# GEOCHRONOLOGY V

## THE U-TH-PB SYSTEM: ZIRCON DATING

Zircon ($ZrSiO_4$) is a mineral with a number of properties that make it extremely useful for geochronologists. First of all, it is very hard (hardness $7^1/_2$), which means it extremely resistant to mechanical weathering. Second, it is extremely resistant to chemical weathering and metamorphism. For geochronological purposes, these properties mean it is likely to remain a closed system. Third, it concentrates U (and Th to a lesser extent) and excludes Pb, resulting in typically very high $^{238}U/^{204}Pb$ ratios. It is quite possibly nature's best clock. Finally, it is reasonably common as an accessory phase in a variety of igneous and metamorphic rocks.

The very high $^{238}U/^{204}Pb$ ratios in zircon (and similar high $\mu$ minerals such as sphere and apatite) provide some special geochronological opportunities and a special diagram, the *concordia diagram*, has been developed to take advantage of them. The discussion that follows can be applied to any other system with extremely high $^{238}U/^{204}Pb$ ratios, but in practice, zircons constitute the principle target for Pb geochronologists.

A concordia diagram is simply a plot of $^{206}Pb^*/^{238}U$ vs. $^{207}Pb^*/^{235}U$. You should satisfy yourself that both of these ratios are proportional to time. In essence, the concordia diagram is a plot of the $^{238}U$–$^{206}Pb$ age against the $^{235}U$–$^{207}Pb$ age. The 'concordia' curve on such a diagram that is the locus of points where the $^{238}U$–$^{206}Pb$ age equals the $^{235}U$–$^{207}Pb$ age. Such ages are said to be *concordant*. Figure 9.2 is an example of a concordia diagram.

The best way to think about evolution of Pb/U ratios is to imagine that the diagram itself evolves with time, along with its axes, while the ac-

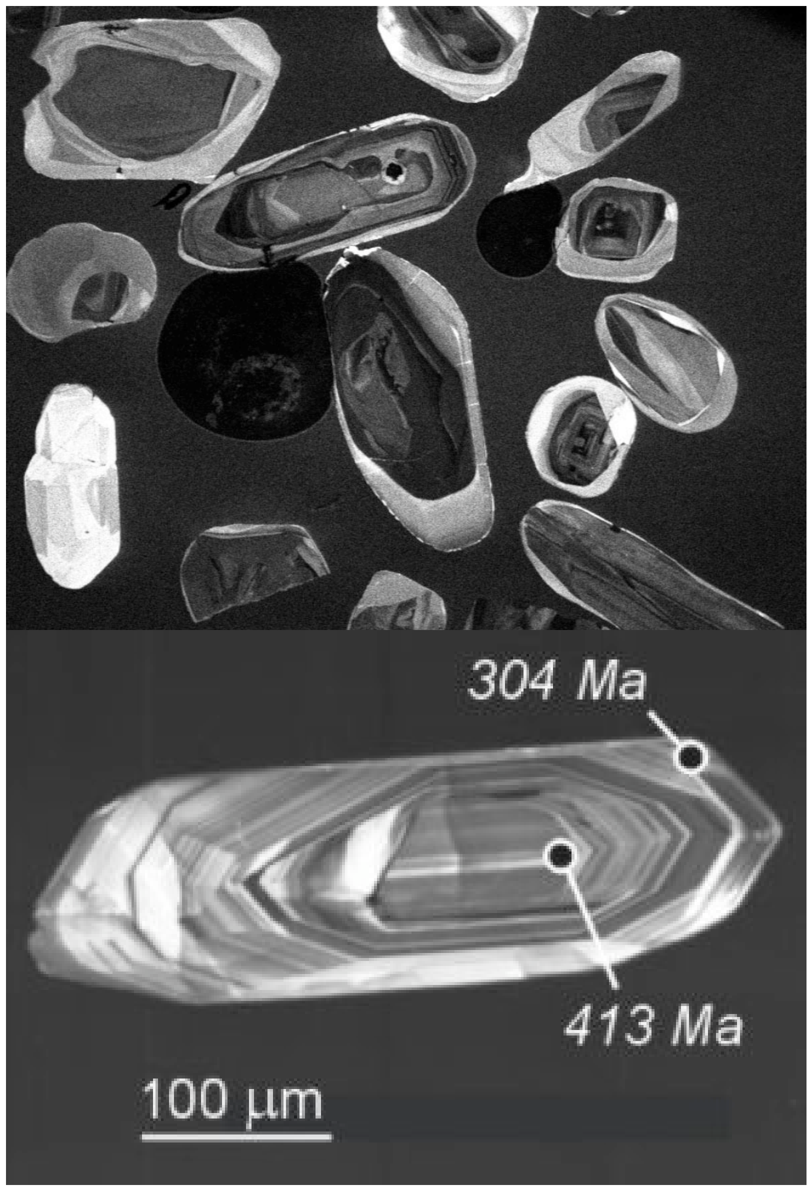


Figure 1. Upper. Separated Zircon crystals. Notice the zoning. Lower. Strongly zoned zircon showing differing ages of spots analyzed by ion probe.

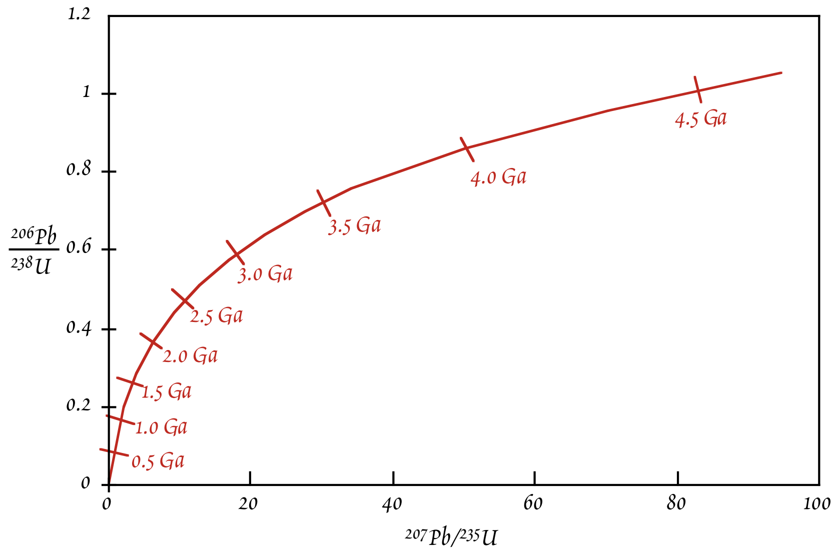


Figure 9.2. The concordia diagram.

tual data point stays fixed. Let's take a 4.0 Ga old zircon as an example. When it first formed, or "closed", it would have plotted at the origin, because had anyone been around to analyze it, they would have found the $^{207}Pb^*/^{235}U$ and $^{206}Pb^*/^{238}U$ ratios to be 0. Initially, $^{207}Pb^*/^{235}U$ would have increased rapidly, while the $^{206}Pb^*/^{238}U$ would have been increasing only slowly. This is because 4.0 Ga ago there was a lot of $^{235}U$ around (recall that $^{235}U$ has a short half-life). As time passed, the increase in $^{207}Pb^*/^{235}U$ would have slowed as the $^{235}U$ was 'used up'. So imagine that the diagram initially 'grows' or 'expands' to the left, expanding downward only slowly. Had someone been around 3.0 Ga ago to determine 'zircon' ages, he would have drawn it as it appears in Figure 9.3 (of course, he would have labeled the 3.0 Ga point as 0, the 4.0 Ga point as 1.0, etc.).

Any zircon that has remained as a completely closed system since its crystallization must plot on the concordia line. What happens when a zircon gains or looses U or Pb? Let's take the case Pb loss, since that is the most common type of open-system behavior in zircons. The zircon must lose $^{207}Pb$ and $^{206}Pb$ in exactly the proportions they exist in the zircon because the two are chemically identical. In other words, a zircon will not lose $^{206}Pb$ in preference to $^{207}Pb$ or visa versa.

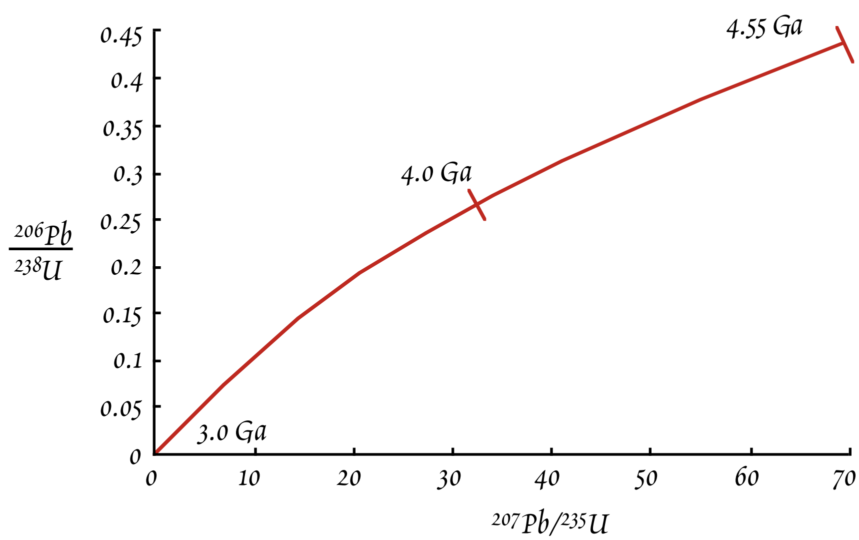


Figure 9.3. A concordia diagram as it would have been drawn at 3.0 Ga.

Let's take the specific case of a 4.0 Ga zircon that experienced some Pb loss during a metamorphic event at 3.0 Ga. If the loss was complete, the zircon would have been reset and would have plotted at the origin in Figure 9.3. We cannot, of course, distinguish a zircon completely reset at 3.0 Ga from one that crystallized at 3.0 Ga, but suppose it lost only half its Pb at that time. During the Pb loss, the $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$

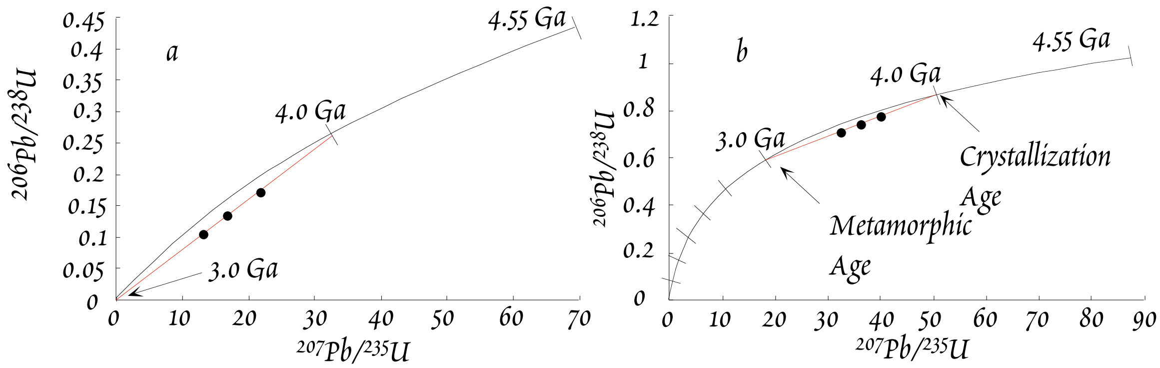


Figure 9.4. (a) Concordia diagram as it would have appeared at 3.0 Ga. Three zircons that experience variable amounts of Pb loss move from the 4.0 Ga point on the concordia curve (their crystallization age) toward the origin. (b) The same three zircons as they would plot at present. The three define a cord between 3.0 Ga and 4.0 Ga. A possible interpretation of this result would be that 4.0 Ga is the crystallization age and 3.0 Ga is the metamorphic age.

would have both decreased by half. Consequently, the point would have migrated half way to the origin. At 3.0 Ga, therefore, it would have plotted on a 'cord', i.e., a straight line, between its initial position on the concordia curve, the 4.0 Ga point, and the origin (Figure 9.4a) at 3.0 Ga. Had it lost some other amount of Pb, say 30% or 80%, it would have plotted on the same cord, but further or nearer the origin. The line is straight because the loss of $^{207}$Pb is always directly proportional to the loss of $^{206}$Pb. The origin in Figure 9.3a corresponds to the 3.0 Ga point on the concordia in Figure 9.4b. So, in Figure 9.4b, the zircon would lie on a cord between the 4.0 Ga and the 3.0 Ga point. We would say this is a 'discordant' zircon.

The intercepts of this cord with the concordia give the ages of initial crystallization (4.0 Ga) and metamorphism (3.0 Ga). So if we can determine the cord on which this discordant zircon lies, we can determine the ages of both events. Unfortunately, if our only data point is this single zircon, we can draw an infinite number of cords passing through this point, so the ages of crystallization and metamorphism are indeterminate. However, we can draw only 1 line through 2 points. So by measuring two zircons (or populations of zircons) that have the same crystallization ages and metamorphism ages, but have lost different amounts of Pb, and hence plot on different points on the same cord, the cord can be determined. The closure age and partial resetting ages can then be determined from the interecepts. (as usual in geochronology, however, we are reluctant to draw a line through only two points since any two points define some line; so at least three measurements are generally made). In practice, different zircon populations are selected based on size, appearance, magnetic properties, color, etc. While zircon is generally a trace mineral, only very small quantities, a few milligrams, are needed for a measurement. Indeed, it is possible to analyze single zircons and even parts of zircons.

U gain would affect the position of zircons on the concordia diagram in the same manner as Pb loss; the two processes are essentially indistinguishable on the concordia diagram. U loss, on the other hand, moves the points away from the origin at the time of the loss (Figure 9.5). In this case, the zircons lie on an extension of a cord above

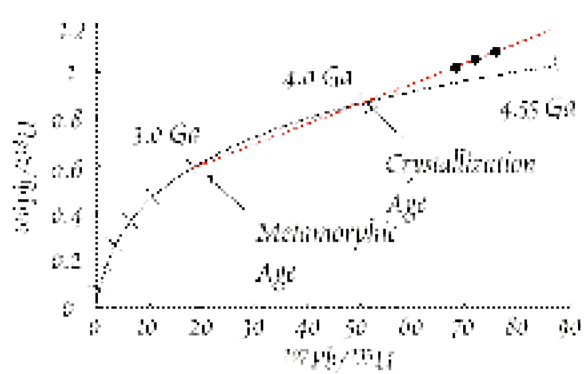


Figure 9.5. A concordia plot showing hypothetical zircons that crystallized at 4.0 Ga and lost U during metamorphism at 3.0 Ga.

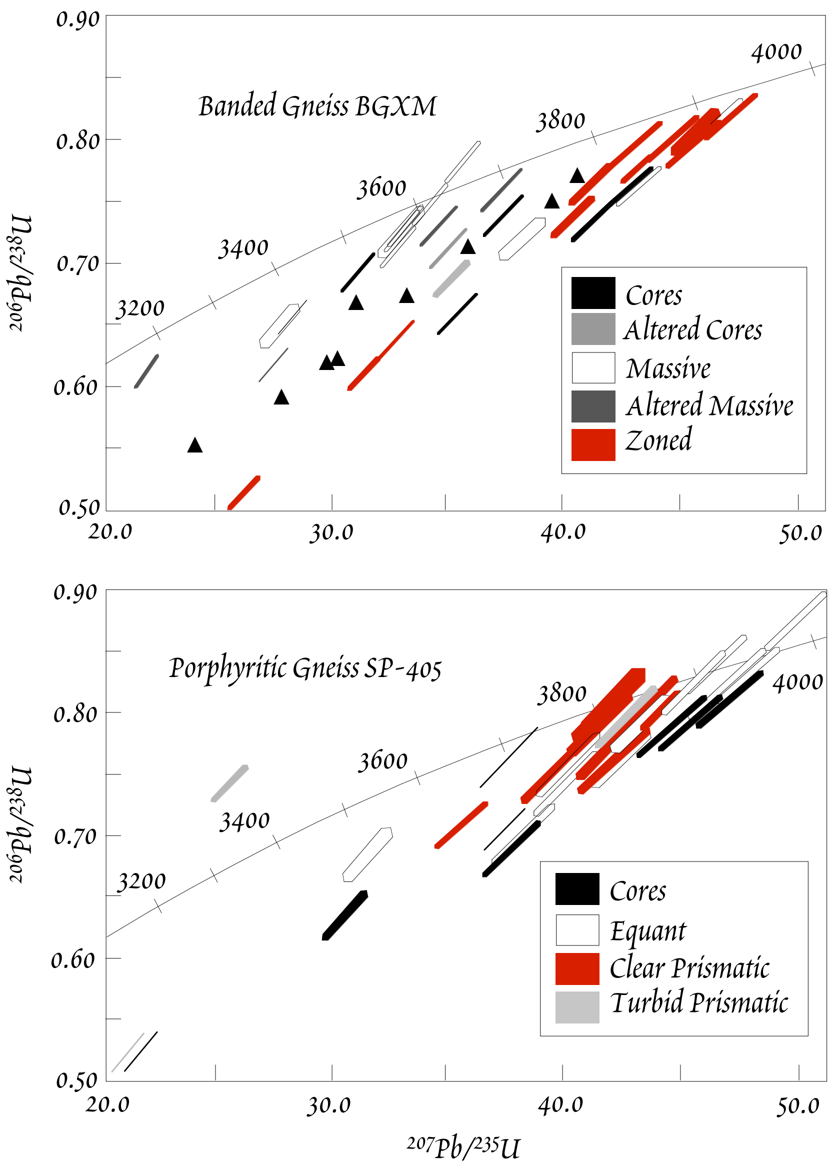


Figure 9.6. Concordia diagrams showing ion probe Pb-U analyses of Acasta gneiss zircons. Size of point is proportional to 1σ analytical uncertainty. Triangles are zircon analyses done by conventional mass spectrometry. From Bowring, et al, 1989.

the concordia. As is the case for Pb loss, the upper intercept of the cord gives the initial age and the lower intercept gives the age of U loss. U loss in less common than Pb loss. This is true for two reasons. First, U is happy in the zircon, Pb is not. Second, Pb will occupy a site damaged by the alpha decay, making diffusion out of this site easier. Radiation damage is a significant problem in zircon geochronology, and one of the main reasons ages can be imprecise. U-rich zircons are particularly subject to radiation damage. Heavily damaged crystals are easily recognized under the microscope and are termed *metamict*.

Pb gain in zircons is not predictable because the isotopic composition of the Pb gained need not be the same as the composition of the Pb in the zircon. Thus Pb gain would destroy any age relationships. However, Pb gain is much less likely than other open system behaviors.

Zircons that have suffered multiple episodes of open system behavior will have U-Pb systematics that are difficult to interpret and could be incorrectly interpreted. For example, zircons lying on a cord between 4.0 and 3.0 Ga that subsequently lose Pb and move on a second cord toward the 2.0 Ga could be interpreted as having a metamorphic age of 2.0 Ga and a crystallization age of between 4.0 and 3.0 Ga.

Continuous Pb loss from zircons can also complicate the task of interpretation. The reason is that in continuous Pb loss, zircons do not define a straight line cord, but rather a slightly curved one. Again imagining that the concordia diagram grows with time, a zircon loosing Pb will always move toward the origin. However, the position of the origin relative to the position of the zircon moves with time in a non-linear fashion. The result is a non-linear evolution of the isotopic composition of the zircon.

Given the mechanical and chemical stability of zircon, it should not be surprising that the oldest terrestrial material yet identified is zircon. Until a decade ago, the oldest dated terrestrial rocks were the Isua gneisses in Greenland. These are roughly 3850 Ma old. Work published in 1989, revealed that the Acasta gneisses of the Slave Province (Northwest Territories, Canada) are 3.96 Ga old. These ages were determined using an ion probe to date the cores of zircon crystals extracted from these gneisses. Concordia diagrams for these gneisses are shown in Figure 9.6.

Zircons having ages in the range of 4100-4260 Ma have been identified in quartzites at Mt. Narryer and the Jack Hills in western Australia (e.g., Compston and Pidgeon, 1986). The quartzites themselves are metamorphosed sandstones that were probably deposited about 3100-3300 Ma. They contain zircons derived from a number of sources. A small fraction of these zircons has cores that are in the range of 4100-4200 Ma. The zircons were analyzed by a specially built high resolution ion probe at the Australian National University nicknamed 'SHRIMP'. The great advantage of this instrument over conventional analysis of zircons is not only that individual zircons can be analyzed, but individual parts of the zircons can be analyzed. The Mt. Narryer zircons have had complex histories suffering multiple metamorphic events between 4260 and 2600 Ma. The principle effect was the growth of rims of new material on the older cores around 3500 Ma. Conventional analysis of these zircons would not have recognized the older ages. The cores of these zircons, however, proved to be nearly concordant at the older ages. These ages determined by ion probe were initially highly controversial. By and large, however, the community has come to accept them as reliable, when performed carefully.

Subsequently even older zircons (would be more correct to say parts of zircons), were discovered in the Jack Hills of Australia. An ion probe date on one part of one of these zircons (Figure 9.6) is shown 4.404 Ga ±8 Ma. Thus the oldest known terrestrial materials are approaching the oldest ages from other planetary bodies, including the Moon, Mars, and asteroids (as represented by meteorites). They remain, however, significantly younger than the age of the Solar System, which is 4.556 Ga. Nevertheless, these very old ages seem to demonstrate that it is zircons, not diamonds, that "are forever".

## REFERENCES AND SUGGESTIONS FOR FURTHER READING

Bowring, S. A., I. S. Williams, and W. Compston, 3.96 Ga gneisses from the Slave province, Northwest Territories, Canada, *Geology*, 17: 971-975, 1989.

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