THERMAL ALTERATION PATHWAY OF ORGANIC MATTER IN SILICIFIED ARCHEAN METASEDIMENTS

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Archean carbonaceous matter is considered to be devoid of hydrogenated organic compounds as a result of thermal alteration. Yet, little is known about the effect of thermal alteration on hydrogenated organic compounds (such as aliphatic moieties) in Archean silicified metasediments, the so-called “cherts”. Experimental studies suggest that silicification promotes organic matter (OM) preservation upon thermal alteration up to 250 °C (Alléon et al., 2016). However, it is difficult to extrapolate these experimental observations to Archean organic matter as 250°C correspond to the lowest metamorphic temperature registered in Archean metasediments. We have then investigated the preservation of hydrogenated organic compounds in a large set of kerogens ranging in age between ca. 0.05 and 3.5 Gyr and having undergone variable metamorphic conditions from unmetamorphosed to greenschist facies. This was performed combining (i) bulk elemental H/C atomic ratio, (ii) the determination of the H content using nanoscale secondary ion mass spectrometry (NanoSIMS), (iii) Raman microspectroscopy and (iv) Rock-Eval pyrolysis.

By linking the *in situ* H/C atomic ratio determined by NanoSIMS and Raman microspectroscopy parameters in the aforementioned set of kerogens, we show that the Full Width at Half Maximum of the Raman default band (FWHM-D1) of kerogens can be related, following the literature, to the presence of aliphatic compounds and/ or bitumen as long as it remains above a minimum value of ca. 100 cm^{-1}. However, in most Archean kerogens, this requirement is not fulfilled, suggesting that hydrogenated compounds have been lost.
The presence of covalently-bound hydrogenated compounds in Archean kerogens was then investigated through Rock-Eval pyrolysis. Rock-Eval pyrolysis revealed that hydrogenated compounds are restricted to covalently bound molecules in Archean kerogens. These covalently bound hydrocarbons did not systematically originate from a unique OM pool in terms of thermal sensitivity since some pyrograms show cracking temperatures ranging between 360 and 580°C. Cracking temperature as low as 360°C appears at variance with the commonly accepted thermal stability of Archean kerogens.
Assessing the metamorphic temperatures underwent by kerogens from Raman spectra-derived parameters (Lafhid et al., 2010), we demonstrate that a large part of the studied Archean kerogens is characterized by an over-hydrogenation compared to their thermal alteration history (Fig. 1a). Such an over-hydrogenation of Archean kerogens is not specific to the presently studied set of kerogens since a literature survey shows that about one third of the studied Archean kerogens presents a bulk H/C atomic ratio higher than 0.3 (Fig. 1b). Therefore, we propose that the relationship between metamorphic temperatures and bulk kerogen H/C atomic ratios reflects (i) a specific thermal alteration pathway specific to OM belonging to silicified Archean metasediments and (ii) the effect of silicification promoting OM preservation.

In the light of the specific metamorphic pathway alteration of kerogens from Archean metasediments, this study shows that silicification promotes the preservation of hydrogenated organic compounds in ancient silicified metasediments.

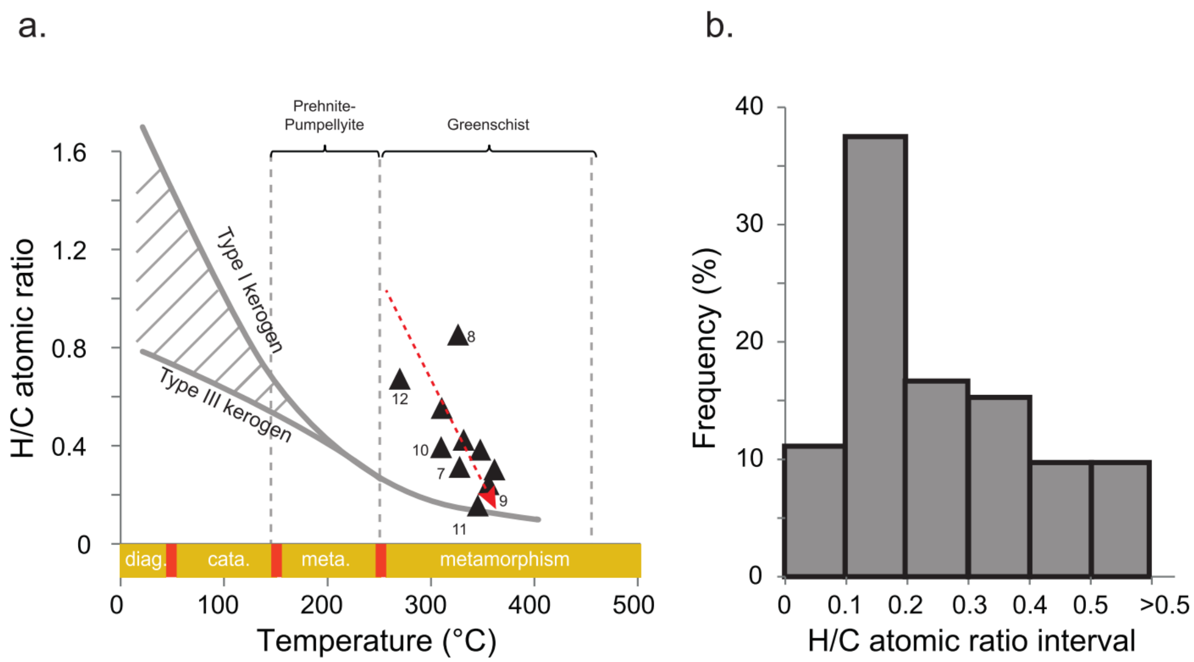

Figure 1 *(a) Comparison between the thermal alteration of type I to type III kerogens (adapted from Hayes et al., 1983) and of Archean kerogens (black triangles, kerogens from this study and from Delarue et al., 2016). Temperatures have been calculated through Raman micro-spectrometry (Lafhid et al., 2010). Thermal alteration stages of kerogens (diag. = diagenesis; cata. = catagenesis; meta. = metagenesis) and metamorphism facies boundaries were drawn according to Hayes et al., (1983). (b) Frequency distribution diagram of bulk H/C atomic ratio values (n = 72) of Archean kerogens from this study and from the literature..*

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