



## **Organic enrichment controlled by smectitic clay minerals in the Miocene Monterey Formation and Cretaceous Pierre Shale**

**M. Kennedy, A. Derkowski**

Department of Earth Science, University of California, Riverside, CA USA  
(martink@mail.ucr.edu)

Studies from modern continental margin sediments indicate a first order relationship between mineral surface area and organic carbon deposition. This relationship also occurs in some ancient black shales such as the Cretaceous aged Pierre Shale in western North America where TOC and Mineral Surface Area (MSA) show a regression of .9 (N=45) over a TOC range of > 12% and the Miocene Monterey Formation. Elevated TOC in these units have previously been attributed to inferred anoxic conditions. The strong relationship with MSA suggests that organic carbon concentration is in part related to some of the same mechanisms that control mineral surface area in sediments. Since MSA is dominated by the fraction and type of clay minerals within the sediment, the relationship between TOC and MSA thus can be further extrapolated to the controls on the clay mineral composition. The dominant source of clay minerals to marine sediments is the terrestrial (soil) environment, and the type of clay minerals precipitated in this environment is determined by regional climate patterns and to a lesser degree local bed rock composition. The marine record of clay minerals thus provides a record of continental climate and the preservative properties of those minerals are responsible in some cases for organic enrichment such as the Pierre Shale or parts of the Monterey Formation. The specific mechanism of organic matter preservation by mineral surfaces is not known partially because of the nano scale at which these interactions occur preclude direct observation, and both clay minerals and labile organic compounds are highly reactive, changing with the redox, pH, DOC concentration, and temperature from the oceanic water column during sedimentation to the diagenetic environment during burial. Determining the physiochemical interactions between clay minerals and organic compounds is, however, critical for understanding the paleoen-

vironmental implications of these deposits and the influences on the system leading to OM concentration. A wide range of different clay mineral properties potentially act to protect labile organic matter from degradation, and these properties may assume different prominence from the water column to the burial environment. Physical relations include: organic matter sheltered by micropores between clay mineral crystallites, crystallites dispersed within organic matter as an exfoliated nanocomposite, thin films (mono layers) of organic compounds on clay mineral surfaces, or polar, non polar and charged organic compounds within interlayers of 2:1 clay minerals (smectite). To determine which of these possible relations is most important, we conducted adsorption, cation-exchange and TGA experiments while monitoring the clay crystal lattice using X-ray diffraction in artificial clay-organic mixtures and from natural thermally immature samples (Monterey Formation) and diagenetically altered samples (illitized Woodford Shale). Our results indicate that both charged and non-charged (polar or non polar) polymerized organic compounds entered and disrupted the interlayer sites of smectitic clay minerals. Illitization of organic bearing smectitic clays resulted in loss of interlayer and mineral surface area but retention of a MSA TOC relation with organic matter expelled from the interlayer sites to form a stable nanocomposite. Our studies showed that a high percentage of smectite was necessary for black shales with TOC > than 6% in non thermally mature sediment, and that desilicification of these sediments using HF acid concentrated amorphous organic matter from the interlayer sites of smectitic clay minerals. The importance of the specific clay mineral (smectite) implies that the continental conditions necessary to produce this type of clay mineral (weathering of volcanic sediments or strongly seasonal climates) must have been operative to produce the organic enrichments in the Pierre Shale and Monterey Formation and fluctuations in the continental climate pattern largely accounted for the periodicity of OM enrichment in these units.