METHANE AT THE AQUA DE NEY HYPERALKALINE SPRING (N. CALIFORNIA USA), A SITE OF ACTIVE SERPENTINIZATION. J. G. Blank[1,2], G. Etiope[3], V. Stamenković[4], A. R. Rowe[5], I. Kohl[6], S. Li[6], and E. D. Young [1]NASA Ames Research Center (Moffett Field, CA, USA; Jennifer.g.blank@nasa.gov), [2]Blue Marble Space Institute of Science (Seattle WA, USA), [3]Istituto Nazionale di Geofisica e Vulcanologia (Rome, IT) [4]California Institute of Technology/Jet Propulsion Laboratory (Pasadena CA, USA), [5]University of Southern California (Los Angels CA, USA), [6]Universify of Californa Los Angeles (UCLA) (Los Angeles CA, USA).

Introduction: Insight in to the processes controlling the origins and forms of methane (CH_4) on Earth, especially in sites of active continental serpentinization, contributes to the understanding of biomarkers in the search for life on other planets. Here, we present new results of stable C and H isotope and isotopologue composition of CH_4 and water chemistry from the Aqua de Ney (California), a site where methane gas is actively bubbling through spring water. We use our measurements of $\delta^{13}C_{CH4}$, $\delta^{2}H_{CH4}$, $^{12}CH_2D_2$ and $^{13}CH_3D$ to constrain an origin for the methane, through comparison with the same parameters in other serpentinization sites [1]. We will discuss our results in the context of the regional geologic setting of the site and a preliminary 16S rRNA study of the microbiological community thriving at the spring.

The Field Site: Aqua de Ney is an hyperalkaline (pH~12) mineral spring located in Siskiyou County, Northern California, known for its high CH_4 content [2]. Stable isotope compositions of O and H, reported for the waters of Aqua de Ney [3], reveal a signature that is much enriched in heavier isotopes than local meteoric water and support a connate origin for the spring waters. Such an origin is consistent with the emplacement setting of ophiolites in the California Coast Range, which are juxtaposed with cherts and deep-marine sedimentary rocks [4]. The Ney spring has unusual chemistry, including extreme dissolved silica content, high boron, sulfide, sodium bicarbonate, and ammonium [5]. The spring also supports unusual microbial ecology and/or microbes extracting energy from fluids of deep origin.

Sample Collection: On-site methane detection was conducted using a portable sensor, and T and pH measurements were determined using portable digital sensors and cross-checked with hand-held thermometers and pH papers. Water and gas samples were collected using sampling techniques employed in prior studies (e.g., [6],[7]), with special treatment for the high-pH water samples [2]. Water samples were passed through 0.2 µm filters and collected in borosilicate and Nalgene bottles. Gas samples were collected in two vessel types: evacuated glass bottles with rubber septa and Giggenbach-style gas bottles.

Laboratory Analyses: Stable C and H isotopes and resolved $^{12}CH_2D_2$ and $^{13}CH_3D$ isotopologues of CH_4 were determined using the novel large-radius high-mass resolution multiple-collector isotope ratio mass spectrometer, *Panorama*, at UCLA. Water aliquots were processed in a commercial laboratory (Thermochem, Santa Rosa CA) for anion and cations and total dissolved solids. Gas samples were analyzed for gas speciation and concentrations by GCMS by Thermochem and UCLA.

Results & Discussion: The measured effluent gas from the spring consisted of >73 vol.% of CH_4. Stable C and H isotope and clumped isotope compositions of CH_4 are similar to those of abiotic methane, rather than microbial methane, typically occurring in other continental serpentinization sites. Isotopologues are in near-equilibrium, suggesting a CH_4 formation temperature of approximately 50°C. Not excluding possible minor microbial components, CH_4 seems to be dominantly abiotic, likely generated by Fischer-Tropsch type reactions at depth [9]. We will compare the microbiology population counts and metabolic activies between the springs, both of which are hosted in the same ophiolite provence. Our reporting on the water and gas chemistry of this unusual site may trigger future detailed microbiological, geochemical and mineralogical studies at Ney.

References: [1] Young E.D. et al. (2017 *in press*). [2] Mariner R.H. et al. (2003) *J. Volcan. Geotherm. Res. 121*, 99-114. [3] Barnes I., et al. (1972) *Contrib. Mineral. Petrol*. **35**, 263-276. [4] Shervais J.W. et al. (2004) *Intl. Geol. Rev.* **46**, 289-315. [5] Feth J.H. et al. (1961) *Geochim. Cosmochim. Acta* **22**, 75-86. [6] Blank J.G. et al. (2009) *Planet. Space Sci.* **57**, 533-540. [7] Etiope G. et al. (2013) *Chem. Geol*. **347**, 161-174. [8] Morrill P. et al. (2013) *Geochim. Cosmochim. Acta* **109**, 222-240. [9] Etiope G. & Sherwood Lollar B. (2013) *Earth. Rev. Geophys*. **51**, 276-299.

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