Neogene to Quaternary U-Th-Pb geochronology using opal, Yucca Mountain, Nevada, USA

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Finding suitable sites for nuclear waste disposal, as well as a wide range of other environmental problems, requires accurate geochronological information to constrain Neogene and Quaternary geologic and hydrogeologic processes. Opal-rich materials in the semi-arid environments of southwest Nevada yield isotopic ages by both U-series dating in the range of 0 to 500 ka (thousand years before present) and U-Pb dating of materials from 10 Ma (million years before present) to 50 ka. These two methods are being used for hydrogeologic and climate studies associated with site characterization of the potential high-level radioactive waste repository at Yucca Mountain.

Opal ($SiO_2{\cdot}nH_2O$) is formed in low-temperature (less than 50°C) environments by precipitation from aqueous solutions or by coagulation of colloidal silica gels. Oxygenated surface and vadose waters dissolve uranium from the felsic volcanic rocks. The limited solubility of thorium and lead in these aqueous solutions with near-neutral pH results in low common Pb and ^{232}Th abundances in opal. Consequently, these opal-rich materials typically have elevated uranium contents and large $^{230}\mathrm{Th}/^{232}\mathrm{Th}_{\mathrm{activity}}$ and $^{238}\mathrm{U}/^{204}\mathrm{Pb}$ ratios, making opal an attractive candidate for ^{230}Th/U and U-Pb dating.

Geological setting and samples

Yucca Mountain is located within the southwestern Nevada volcanic field (USA) and is composed of a 1 to 3 km-thick sequence of 12 to 13 Ma felsic volcanic rocks (Sawyer *et al.*, 1994). Site characterization studies require reliable dating of surficial deposits, ground water discharge deposits and vadose zone hydrogenic deposits to establish hydrologic response to past climate variations. Hydrogenic silica in two fundamentally different environments has been dated by ^{230}Th-U and U-Pb methods. 1) *Soil environments.* Thin (a few tenths of mm to several mm) rinds of calcite plus opal occur on rock clasts in soils. Innermost layers of these clast rinds are the oldest pedogenic materials within a given horizon and reflect soil-formation ages that are relatively close to alluvial deposition events. Opal-rich rhizoliths (petrified plant roots) from buried soils also yield precise ^{230}Th/U ages; however, these materials may or may not be closely associated with depositional events. 2) *Subsurface fracture and cavity coatings.* Opal and chalcedony samples were obtained from drill core and collected from tunnel walls. Dating of subsurface mineral deposits provide insights into the processes of vadose-zone fracture flow and the links between percolation and climate change.

The surficial and subsurface opal deposits are morphologically distinct. Opal-rich material in surface deposits is typically tan, opaque, and finely intergrown with authigenic calcite. Although coarse detritus is commonly excluded from innermost rinds, a fine-grained detrital component is invariably present and cannot be separated mechanically. These samples are totally digested and subsequent analyses represent a mixture of opal and calcite components. In contrast, vadose-zone opal is generally clear, high-purity silica that fluoresces bright green under ultraviolet illumination due to elevated uranium contents. It is commonly interlayered with calcite, but remains discrete so that physical separation of the two phases is possible.

Analytical techniques

Silica-enriched materials were obtained by microsampling techniques using dental burrs and picks under binocular magnification. Subsamples were digested using hydrofluoric acid (HF) and nitric acid (HNO_3) and spiked either with ^{229}Th-^{236}U spike (for U-series studies), or with ^{229}Th-^{236}U-^{233}U-^{205}Pb spike (for combined U-series and U-Pb studies). After equilibration, U, Th and Pb were purified using ion-exchange chromatography, and analysed by thermal ionization mass-spectrometry (TIMS). Blanks during this study were less than 5 picograms (pg) for U and Th, and approximately 1 pg for Pb.

An acid wash (1N HCl or 10% acetic acid) may be used for vadose-zone opals to remove surface contamination and any admixed calcite. The effect of this acid treatment on the U-Th-Pb system was tested by two series of experiments: one on a calcite and opal mixture and another on a pure opal sample. Resulting data do not show any appreciable effects on the U-Th-Pb system, which demonstrates the robustness of opal to at least short-lived interactions with corrosive solutions.

Results

Opal-rich clast rinds and rhizoliths from the soil zone have U concentrations of 5 to 30 ppm and have measured ^{230}Th/^{232}Th activity ratios from approximately 3 to several hundred. The presence of ^{232}Th in these materials requires small corrections for initial ^{230}Th from the detrital components. Corrected ^{230}Th/U ages typically have 2σ errors less than 2 percent of the stated value. Resulting ^{230}Th/U ages range from several thousand years to finite ages over 500 ka (albeit the latter has large uncertainties). Ages are generally in agreement with observed growth stratigraphy of the samples and with limited dates by radiocarbon and thermoluminescence methods obtained for the same soil horizons. In addition, a consistent range of values between about 1.4 and 1.9 for initial ^{234}U/^{238}U ratios is observed for pedogenic materials, which is a good indication of the veracity of a given analysis.

In contrast with surficial opal occurrences, detrital components are absent in vadose-zone opal and chalcedony, resulting in extremely low Th/U ratios (10^{-2} to 10^{-5}), high ^{230}Th/^{232}Th activity ratio (up to 10^6) and ^{238}U/^{204}Pb (up to 10^8). Consequently, correction for initial ^{230}Th is negligible for age determinations. Opal is richer in uranium than chalcedony (typically 50-200 ppm in opal compared to 5-15 ppm in chalcedony). Low common Pb abundances in opal (in most samples, measured ^{206}Pb/^{204}Pb ratios are greater than 100) allowed determination of common lead-corrected ^{206}Pb*/^{238}U and ^{207}Pb*/^{235}U ratios with typical 2σ errors of less than 3% and 10%, respectively. Uranium-series determinations of opal and calcite younger than 100 ka indicate that a wide range in initial ^{234}U/^{238}U is present (activity ratios of 4 to 9.5). This range in initial ratios limits the U-Pb technique based on ^{206}Pb*/^{238}U ratios, because the initial ^{234}U/^{238}U activity ratio should be known. To overcome this limitation in the youngest opals, U-Th-Pb data are interpreted using a new set of concordia diagrams with ^{234}U/^{238}U, ^{206}Pb*/^{238}U, ^{230}Th/^{238}U and ^{207}Pb*/^{235}U axes. Initial ^{234}U/^{238}U activity ratios and ages (both ^{206}Pb*/^{238}U and ^{230}Th/U) are calculated assuming the system has remained closed to parent-daughter isotope mobility since deposition. The closed system assumption is tested using the ^{206}Pb*/^{238}U-^{207}Pb*/^{235}U concordia, consisting of a family of curves for different initial ^{234}U/^{238}U activity ratios. Outermost opal layers show nearly concordant U-Pb ages from 50 to 1611 ka. Use of the U-Pb technique to date these Quaternary opals significantly extends the age range beyond that of conventional U-series methods.

Opal and chalcedony in the interiors of these mineral coatings have U-Pb ages that are consistent with the mineral growth microstratigraphy. U-Pb ages for clear opal in intermediate stratigraphic positions range from 0.5 to 8 Ma whereas ages between 8 to 10 Ma are obtained from translucent gray chalcedony at the base of some of the coatings. Combined U-Pb and ^{230}Th/U ages of multiple horizons within the sample support an interpretation of low and uniform rates of mineral deposition (approximately 1 to 4 mm per million years) resulting in the observed micrometer-scale layering.

Conclusion

The data obtained indicate that low-temperature secondary opal-rich material from soil environments and subsurface fracture coatings at Yucca Mountain, Nevada have elevated uranium concentrations and low contents of ^{232}Th and common lead. These materials can be used for U-series and U-Pb age determinations in the age range from several thousands to greater than 10 million years.

References

Sawyer, D.A., Fleck, R.J., Lanphere, M.A., Warren, R.G., and Broxton, D.E., (1994) *GSA Bull.*, **106**, 1304–18.