High-pressure high-temperature Raman spectroscopy of kerogen: Relevance to subducted organic carbon

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ABSTRACT

The amount of insoluble macromolecular organic matter in the Earth’s crust, commonly referred to as kerogen, far exceeds the mass of living organic matter. The fraction of kerogen in sediments subducted into the mantle remains poorly constrained and will vary depending on the physical-chemical properties of kerogen along different slab geotherms. We studied the pressure-temperature evolution of carbon vibrational frequencies in isolated kerogen, previously not subjected to metamorphism, using Raman spectroscopy in a sapphire optical cell up to 3.2 GPa and 450 °C, corresponding to colder subduction geotherms. For blue-green laser excitation, we find optical irradiance exceeding ~3 kW/cm² induces changes in spectral features of the primary graphitic (G-band) and two main disordered modes (D1 and D2) that might otherwise be mistaken for thermal maturation. Whereas previous in situ studies have investigated the changes in these molecular vibrations of kerogen at high temperature or high pressure, we collected Raman spectra of isolated kerogen at simultaneous high P-T conditions. Although instantaneous and irreversible changes in band ratios of isolated kerogen were observed above ~350 °C at room-pressure, long-duration (2–8 h) heating experiments at 450 °C and 2.7–3.0 GPa reveal no permanent change in band structure. The reduction in vibrational frequencies of the disordered carbon modes with temperature (dν/dT) at pressures >1 GPa is slightly less than found at room pressure, further indicating that pressure effectively increases the thermal stability of kerogen. Our results suggest that kerogen reaching depths of 60 km where the temperature is below ~450 °C may subduct into the mantle, providing a potential source for the organic-rich component of carbon recently detected in certain lower-mantle diamonds.

Keywords: Kerogen, Raman spectroscopy, subduction, sapphire anvil

INTRODUCTION

The transport, burial, and transformation of organic carbon along active margins is an important but still poorly constrained component of the global biogeochemical carbon cycle. Along active continental-oceanic tectonic boundaries associated with small mountainous rivers, such as Cascadia, Alaska, Taiwan, and South America, exported kerogen (fossil carbon) often dominates riverine sediments, and can constitute as much, and potentially more than 75% of the total particulate organic load (Leithold et al. 2006; Drenzek et al. 2009; Blair et al. 2010; Hilton et al. 2010). High sediment transport rates, coupled with close proximity to sediment sources, promotes the efficient burial and preservation of organic carbon in the marine environment. Kerogen forms by diagenetic to metasomatic processes imposed on organic matter, resulting in a highly recalcitrant and structurally complex compound capable of persisting in the sedimentary record for geologic timescales and likely exceeding the mass of carbon in living organic matter by four orders of magnitude (Durand 1980). Understanding the high-pressure, high-temperature properties of kerogen will lead to a better understanding of the behavior of kerogen during subduction.

Raman spectroscopy has been widely used to characterize carbonaceous material (CM) in Earth and planetary materials for some time. Detection of biosignatures in CM is a primary focus in the study of early life on Earth (Pasteris and Wopenka 2002; Schopf et al. 2002; Schopf and Kudryavtsev 2005; Kremer et al. 2012) with potential application to Mars (e.g., Ellery et al. 2004; Dunn et al. 2007; Dartnell et al. 2012; Steele et al. 2012), where the ExoMars rover, expected to launch in 2018, will deploy a Raman spectrometer to analyze potential organic compounds using a 532 nm continuous excitation wavelength (Courrèges-Lacoste et al. 2007; Rull et al. 2013; Hutchinson et al. 2014). Characterization of CM by Raman spectroscopy has also been used to infer the thermal history of meteorites (Quirico et al. 2003; Hochleitner et al. 2004; Bonal et al. 2006; Busemann et al. 2007; Matsuda et al. 2010) and interplanetary dust particles (Wopenka 1988; Sandford et al. 2006), as well as to characterize riverine particulate organic carbon (Galy et al. 2007, 2008; Bouchez et al. 2010). Interpretation of CM Raman spectra in Earth and planetary materials requires caution because of its sensitivity to the laser (Kagi et al. 1994; Morishita et al. 2011), ionizing radiation (Dartnell et al. 2012) and polishing in sample preparation (Ammar et al. 2011).

In terrestrial meta-sedimentary rocks, the evolution of CM crystallinity measured by Raman spectroscopy has been used to develop a geothermometer of peak metamorphic temperature in the 300–700 °C range (Wopenka and Pasteris 1993; Beyssac et al. 2002a, 2002b; Rahl et al. 2005). Application to lower grade metamorphism or metasomatism at 25–300 °C is not as well

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