THE ORIGIN OF CARBON-BEARING VOLATILES IN A CONTINENTAL HYDROTHERMAL SYSTEM IN THE GREAT BASIN: WATER CHEMISTRY AND ISOTOPE CHARACTERIZATIONS Qi Fu[1], Richard A. Socki[2], Paul B. Niles[3], Christopher Romanek[4], Saugata Datta[5], Mike Darnell[6] [1]Lunar and Planetary Institute, USRA, Houston, TX 77058 (fu@lpi.usra.edu), [2]ESCG, [3]KR, Astromaterials Research and Exploration Science, NASA Johnson Space Center, Houston, TX 77058, [4]Dept. of Earth and Environmental Sciences, University of Kentucky, Lexington, KY 40506, [5]Dept. of Geology, Kansas State University, Manhattan, KS 66506, [6]Dept. of Earth and Atmospheric Sciences, University of Houston, Houston, TX 77204.

Introduction: Hydrothermal systems on Earth are active centers in the crust where organic molecules can be synthesized biotically or abiotically under a wide range of physical and chemical conditions [1-3]. Not only are volatile species (CO, CO_2, H_2, and hydrocarbons) a reflection of deep-seated hydrothermal alteration processes, but they also form an important component of biological systems. Studying carbon-bearing fluids from hydrothermal systems is of specific importance to understanding (bio-)geochemical processes within these systems. With recent detection of methane in the martian atmosphere [4-7] and the possibility of its hydrothermal origin [8, 9], understanding the formation mechanisms of methane may provide constraints on the history of the martian aqueous environments and climate.

The carbon isotopic compositions of methane and other alkanes have long been used for recognition of their origins. For example, to distinguish methane of abiotic origin, one suggested criteria is $\delta^{13}C$ values higher than -25‰ (V-PDB) [10]. Another criterion is "inverse correlation" of $\delta^{13}C$ and δ^2H values of *n*-alkanes. $\delta^{13}C$ value of alkanes decreases and δ^2H increases with carbon numbers due to kinetic fractionation effect during polymerization reactions that produce abiotic hydrocarbons [10-12]. Recent studies, however, showed that production of abiotic methane during serpentinization reactions can result in very low $\delta^{13}C$ values [13], which may overlap values typical for bacterial methane, and "inverse correlation" of $\delta^{13}C$ and δ^2H values is not necessarily the case for abiotic hydrocarbons [14-16]. Furthermore, there are several secondary processes that may generate variations in isotope compositions of methane: re-equilibration with CO_2, mixing with methane of other sources, and oxidation. Therefore, using the above suggested criteria alone is insufficient to identify the origin of methane and other organics.

There are numerous hydrothermal fields within the Great Basin of North America, some of which have been exploited for geothermal resources. While methane and other alkanes are also observed, in some cases with high concentrations, the origin and formation conditions of these organic compounds remain unknown. Thus, studying hydrothermal springs in this area provides us an opportunity to expand our knowledge of subsurface chemical processes that generate organic compounds in hydrothermal systems, and aid in future development and exploration of potential energy resources as well.

Geological Settings: Surprise Valley Hot Springs (41º32'N, 120º5'W), located in northeastern California, is a terrestrial hydrothermal spring system of the Great Basin. The Surprise Valley is regarded as a typical basin and range province valley, bounded by the Warner Range on the west that consists of Tertiary volcanic and intrusive rocks, and the east-dipping Surprise Valley Fault on the east [17]. Geophysical studies in this area indicated the presence of clay-rich volcanic and sedimentary rock of Tertiary age beneath the lava flows in late Tertiary and Quaternary.

Results and Discussion: Water and gas samples were collected from the Surprise Valley Hot Springs (SVHS) for a number of chemical and isotope composition analyses, including *in-situ* pH, alkalinity, conductivity, oxidation reduction potential (ORP), major and trace element, and C and H isotope measurements.

Water chemistry The SVHS fluids are slightly alkaline, with the average pH value of 8.37. The measured alkalinity ranges from 19.74 to 26.32 mg/L as $CaCO_3$, with the average value of 22.70 mg/L.

The major anion in hydrothermal fluids is SO_4^{2-} with concentrations varying from 308 to 319 ppm. Other anions are Cl^- of $\sim$ 200 ppm, and F^- in trace amounts. The dominant anion is Na^+ with the average concentration of 314 mg/L. Other major cations include SiO_2 and Ca^{2+}, averaging 45.2 and 17.3 mg/L, respectively. The concentration of K^+ is low and less than 8 mg/L. Metal elements detected in trace amounts include Sr, As, Li, Mo, and W. Based on the high contents of Na^+ and SO_4^{2-} with previous results of other springs in surrounding area, the fluid from SVHS can be classified as Na-(Cl)-SO_4 type [18, 19]. Thermodynamic calculation using ORP and major element data indicated that log$f$ O_2 values are $\sim$ -57.3. Under this condition, sulfate is the most dominant sulfur species, which is consistent with anion analysis results.

The concentrations of dissolved SiO_2, Na^+, K^+, and Ca^{2+} are used for estimations of aquifer temperatures at depth by dissolved SiO_2 and Na-K-Ca geothermometer calculations [18]. The average temperature of SVHS is

125.0 °C by the Na-K-Ca geothermometer, and 135.4 °C by dissolved SiO_2. Both temperatures are higher than the values measured at the orifice of spring which are in the range of 77.3 to 90.0 °C.

Carbon and hydrogen isotopes. CO_2 and homologs of alkanes (C_1-C_5) were identified in gas samples. The $\delta^{13}C$ values of CO_2 range from -21.12 to -14.97‰ (V-PDB). In contrast, the data of alkanes showed less variation. The average $\delta^{13}C$ value of methane is -48.41 ± 0.34‰ for 3 samples with the exception of a value of -44.95‰ (Fig. 1). Two isomers, *iso-* and *n-*, were observed for C_4 and C_5. The straight chain (*n-*) isomers always have higher $\delta^{13}C$ values than branched (*iso-*). Overall, the carbon isotope value increases with carbon numbers for straight chain alkanes (Fig. 1). Hydrogen isotope values of C_1-C_3 alkanes have shown more uniform δD values than C_4 and C_5. The δD values of CH_4 ranged from -247.75 to -229.65‰ (V-SMOW), and most values of C_2H_6 and C_3H_8 were in the range of -245.00 to -235.00‰.

The carbon isotope measurements of dissolved carbon species were also conducted. Results showed that $\delta^{13}C$ values of dissolved inorganic carbon (DIC) were highly uniform, with the average of -9.14 ± 0.08‰. Compared with gaseous alkane data, the difference in $\delta^{13}C$ between gaseous and dissolved alkanes were small, most of which are < 1‰. Dissolved CO_2 has $\delta^{13}C$ values less than CO_2 gas, with the difference of 0.02‰ to 10.60‰. Both CO_2 phases are out of ^{13}C equilibrium with DIC based on the theoretical prediction of C isotope fractionation between HCO_3^- and CO_2 at ~ 90 °C [20].

The combination of $\delta^{13}C$ and δD values of methane has been used to identify different sources of natural gas [21]. Along with geological evidence obtained in this and previous studies, the hypothesis regarding the formation of carbon-bearing compounds in hydrothermal fluids might involve two processes: 1) Under high heat flow conditions which are caused by regional faulting and crustal extension, original high molecular weight organic compounds (kerogens) in clay-rich volcanic and sedimentary rock decomposed to generate methane and other alkane homologs. The isotope values of these thermogenic hydrocarbons are constrained by several factors, including precursor organic compounds, kinetic isotope effects during decomposition reactions, and temperature. 2) The SVHS area is associated with outflow structures, and distant from the heat source [18]. Anaerobic oxidation of methane (AOM) at shallow depth (< 90 °C) is suggested as being responsible for the generation of CO_2 in SVHS.
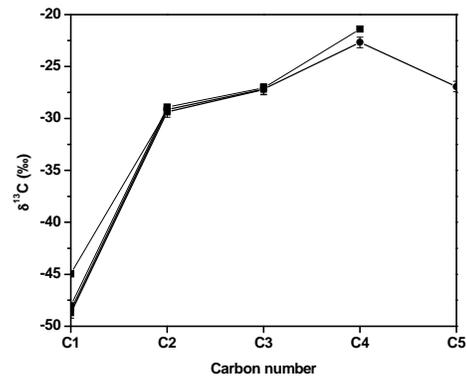

Fig 1. The ^{13}C value increases with carbon number for *n*-alkane homologs collected from SVHS in the Great Basin. Combined with other evidence, the alkanes are likely of thermogenic origin.

Conclusions: Two processes accounting for the observed isotope values of carbon-bearing compounds in SVHS are proposed: thermogenic production of alkane homologs and formation of CO_2 by AOM. In addition to isotope measurements, the geological background and fluid chemistry data are utilized to support the proposed scenario. This knowledge may prove useful to unravel the origin and history of carbon-bearing gases in hydrothermal systems on Earth and other planets.

References: [1] Giggenbach W.F. (1980) *Geochim. Cosmochim. Acta, 44,* 2021–2032. [2] Des Marais D.J. (1981) *Nature, 292,* 826–828. [3] Schoell M. (1988) *Chem. Geol., 71,* 1–10. [4] Formisano V. et al. (2004) *Science, 306,* 1758–1761. [5] Krasnopolsky V.A. et al. (2004) *Icarus, 172,* 537–547. [6] Geminale A. et al. (2008) *Planet. Space Sci., 56,* 1194–1203. [7] Mumma M.J. et al. (2009) *Science, 323,* 1041–1045. [8] Lyons J.R. et al. (2005) *Geophys. Res. Lett., 32,* doi:10.10292004GL022161. [9] Oze C. & Sharma M. (2005) *Geophys. Res. Lett., 32,* L10203. [10] Jenden P.D. et al. (1993) *USGS Prof. Paper, 1570,* 31–56. [11] Schoell M. (1983) *Am. Assoc. Petrol. Geol. Bull.* 67, 2225-2238. [12] Sherwood Lollar B. et al. (2002) *Nature, 416,* 522–524. [13] Horita J. & Berndt M.E. (1999) *Science, 285,* 1055–1057. [14] Yuen G.U. et al. (1990) *LPSC, XXI,* 1367–1368. [15] Hu G. et al. (1998) *Sci. China, 41,* 202–207. [16] Fu Q. et al. (2007) *Geochimica et Cosmochimica Acta, 71,* 1982-1998. [17] Rigby F.A. & Zebal G.P. (1981) *USDoE, Los Alomos Sci. Lab. Pub., LA-8598-MS.* [18] Mariner R.H. et al. (1993) *Geothermics, 22,* 1-15. [19] Sladek C. et al. (2004) *Geotherm. Res. Council Annual Meeting, Aug–Sept.* [20] Mook W.G. et al. (1974) *Earth Planet. Sci. Lett., 22,* 169-176. [21] Whiticar M.J. (1999) *Chem. Geol., 161,* 291-314.