# *In situ* O & Si isotopic microanalysis of diagenetic cements: Basin brines vs. weathering, low vs. high T

ANTHONY D. POLLINGTON*, REINHARD KOZDON,
KOUKI KITAJIMA, ARIEL STRICKLAND
AND J.W. VALLEY

WiscSIMS, Dept. Geoscience, Univ. Wisconsin, Madison, WI 53706, USA
(*correspondence: apolling@geology.wisc.edu)

Secondary minerals, such as diagenetic overgrowths, are potential recorders of processes in surface and shallow subsurface environments. Quartz overgrowths incorporate chemical and isotopic signatures of the fluids from which they grow; the composition of these fluids in turn being influenced by factors such as chemical weathering of the source region and interactions with rocks along a flow path.

*In situ* microanalyses of $\delta^{18}O$ in isotopically-zoned quartz overgrowths from the Cambrian Mt. Simon Sandstone in central North America reveal growth from a compositionally ($\delta^{18}O$) constant fluid during an evolving temperature history of burial and heating [1]. The temperatures calculated from $\delta^{18}O$ values indicate that drill core samples from the Illinois Basin grew in response to burial/heating and are consistent with geotherm temperature-depth estimates (50 to 110°C). However, overgrowths from most outcrop samples on the Wisconsin Dome, which have never been deeply buried, indicate growth at low temperatures (~35°C).

We have also measured Si isotope ratios and trace element concentrations in the same overgrowths. The $\delta^{30}Si$ values for most samples indicate growth from a source dominated by primary igneous Si (such as detrital sand grains). However, samples from one outcrop, ~5m above the Precambrian unconformity, have $\delta^{30}Si$ values that are among the lowest terrestrial values reported (-5.44‰ to -0.40‰) as well as unusually low $\delta^{18}O$ values suggesting hydrothermal precipitation. Chemical weathering has been proposed as a mechanism to explain low $\delta^{30}Si$ values in overgrowths [2].

Trace element concentrations are relatively low in detrital quartz, and overgrowths from the basin samples. In quartz overgrowths from outcrop samples though, concentrations of some elements (in particular Li and Al) are at least 1-2 orders of magnitude higher than the detrital material. Trace element concentrations, $\delta^{18}O$ and $\delta^{30}Si$ values are distinctly different for outcrop samples versus basin samples. This possibly reflects interaction of fluids with a weathered protolith, such as the nearby paleosol that underlies the formation on the Cambrian-Precambrian unconformity.

[1] Pollington *et al.* (2010) *Geochimica et Cosmochimica Acta Suppl.* **74**, A823. [2] Basile-Doelsch *et al.* (2005) *Nature* **433**, 399–402.

---

# Reaction paths and volume changes of solid solutions in coupled dissolution-precipitation reactions: The role of endmember solubility

K. POLLOK[1]*, C.V. PUTNIS[2] AND A. PUTNIS[2]

[1]Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany
(*correspondence: kilian.pollok@uni-bayreuth.de)
[2]Institut für Mineralogie, Universität Münster, Corrensstr. 24, D-48149 Münster, Germany

Mineral-fluid reactions towards equilibration involve readjustment of the phase assemblage and its composition. Such reequilibration is commonly accomplished by dissolution and precipitation reactions at Earth's surface and at crustal conditions when fluid flow is pervasive. As most rock-forming mineral systems are, to various extents, solid solutions, they respond to the fluid chemistry by readjusting their composition. This can be often observed as a pseudomorphic replacement. In this context, the concept of solubility becomes complicated once solid solution-aqueous solution (SS-AS) relationships are taken into account [1].

Based on the internally consistent description of solubility and SS-AS equilibrium states in the model $KBr\text{-}KCl\text{-}H_2O$ system [2] a quantitative treatment of various reaction paths and their associated volume changes is presented. It allows to derive various scenarios for dissolution-precipitation reactions based on solid-fluid ratio, local equilibrium or limited transport at the reacting interface which in turn can provide qualitative predictions on the kinetics of the replacement reaction.

In many cases, volume changes are preserved in replaced minerals as intracrystalline porosity which can facilitate transport from and to the reaction front [3]. Data on the solubility of solid solutions in complex aqueous fluids at higher temperature and pressure is still limited. However, the determined porosity in partly replaced minerals (either natural or experimental) can be used to roughly estimate the solubility difference of the parent and product phases. This concept as well as its limitations will be demonstrated for various rock-forming minerals and is intended to facilitate more experimental work to ascertain the role of porosity generation in interface-coupled dissolution-precipitation reactions.

[1] Prieto, M. (2009) *Rev Min Geochem* **70**, 47–85. [2] Pollok, K. *et al.* (2011) *Am J Sci* **311**, DOI: 10.2475/03.2011.02. [3] Putnis, A. (2009) *Rev Min Geochem* **70**, 87–124.