn 1953). Differential expansion produces internal stress that often pervasively cracks the crystal (Fig. 6B) and provides access to aqueous fluid that can alter the damaged domains as documented by Krogh and Davis (1974, 1975b). Some later discussions of radiation damage in zircon are given in Ewing et al. (1987), Chakoumakos et al. (1987) and Lee and Tromp (1995).

The dependence of zircon-Pb loss characteristics on local conditions is shown by examples where discordia lines with a wide range of lower intercept ages are found from coeval rocks in the same area (e.g., Davis et al. 1985). Such observations suggest that Pb loss is not an inevitable property of zircon and potentially can be eliminating altogether. If portions of zircon grains that have escaped alteration or leaching can be identified and separated, they should produce concor-

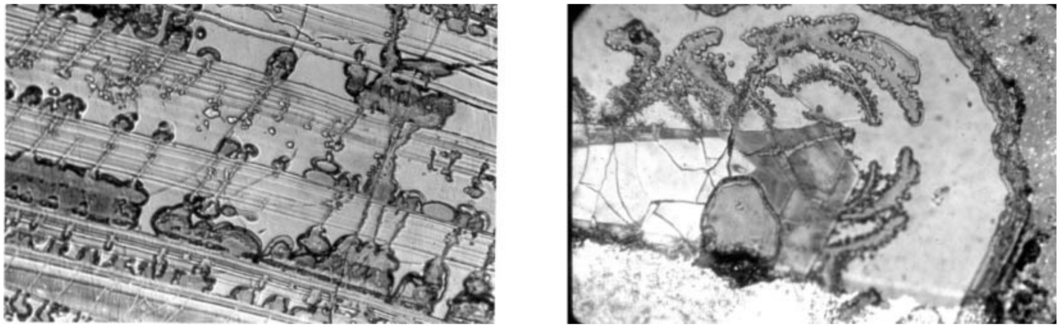

Figure 6. Optical images of alteration in zircon revealed by HF vapour etching of polished grains. (A, left) Oscillatory zoned zircon in which alteration appears to have developed preferentially in high-U zones. Alteration is localized where micro-fractures that cross the high-U zones provided access for fluid. (B, right) High-U zircon with a low-U core. Note how altered domains in the metamict outer zone are rooted at fluid-access cracks in the low-U central zone, which may have ruptured due to expansion of the damaged zone.

dant U-Pb data. In many cases careful visual observation can effectively identify altered crystals while etching with HF or NaOH makes alteration highly visible (Krogh 1994). Because most Precambrian zircon populations are highly damaged, however, dating the rare primary concordant phase usually requires the ability to analyze a few grains (or less) of zircon.

During this period, the isotope group at the Université de Paris under Claude Allègre began dating zircon at the single-grain level. The first such study was by Lancelot et al. (1976) on a charnockite paragneiss from West Africa. Bulk zircon fractions gave an age of ca. 2.05 Ga in agreement with regional metamorphism but in conflict with the Rb-Sr whole rock age of ca. 3.1 Ga. Single clear zircon crystals gave a roughly consistent age of 2.04 Ga while single brown grains gave a scattered array pointing toward ca. 3.0 Ga. Analyses of single grains were thus able to reveal an older age component that was not evident in the bulk analyses. A subsequent paper by Michard-Vitrac et al. (1977) applied single-grain analysis to early Precambrian rocks. Zircon from clasts in a metaconglomerate at Isua, Greenland, pushed the oldest terrestrial age back to 3769±11 Ma. The single-grain approach was first applied to detrital zircon by Gaudette et al. (1981) who sampled a Cambrian sandstone in the eastern United States. Only 5 single zircon grains were analyzed, however, the main aim of the study being to resolve age differences by identifying distinct detrital populations based on color and morphology then dating them in bulk. The single-grain analyses fell within the cluster of bulk fraction compositions, which scattered along distinct mixing lines although most of the analyses may have been significantly affected by secondary Pb loss as well as mixing from multiple sources. Single detrital zircon dating was applied more successfully to metaturbidites of the Archean Slave and Superior provinces by Schärer and Allègre (1982a) and Gariépy et al. (1984), respectively. As shown by later studies, their data roughly but correctly reflected the age distribution of probable source rocks.

Early single-grain studies unfortunately suffered from secondary Pb loss as well as analytical blanks that were too high to permit precise age determinations. Such problems generally limited errors to about ±30 Ma in the above Archean studies. The data were useful, however, for distinguishing widely spread age components and the studies demonstrated the utility of analyzing zircon from complex rocks at the single-grain level. This approach was carried a step further with the analysis of fragments of a single zircon, albeit a large one (500 μg), by Schärer and Allègre (1982b). The zircon, from a syenite in the Pikes Peak batholith, was broken into 11 fragments that were dated individually and the results compared to those from smaller single grains. The main importance of this study was in showing that the zircon fragments produced a much broader spread of data than the whole grains. In particular, some fragments were concordant or near-concordant, whereas all the single whole-grain analyses were quite discordant. As stated by the authors: "These results suggest that the discordancy phenomenon should be discussed in terms of domains within a single grain and not in terms of grain dimensions or volume diffusion relative to grain size" (Schärer and Allègre 1982b, p. 587). This conclusion, the same as that of Steiger and Wasserburg fifteen years earlier, aptly summarized the approach necessary to solve the discordance problem. At the same time, two quite different solutions to the problem were being pursued.

RESOLUTION OF THE PB LOSS PROBLEM — 1982 TO THE PRESENT

Further advances in ID-TIMS methods

In the mid-1970s John Wood and Ken Card at the Ontario Geological Survey (OGS) along with Syd Lumbers at the Royal Ontario Museum arranged funding for a U-Pb geochronology lab at the museum under the directorship of Tom Krogh. It was a natural decision, although not without controversy, to exploit the new methods of precise geochronology developed at the CIW in order to resolve complex geologic problems that had arisen as a result of the Survey's mapping programs. The Jack Satterly Geochronology Laboratory (JSGL), named for a pioneering Ontario geologist, opened in 1977. Paul Nunes was hired to help set up the laboratory and function as the OGS geochronologist. Don Davis joined as a post-doctoral fellow in 1978 to apply the method in the western Wabigoon greenstone belt of the Superior province. Fernando Corfu arrived in 1980 and eventually carried on the program of OGS dating.

Pb blanks at the time were about 50 pg and zircon sample sizes about 1 mg. Even picking the most pristine-looking grains from low-U zircon populations would usually produce data that were several percent discordant. Although some greenstone belts were found to have developed over hundreds of million years (Nunes and Thurston 1980), results from others, such as the western Wabigoon belt, suggested time spans of less than 50 Myr. Locally, volcanic and plutonic sequences might record much shorter periods but these could not be resolved with discordant data. While mass spectrometer data from large zircon fractions were very precise, and upper intercept ages gave precisions of a few million years, in some cases these ages were shown to be inaccurate, such as plutons appearing older than their host rocks. Failing to solve such geological problems despite so much work created considerable frustration. There was ongoing discussion in the lab on how to best interpret data and a great deal of time was spent experimenting with a variety of new sample preparation and analytical techniques.

The paramagnetic response of discordant zircon, which had first been exploited by Silver and Deutsch (1963) to increase the spread of discordance using the Frantz separator, could be enhanced using the high-gradient magnetic field around a pointed soft iron wire connected to a hand-held bar magnet (Krogh 1982a). The least magnetic fraction from the Frantz thereby could be split further by testing individual grains. Low-U unaltered grains were repelled from the wire tip due to the natural diamagnetism of zircon, while grains in which only one end was altered showed a much stronger paramagnetic attraction from that end. It was observed however, that paramagnetism sometimes correlated not only with degree of alteration, but also with high-U content (a desirable feature for small samples), so concordant high-U zircon grains could not be effectively separated.

The most important advance was a method for removing the outer layer of zircon crystals by air abrasion (Krogh, 1982b). For the first time, this allowed concordant, precise data to be extracted from a wide variety of samples. Combined with careful selection, it made redundant the question of how secondary (low-temperature) discordance should be interpreted because it eliminated such discordant domains from the analyzed sample.

Krogh used fission track maps and etched grain mounts to show that many zircon crystals are surrounded by a thin high-U layer. Damage to this layer, even if it is not unusually U-rich, could easily result in alteration and Pb loss because it is directly accessible to the outside environment. Removing the primary crystal surfaces therefore seemed a promising approach for achieving concordance. The air abrasion method was inspired by a technique developed in India to prepare single crystals for X-ray diffraction. In the Krogh design, zircon is placed in a steel chamber in a circulating stream of air that exits through a fine nylon sieve. After several hours, the grains become rounded through collisions with the chamber walls. Analyses of abraded zircon from early experiments were more concordant than those of the starting material but abrasion alone often failed to eliminate all Pb loss. To achieve concordant data it was essential to choose abraded zircon grains with no visible cracks or internal alteration. The clearest, crack-free crystals with primary magmatic morphology were picked, abraded, and then carefully re-picked. Davis et al. (1982) found that the presence of pyrite during the abrasion process polished the surface of the grains, making it much easier to examine their interiors for any alteration, inclusions or fractures.

Some of the first abrasion experiments used zircon from noritic phases of the Sudbury mafic complex, which Krogh and others had attempted to date using discordant zircons. Analyses of carefully picked abraded samples are mostly concordant and show that all phases of the mafic complex are precisely coeval at 1850±1 Ma (Krogh et al. 1984). The complex is now thought to be a total crustal melt that resulted from a large meteorite impact. Application of abrasion to samples from Superior province greenstone belts resulted in a marked improvement in concordance and, for inheritance-free samples, produced more accurate ages that accord with geological relationships (e.g., Davis et al. 1982, Corfu and Ayres 1984).

When the main objective of zircon geochronology had been to define discordia, large magnetic and size fractions were often analyzed to give maximum precision. The uncertainty in the age arose mainly from having to extrapolate discordant data. After the introduction of abrasion it became clear that discordance is not an unavoidable property of zircon. It also became clear that achieving a concordant but less precise datum was better than attaining greater analytical precision with a larger sample, but one of lower quality, and be left with having to interpret discordant results. Discordance was thus eliminated as an acceptable option. However, only a minute amount of totally undamaged zircon could be separated from many rocks, especially Precambrian ones. Therefore there was an ongoing need to reduce sample sizes, which created the need for ever-lower blanks. For ID-TIMS, abrasion ended the period of acceptance of milligram-size samples. It created another cycle of innovation that led to routine precise analysis of single grains and parts of grains. This greatly reduced the problem of secondary Pb loss and enabled samples with polyphase zircon and multiple age populations to be studied more effectively.

High blanks and limited sensitivity on conventional mass spectrometers such as the Micromass 30 initially continued to limit sample selection. This situation improved dramatically during the early 1980s. The JSGL achieved a reduction in Pb blank to several picograms by including a high-temperature 6N HCl wash in the Teflon bomb cleaning procedure and by reducing bomb and column sizes. The introduction of extended geometry mass spectrometers with improved source design such as the VG54/354 and MAT260 increased ion transmission by a factor of five. For silica gel loads, ionization efficiency increases as the sample size is reduced, a virtue of many TIMS loading methods. This method therefore is even more effective for the analysis of picogram-sized samples. The Daly collector used on the VG354 proved to have exceptionally stable linearity and mass fractionation relative to electron multipliers so it began to be used routinely for all isotopic ratios, instead of the less sensitive Faraday collector.

Throughout the 1980s the JSGL hosted a large number of students and visitors who applied the new method to a wide range of geologic problems. Many of these individuals, such as Larry Heaman, Greg Dunning, Bob Tucker, Nuno Machado, Urs Shärer and later Urs Schaltegger and Fernando Corfu went on to lead geochronology labs elsewhere. The new techniques were adopted at other labs such as the Geological Survey of Canada, where Otto van Breeman assembled a team of geochronologists including Randy Parrish, Chris Roddick and Jim Mortensen, later followed by Bill Davis, who added their own innovations. Parrish (1987) introduced a design for Teflon microdissolution capsules that allowed many parallel dissolutions to be carried out inside one larger capsule. This approach was inspired by the earlier efforts of Krogh (1978) to build capsules in which zircon could be dissolved by HF vapor. Another variant was introduced later by Wendt (1991). Methods for zircon U-Pb isotopic analysis by multicollection (Roddick et al. 1987) and efficient data reduction software (Roddick 1987) were developed at the GSC. Parrish and Krogh (1987) synthesized a new batch of ^{205}Pb using the accelerator at the University of British Columbia and aliquots were sold to numerous laboratories. Automated data-reduction software and automated zircon analytical software developed by Ludwig were in routine use at the USGS by the early to mid 1980s. Fully automated U/Pb TIMS analyses for even single Phanerozoic zircons, using both commercial (VG Sector54) and custom (Ludwig, USGS) software became routine at some laboratories thus improving the time efficiency of the mass spectrometry. The database of precise zircon ages grew rapidly after 1982 and U-Pb zircon geochronology became recognized as an essential tool for understanding the record of ancient orogenies (e.g., Corfu 1993). From this time onward, progress in ID-TIMS methods would be a matter of incremental refinements in technique and improvements in understanding the zircon U-Pb system.

An outstanding example of precise U-Pb dating using abrasion is the work on the Duluth layered mafic complex, part of the Midcontinent Rift structure in Minnesota, by Paces and Miller (1993) at the U.S. Geological Survey. Multiple zircon fractions from four anorthositic and troctolitic rocks gave concordant data with ages that range from 1099.3±0.3 Ma to 1098.6±0.5 Ma. ^{208}Pb-^{232}Th isotopes were also measured and agree at the 1% level but give more discordant, scattered ages.

The Th-Pb system has never proved to be as useful as U-Pb in zircon, although attempts have been made to apply it since the earliest papers. Modeling of the U-Th-Pb system was discussed by Steiger and Wasserburg (1966). Tilton et al. (1955) noted early on that Th-Pb ages on zircon and titanite were much younger than U-Pb ages. They suggested that Th and U might be concentrated in different parts of the crystal and ^{208}Pb preferentially lost from the Th-rich phase. As seen with the Duluth data, Th-Pb discordance persists at a reduced level even for unaltered zircon where the U-Pb system is concordant. This might be due to differential loss of U (as well as Pb) relative to Th, or to the difficulty of keeping Th in solution during sample processing, which could result in poor equilibration between sample and spike. Further, the ^{232}Th decay constant is not as well determined as the U decay constants.

For mid to early Precambrian samples, by combining abrasion with reasonably careful sample selection, it was possible in most cases where the zircon population is cogenetic and has experienced only low temperature Pb loss to achieve data showing less than 1-2% discordance. An added bonus was that common Pb levels in near-concordant fractions fell to the point where they were indistinguishable from laboratory blank, showing that excess common Pb in discordant zircon is probably added at the time of radiogenic Pb loss. It was often difficult to eliminate all discordance so a common procedure in the early 1990s was to analyze two or more fractions of abraded zircon and one of unabraded grains, which would produce a more discordant datum. It was thought that this allowed correction for the small amount of residual Pb loss that affected the abraded fractions. Extensive later experience has shown, however, that near-concordant data from abraded fractions tend to agree in their radiogenic ^{207}Pb/^{206}Pb and give the correct age. The reasons for the small amount of relatively recent (<100 Ma) Pb loss are still not clearly understood. Regression with data from unabraded fractions which lie on an older Pb-loss line can in fact produce an intercept age that is spuriously high (examples are discussed in Davis and Krogh 2000). The difference is small if the best data are nearly concordant, but it can exceed the inferred error.

An alternative approach to achieving concordance in a single age population is to avoid or dissolve out altered domains by chemical attack. Krogh and Davis (1974, 1975b) and Krogh (1994) observed that a few minutes of attack by 5% HF turned otherwise invisible zircon alteration chalky-white so it could be easily avoided during picking. Mattinson (1994) used hot HF to dissolve discordant domains in Mesozoic zircons, extracting a small amount of concordant residue after a series of leaches that lasted several days. Krogh (1994) and Krogh et al. (2002) used a variation of this method on Precambrian zircon in which the extent of radiation damage was revealed by a 2-hour leach in NaOH or HF at 200°C. The few grains that show no sign of attack, once abraded, typically have U values up to ten times lower than selected high-quality untreated grains from the same population. They give data that are more concordant and that are collinear with data from grains that were abraded but untreated with acid. This result is consistent with the findings of Mattinson (1994) but is in conflict with leach results of Davis and Krogh (2000) and Corfu (2000). These authors leached non-magnetic unabraded Archean zircon in warm HF. Data from analyses of the residues are 5-10% discordant but give ^{207}Pb/^{206}Pb ages older than those of concordant analyses from unleached abraded zircons. This implies that the Pb that accumulated during the early part of the sample history is less susceptible to leaching. One explanation could be that the zircon suffered early annealing during metamorphism. Apparently zircon that remains inert to chemical attack was not affected by this process and also remained as a closed system over geologic time.

Mattinson (1987) pointed out that many zircon geochronology papers were still using inadequate error analysis. He discussed the factors limiting U-Pb age precision and emphasized the effect of uncertainty in the U decay constants. Optimal statistical methods for dealing with concordant data were devised by Ludwig (1998a, 2001). Ludwig's refinements of data analysis and reduction software, especially the ISOPLOT program (Ludwig 1998b), have been a major ongoing contribution to zircon geochronology and to a wide range of other isotopic studies.

The increased activity stimulated by the new methods opened up new environments and minerals to precise U-Pb geochronology. Zircon was found to be common in plagiogranites, providing a means to date oceanic crust in ophiolites (Dunning and Krogh 1985). Van Schmus and Bickford used zircon ages from drill cores to map the sub-surface Precambrian basement of North America (later summarized in Van Schmus et al. 1996). Metamorphic zircon, often distinguishable by low Th/U (Krogh and Davis 1973), was found to be common in high-grade mafic rocks (Percival and Krogh 1983). Other minerals besides titanite and rare earth phosphates were found to contain radiogenic Pb, for example perovskite (Heaman 1989), rutile (Richards et al. 1988) and opal (Ludwig et al. 1980). The most important of these is baddeleyite (ZrO_2), which typically has several hundred ppm U, virtually no common Pb and is not as easily altered as zircon, so it usually produces near-concordant data without abrasion. Baddeleyite was one of several U-rich minerals from lunar rocks on which ^{207}Pb/^{206}Pb ages were measured with an early ion probe by Andersen and Hinthorne (1972). It was first utilized for precise dating in ID-TIMS studies by Krogh et al. (1984, 1987). The mineral is relatively rare in terrestrial rocks but is sometimes found in mafic dikes, which often cannot be precisely dated in any other way (Krogh et al. 1987, Heaman and LeCheminant 1993). Swarms of mafic dikes are important markers in the geological record since they probably record the impacts of ancient mantle plumes and sometimes accompany continental breakup (LeCheminant and Heaman 1989, Kamo et al. 1989).

By the late 1980s, Pb blanks at the JSGL had fallen to the 1-2 pg range and single zircon dating began. This, combined with abrasion, finally allowed precise ages to be measured on single detrital zircon grains in sedimentary rocks. The first such study was carried out on Archean sandstones from the Rainy Lake area of the western Superior province. Historically this has been considered a type area for Archean geology. It was first mapped by Andrew C. Lawson in the mid-1880s, and the geologic relationships have been debated ever since. Zircons from the area, including bulk fractions from metasandstones, had been dated by Hart and Davis (1969). These early data scattered around a discordia with an upper intercept age of about 2720 Ma (Fig. 2) so individual igneous events could not be resolved. The new concordant data (Davis et al. 1989) revealed a clear pattern of discrete events over a 2728-2685 Ma age range (Fig. 7A). In the classic stratigraphy of Lawson, the oldest units were turbiditic sandstones because they appeared to be at the base of the section. However, precise concordant ages from single detrital zircon grains showed that the sandstones were some of the youngest supracrustal units (Fig. 7B). They were probably over-thrust by older rocks and structural evidence indicated that the section had been overturned. Data from else-

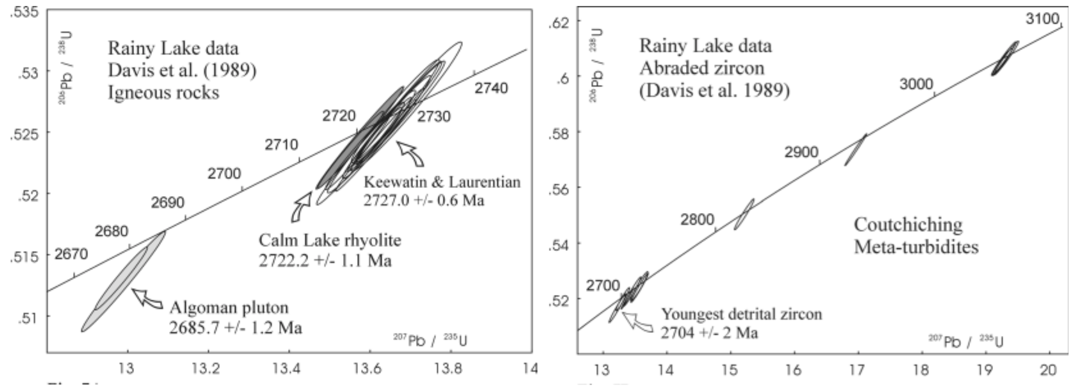

Figure 7. (A) U-Pb data on abraded zircon from igneous rocks in the Rainy Lake area, NW Ontario, Canada by Davis et al (1989). Compare to Hart and Davis (1969) data on the same units in Fig 2. (B) U-Pb data on single detrital zircon grains from Archean metasandstone in the Rainy Lake area.

where in the Superior province revealed that some other stratigraphic packages were out of sequence and supported models of thrust deformation similar to that at modern collisional boundaries (Davis et al. 1988, Corfu and Ayres 1991). Such studies helped initiate a conceptual change from regarding Archean tectonic processes as unique to the early Earth to explaining them in terms of actualistic models.

Krogh (1993) further extended the single grain method by dating single zircon cores and metamorphic overgrowths that he broke off average-size grains from the Kapuskasing structural zone of Ontario, an upthrust section within the Superior province that exposes deep levels of the Archean crust. Precise dating of such tiny fragments was only possible because of the low procedural blanks. Corfu (1987) had previously found that metamorphic zircon growth became younger at deeper paleo-levels of the crust. Krogh (1993) showed that metamorphic overgrowths surrounding metamorphic cores in zircon from amphibolites corresponded in age to metamorphic zircon cores in mafic granulites at deeper crustal paleo-levels. The data can be explained if the deep continental crust in this area had been built up progressive underthusting and dehydration of oceanic crust. Fluids released during granulite metamorphism apparently re-hydrated higher-level thrust sheets that had been emplaced and metamorphosed earlier, growing a new generation of metamorphic zircon. The most compelling evidence came from igneous zircon ages in granitoid clasts from a deep-level metaconglomerate. These gave ages younger than the youngest Archean supracrustal rocks in adjacent structurally overlying greenstone belts, implying that they must have been emplaced by late underthrusting rather than by burial.

A novel application was the use of zircon in meteorite ejecta layers to identify the impact site. Shock metamorphism associated with meteorite impacts produces characteristic planar deformation features in zircon. Such features were documented in zircon from Archean rocks adjacent to the Sudbury structure (Krogh et al. 1984, 1996) and from the thin world-wide ejecta layer associated with the K-T (end-Cretaceous) impact (Bohor et al. 1994). Single-grain dating of shocked zircon from this layer in several locations showed a predominant pattern of Pb loss at 65 Myr from a primary age of about 550 Ma, identical to that found in the basement to the Chicxulub crater in Mexico. This implicated Chicxulub as the impact site (Krogh et al. 1993, Kamo and Krogh 1995).

Routine sub-picogram blanks were achieved at some labs in the mid-1990s. Single zircon dating had become the norm for most samples by that time. Column separation of U and Pb from small zircon samples was shown to be unnecessary long before (Ludwig and Stuckless 1978) making low blanks easier to maintain. Pb blanks are now routinely in the range 0.2-0.8 pg at JSGL. This represents a drop of six orders of magnitude since the 1960s largely because of improvements in technique but also likely due to a progressive reduction in environmental Pb pollution over the past three decades. The factor of ten drop since the mid-1980s is difficult to explain in any other way since analytical procedures changed only in minor ways over that period to make the process more efficient. Blank levels at the JSGL are all the more remarkable since, unlike most clean labs, workers do not use any special clothing and the actual clean environment is restricted to small filtered air boxes that were constructed at the lab's inception. Such basic equipment is sufficient to produce the cleanest analyses, along with skill and concentration on the part of the analyst.

The Sensitive High-Resolution Ion Micro-Probe (SHRIMP)

Despite the improvements introduced at CIW, zircon dating in the 1970s was still limited by complex chemical procedures and high laboratory blanks. Single-grain analyses were imprecise and bulk fraction analyses risked being inaccurate because of discordance and inheritance. Efforts began to overcome these limitations by analyzing zircon directly at the intra-grain level using secondary ion mass spectrometry (SIMS).

SIMS instruments (ion probes) designed for geoscience use a focused beam of high-energy ions to sputter (ablate) a small area (usually ~20 μm diameter) on the polished surface of a sectioned target crystal, producing secondary ions from the crystal which are analyzed for their isotopic composition in a double-focusing mass spectrometer. The process is almost non-destructive, about 3 ng of sample being consumed per analysis. The small sample size limits the analytical precision, however, so the most appropriate use of ion probes is in analyzing mineral samples that are scarce, complexly structured or of composite age.

The potential of SIMS for U-Pb geochronology was first demonstrated by Andersen and Hinthorne (1972) who used an ARL ion microprobe at the Hasler Research Center in California to measure $^{207}Pb/^{206}Pb$ ages in zircon and other U-bearing minerals from lunar samples. The ages compared favorably with those measured on the host rocks by other techniques, but the sensitivity of their probe was too low to detect ^{204}Pb, so no corrections were made for common Pb. Also Pb/U was not measured so there was no test for concordance. Both these shortcomings were addressed by Hinthorne et al. (1979). Using a prediction from the work of Andersen and Hinthorne (1973) that the secondary ion ratios Pb^+/U^+ and UO^+/U^+ should co-vary for any target of uniform Pb/U, they analyzed zircon grains from Proterozoic pegmatite from Ontario and Archean gneiss from the Stillwater complex against silicate and glass standards with known Pb and U contents. Because the ARL probe had low mass resolution it was necessary to make large corrections for molecular interferences. Further, ^{204}Pb was still below detection limits, so common Pb was corrected using the measured $^{208}Pb/^{206}Pb$ and Th/U. Nevertheless, the analyses agreed reasonably well with bulk zircon data from the two samples (Tilton et al. 1957), and one grain from the Stillwater gneiss gave a near-concordant composition 300 Ma older than the others, supporting the suggestion of Nunes and Tilton (1971) that the gneiss contained inheritance from an older terrane.

Hinton and Long (1979) reduced the effects of molecular interferences by operating their AEI ion microprobe at higher mass resolution (3200). They succeeded in measuring ^{204}Pb, but the loss in sensitivity was such that each analysis took several hours. One of their samples, a gneiss from Lac Seul, Ontario, had previously been dated by Krogh et al. (1976) at 3040±40 Ma. The ion probe analyses showed the central regions of the zircons, some of which had visible discrete cores, to have higher average $^{207}Pb/^{206}Pb$ than the rims. The difference was interpreted to reflect the effects of metamorphism at ~2.7 Ga, the original age of the zircon being at least 3.3±0.1 Ga. Although later ID-TIMS dating of another sample by Corfu et al. (1995) yielded 3040±3 Ma, confirming the Krogh et al. (1976) result, the Hinton and Long (1979) analyses were the first direct evidence that an isotopic record of two stages of zircon growth could be preserved within individual crystals.

The need to achieve sufficient mass resolution to resolve molecular interferences (about 5000) without a major loss of sensitivity drove subsequent advances in ion microprobe design. The approach adopted by a group led by Bill Compston at the Australian National University was to use a larger analyzer magnet (1 m radius), which provided high mass resolution without the need to narrow the analyzer slits and cut secondary ion transmission. Commercial ion probe manufacturers followed the same course several years later. The project to build a Sensitive High-Resolution Ion Micro-Probe (SHRIMP) was initiated in 1974. Designed by Steve Clement, Gordon Newstead and Compston using a low-aberration ion optic configuration devised by Matsuda (1974), the first SHRIMP became operational in 1981. SHRIMP proved to be much more successful than its predecessors, a typical analysis taking about 20 minutes, and opened up a new chapter in zircon geochronology (Compston 1996, Williams 1998). It was a major contributor to the notable increase in the publication rate of U-Pb zircon papers after 1982 (Fig. 5).

Some of the first SHRIMP U-Pb analyses (Williams et al. 1983) were carried out on the same zircon crystals from Antarctic orthogneisses on which the low resolution ARL probe had measured ages of 1600-3500 Ma (Lovering et al. 1981), much older than those determined by Rb-Sr (950-1400 Ma). The SHRIMP results were consistent with the Rb-Sr data, validating concerns that the $^{207}Pb/^{206}Pb$ measurements by the ARL probe had been under-corrected for isobaric interferences and common Pb. Another early application was to date rare lunar zircon grains discovered in sawdust and thin sections from breccias (Compston et al. 1984). Of particular value were those zircon grains contained within minute lithic fragments, from which the source lithologies could be inferred. Zircon as old as 4.37 Ga provided evidence for early solidification of the lunar magma ocean, a wide range of ages from 4.32 to 3.88 Ga in granopyhres recorded a protracted but episodic history of differentiated magmatism, and some cases of extreme discordance reflected late isotopic disturbance by large impactors (Meyer et al. 1996). Zircon from the Vaca Muerta mesosiderite, also dated in thin section, gave an age for meteorite formation near the beginning of the solar system, 4563±15 Ma (Ireland and Wlotzka 1992).

The high productivity of SHRIMP is ideally suited to studies of sediment provenance, in which it is necessary to date large numbers of grains individually (a minimum of 60 to have a 95% chance of sampling every component present at above 5% abundance). Searching for evidence of the oldest terrestrial crust, Froude analyzed hundreds of zircon grains from numerous early Archean quartz-rich metasedimentary rocks in the Murchison district of Western Australia, finding one quartzite at Mt. Narryer in which ~2.5% of the zircon had ages of 4.1-4.2 Ga (Froude et al. 1983), at the time more than 300 Myr older than the oldest-known terrestrial mineral. Given the checkered history of ion probe analysis the result was received with skepticism by some of the geoscience community (Moorbath, 1983), especially when single grain ID-TIMS analyses of zircon from the same rock failed to find any grains older than 3.5 Ga (Schärer and Allègre 1985). Further old grains were soon unearthed, however, in metasedimentary rocks at nearby Jack Hills (Compston and Pidgeon 1986 and Fig. 8), and the SHRIMP ages were confirmed by the zircon evaporation method (Kober et al 1989, method described below) and by ID-TIMS (Fanning and McCulloch 1990, Amelin 1998). The Murchison region remains the only place where such ancient remnants of the early Earth are known.

SHRIMP microsampling was also instrumental in the discovery of the oldest-known terrestrial rocks, the Acasta gneiss from the western Slave Province in the Northwest Territories, Canada. ID-TIMS analyses by Bowring et al. (1989a) of small zircon fractions and single grains from one Acasta sample yielded discordant analyses with a range of ^{207}Pb/^{206}Pb ages up to 3.83 Ga, clearly indicating the antiquity of the rock but only loosely defining its actual age. SHRIMP analyses showed the zircon grains to be a mixture of cores and rims, and zoned, structureless and altered domains, only a small portion of which recorded the primary crystallization age of 3962±3 Ma (Bowring et al. 1989b). Further ion probe work in the area (Stern and Bleeker 1998, Bowring and Williams 1999) has since located gneiss with ages up to 4031±3 Ma, but the complexity of the zircons is such that these ages have yet to be resolved by ID-TIMS.

A decade of development of SHRIMP I was followed by the introduction of SHRIMP II in

Figure 8. Bill Compston and Bob Pidgeon with a sample of Jack Hills conglomerate, taken at Curtin University in 1986.

1992. Improvements in the ion extraction optics gave the new instrument four times the sensitivity of its predecessor, Köhler focusing produced a more sharply defined, uniform primary ion beam, increasing the accuracy of the measurements of Pb/U, and better magnet design reduced analysis times. SHRIMP II was also a more versatile instrument, being designed to accept a Cs ion source for stable isotope analysis and a multiple collector. At about the same time, high-resolution ion microprobes manufactured by VG (Isolab 120) and Cameca (Cameca 1270) also became available. In 1998 a SHRIMP with even higher mass resolution, the SHRIMP RG, was brought on line, further expanding the scope for analyses free of isobaric interferences. The Cameca Nanosims 50 introduced in 2000 reduced the scale of isotopic analysis to sub-micron, but its accuracy and precision for geochronology at this scale have yet to be thoroughly evaluated.

High-resolution ion probes are now distributed in isotope laboratories throughout the world, but they are limited by their high price to major research institutions. Most are operated by consortia, many of which have strong links to government. The high productivity of the instruments is particularly attractive to government geological surveys, ion probe geochronology now being an integral part of regional geological mapping programs in several countries (e.g., Stern 1997). The body of ion microprobe data is now comparable to, or greater than, that of ID-TIMS.

High-resolution ion probes expanded the scope of U-Pb geochronology. Not only did the higher speed of analysis make it practical to date more samples and many more grains per sample, but the high spatial resolution made it possible to study individual grains containing several generations of growth. Studies of sediments, poly-metamorphosed rocks and polychronic inheritance flourished. For example, Pell et al. (1997) used the composite detrital zircon populations in desert dune sands from throughout Australia to determine the geographic regions from which the sands were derived, demonstrating unexpectedly that the principal sediment transport mechanism was water, not wind. Armstrong et al. (1990) showed that, contrary to earlier interpretations, the Barberton Greenstone Belt was not a simple stratigraphic succession, but part of an allochthonous sequence with major tectonic and stratigraphic breaks and inversions evolved in a tectonically active convergent environment. Taking the large scale approach, Kalsbeek and Nutman (1996) revealed the general history of an entire Greenland orogen in one week analyzing a few zircon grains from each of 90 samples, sketching out the principal tectonic units, their ages and metamorphic histories. Williams (1992) showed that inherited zircon in Paleozoic S-type granites from Australia was composite in age, the ages and relative abundances of the inherited components accurately matching those of detrital zircon populations in the host metasedimentary rocks.

Analysis of ^{207}Pb/^{206}Pb by ion probe is straightforward but measuring Pb/U isotopic ratios is more difficult because Pb and U have different secondary ionization efficiencies which change during each analysis. The efficiencies are also matrix dependent, so Pb/U and Pb/Th are measured relative to concordant reference minerals, a procedure currently reliable to about 1%. These reference standards must be dated independently by ID-TIMS. Early zircon work in the ANU lab was referenced to a U-rich Sri Lankan zircon megacryst, SL3. As techniques improved, this metamict crystal was replaced by another megacryst with lower U and more uniform composition, SL13 (Williams et al. 1988, Claoué-Long et al. 1995). This also proved heterogeneous on the microscale, however (Compston 1999), and has been abandoned except as a U concentration reference. As ion probe geochronology has expanded, so have attempts to identify minerals suitable for international standards, but reference minerals still remain largely laboratory specific. Fragments of zircon megacryst 91500 from a syenite complex near Kuehl Lake, Ontario (Wiedenbeck et al. 1995) have been widely distributed, but they are heterogeneous. The Australian geological survey (Geoscience Australia) and ANU now use zircon from a Paleozoic diorite (Temora; Black et al., submitted). ANU also uses zircon from the Duluth complex (Paces and Miller 1993), a standard also adopted in Stanford and at NIPR, Tokyo. SHRIMP and ID-TIMS groups continue to work together to intercompare and evaluate zircon standards (Roddick and van Breemen 1994, Black et al., submitted).

One of the most demanding applications of U-Pb geochronology is precise calibration of fossil-based stratigraphic boundaries, the Paleozoic time scale. Questions about standardization as well as small-scale cryptic Pb loss and inheritance from zircons analyzed by SHRIMP versus ID-TIMS have been sources of argument between groups using each method (e.g., Compston and Williams 1992, Tucker and McKerrow 1995). Valid points have been raised on both sides. SHRIMP does have difficulty achieving better than 1% accuracy in Pb/U measurements, but it has demonstrated that zircon grains in volcanic rocks commonly are the product of igneous episodes of subtly different ages, an observation that is supported by ID-TIMS (Mundil et al. 2001, Oberli et al. 2002). Of further concern for accurate zircon dating of young volcanism, ion probe U-series disequilibrium studies of zircon from very young eruptive sequences show that magma chambers persist for hundreds of thousands of years, the zircon age of volcanic rocks recording not crystallization after eruption but an earlier time when the magma chamber became saturated in Zr (Reid et al. 1997).

The ion microprobe has advanced U-Pb geochronology, not only through instrumental improvements but also through a better understanding of zircon itself. It has been difficult to determine the closure temperature of zircon, mainly because Pb, U and Th diffuse so slowly in well-crystallized zircon that the rates are very difficult to measure (Cherniak et al. 1997). Operating SHRIMP II in depth profiling mode, Lee et al. (1997) were able to measure Pb, U and Th diffusion profiles only a few nanometers deep produced in chips of SL13 by laboratory heating experiments up to 1100°C. The volume diffusion closure temperature for a 100 μm diameter grain, determined mainly by the diffusivity of Pb, was calculated to be ~900°C, about 100°C less than diffusion closure temperatures later measured on natural and synthetic zircon by Cherniak and Watson (2000) using Rutherford backscattering. These results are in agreement with numerous observations that zircon is highly resistant to isotopic resetting at high-grade metamorphic and even magmatic temperatures. For example, Williams (2001) found the U-Pb ages of detrital zircon in a regionally metamorphosed turbidite sequence at Cooma, Australia, to be unaffected by metamorphism, even where that zircon survived only as cores in an anatectic granite (Fig. 9). There is evidence that in some situations the U-Pb closure temperature of zircon might be even higher. Kinny et al. (1989), for example, found Archean mantle zircons in Cretaceous kimberlites. Although the thermal history of the grains was not known, they inferred that the zircon had remained closed to diffusion of Pb and U at a temperature greater than 1100°C over billions of years. More convincing is the work of Möller and others (2002), who documented preservation of U-Pb ages in zircon subjected to dry contact metamorphism up to 950°C lasting at least 1 Myr, implying a diffusion closure temperature >1000°C.

The need for accurate targeting of SHRIMP analyses stimulated the development and application of methods for imaging chemical and structural zonation in zircon such as cathodoluminescence (CL) and backscattered electron (BSE). Such images reveal features such as cores, magmatic and metamorphic overgrowths and areas of recrystallization (Fig. 10). They also show up alteration, fractures and inclusions. Zoning patterns provide clues to the U content of each domain and the environment in which it formed. Sampling complex grains can pose a significant challenge to the ID-TIMS method but is a strength of the ion microprobe. In two early studies, Williams et al. (1984) and Black et al. (1986) showed that within the zircon from one sample of early Archean orthogneiss from the Napier complex, Antarctica, there were three distinct generations of zircon growth recording at least four thermal events that spanned 2 Gyr. Some zircon domains contained unsupported radiogenic Pb characterized by ^{207}Pb/^{206}Pb 'ages' older than the grains, probably resulting from intra-grain redistribution of radiogenic Pb during high-grade metamorphism. Gebauer et al. (1988) used CL imaging combined with SHRIMP dating to resolve ages of primary magmatic phases from older xenocrysts and younger metamorphic overgrowths in an eclogite. SHRIMP dating of cores and metamorphic overgrowths in single detrital zircons from Hercynian paragneisses produced concordant data with ages ranging from 3.84 Ga to 0.32 Ga (Gebauer et al. 1989). Bulk zircon dating on these rocks during the 1970s had produced quasi-linear arrays of discordant data similar to those measured on paragneisses from the Swiss Alps. The SHRIMP results resolved earlier debates over the interpretation of these arrays by showing that they resulted from mixtures of diverse

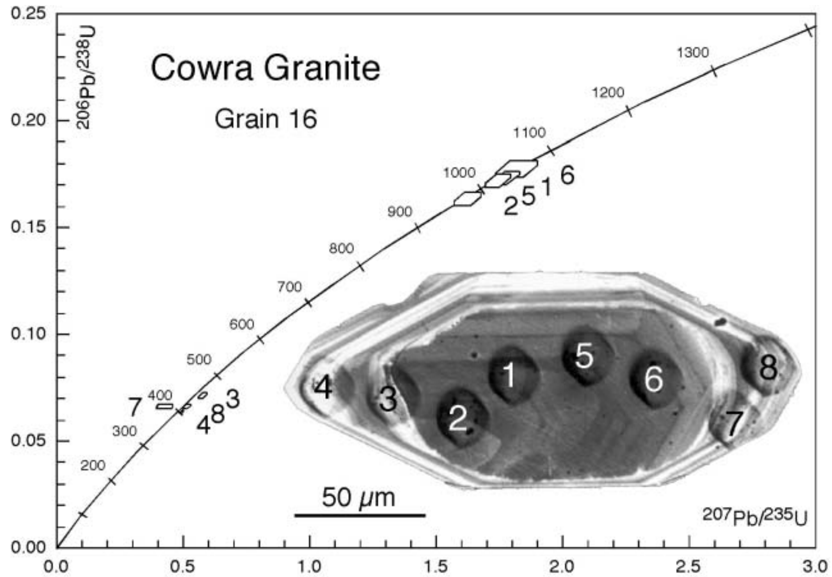

Figure 9. CL image of polyphase zircon from the Cowra granite, Australia, showing pits produced by the SHRIMP primary ion beam. Concordia data show that the overgrowth is about 600 Myr younger than the core.

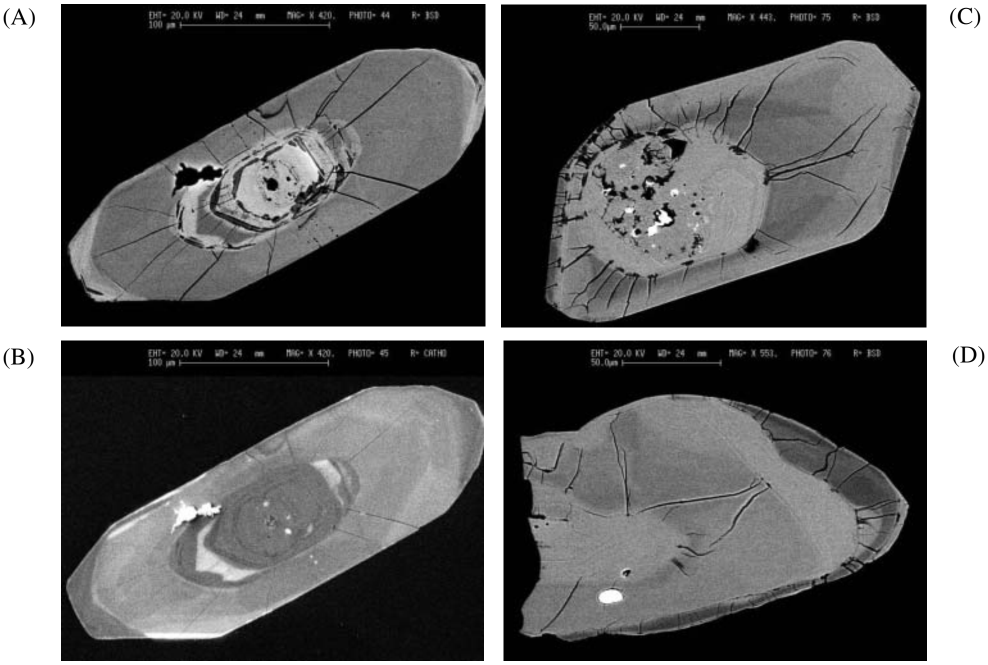

Figure 10. Images of zircon from Archean gneisses in the Winnipeg River belt, NW Ontario, Canada. (A) BSE image of a grain with a core from a ca. 2700 Ma gneiss. BSE is sensitive to the average atomic number so trace element enriched areas are brighter. (B) CL image of the grain in A. CL is sensitive to both elemental composition and structural state. Emission is suppressed by radiation damage so areas that are bright in BSE are often dark in CL. (C) BSE image of a zircon from a 2880 Ma old gneiss with 3060 Ma inheritance. The overgrowth has been cracked by differential expansion of the higher U core. The core is altered (dark regions) and contains bright inclusions that are probably REE phosphate. (D) BSE image of zircon from the older gneiss with four phases of growth. Lower-U phases are preferentially cracked.

concordant ages rather than metamorphically induced Pb loss. Similarly, SHRIMP dating of individual zircon cores and overgrowths in granites intruding the Dalradian of Scotland (Pidgeon and Compston 1992) showed that the data arrays generated by earlier analyses of bulk zircon fractions (e.g., Pankhurst and Pidgeon 1976) were the result of mixing magmatic zircon with inherited cores that showed little evidence of Pb loss despite having been heated to magmatic temperatures (Fig. 3 inset).

Serious application of imaging really began in the early 1990s with the study by Vavra (1990), who produced high quality CL images of complex zircon structures and used these to interpret magmatic growth histories. This was an extension of earlier work by Pupin (1980) who had classified zircon morphologies and attempted to relate them to the temperature and composition of the host magma. High-quality BSE images of inherited cores in zircons that had been dated by SHRIMP were published by Paterson et al. (1992). Hanchar and Miller (1993) discussed the potential of BSE and CL imaging combined with SHRIMP as a tool for investigating complex growth histories due either to changes within the crystallization sequence or to episodic growth events that were sufficiently different in age to be dated separately. High-quality imaging was combined with SHRIMP dating to help define metamorphic P-T-t paths in the Swiss Alps by Gebauer (1996) and by Vavra et al. (1996). Schaltegger et al. (1999) studied metamorphic and igneous zircon in the Variscan belt of France using SHRIMP and ID-TIMS combined with CL imaging and intra-grain trace element studies. They found that zircon grew under granulite facies conditions at 335 Ma but was apparently reset during amphibolite facies overprinting about 10 Myr later by a process of annealing or recrystallization. This occurred at about 700°C, substantially below the normal closure temperature for volume diffusion of Pb. Unexpectedly, coexisting monazite, which was thought to have a lower closure temperature, was not reset. How and why zircon recrystallizes and is reset under some low temperature metamorphic conditions is not yet understood. Recrystallization fronts due to metamorphism and/or magmatic cooling have been documented by Hoskin and Black (2000) and by Pidgeon et al. (1998). Without the spatial resolution of the SHRIMP, such intra-grain structures would be difficult or impossible to date and there would be much less incentive to understand them.

The accuracy of SHRIMP microanalyses is achieved at the expense of precision, a consequence of the small number of ions available from the sampled volume. Age precisions from SHRIMP are normally 5 to 10 times worse per spot than they are from analyzing a whole grain by ID-TIMS. Uncertainty can be reduced by pooling analyses from different spots but the fact that the error varies inversely with the square-root of the number of analyses makes for a law of diminishing returns. Also, large individual uncertainties make it difficult to detect small amounts of secondary Pb loss or inheritance, either of which can bias the mean beyond its measured precision. On the other hand, the ion microprobe approach excels for complex zircons and/or where very high age-precision is not essential. For example, sufficient data can be acquired from detrital zircon populations to define statistically robust age populations, allowing the application of sophisticated numerical methods to study provenance (e.g., Sircombe 2000). Also, zircons for which a more precise age determination would be valuable (usually the youngest) can be removed from the mount and dated by ID-TIMS. The strengths of SHRIMP are largely complementary to those of ID-TIMS. Unfortunately, until recently a degree of competitiveness tended to prevail between their practitioners and the two techniques were largely developed and applied independently of each other. Early publications from the SHRIMP group often claimed a superiority over 'conventional' zircon dating. This was true by comparison with traditional bulk zircon methods. However early SHRIMP results often showed considerable discordance, because of difficulty in seeing alteration, and gave imprecise U/Pb ratios, because of difficulty with standardization, while advances in ID-TIMS methods had largely eliminated secondary discordance as a serious problem. Discordance ceased to be a problem with SHRIMP analyses as well once sampling became guided by high quality imaging of the grains. Competition between the two methods produced some interesting debates (e.g., Schärer and Allègre 1985, Corfu and Davis 1991) but was ultimately of little value to the progress of geochronology. The most effective strategy for dating complex terranes is to utilize the strengths of both.

The zircon evaporation method

Kober (1986, 1987) developed a method for selective evaporation of Pb from single zircons at progressively higher temperature. Evaporation of Pb from single zircons had been experimented with earlier by Buchs et al. (1970) and Coppens et al. (1965) using a single filament. In the Kober method, Pb evaporated from zircon on a side filament is deposited on a blank center filament from which it can be re-evaporated. The effectiveness of this technique relies on the fact that zircon converts to ZrO_2 (baddeleyite) when it is heated (Chapman and Roddick 1994) releasing SiO_2, which acts as an ionization activator, as well as Pb. A wide rhenium side filament is wrapped partly around the sample grain and heated step-wise in the mass spectrometer. Evaporated silica and Pb are deposited on a cooler center filament which can then be re-heated to measure the Pb isotopic composition. The double filament approach gives greater stability of emission and more control of the evaporation process.

Like SHRIMP, this method dispenses with the necessity of chemical extraction but, most importantly, Pb in undamaged parts of the zircon evaporates at a higher temperature than Pb in altered or damaged domains. In partly altered zircons, the $^{207}Pb/^{206}Pb$ age can be seen to increase with temperature and the ^{204}Pb to decrease until a plateau is reached where ^{204}Pb is negligible. This should represent the age of the pure radiogenic component from undamaged domains and therefore the primary age of the zircon. Because the Pb is extracted at the atomic scale, even pervasively cracked zircons where unaltered domains would be too small for analysis by ID-TIMS or SHRIMP can theoretically be dated. A disadvantage of the method is that Pb/U information is lost. However, this may not be a severe problem for rocks having simple zircon populations. Demonstrating reproducibility of $^{207}Pb/^{206}Pb$ ages from different grains is probably a reliable test that the age is meaningful. Another disadvantage is that the small ion beams and the necessity for stepped analyses require large amounts of mass spectrometer time, sometimes as much as one day per sample. Results from the evaporation method may be unreliable if good measurement protocols are not followed in order to ensure that the labile Pb component is completely removed. Correctly applied, the method has produced reliable and moderately precise zircon ages from many rocks (e.g., Kröner et al. 1991, 1993).

Other developments

Fission track dating of zircon will not be covered here except to say that it has been very useful for constraining thermal and uplift histories (Gleadow and Brooks 1979). It was developed over the same period as isotopic analysis and has produced a voluminous literature that would require a review on its own. Zircon also shows significant promise for thermoluminescence (TL) and optically stimulated luminescence (OSL) dating (Smith 1988), which are useful over archeological time scales.

Over the past two decades a number of other methods have been developed for drawing geological information from zircon. Dating by laser ablation – inductively coupled mass spectrometry (LA-ICPMS), where zircon is volatilized and U and Pb isotopes ionized in an inductively coupled plasma source followed by mass analysis in a quadrupole or multi-collector mass spectrometer, is still in a state of active development. This, along with studies of Hf and O isotopes, trace element compositions, and melt inclusions in zircon are reviewed elsewhere in this volume.

THE LEGACY OF ZIRCON DATING

The first half-century of U-Pb geochronology was a time of fundamental discovery when the problem of dating was tied to broader questions about the nature of matter. At that time, the true breadth of geologic time was poorly understood. Isotopic dating of zircon subsequently began as an arcane and difficult art developed in large measure by physicists and chemists with an interest in geology. There followed an extended period of technical advances that vastly increased its capabilities. Smaller samples, more efficient ID-TIMS analytical protocols and the development of the SHRIMP broadened the range of rock samples that could be dated and made the method much more accessible. Dating zircons is still demanding but much less so than in the early days. Today most zircon geochronologists are geologists by training who have adopted the method to help them with field-based studies.

The history of zircon geochronology illustrates some of the factors that drive, and in some cases retard, scientific progress. The general pattern of development is stepped rather than smooth: extended periods of application and refinement are interspersed by relatively brief periods of revolutionary advance. The early Pb-α method (1950-1957), was quickly replaced by isotope dilution (Tilton et al. 1955) but the next major advances required nearly 15 years until the silica gel ionization activator was widely adopted (Cameron et al. 1969) quickly followed by bomb dissolution, miniaturized column chemistry, and ^{205}Pb spike (Krogh 1973). Subsequently, after about a decade of applications but few major advances in technique, zircon abrasion was introduced (Krogh 1982) at almost the same time as effective SIMS dating using the SHRIMP (Compston et al 1982). SIMS opened up a new approach to zircon dating and was followed by zircon evaporation (Kober 1986), a new branch of TIMS dating. Again, an extended period of applications followed accompanied by gradual refinements such as blank reduction in ID-TIMS and improvements in SIMS instrumentation. At present, LA-ICPMS has begun to emerge as a new technology that may eventually challenge earlier methods. Overcoming technical problems in mass spectrometer design was an obvious limiting factor in the progress of methods such as SIMS and LA-ICPMS, which have shown a measured and continuous advance in capabilities. Progress in ID-TIMS is less easily explained in this way since much of the technology necessary to eliminate secondary Pb loss and perform precise single grain analysis was available long before it was actually used. For example ionization activators (Akishin et al. 1957), the use of high-pressure Teflon dissolution capsule for dissolving minerals (Ito 1961) and picogram blank chemistry (Tera and Wasserburg 1975) were experimented with many years before they came to be perfected and widely adopted for zircon geochronology. With ID-TIMS the rate of progress seems to have depended more on psychological and philosophical factors and it is here that the 'revolutionary' pattern of progress shows most strongly.

An important factor in innovation was having the right research environment, a critical mass of researchers focused on zircon dating who were in a position to experiment, as well as the existence of personalities with the imagination to conceive new ways of doing things and the determination to perfect them. The perception of an impasse that existing methods could not overcome was perhaps the most important trigger for major advances. The Pb-α method had shown the potential of zircons for dating but workers must have been frustrated by the limitation in precision. This was greatly improved by the introduction of isotope dilution by the Chicago group, made possible by the availability of enriched isotopes from the nuclear program. There followed a long period of applications during which U-Pb geochronology started to be used, for the first time, as a practical method of detailed geologic investigation. The complications presented by discordance in zircon became obvious and understanding these occupied much of the subsequent research effort. The Caltech lab of Silver was active at this time and was particularly influential as Silver introduced mineralogy into the interpretation of zircon U-Pb ages, which laid the groundwork of present-day research on complex zircons. Despite the enormous amount of work involved in performing zircon analyses, there does not seem to have been a general ongoing effort to further improve techniques until the early 1970s at CIW. The CIW innovations greatly increased the number of zircon dates by making the analytical process more efficient in terms of time and sample consumption. There followed again a period of intense application but groups like ETH ran into problems of inheritance in Alpine zircons while others still found that accuracy of ages was limited by secondary Pb loss. Insightful studies by Steiger and Wasserburg (1966, 1969) and Grünenfelder (1964) suggested early on that zircon consists of a mixture of concordant and discordant phases. The logical conclusion is that one can eliminate discordance by identifying and isolating concordant phases. A wider appreciation of these observations might have provided an early impetus to isolate concordant phases and strive for the low blanks necessary to do precise single zircon work. Instead, for a long time efforts were more focused on debates over the nature and meaning of Pb loss and the most appropriate methods of data treatment. Ultimately, it was the failure of theory to produce consistent reliable ages that created the impasse leading to developments such as abrasion, ultra-low blanks and SHRIMP. Perhaps the key lesson from this is that the urge to push measurements into new regions of sensitivity and precision is the most important force driving scientific progress.

The cumulative legacy of zircon dating is the precise calibration of most of geologic time. This is a great achievement resulting from the perseverance of many dedicated individuals. Its scientific value lies in the power to test geologic models and resolve controversies that commonly arise due to the incompleteness of the geologic record. Perhaps the best example is the impact of zircon dating on understanding the history and pace of evolution. Precise dating of volcanic ash beds by Tucker et al. (1990), Compston and Williams (1992) and others served to establish an absolute time scale for the paleontological record. By dating units that closely bracket era boundaries, Bowring has shown that the pace of evolution was explosive following major extinctions such as at the base of the Cambrian (Bowring et al. 1993). The greatest known mass extinction, the Permo-Triassic boundary, can now be correlated at the sub-million year level with the Siberian Traps, the largest known flood volcanic province (Bowring et al. 1998, this volume; Kamo et al. 1996, submitted). Unlike the earlier debate with Lord Kelvin, results from this work have gone against uniformitarianism. They have favored episodic evolutionary events associated with global catastrophes as the driving force for major evolutionary change. Thus, U-Pb dating continues to influence and modify Darwin's theory.

The rich chronological record revealed by zircons does not quite end at 4.0 Ga, the age of the oldest rocks. The Hadean eon remains almost hidden from direct observation, except for a single area in western Australia where zircons older than 4.0 Ga are preserved as detrital grains and xenocrysts. The oldest is now dated at 4404 Ma (Valley et al. 2002), only about 100 Myr younger than the massive collision that formed the Earth-Moon system. These zircons are our only window into the first 500 Myr of Earth's history. Their ages have been precisely established by U-Pb dating. The pre-history of crust-mantle differentiation reflected in their magmatic reservoirs has been studied using Hf isotopes (Amelin et al. 1999). Their O isotopes give tantalizing indications of an early hydrosphere (Mojzsis et al. 2001, Wilde et al. 2001), while mineral inclusions show that they were derived from granitoid rocks, a major component of continental crust (Maas et al. 1992). What a rich trove of information to be mined from such tiny specks of matter. Without zircon, the details of our planet's history would be mostly lost. We are indeed fortunate to have such a wonderful mineral.

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