Precise two chronometer dating of pleistocene travertine: the ^{230}Th/^{234}U and ^{226}Ra$_{ex}$/^{234}U approach

J. Eikenberg
G. Vezzu

Paul Scherrer Institute, 5232 Villigen (PSI), Switzerland

G. Wyssling

Buero Wyssling AG, 8803 Pfaffhausen (ZH), Switzerland

Until recently it was not possible to develop a generally accepted model of the geological setting and evolution of the most impressive Swiss limestone caves near Lucerne. Nevertheless, the underlying sedimentary strata suggests that the impressive caves formed in the cause of the global warming following the last glacial period (i.e. less than 10^4 y before present). Fresh precipitates indicate further-more, that the formation of travertine is still active on this locality. Previous attempts using the most suitable dating methods (^{14}C radiocarbon method, pollen analyses) for such a young setting failed, because the carbon isotope composition in the extremely small fractions of fossil organic residues is strongly disturbed by carbon of inorganic origin from precipitating calcite. However, for geological systems which have been developed less than 3×10^5 y ago, radionuclides from the U and Th decay series may be used as chronometers, provided that fractionation processes such as different solubilities cause activity disequilibria between the different members (^{238,234}U, ^{230}Th, ^{226}Ra etc.) in the waters from where the preci-pitates are formed (e.g. Attendorn and Bowen, 1997).

Analytical techniques

After complete sample dissolution in HNO_3 and addition of the chemical yield calibration spikes (^{232}U, ^{228}Th, ^{209}Po) the following nuclides were analysed mainly using α-spectrometry: ^{238}U, ^{234}U, ^{232}Th, ^{230}Th and ^{226}Ra (the latter via its short lived progenies ^{222}Rn and ^{210}Po). U and Th were separated chromato-graphically and the sample discs were prepared using electrolytic deposition in $HNaSO_4$-medium. ^{226}Ra was determined indirectly by spontaneous deposition of ^{210}Po on silver discs and via emanation of ^{222}Rn into an organic cocktail which was counted using $\alpha\beta$-LSC. This was useful to select samples with ages below 100 years.

Results and discussion

Reducing the complex ^{238}U decay series into geologically relevant subsystems (i.e. oder than a few years) the following precursor-progeny relations hold

$$^{234}\text{U} \rightarrow {}^{230}\text{Th} \rightarrow {}^{226}\text{Ra} \rightarrow {}^{210}\text{Pb} \rightarrow {}^{210}\text{Po} \qquad (1)$$
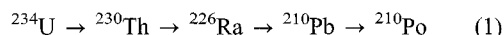
So far, two methods employing this decay chain have been applied successfully in the field of sedimentology. (i) ^{230}Th/^{234}U ingrowth dating for rock formations which evolved between $(0.5-3) \times 10^5$ y ago (e.g. Kaufmann, 1993) and (ii) ^{210}Pb excess decay dating (supplied from of soil-emanated ^{222}Rn into the atmosphere), i.e. a method which is mainly applied to determine sedimentation rates in lakes for the last 100 years (e.g. Robbins, 1978). There are, however, additional mother-daughter couples that are potentially useful for dating geological young systems. Figure 1 shows the evolution of the activity ratios in the ^{238}U series for hypothetical cases with initial daughter/parent ratios of 2 (two times daughter excess) and 0 (i.e. zero inherited daughter activity at the time of sample formation). The figure implies that the different chronometers can be applied in both directions, (i) decay of daughter excess and (ii) daughter ingrowth.
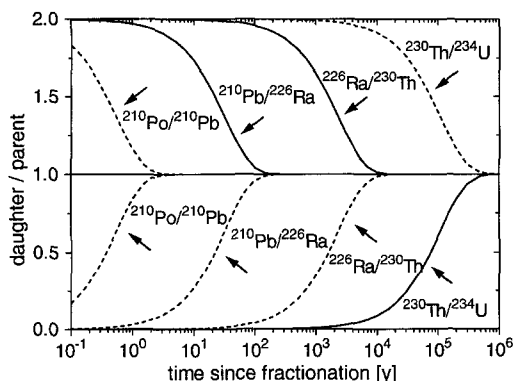

FIG. 1. Schematic illustration of time scales over which different pairs of the ^{238}U decay series members decay towards secular radioactive equilibrium.
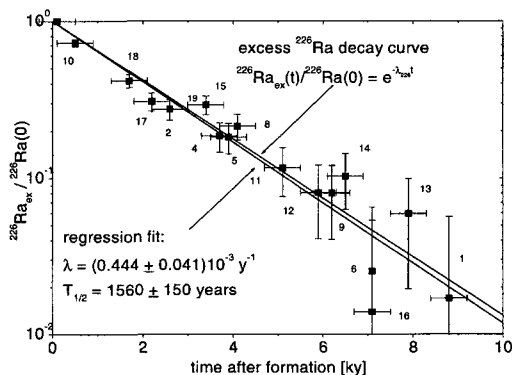
FIG. 2. Comparison of the analytical data to the theoretical decay of ^{226}Ra in a semi-log diagram with ^{226}Ra$_{ex}$/^{226}Ra(0) as a function of time.

Of special focus is the couple ^{226}Ra/^{230}Th, because this system ($T_{1/2}$ of ^{226}Ra = 1600y) may be suitable for dating rocks with formation ages between $\approx$ 100 years and about 8×10^3 y, i.e. an interval which would exactly close the time gap between the established systems ^{230}Th/^{234}U and ^{210}Pb$_{ex}$/^{226}Ra in a sedimentary environ-ment. These two systems of geological relevance as well as the presented ^{226}Ra$_{ex}$/^{230}Th chronometer (see below) are given as bold lines in Fig.1, while the dashed lines display all other hypothetical chronometers in sedimentology. Equations (2-4) show theoretically the ^{230}Th/^{234}U ingrowth and ^{226}Ra$_{ex}$/^{234}U excess decay relationship for an ideal system which started under the following boundary conditions: no initial ^{230}Th, i.e. ^{230}Th(t=0) = 0, no significant change of the ^{234}U activity with time, i.e. ^{234}U(t) = ^{234}U(0) and constant initial values of ^{226}Ra(0) in all samples independent of time.Provided that these boundary conditions are valid the following analytical solutions are obtained:

$$^{234}U(t) = {}^{234}U(0) \times e^{-\lambda_{238}t} \qquad (2)$$

$$^{230}Th(t) = {}^{234}U(t) \times (1 - e^{-\lambda_{230}t}) \qquad (3)$$

$$^{226}Ra(t) = {}^{226}Ra_{ex}(0) \times e^{-\lambda_{226}t} + \qquad (4)$$

$$^{234}U(t) \cdot \frac{\lambda_{226} \cdot (1 - e^{-\lambda_{226}t}) - \lambda_{230} \cdot (1 - e^{-\lambda_{230}t})}{\lambda_{226} - \lambda_{230}}$$

These relations show clearly that (i) the ^{230}Th ingrowth is dependent only on the uranium activity and, therefore, the ^{230}Th supported ^{226}Ra ingrowth is also dependent only on the ^{234}U activity. Since this coupled system is completely independent of ^{230}Th, we will refer to this couple as the ^{226}Ra$_{ex}$/^{234}U chronometer. Since the second term in equation (4) is nothing other than the U/Th supported ^{226}Ra ingrowth (^{226}Ra$_{sup}$), the amount of the residual excess ^{226}Ra surviving the decay of initially

incorporated Radium can be calculated as follows:

$$^{226}Ra_{ex}(t) = {}^{226}Ra_m - {}^{226}Ra_{sup}(t), \qquad (5)$$

where ^{226}Ra$_m$ is the measured total activity of ^{226}Ra. Normalizing this relationship to ^{226}Ra(0) (taken from samples with ^{230}Th/^{234}U < 10^{-3} and with ^{222}Rn/^{210}Po < 1) the ^{226}Ra$_{ex}$/^{234}U ages can be obtained in a similar manner to other dating systems based on decay of an excess component (such as ^{14}C dating), or,

$$\frac{{}^{226}Ra_m - {}^{226}Ra_{sup}(t)}{{}^{226}Ra_{ex}(0)} = e^{-\lambda_{226}t} . \qquad (6)$$

To calibrate the ^{226}Ra$_{ex}$/^{234}U chronometer, the boundary conditions mentioned above must be valid (all proofs discussed in Eikenberg et al., 1998) and the sample ages have to be known from independent determinations. The sample ages were obtained using precise ^{230}Th/^{234}U isochrone dating (Eikenberg et al, 1998). The resulting data are shown in Fig. 2 as ^{226}Ra$_{ex}$(t)/^{226}Ra(0) versus time on a semi-log plot. All those samples which started with identical ^{226}Ra(0) to the most recently formed travertine should plot on the theoretical ^{226}Ra$_{ex}$/^{226}Ra(0) decay curve. Indeed, most of the data plot on or are close to the curve and even samples which exhibit ages of 4 times the half live of ^{226}Ra still fit well to the decay curve. From the youngest to the oldest samples the data cover, in summary, a range of more than one order of magnitude with respect to ^{226}Ra$_{ex}$(t)/^{226}Ra(0).

Although the data argue strongly for a constant initial input of ^{226}Ra into the precipitating material, there is a further proof to justify this conclusion. In particular, as the earth alkaline element Ba behaves chemically very similar to Ra, it is interesting to study the variation of Ba in the rocks samples. Since the concentration of Ca in the authigenic phase is constant (pure calcium carbonate) it is most suitable to use the Ba/Ca ratios as a measure on the variability of initial ^{226}Ra. Analysis of six samples yielded highly constant values of $(4.90 \pm 0.2) \times 10^{-3}$ g/g, hence suggesting invariant ^{226}Ra concentrations at any time of travertine formation at this locality.

References

[1] Attendorn, H.G. and Bowen, R.N.C. (1997) Chapman & Hall, London-New York, 522 pp.

[2] Kaufmann, A. (1993) Geochim. Cosmochim. Acta, 57, 2303–17.

[3] Robbins, J.A. (1978) In: The Biochemistry of Lead in the Environment, ed. J.O. Niagru. Elsevier, Amsterdam.

[4] Eikenberg, J., Vezzu, G., Zumsteg, I., Bajo, S., Rüthi, M. and Wyssling, G. (this work, submitted to Geochim. Cosmochim. Acta, 1998).