U-Pb dating of paleocaliche in the Triassic New Haven Arkose, Hartford Basin, Connecticut

Z S Wang, E T Rasbury, G N Hanson, W J Meyers
Department of Earth and Space Sciences
SUNY at Stony Brook, NY 11794-2100, USA
Tel: 516-632-8294; E-mail: Zhwang@ccvm.sunysb.edu

A long-standing problem in geology has been the inability of directly determining the absolute age for the time of sedimentation of sedimentary rocks. The absolute ages for geologic time scale boundaries in the early Phanerozoic have been determined generally by extrapolating from a relatively few, precisely dated intrusive and volcanic rocks (Harland et al., 1990). Significant errors have been introduced and perhaps magnified by correlation of stage boundaries and by extrapolation to zonal or other boundaries within stages. Therefore, most stage, epoch and period boundaries prior to the Cretaceous have uncertainties of 10 to 30 Ma (2σ). In many cases the uncertainty in the boundary ages is equivalent to or greater than the period of time between boundaries.

The ultimate goal of our research is to directly date times of sedimentation. We have chosen pedogenic paleocaliches for absolute age determination because they are very common in terrestrial and shallow marine sedimentary sequences; and paleosols represent paleo-exposure surfaces, or unconformities, which are stratigraphic or sequence boundaries possibly. Caliche or calcrete layers in paleosol are good candidates for U-Pb dating because:

(1) caliche consists of low-mg calcite which is not easily recrystallized during later diagenesis;
(2) uranium is enriched in pedogenic calcite relative to lead;
(3) pedogenic calcite can be identified and distinguished from later calcite in the field, petrographically and geochemically;
(4) U-Pb dating system has the potential of being precise; and
(5) caliches are common in many rapidly deposited sediments throughout the Phanerozoic.

Here we present early results of U-Pb dating of paleocaliche in the Triassic New Haven Arkose, Hartford Basin, Connecticut. The New Haven Arkose consists of 2000 meters of fluvial and alluvial facies with numerous caliche horizons. The section near Meriden is about 130 meters thick and is several hundreds of meters (?) below the Triassic/Jurassic boundary. There are two major problems in U-Pb dating of paleocaliche: (1) recognizing calcite samples which are pedogenic, U-enriched, and free of later diagenetic overprint; (2) separating about 1ppm U and Pb from 400,000ppm Ca.

Petrographic studies reveal at least three generations of calcite that coexist in the caliches. The first generation is micritic calcite with dull cathodoluminescence. The second generation is blocky calcite with dark cathodoluminescence. The third generation is blocky calcite with very bright cathodoluminescence. The first two generations of calcite are closely associated with root related fabrics and precipitated before the internal sediments. The third generation fills pore space left by the first two generations of calcite and precipitated after the internal sediments. Each generation has distinct trace element, carbon isotope and oxygen isotope signatures (Table 1).

U and Mn abundance in calcite are good indicators of redox conditions of aqueous solutions in which calcite precipitated. Although the redox condition is not the primary control on the precipitation of calcite, it is a major factor in determining the mobility of U and Mn in soil profile. Mn is very insoluble under oxidizing conditions, but is mobile under reducing conditions. U, however, is mobile under oxidizing conditions and immobile under reducing conditions. In a soil profile the redox conditions are generally a function of depth. With increased depth, the conditions become more reducing. Thus, U and Mn abundance in calcite are dependent on the depth at which calcite was precipitated.

Table 1, Petrographic and chemical characteristics of calcite

Generation	First	Second	Third
Type	Micritic	Blocky	Blocky
Mg ppm (Electron microprobe)	1600 (n=4)	1085 (n=3)	15 (n=3)
Mn ppm (Electron microprobe)	345 (n=4)	<200 (n=3)	1915 (n=3)
Uranium (Fission track density)	Relatively high	Relatively high	Relatively low
$\delta^{13}C_{PDB}$ ‰	-8.6 to -6.4 (n=22)	-7.7 to -6.4 (n=8)	-9.2 to -6.9 (n=9)
$\delta^{18}O_{PDB}$ ‰	-6.5 to -4.6 (n=22)	-6.4 to -5.7 (n=8)	-10.7 to -5.9 (n=9)

The U and Mn data for the three generations of calcite (Table 1) suggest that the first two generations of calcite precipitated under more oxidizing conditions, i.e. they have lower Mn and higher U or nearer the groundsurface. The third generation calcite precipitated in a relatively more reducing environment as suggested by the lower U and higher Mn abundances. All three generations of calcites have similar $\delta^{13}C$ which is typical of soil carbonate. The oxygen isotope data are also typical of soil calcite. The third generation, however, has a larger range of $\delta^{18}O$ than that of other two generations. Based on above petrographic and geochemical evidence, we interpret the first two generations of calcite to be pedogenic calcite, while the third generation may include not only pedogenic calicite but also burial or groundwater calcite. Thus the first two generations of calcite are good candidates for U-Pb dating of the time of pedogenesis.

The U-Pb isotopic analysis of first generation micritic calcite in the Meriden section gives very encouraging results (Table 2). We have selected multiple aliquots of a *ca.* 100 gram sample from a horizontal sheet crack which is several hundreds of meters below the Triassic/Jurassic boundary. This pure, U enriched, pedogenic calcite sample has been dated independently by Z.S.Wang and E.T. Rasbury. They used different chemistries, different sized aliquots, and different isotopically enriched spikes. The U-Pb ages overlap each other within uncertainty (Table 2). We have calculated $^{238}U/^{206}Pb$ ages using two different isochron systems. The uncertainty in the $^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$ isochron (Rasbury *et al*, 1996) is about half that of the $^{238}U/^{204}Pb$-$^{206}Pb/^{204}Pb$ isochron because the $^{207}Pb/^{206}Pb$ ratio can be measured more precisely than the $^{206}Pb/^{204}Pb$ ratio and there is probably less variation in the $^{207}Pb/^{206}Pb$ initial ratio. The average age of 214 ± 3 Ma is in good agreement with the Triassic/Jurassic boundary age of 208±16 Ma (2σ) (Harland *et al*, 1990). These data suggest that it is possible to get precise ages with uncertainties of less than 3 Ma on paleocaliche using the U-Pb system.

Table 2, U-Pb isochron ages of aliquots of a caliche sample from the New Haven Arkose, Hartford Basin, Connecticut

Analyst	$^{238}U/^{204}Pb$-$^{206}Pb/^{204}Pb$ isochron age (Ma)	$^{238}U/^{206}Pb$-$^{207}Pb/^{206}Pb$ isochron age (Ma)
Rasbury	218 ± 5.4 (2σ) n=6	216.2 ± 3.1 (2σ) n=6
Wang	212.7 ± 4.8 (2σ) n=9	211.9 ± 2.1 (2σ) n=9

References Cited

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