

## Appendix: Brief summary of the main features of the U-Pb technique

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The U-Pb dating method is based on the radioactive decay of  $^{238}\text{U}$  to  $^{206}\text{Pb}$  and  $^{235}\text{U}$  to  $^{207}\text{Pb}$ , both involving a chain of intermediate decay products and the emission of 8 and 7  $\alpha$  particles, and 6 and 4  $\beta^-$  particles, respectively. The currently adopted half-life time of  $^{238}\text{U}$  is 4.468 b.y. and that of  $^{235}\text{U}$  is 0.7038 b.y. (Jaffey et al., 1971). The different speeds of the two chronometers result in a continuous change of the ratio of radiogenic  $^{207}\text{Pb}$  to  $^{206}\text{Pb}$  with time. This ratio, therefore, is itself a direct expression of the age. The main advantage of the two U-Pb systems is the fact that they are overdetermined allowing the calculation of two separate ages whose agreement implies that the U-Pb system is in isotopic equilibrium, which in turn implies that there has been no disturbance and that the age is accurate. Disagreement between the two ages (i.e. discordance) shows that the system has not remained closed over its lifetime or, for young samples, lack of secular equilibrium in the decay chain. In most cases the open system behaviour is due to differential loss of daughter Pb.

The third related system is  $^{232}\text{Th}$  decaying to  $^{208}\text{Pb}$  with the emission of 6  $\alpha$  and 4  $\beta^-$  particles. Because Th is chemically distinct from U it may respond differently than U to geological processes affecting its host. Hence isotopic disturbances can develop for different reasons for Th-Pb than for U-Pb making the direct comparison between the two systems more problematic. The Th-Pb method is thus less commonly used than U-Pb, also due to some technically challenging aspects of the analysis.

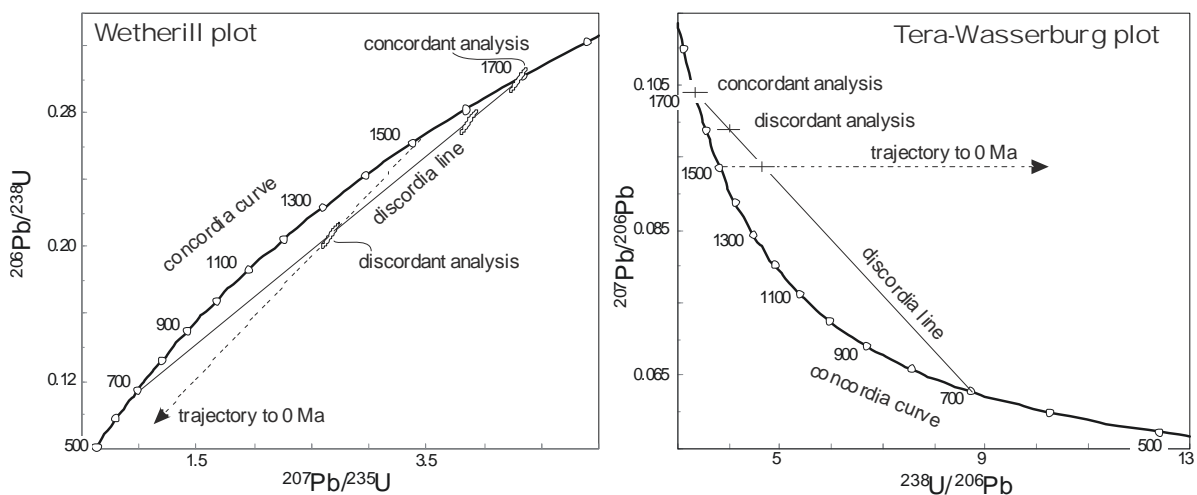


Fig. A1. Comparison of the two commonly used concordia plots.

It is convenient to examine U-Pb data graphically in concordia plots. The more commonly used Wetherill diagram, depicted in figure A1, is a plot of  $^{206}\text{Pb}/^{238}\text{U}$  vs.  $^{207}\text{Pb}/^{235}\text{U}$  (Wetherill, 1956a,b). Pairs of these ratios calculated for different ages define the concordia curve. The alternative Tera-

Wasserburg diagram is based on the relation between  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{238}\text{U}/^{206}\text{Pb}$  (Tera and Wasserburg, 1972). The age information that one can extract from these plots is essentially the same, but Tera-Wasserburg is preferred by some as there is a much smaller error correlation between  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{238}\text{U}/^{206}\text{Pb}$  than between  $^{206}\text{Pb}/^{238}\text{U}$  and  $^{207}\text{Pb}/^{235}\text{U}$ . In both diagrams, results obtained for closed systems plot on the concordia curve (concordant) whereas those obtained from open systems will plot off the curve (discordant), in simple cases with multiple analyses defining a discordia line whose intersections with the concordia curve indicates the time of formation and that of disturbance of the system. The Tera-Wasserburg plot can be expanded into a three-dimensional plot where the third axis is defined by  $^{204}\text{Pb}/^{206}\text{Pb}$ . This 3-D plot allows to deal with samples comprising substantial amounts of common Pb without requiring a priori correction. The data, uncorrected for common Pb are generally visualized as projections on the  $^{207}\text{Pb}/^{206}\text{Pb}$  and  $^{238}\text{U}/^{206}\text{Pb}$  plane, and for concordant populations having different proportions of radiogenic to common Pb they define a line whose intersection with concordia yields the age of crystallization. A version of the plot reduced to 2-D is used occasionally to visualize and interpret high common Pb data obtained by SIMS and LA-ICP-MS without measuring  $^{204}\text{Pb}/^{206}\text{Pb}$ .

The analytical uncertainties on individual U-Pb analyses integrate various components, including the measurement statistics, uncertainties arising from fractionation during ionization and systematic biases from the instrument, uncertainties in the tracer composition (for ID-TIMS) or those arising from the measurements of standards used to calibrate U-Pb ratios (for SIMS and LA-ICP-MS), uncertainties in the contribution and composition of the analytical blank and initial common Pb. The uncertainties on U-Pb ages determined from these data depend further on the coherence of multiple analyses and their closeness to the Concordia curve, or collinearity in defining discordia line. The precision of intercept ages is also dependent on the angle of intersection of a discordia line with the concordia curve, the uncertainty increasing with decreasing angle of intersection. External components contributing to the age uncertainties stem from the decay constants and the adopted values for the U composition.

The latter, systematic errors are relatively small, at the permil level or less, but become an important factor for high-precision data obtained by ID-TIMS whose precisions is at the level of a few permil for U-Pb and Pb-Pb ratios.

The percentage error on U-Pb ratios translates into proportionally smaller and smaller age uncertainties with time, for example, an uncertainty of 0.5% on  $^{206}\text{Pb}/^{238}\text{U}$  corresponds to about  $\pm 5$  Ma at 2700 Ma, but only  $\pm 0.3$  Ma at 50 Ma. By contrast, a typical error of 0.1% on the  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio corresponds to about  $\pm 1.7$  Ma at 2700 Ma but will increase to about 2.4 Ma at 50 Ma. In addition, very young samples contain proportionally much less radiogenic Pb, especially  $^{207}\text{Pb}$ , at 50 than at 2700 Ma, while the levels of analytical contamination or initial Pb remain constant. Thus, the measurement of  $^{207}\text{Pb}/^{206}\text{Pb}$  in young samples is less precise, both because of the weak signal in the mass spectrometer and the greater correction for common Pb. The  $^{207}\text{Pb}/^{235}\text{U}$  ratio of young samples is generally afflicted by the same difficulties, whereas  $^{206}\text{Pb}/^{238}\text{U}$  is much less affected by these problems because  $^{206}\text{Pb}$  is more

abundant than  $^{207}\text{Pb}$ . The ID-TIMS approach can counteract these problems to some degree by measuring for longer periods of time and collecting more data or by increasing the sample size. For SIMS and LA-ICP-MS these approaches are generally less of an option due to the practical limitations in the size of the beam and the depth of penetration into the grains. The difficulties in measuring  $^{207}\text{Pb}$  and  $^{204}\text{Pb}$  by the latter techniques can have an important impact on the obtained precision.

As a consequence of these various factors the  $^{207}\text{Pb}/^{206}\text{Pb}$  ages are generally most useful for Precambrian samples whereas for Phanerozoic samples the  $^{206}\text{Pb}/^{238}\text{U}$  becomes more informative.

More detailed description of various aspects of the analytical technique and error analysis can be found in Heaman and Parrish (1991), Parrish and Noble (2003), Bowring and Schmitz (2003) and Condon and Bowring (2012).

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