Abiogenic methane in volcanic emissions can be non-genetic with the higher hydrocarbons

J. FIEBIG* AND A.B. WOODLAND

Institut für Geowissenschaften, J.W. Goethe Universität, Altenhöferallee 1, 60438 Frankfurt am Main, Germany (*correspondence: Jens.Fiebig@em.uni-frankfurt.de)

The emission of methane and the higher hydrocarbons is observed in both mid-ocean ridge and subduction-related hydrothermal systems. It has been recently reported that methane emanating from an extensional ultramafichydrothermal system originates from the abiogenic reduction of (mantle) CO_2 (1). The same process is also known to occur in subaerial subduction-related systems (2). These findings implied that abiogenic hydrocarbon production is not ultramafic-hydrothermal restricted to extensional environments, but also occurs under the more oxidizing conditions encountered at convergent plate boundaries. (Submarine) volcanic-hydrothermal systems associated with convergent tectonics might, therefore, have been suitable places for the emergence of life, too.

The identification of three subduction-related sources where the vast majority of methane has an abiogenic origin makes these places ideal sites to study the genetic relationship between methane and the higher hydrocarbons. We present hydrocarbon distribution data from one of these places, Nisyros, Greece, for whose hydrothermal system redox and temperature conditions are well constrained. Data indicates that the higher hydrocarbons are non-genetic with the abiogenic methane suggesting two important implications: 1) carbon isotope reversal between methane and the higher hydrocarbons is not a reliable indicator of abiogenic production of hydrocarbons other than methane and 2) abiogenic methane should be more widespread than previously assumed. These two points could also be valid for ultramafic-dominated systems in mid-ocean ridge as well as subduction settings.

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Alternative data reduction for precise and accurate isotope ratio determination via LA-MC-ICP-MS

J. FIETZKE¹*, V. LIEBETRAU¹, D. GÜNTHER², M. FRISCHE³, K. ZUMHOLZ¹, T.H. HANSTEEN¹ AND A. EISENHAUER¹

 ¹IFM-GEOMAR, Kiel, Germany (*correspondence: jfietzke@ifm-geomar.de)
²ETH Zurich, Switzerland
³SFB574, Univ. Kiel, Germany

An alternative approach for the evaluation of isotope ratio data using LA-MC-ICP-MS will be presented. In contrast to previously applied methods it is based on the simultaneous responses of all analyte isotopes of interest and the relevant interferences without performing a conventional background correction.

Significant improvements in precision and accuracy can be achieved when applying this new method and will be discussed based on the results of two first methodical applications:

- a) radiogenic and stable Sr isotopes in carbonates
- b) stable chlorine isotopes of pyrohydrolytic extracts.

In carbonates an external reproducibility of the ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ ratios of about 19 ppm (RSD) was achieved, an improvement of about a factor of 5. For recent and sub-recent marine carbonates a mean radiogenic strontium isotope ratio ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ of 0.709170 \pm 0.000007 (2SE) was determined, which agrees well with the value of 0.7091741 \pm 0.0000024 (2SE) reported for modern sea water [1].

Stable chlorine isotope ratios were determined ablating pyrohydrolytic extracts with a reproducibility of about 0.05% (RSD). For basaltic reference material JB1a and JB2 chlorine isotope ratios were determined relative to SMOC (standard mean ocean chlorinity) $\delta^{37}Cl_{JB-1a} = (-0.99 \pm 0.06) \%$ and $\delta^{37}Cl_{JB-2} = (-0.60 \pm 0.03) \%$ (2SE), respectively, in accordance with published data [2].

The described strategies for data reduction are considered to be generally applicable for all isotope ratio measurements using LA-MC-ICP-MS.

[1] McArthur, Rio, Massari, Castradori, Bailey, Thirlwall & Houghton (2006) *Palaeogeo. Palaeoclim. Palaeoeco.* 242, 126, doi: 10.1016/j.palaeo.2006.06.004 [2] Fietzke, Frische, Hansteen & Eisenhauer (2008) *J. Anal. At. Spectrom.* 2008, doi:10.1039/B718597A.

A267