

Tracking Fluids, Climate and Crystal Chemistry using the Stable Isotope Compositions of Clays

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The use of stable hydrogen and oxygen isotopic compositions of clay minerals to determine the origin and evolution of pore water in low temperature environments, and to deduce temperatures in these systems, was first elucidated by Sheppard *et al.* (1969), Savin and Epstein (1970) and Lawrence and Taylor (1971, 1972). Today's presentation provides an overview of our group's applications of these principles in sedimentary systems, and outlines some current challenges.

The stable isotopic analysis of secondary minerals in the pore-systems of sedimentary rocks has been a standard technique for elucidating fluid movement and evolution in sedimentary basins since the 1980s. For example, diagenetic clays provided a definitive stable isotopic record of Eocene influx of meteoric water into most sandstones in the northern portion of the Western Interior Basin of North America. This occurred in response to mountain-building during latter stages of the Laramide Orogeny (Longstaffe, 1993). Likewise, H- and O-isotope analyses of secondary chlorite and illite provided evidence for tectonically motivated, multiple episodes of rock-water interaction along the Precambrian-Paleozoic unconformity in the Appalachian Basin of North America (Ziegler and Longstaffe, 2000a,b). Hot basinal brines, driven westward by Taconic orogenic events, controlled chlorite formation. Illitic clays formed later from local meteoric water during basement reactivation related to distal Acadian and Alleghanian orogenic activity. A similar approach was possible in the quite different tectonic setting of the Dead Sea Graben. There, the stable isotopic compositions of secondary minerals provided evidence for multiple (and layered) fluid regimes (Longstaffe et al., 2003). In each case, the understanding

of regional paleofluid behaviour provided insight into the distribution of hydrocarbon and mineral deposits.

There have also been practical applications to petroleum exploitation. For example, steam is injected into very viscous deposits of the Alberta oil sands (the largest hydrocarbon accumulations in the world) to facilitate *in situ* hydrocarbon recovery. Steam generation adds considerably to the cost of hydrocarbon extraction. Hence there is interest in understanding its movement in the subsurface, and in particular, whether or not the steam is interacting with the targetted reservoir as planned. Changes in the hydrogen and oxygen isotopic compositions of clay minerals can be used to trace the extent and temperature of contact between the injected fluid and the reservoir.

The climate archive stored in the isotopic compositions of hydrous minerals from ancient soils has been pursued with increasing interest since the mid-1990s. The goal is to understand the nature and rates of fluctuations in Earth's temperature and humidity, particularly in mid-continental regions. We have examined the hydrogen and oxygen isotopic compositions of pedogenic clay minerals from Cretaceous paleosols from northern regions of the Western Interior Basin. These results have been used as a proxy for paleoprecipitation, whose isotopic composition, in turn, can be used to infer temperature and prevailing atmospheric moisture conditions at that time (Vitali et al., 2002). Holocene climate change in mid-continental North America is of more pressing interest. The complex relationships amongst the oxygen isotopic compositions of grass phytoliths (opal-A) and coexisting cellulose on one hand, and source water, temperature and humidity, on the other hand, are gradually being deciphered (Webb and Longstaffe, 2002, 2003). As a result, grass phytoliths and cellulose have potential as isotopic paleoclimate proxies in ancient soils where both phases accumulate.

The stable isotope approach presumes that hydrous minerals can be isolated and analyzed without changing their original isotopic compositions. We have evaluated most of the common pretreatment methods. We have learned that 'less is best'. Stable isotopic study of hydrous minerals also depends upon reliable knowledge of mineral-water fractionation factors. Patience is a virtue in measurement of mineral-water fractionation factors at low temperatures. Years of growth, for example, were needed to provide convincing experimental measurements of the O- and H-isotope fractionation factors for gibbsite (Vitali et al., 2001). Post-formational isotopic exchange between hydrous minerals and ambient water is also of concern. Debate still rages concerning the coupled (hydroxyl group) versus decoupled (proton) nature of isotopic exchange between hydrous phases and water.

Different minerals are affected differently, in ways still being discovered. For example, 1.0nm halloysite exhibits significant oxygen (in addition to hydrogen) isotopic exchange at room temperature, a feature largely absent from the 0.7nm variety. A still greater challenge is provided by the possibility that some hydrous minerals inherit part of their compositions from precursors. Experiments involving transformation of berthierine (a 1:1 layer, Fe-rich clay mineral) to saponite (a 2:1 layer smectite) suggest that such inheritance can occur. This observation challenges yet another assumption commonly employed in interpretation of the stable isotopic compositions of clay minerals.

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