The role of mineral surfaces in the preservation and transformation of organic carbon: meso- to nano– scale spatial complexity of organic matter forms in organic-rich shales

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Introduction

Sequestration of organic matter (OM) in sediments is a fundamental biogeochemical process that regulates planetary temperature, the flux of free oxygen to the atmosphere and oceans, and the distribution and quality of hydrocarbon source rocks (Kennedy et al., 2006). The discovery of a first-order control of mineral surface area (MSA) on OM concentrations in sediments and shales has fundamentally changed current understanding of OM sequestration in marine systems (Mayer, 1994; Kennedy et al., 2002; Kennedy & Wagner, 2011). This relationship suggests that high-MSA minerals such as smectite play a dominant role in OM preservation and burial in shales, and that factors such as oxygen exposure time, overall sedimentation rates and productivity are of secondary importance. However, studies of OM – MSA associations have been restricted to assessments of bulk samples and their derived empirical relationships do not provide a mechanistic explanation for OM preservation. The mechanisms of OM preservation remain unknown, largely because analytical methods for the direct assessment of mineral-OM associations at the appropriate scales were lacking. Shales in particular are highly heterogeneous materials at meso to nano scales (Loucks et al., 2009) and the spatial complexity and associations of OM forms and mineral surfaces at these scales are not understood. For instance, the importance of adsorption and surface facilitated polymerisation *vs* physical occlusion, mineral type and OM type remain largely unknown (Burdige, 2007).

Recently, synchrotron spectromicroscopy (STXM, C NEXAFS, FTIR) has enabled the integrated study of spatial variability of OM forms at meso to nano scales (100’s µm – 0.05 µm). Studies of soil microaggregates have demonstrated that the distribution of OM is complex and varies with OM class (Kinyangi et al., 2006; Lehmann et al., 2007; 2008). These studies have also provided, for the first time, direct evidence of preferential associations between particular OM types (e.g. aliphatic or aromatic) and OM location (pore *vs* mineral surface, illite *vs* kaolinite). This approach has also shed new light on the bonding mechanisms between OM and minerals (Lehmann et al., 2007). Clearly, application of synchrotron microspectroscopy techniques has the potential to answer many of the long-debated questions about preservation of OM in terrestrial and marine systems. However, application of these techniques has largely been restricted to studies of soil OM and there is tremendous scope for the study of OM preservation in both modern and ancient marine sediments.

Approach

Our study aims to investigate the mechanisms of OM preservation in organic-rich shales by characterising the types of OM and their association with mineral surfaces at meso to nano scales. This will be achieved through a combination of FTIR and STXM/ C NEXAFS microspectroscopy. We have obtained FTIR beamtime at the Australian Synchrotron for March 2012 and have prepared an application to the Swiss Light Source for STXM/ C NEXAFS analysis of the same samples in mid-2012.

The shale samples selected for our study are from the Naples Beach outcrop of the Miocene Monterey Formation, considered to be California's most important source rock. These thermally immature, smectite-rich samples are well characterised at a macro scale, and a strong relationship between MSA and OM content has already been demonstrated (Figure 1A). We hypothesise that 1) particulate OM is rare, 2) most OM is of sub-μm size and is closely associated with clay mineral surfaces 3) OM associated with mineral surfaces is compositionally distinct from pore or particulate OM. To test the effect of clay mineralogy we have also included several samples of the Devonian Woodford Shale, a thermally mature, organic-rich shale that is dominated by illite.

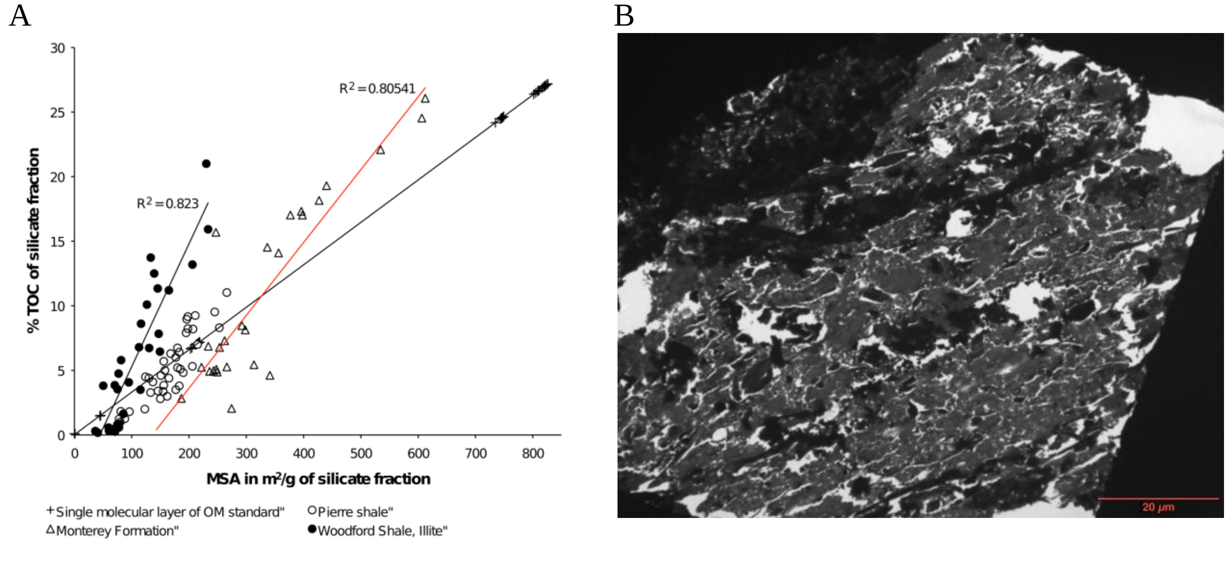

Fig 1. A) Strong positive relation between MSA and OM content in shales, reflecting interaction between clay mineral surfaces and OM. Different slopes indicate different OM loadings or different organic affinities in these three environments. Illite-rich Woodford Shale has a significantly steeper slope compared to smectite-rich Monterey and Pierre Shale, illustrating the effect of clay mineral type (Unpublished data). B) TEM image of cryomicrotomed 300 nm thick section of Monterey shale sample. Sample preparation for synchrotron microspectroscopy is challenging as standard carbon-based embedding materials cannot be used, and cryosections of shales are fragile and do not readily adhere to the sample grids.

The FTIR data will permit us to determine the spatial distribution of OM types at meso and micro scales (100s µm – 5 µm; Figure 2). We anticipate that correlation of mineral and OM functional groups will permit us to infer bonding mechanisms to mineral surfaces. This information will allow us to test the relative importance of sorption and physical occlusion as protective mechanisms. Characterisation of the same samples using STXM and C NEXAFS will complement our findings from the FTIR experiments and allow us to identify mechanisms controlling associations of OM forms with mineral surfaces at near to molecular scales (30 nm).

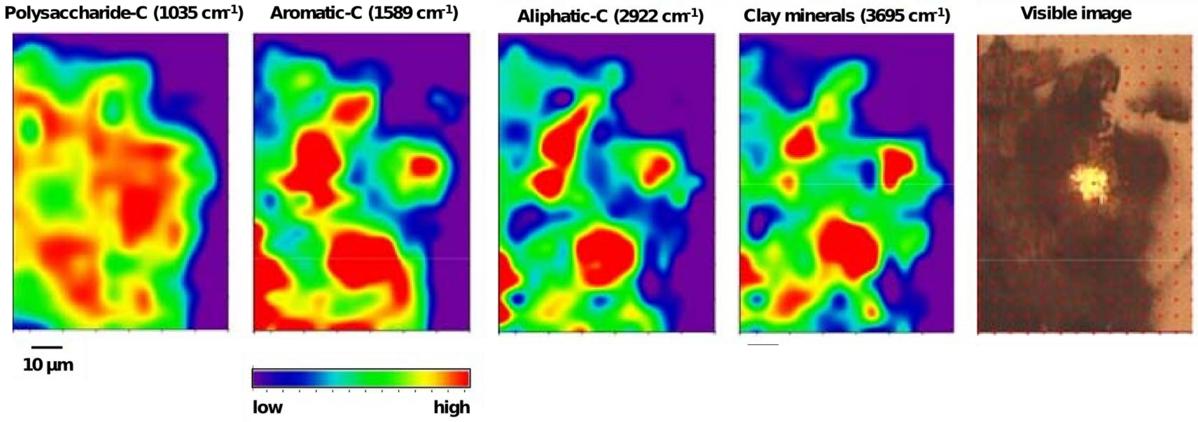

Fig 2. Distribution of polysaccharide C, aromatic C, aliphatic C and kaolinite O-H in soil microaggregates from Kenya, using FTIR spectroscopy (5 µm resolution). Aliphatic C is closely associated with kaolinite, while polysaccharide C is more broadly distributed. Figure modified from Lehmann et al., 2007. Distribution of various OM classes and associations with mineral surfaces in shales is currently unknown, our research will address this knowledge gap.

Nine samples across a MSA/TOC gradient have been selected to address the study aims, three each from low, medium and high MSA/TOC categories. As standard embedding procedures using C-based epoxies or resins cannot be used, multiple replicates of each samples were soaked in DI water and shock-frozen in liquid nitrogen before cryomicrotoming (≈300 nm section thickness) and mounting on C-free SiO coated Cu grids. The quality of the sections was verified by TEM imaging (Figure 1B).

Conclusions

Sequestration of organic matter (OM) in sediments is a fundamental biogeochemical process of global significance. High surface area minerals such as smectite play a dominant role in OM sequestration in sediments and, after burial, in shales. However, the exact role that mineral surfaces play in OM preservation is not understood because of the sub-µm scale at which these processes occur. Synchrotron microspectroscopy now permits us to investigate nano and microscale associations of OM with mineral surfaces and to test whether particular OM classes are preferentially associated with mineral surfaces *vs* occlusion within pores, as well as infer bonding mechanisms to mineral surfaces. We have commenced work on samples from the Monterey Formation, an important California important source rock, to determine the mechanisms of OM preservation in organic rich shales. Results are anticipated for late 2012.

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