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Thermally evolved gas analysis (TEGA) of hyperarid soils doped with microorganisms from the Atacama Desert in southern Peru: Implications for the Phoenix mission

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Abstract

TEGA, one of several instruments on board of the Phoenix Lander, performed differential scanning calorimetry and evolved gas analysis of soil samples and ice, collected from the surface and subsurface at a northern landing site on Mars. TEGA is a combination of a high temperature furnace and a mass spectrometer (MS) that was used to analyze samples delivered to the instrument via a robotic arm. The samples were heated at a programmed ramp rate up to 1000 °C. The power required for heating can be carefully and continuously monitored (scanning calorimetry). The evolved gases generated during the process can be analyzed with the evolved gas analyzer (a magnetic sector mass spectrometer) in order to determine the composition of gases released as a function of temperature. Our laboratory has developed a sample characterization method using a pyrolyzer integrated to a quadrupole mass spectrometer to support the interpretations of TEGA data. Here we examine the evolved gas properties of six types of hyperarid soils from the Pampas de La Joya in southern Peru (a possible analog to Mars), to which we have added with microorganisms (*Salmonella typhimurium*, *Micrococcus luteus*, and *Candida albicans*) in order to investigate the effect of the soil matrix on the TEGA response. Between 20 and 40 mg of soil, with or without ~5 mg of lyophilized microorganism biomass (dry weight), were placed in the pyrolyzer and heated from room temperature to 1200 °C in 1 h at a heating rate of 20 °C/min. The volatiles released were transferred to a MS using helium as a carrier gas. The quadrupole MS was ran in scan mode from 10 to 200 m/z. In addition, ~20 mg of each microorganism without a soil matrix were analyzed. As expected, there were significant differences in the gases released from microorganism samples with or without a soil matrix, under similar heating conditions. Furthermore, samples from the most arid environments had significant differences compared with less arid soils. Organic carbon released in the form of CO_2 (ion 44 m/z) from microorganisms evolved at temperatures of $\sim 326.0 \pm 19.5$ °C, showing characteristic patterns for each one. Others ions such as 41, 78 and 91 m/z were also found. Interestingly, during the thermal process, the release of CO_2 increased and ions previously found disappeared, demonstrating a high-oxidant activity in the soil matrix when it was subjected to high temperature. Finally, samples of soil show CO_2 evolved up to 650 °C consistent with thermal decomposition of carbonates. These results indicate that organics mixed with these hyperarid soils are oxidized to CO_2. Our results suggest the existence of at least two types of oxidants in these soils, a thermolabile oxidant which is highly oxidative and other thermostable oxidant which has a minor oxidative activity and that survives the heat-treatment. Furthermore, we find that the interaction of biomass added to soil samples gives a different set of breakdown gases than organics resident in the soil. The nature of oxidant(s) present in the soils from Pampas de La Joya is still unknown.

Keywords: Thermal analysis; TEGA; Atacama Desert; Pampas de La Joya; Hyperarid soils; Phoenix mission

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1. Introduction

Thermal analysis is a convenient processing technique for the transformation of relatively large substances into volatile compounds suitable for analysis by mass spectrometry (MS). High temperatures during rapid heating (pyrolysis) or slow heating (thermolysis) have been used for bond breakage and fractionation of molecules in different types of samples, such as, agricultural soils (Schulten and Leinweber, 1993a,b), microorganisms (Miketova et al., 2003; Snyder et al., 2005), ancient soils (Wang et al., 2000), minerals (Boynton and Ming, 2007; Lauer et al., 2006), soils samples for organic matter quantification (Manning et al., 2005; De la Rosa et al., 2008) and martian regolith by the Viking landers (Biemann et al., 1977).

A key goal in the search for evidence of life on Mars is the detection of organic matter. Since thermal analysis does not require any solvents for organic extraction, it has been the method of choice for searching organics on Mars. Thus, one of the primary objectives of the Phoenix scout mission, which landed on Mars on May 25, 2008 was to search for habitable zones by assessing organic or biologically interesting material in icy soils on the surface, using thermal volatilization followed by mass spectrometry (TV–MS) (Smith, 2004; Hoffman et al., 2008).

For the Viking landers the detection limit of the GC–MS was ppb for organics (Biemann et al., 1979). However, this does not mean that the overall limit on organics in the soil set by Viking is ppb. The reason is that the method (thermal volatilization) used to release organics from the soil and get them into the GC–MS was not very efficient. In this regard, recent studies have shown that the pyrolysis technique has limitations in transferring intact organic fragments into the GC–MS when the soil contains low levels of organics (Skelley et al., 2005; Navarro-Gonzalez et al., 2006). Navarro-González et al. have shown two important limitations of the pyrolysis technique. First, when organics are present as low level refractory substances, the temperatures reached by Viking (up to 500 °C) may be inadequate to release the organics. Second, the iron present in the soil oxidizes the organics when heated resulting in the formation of CO_2 and H_2O. The organics have to be present at high levels to overcome this effect. Thus it is probable that the real limit set by Viking on organic content of the soil is more likely to be at ppm even though the instrument detection limit was ppb (Navarro-Gonzalez et al., 2006). It is important to emphasize that the work of Navarro-Gonzalez et al. (2006), only raised limitations in the pyrolysis step but not on the GC–MS instrument, which they concluded it operated flawlessly as the GC–MS was designed and built (Biemann, 2007; Mukhopadhyay, 2007). In addition, other studies using flash TV–GC–MS have shown earlier no reliable detection of organics in agricultural soils if the level of organics were below 50,000 ppm C or in the presence of iron oxides (Schulten and Leinweber, 1993a). Given that martian regolith may have low levels of organic matter and contain high levels of metal oxides, including iron oxides (Navarro-Gonzalez et al., 2003), it is useful to investigate the thermal response of certain type of soils considered as "Mars analogs" to understand the effect of the matrix in the breakdown of organic matter during thermal processing.

The Atacama Desert, in northern Chile and southern Peru, is one of the most, if not the most, arid regions on Earth (McKay et al., 2003) and the arid core of the Atacama near Yungay Chile contains Mars-like soil (Navarro-Gonzalez et al., 2003). These soils are Mars-like in that they contain very low levels to organic matter (20–40 ppm of organic C), a non-biological oxidant, the virtual absence of microscopic life, and exotic mineralogical composition including iron oxides, which are common characteristics expected on Mars (Navarro-Gonzalez et al., 2006; Fletcher et al., submitted for publication). However, Pampas de La Joya, the Atacama region located on southern Peru between 15 and 17 °S, has recently had an astrobiological interest because it exhibits hyperarid soils with the lowest levels to organics. This fact suggests that this region may also contain Mars-like soils (Valdivia-Silva et al., 2005). In this paper, we examine the thermal and evolved gas properties of six types of hyperarid soils from the Pampas de La Joya (Atacama Desert in southern Peru). We examine untreated soil samples and samples enriched with three different types of the microorganisms (*Salmonella typhimurium, Micrococcus luteus,* and *Candida albicans*), in order to answer two basic questions: what is the TV response of the hyperarid soils from Mars-like soils? and can these soils alter the TV response of the microorganisms present in them? Our experiments simulate the TV approach of the Phoenix Lander by subjecting samples to a slow heating followed by mass spectrometry of the evolved gas analysis (EGA).

2. Methods

2.1. Soil samples and microorganisms

Soil samples used in this study were collected from 2004 to 2007 in the Pampas de La Joya, Atacama Desert in southern Peru, located about 50 km from the city of Arequipa between 15 and 17 °S. This extreme hyperarid location is under studied because of geomorphologic, paedologic and climatologic characteristics of astrobiological interest (Navarro-Gonzalez et al., 2006; Valdivia-Silva et al., 2005). The hyperarid zones were derived from an Aridity Index (AI) which is calculated as the ratio P/PET (evotranspiration/precipitation) <0.05 (Thornwaite's, 1948; UNEP, 1997). The total area of the desert is approximately 150 km^2 and it was divided into six types of soils based on texture and mineralogy. Around 200–400 g representing a composite of five individual nearby sites (∼1.5 m in radius) of each one of these six types of soils were collected from the surface to a depth of 5–10 cm using sterile scoops and stored in sterile polyethylene (Whirlpak™) bags for