

Broken $^{206}\text{Pb}/^{238}\text{U}$ carbonate chronometers and $^{207}\text{Pb}/^{235}\text{U}$ fixes

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Carbonate U-Pb dating has become a key tool for Quaternary palaeoclimatology and palaeoanthropology beyond the ~800ka age limit of Th-U disequilibrium dating.

U-Pb geochronology is based on the paired radioactive decay of ^{238}U to ^{206}Pb and of ^{235}U to ^{207}Pb . Current carbonate U-Pb data processing algorithms rely mostly on the $^{206}\text{Pb}/^{238}\text{U}$ clock and attach little weight to the $^{207}\text{Pb}/^{235}\text{U}$ data. A key weakness of this approach is the need to correct the $^{206}\text{Pb}/^{238}\text{U}$ data for initial $^{234}\text{U}/^{238}\text{U}$ disequilibrium, which may cause an excess (or deficit) in radiogenic ^{206}Pb compared to secular equilibrium. The disequilibrium problem can be elegantly captured by matrix exponentials, using either an assumed initial composition, or a measured set of modern $^{234}\text{U}/^{238}\text{U}$ (and optionally $^{230}\text{Th}/^{238}\text{U}$) activity ratios.

When coupled with a deterministic Bayesian inversion algorithm, the matrix exponential formulation indicate that disequilibrium corrections work well for relatively young samples but become unreliable beyond 1.5Ma and impossible beyond 2Ma (Figure 1). Theoretical models and real world examples from Siberia, South Africa and Israel show that disequilibrium correction of such old samples can do more harm than good.

Previous 'Monte Carlo' error propagation methods underestimate these uncertainties by up to an order of magnitude. The $^{207}\text{Pb}/^{235}\text{U}$ isochron method is a more accurate and precise alternative to $^{206}\text{Pb}/^{238}\text{U}$ geochronology for >2Ma carbonates that are suspected to have experienced significant levels of initial $^{234}\text{U}/^{238}\text{U}$ disequilibrium.

Figure 1 shows the relative magnitude (a) and precision (b) of the initial $^{234}\text{U}/^{238}\text{U}$ disequilibrium correction against the corrected carbonate $^{206}\text{Pb}/^{238}\text{U}$ date for different values of the initial $^{234}\text{U}/^{238}\text{U}$ activity ratio (solid lines). The dashed line in panel b) marks the relative uncertainty interval when no disequilibrium measurement is available, defined as the difference between corrected dates using assumed initial $^{234}\text{U}/^{238}\text{U}$ activity ratios of 1 and 12. t_r = uncorrected ('raw') date, t_c = disequilibrium corrected data, t_l and t_u = lower and upper confidence limits of the disequilibrium correction, assuming 2 permil reproducibility of the $^{234}\text{U}/^{238}\text{U}$ activity ratio.

