Comprehensive screening of geochemical proxies using RADAR mode FTICR-MS

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Classical development of geochemical proxies involves identification and target analysis of priori defined, specific molecular couples relating to a process of interest (e.g. oil maturity level). Typically, these analyses are based on GC or LC methods with MS detection and often include LC fractionation steps prior to analysis. Consequently, targeted approaches have a high probability of missing unexpected geochemical markers in complex systems with multiple proxy sources and high degrees of mixing, such as subsurface environments.

Here, we describe a screening strategy, acronymed RADAR for "Rapid Analyte Detection And Reconnaissance", aimed to overcome the limitations of the classical compound-specific methods and that engages all the analytical advantages of ultrahigh resolution Fourier transform mass spectrometry (FTICR-MS). These include broad mass range, high resolution and sensitivity of mass detection, which in conjunction with diverse ionization modes (e.g. atmospheric pressure photoionization, electrospray ionization) can enable a comprehensive multi-target screening of species present in complex systems, after minimal sample preparation. Furthermore, it allows the screening for possible candidates of new, unexpected proxy systems. Such information can guide and streamline the subsequent development of methods based on conventional GC and LC technologies to confirm and specifically target these novel geochemical markers.

We illustrate the potential of this strategy using data from the FTICR-MS analysis of recent marine sediments and some oil suites. For instance, we illustrate the rapid, putative identification of a suite of glycerol dialkyl glycerol tetraether lipids (GDGTs), containing a range of cyclic moieties (0-8), as well as of their hydroxylated analogues. In addition, we speculate on the possible presence of some novel GDGTs, and high molecular weight intact polar lipids. These findings could improve the understanding of the relationship between the GDGT distribution and the environmental factors, such as Sea Surface Temperature. Novel proxies related to petroleum generation and alteration will be shown.