



Quantifying time in sedimentary successions by radio-isotopic dating of ash beds

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Sedimentary rock sequences are an accurate record of geological, chemical and biological processes throughout the history of our planet. If we want to know more about the duration or the rates of some of these processes, we can apply methods of absolute age determination, i.e. of radio-isotopic dating. Data of highest precision and accuracy, and therefore of highest degree of confidence, are obtained by chemical abrasion, isotope-dilution, thermal ionization mass spectrometry (CA-ID-TIMS) ^{238}U - ^{206}Pb dating techniques, applied to magmatic zircon from ash beds that are interbedded with the sediments. This techniques allows high-precision estimates of age at the 0.1% uncertainty for single analyses, and down to 0.03% uncertainty for groups of statistically equivalent $^{206}\text{Pb}/^{238}\text{U}$ dates.

Such high precision is needed, since we would like the precision to be approximately equivalent or better than the (interpolated) duration of ammonoid zones in the Mesozoic (e.g., Ovtcharova et al. 2006), or to match short feedback rates of biological, climatic, or geochemical cycles after giant volcanic eruptions in large igneous provinces (LIP's), e.g., at the Permian/Triassic or the Triassic/Jurassic boundaries. We also wish to establish as precisely as possible temporal coincidence between the sedimentary record and short-lived volcanic events within the LIP's. Precision and accuracy of the U-Pb data has to be traceable and quantifiable in absolute terms, achieved by direct reference to the international kilogram, via an absolute calibration of the standard and isotopic tracer solutions. Only with a perfect control on precision and accuracy of radio-isotopic data, we can confidently determine whether two ages of geological events are really different, and avoid mistaking interlaboratory or interchronometer biases for age difference.

The development of unprecedented precision of CA-ID-TIMS ^{238}U - ^{206}Pb dates led to the recognition of protracted growth of zircon in a magmatic liquid (see, e.g., Schoene et al. 2012), which then becomes transferred into volcanic ashes as excess dispersion of ^{238}U - ^{206}Pb dates (see, e.g., Guex et al. 2012). Zircon is crystallizing in the magmatic liquid shortly before the volcanic eruption; we therefore aim at finding the youngest zircon date or youngest statistically equivalent cluster of ^{238}U - ^{206}Pb dates as an approximation of ash deposition (Wotzlaw et al. 2013). Time gaps between last zircon crystallization and eruption (" Δt ") may be as large as 100-200 ka, at the limits of analytical precision.

Understanding the magmatic crystallization history of zircon is the fundamental background for interpreting ash bed dates in a sedimentary succession. Ash beds of different stratigraphic position and age may be generated within different magmatic systems, showing different crystallization histories. A sufficient number of samples (N) is therefore of paramount importance, not to lose the stratigraphic age control in a given section, and to be able to discard samples with large Δt – but, how large has to be "N"?

In order to use the youngest zircon or zircons as an approximation of the age of eruption and ash deposition, we need to be sure that we have quantitatively solved the problem of post-crystallization lead loss – but, how can we be sure?! Ash bed zircons are prone to partial loss of radiogenic lead, because the ashes have been flushed by volcanic gases, as well as brines during sediment compaction. We therefore need to analyze a sufficient number of zircons (n) to be sure not to miss the youngest – but, how large has to be "n"?

Analysis of trace elements or oxygen, hafnium isotopic compositions in dated zircon may sometimes help to distinguish zircon that is in equilibrium with the last magmatic liquid, from those that are recycled from earlier crystallization episodes, or to recognize zircon with partial lead loss (Schoene et al. 2010).

Respecting these constraints, we may arrive at accurate correlation of periods of global environmental and biotic disturbance (from ash bed analysis in biostratigraphically or cyclostratigraphically well constrained marine sections) with volcanic activity; examples are the Triassic-Jurassic boundary and the Central Atlantic Magmatic Province (Schoene et al. 2010), or the lower Toarcian oceanic anoxic event and the Karoo Province volcanism (Sell et al. in prep.). High-precision temporal correlations may also be obtained by combining high-precision U-Pb dating with biochronology in the Middle Triassic (Ovtcharova et al., in prep.), or by comparing U-Pb dates with

astronomical timescales in the Upper Miocene (Wotzlaw et al., in prep.).

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