

**STABLE ISOTOPE CHARACTERIZATION OF A TERRESTRIAL KIESERITE WITH COMPARISONS TO OTHER SULFATE MINERALS.** V.W. Lueth<sup>1</sup>, A.R. Campbell<sup>2</sup>, and J.J. Papike<sup>3</sup>, <sup>1</sup>New Mexico Bureau of Geology & Mineral Resources, New Mexico Tech, Socorro, NM 87801 (vwlueth@nmt.edu); <sup>2</sup>Dept. of Earth & Environmental Sciences, New Mexico Tech, Socorro, NM 87801; <sup>3</sup>Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131

**Introduction:** Previous missions to Mars have documented that sulfate minerals are important components in the Martian regolith. Kieserite, gypsum, and jarosite are among the sulfate minerals identified and represent an important opportunity to understand water-rock-atmospheric interactions that led to their formation via stable isotope analysis. Here we characterize the stable isotope compositions of a terrestrial kieserite ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ) from Lehrte, Niedersachsen (Lower Saxony), Germany, kindly provided by the Smithsonian Institution. Some nonisotopic analytical results from this same sample were reported earlier [1]. This sample appears to be from Permian evaporates in the Hansa mine area where the Stassfurt bed consists mostly of a kieserite-sylvite-halite assemblage. We then compare the results of the kieserite analysis to gypsum from similar marine environments and speculate on the reliability of kieserite isotopic analyses.

**Stable Isotope Analysis:** Stable isotopes of sulfur, oxygen (sulfate oxygen only), and hydrogen were run at New Mexico Tech in conjunction with a number of other sulfate minerals (gypsum, barite, and jarosite). Analytical techniques are reported in [2]. Stable isotopes of sulfate oxygen and sulfur were originally performed on similar materials by [3] and are used for discussion.

**Sulfur.** The average  $\delta^{34}\text{S}$  value from replicate analyses of the sample was 11.1 ‰ (CDT), typical of sulfur values for sulfate precipitated from a Permian sea [4]. This result is very close to values published earlier [3] for kieserite samples analyzed from the “Strassfurt” potash seams that ranged between 8.4 to 10.6 ‰ (CDT). Reported sulfur values from other Permian marine evaporites worldwide typically range from 10 to 15 ‰ [4].

**Oxygen.** An average  $\delta^{18}\text{O}_{\text{SO}_4}$  value from replicate analysis was 15.6 ‰, approaching the highest values for Permian ocean water but not unexpected for evaporates precipitating from a restricted marine basin. Permian ocean waters exhibit a wide range of  $\delta^{18}\text{O}_{\text{SO}_4}$  values from 10 to 15 ‰ [4]. A comparable  $\delta^{18}\text{O}_{\text{SO}_4}$  value of 13.0 ‰ was reported for sulfate from gypsum of the Permian Yeso Fm of equivalent age [5]. Based on these values, the sample accurately reflects the environment from which it precipitated, a restricted marine evaporite basin. Earlier workers [3] published  $\delta^{18}\text{O}_{\text{SO}_4}$  values ranging from 7.7 to 10.8‰ for kieserite from the “Strassfurt” potash seams. These values are significantly different from our analysis and low for

published Permian values [4]. They interpreted these values and ranges as a result of exchange with another water (diagenetic?). Exchange with other waters is possible but would require significant changes from the original environment of deposition. Alternatively sulfate reduction and re-oxidation could also result in lower  $\delta^{18}\text{O}_{\text{SO}_4}$  values but recognizable changes in sulfur isotope compositions would be expected [6].

**Hydrogen.** Replicate  $\delta\text{D}$  analysis of the kieserite gave values of  $-71$  and  $-68$  ‰ (SMOW). These values are far removed from both modern and ancient ocean waters reported in the literature [7] and probably represent exchange with meteoric water.

**Summary:** Stable isotope analysis of sulfate minerals provides unique opportunities to understand the origin and perhaps recognize later processes that have affected the minerals. Sulfur isotope values appear quite robust, reflecting the origin of the sulfur in the sulfate – in this case derived from the vast Permian ocean reservoir. In other sulfates, such as gypsum and jarosite, sulfur values reflect their origin from other reservoirs such as oxidation of preexisting sulfide minerals [2] or, in hydrothermal systems, the oxidation of sulfur dioxide [8] or hydrogen sulfide [5]. Sulfate oxygen values also fairly consistently reflect the source of oxygen at the time of oxidation to sulfate – in the case of this kieserite, the Permian marine reservoir. Abiotic variations in sulfate oxygen without changes in sulfur values require low pH, higher temperature, and/or varying solution compositions that require significantly long residence times. Alternatively, bacterially mediated sulfate reduction and re-oxidation are required for significant oxygen isotope exchange that also results in changes in the sulfur values [6]. Hydrogen, in contrast, appears to be readily exchangeable in kieserite and some other sulfates (notably gypsum) but not jarosite [5,8]. The applicability of hydrogen isotopes as a recorder of ancient processes is thus much more problematic in kieserite and gypsum.

**References:** [1] Papike et al (2007) 7<sup>th</sup> Intl. Conf. On Mars, # XXXX. [2] Campbell and Lueth (2007) *Appl. Geochem.*, (in press). [3] Wenzel et al. (1986) 4<sup>th</sup> Working Mtg, Isotopes in Nature, Leipzig, Proceedings, p.669-678. [4] Claypool et al. (1980) *Chem. Geol.* v. 28, p. 199-260. [5] Lueth et al. (2005) *Chem. Geol.*, v. 215, p. 339-360. [6] Alpers et al. (1992) *Chem. Geol.* v. 96, p. 203-226. [7] Sheppard, (1986) *Reviews in Mineralogy*, v.16, p. 165-183. [8] Rye and Alpers (1997) USGS *OFR* 97-88.