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Stable isotope records of hydrologic change and paleotemperature from smectite in Cenozoic western North America

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Abstract

The oxygen and hydrogen isotopic composition of soil water ($\delta^{18}O_w$ and δD_w hereafter) reflect the history of water through processes such as source evaporation, precipitation and vapor recycling. Temperature, humidity, evaporation, and post-condensation processes can affect $\delta^{18}O_w$ and δD_w. As such, isotope proxy records are often limited in their ability to constrain paleoclimate, paleoecology or paleoelevation without independently corroborating data. Smectite preserves both the hydrogen and oxygen isotope signature of parent water, and therefore provides critical insight into meteoric water line relationships and paleotemperature. Here, we use *in situ* pedogenic smectite $\delta^{18}O$ and δD records to characterize the evolution of the hydrologic cycle in Cenozoic western North America. We incorporate 192 samples, 119 of which are previously unpublished, from 11 Cenozoic basins representing a range of environments in the Basin and Range, Rocky Mountains and Great Plains. Our results indicate that the processes controlling smectite isotopic compositions vary both regionally and temporally. In some localities such as Oligocene to Pleistocene western Nebraska, change in temperature is the primary control on smectite isotopic composition. In other basins such as in Miocene Trapper Creek, ID, isotope values lie along the meteoric water line, suggesting change in meteoric water composition is responsible for the variation. In most basins, especially those in the Neogene Basin and Range, smectite line slope suggests either evaporation of previously meteoric water or a combination of change in paleotemperature and meteoric water composition. Smectite geothermometry suggests mineral formation temperatures of 30–40 °C in the Middle Miocene in the Rocky Mountains, Great Plains and Basin and Range, and a decrease of 10–15 °C since the Middle Miocene Climatic Optimum, consistent with clumped isotope and paleofloral temperature estimates.

1. INTRODUCTION

The oxygen and hydrogen isotopic compositions of soil water ($\delta^{18}O_w$ and δD_w hereafter) reflect the history of water as they are affected by processes such as source evaporation, precipitation and vapor recycling (e.g., Craig, 1961; Craig and Gordon, 1965). A variety of geochemical proxies such as calcium carbonate, silicates, hydrated volcanic glass, and mammalian tooth enamel record the isotopic signature of ancient water, and have been widely applied to interpret and constrain paleoclimatic and paleotopographic change in western North America (e.g., Kohn et al., 2002; Poage and Chamberlain, 2002; Horton et al., 2004; Mulch et al., 2006, 2007, 2008; Mix et al., 2011, 2013). Since many factors can affect $\delta^{18}O_w$ and δD_w, isotope records are often limited in their ability to constrain paleoclimate, paleoecology or paleoelevation without independently

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corroborating data. This is particularly true for studies of a single isotope system, as these techniques are unable to constrain critical features of the hydrologic regime such as local meteoric water line slope and evaporation.

Smectite, along with other clay minerals, chert, goethite, gibbsite and some other materials provide the advantage of recording both the hydrogen and oxygen isotopic signatures of parent water (e.g., Lawrence and Taylor, 1971, 1972; Yeh and Epstein, 1978; Yapp, 1987), but have been less frequently applied (Stern et al., 1997; Chamberlain and Poage, 2000; Takeuchi and Larson, 2005; Abruzzese et al., 2005; Sjostrom et al., 2006; Mulch et al., 2006). Smectite refers to a family of 2:1 clay minerals that typically form as weathering products of aluminosilicates. The Cenozoic stratigraphy of western North America is well suited to the use of smectite as a proxy due to its abundant silicic ashes that weather rapidly to smectite in the shallow subsurface (Stanley and Benson, 1979; Stanley and Faure, 1979). Furthermore, these spatially-extensive ashes have been well studied and provide high quality radiometric age control for paleoclimate reconstructions.

Herein, we incorporate pedogenic smectite samples from a range of environments in the Basin and Range, Rocky Mountains and Great Plains (Fig. 1). First, we apply a combined oxygen and hydrogen isotope approach to characterize meteoric water relationships in the past. We use the slope of δ^{18}O–δD data to distinguish among meteoric water composition, temperature, and/or aridity as drivers of isotopic change. Second, due to differences in the equilibrium fractionation of hydrogen and oxygen, the temperature of mineral formation can be reconstructed with smectite δ^{18}O and δD values. In this study, we produce long-term temperature records from smectite in western North America. In short, our findings demonstrate that causes of isotopic change in smectite vary both spatially and temporally, and that mineral formation temperatures decreased since the Middle Miocene.

2. COMBINED OXYGEN AND HYDROGEN ISOTOPE APPROACH

2.1. δ^{18}O–δD relationships in meteoric water and smectite

δ^{18}O and δD of meteoric water reflect many aspects of the hydrologic cycle, and have since been used in a number of applications including studies of paleoelevation, decoupling evaporation and transpiration and delineating air mass trajectories (Craig, 1961; Dansgaard, 1964; Rozanski et al., 1993). Globally, precipitation falls on a meteoric water line (GMWL) with a slope of approximately 8, and a y-intercept, or deuterium excess, of approximately 10 (Friedman, 1953; Craig, 1961) (Fig. 2). Regional variations in these slopes and intercepts in meteoric and surface waters are large, however. In the continental United States, the slopes of local meteoric water lines (LMWLs) inferred from stream waters range from 5 to 13, with an average of 6.1 (Kendall and Coplen, 2001). LMWL slopes are often lower than the GMWL value of ~8 due to low humidity and evaporation (Yurtsever and Gat, 1981). This relationship reflects differences in the kinetic effects of oxygen and hydrogen associated with evaporation, driving waters to evolve along an evaporation trend of a lower slope than the GMWL. The slope decreases as relative humidity decreases. For example, in arid environments with relative humidity less than 25%, surface water line slopes are ~4, whereas for a relative humidity of over 95%, the evaporation-driven trend approaches the GMWL slope of ~8 (Clark and Fritz, 1997). Smectite that forms in equilibrium with these waters will create linear arrays on δ^{18}O–δD diagrams, hereafter referred to as *smectite lines*. The gap between the smectite lines and the meteoric water line represent the temperature-dependent equilibrium fractionation between smectite and water (Fig. 2).

For each stratigraphic section included in this study, we plotted δ^{18}O vs. δD in order to examine the relationships

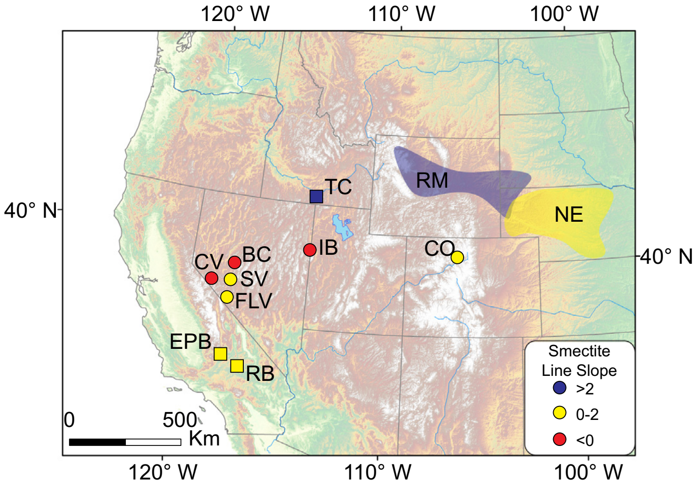

Fig. 1. The eleven stratigraphic sections used in this study. Circles indicate new data while squares shows previously published work. Color represents ancient meteoric water line slope reconstructed from smectite. The two shaded regions show the sampled area for composite sections of the east-flank of the Rocky Mountains of Sjostrom et al. (2006) and Nebraska (this study). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)