A field study of the chemical weathering of ancient sedimentary organic matter

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Organic carbon oxidation during weathering of sedimentary organic matter [SOM] on the continents is a crucial component of the geochemical carbon cycle. On long time scales, SOM weathering balances O_2 release to and CO_2 removal from the atmosphere due to burial of organic matter in sediments, and in this way play an important role in maintaining equable levels of atmospheric O_2 and to a lesser degree, CO_2 (Garrels *et al.*, 1975; Berner, 1989). Little is known about the chemical alterations in SOM structure and composition that develop during weathering. Thus, the rate of SOM weathering, those factors that influence this rate, and their role in regulating the composition of Earth's atmosphere remain poorly constrained. Limited previous work has shown that organic carbon content decreases from less to more intensely weathered samples of black shales. This is attributed to both oxidation to CO_2 and removal of water-soluble organic matter (Littke *et al.*, 1991). Also, preferential loss of extractable aromatic versus saturated hydrocarbons and of isotopically depleted SOM (Leythäuser, 1973; Clayton and Swetland, 1978) and the selective resistance to weathering of aliphatic biopolymers (Nip *et al.*, 1991) point to the enhanced weathering of specific SOM structural elements.

The goal of the present study is to characterize the changes in abundance and composition of sedimentary organic matter that develop during the progressive weathering of a black shale in order to better constrain the rate of SOM weathering and the role that initial organic matter type may play in controlling this rate. This study also investigates the selective resistance to weathering of specific SOM structural elements to predict the composition of the organic matter that escapes complete oxidation within the weathering profile to be delivered to downstream sediments.

Sampling strategy and results

Whole rock samples were collected from weathering profiles developed on the following formations: Green River (Eocene, Utah, USA); Monterey, (Miocene, California, USA); Mancos (Cretaceous, Utah, USA); Woodford (Devonian, Oklahoma, USA); New Albany (Devonian, Kentucky, USA); and Marcellus (Devonian, New York, USA). These formations were chosen for two major reasons. One, the composition and structure of unaltered organic matter in these formations has been extensively studied, and therefore weathering-related changes can be directly compared with the body of literature on the unweathered shales. Two, these formations vary significantly in depositional environment, organic matter source and kerogen type, and thus selective weathering of specific SOM structural elements is more clearly revealed by the comparing weathering between profiles.

Samples were obtained where roadcuts into weathered black shales expose light-coloured weathered material 2–4 m thick grading into dark, blocky unweathered rock. The surface rind at all sampling sites follows topography. A single stratigraphic horizon was followed at each site outward from the unaltered rock through the weathered rind into the soil developed on the shale, with samples collected at 10–50 cm intervals. Weathering profile lengths range from 3–7 m (measured normal to topography). Weight percent total organic carbon [TOC] analyses are shown in Fig. 1. These profiles clearly demonstrate substantial, but not complete, TOC loss from the surface of each weathering profile. TOC loss ranges from 70–95% at the surface relative to deeper, unaltered material.

Analytical pyrolysis combined with gas chromatography and gas chromatography-mass spectroscopy reveals that kerogen isolated from each weathering

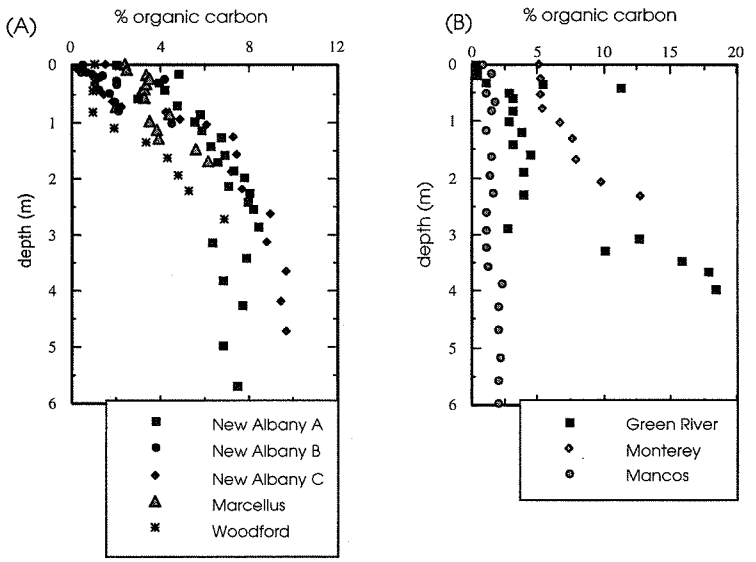

FIG. 1. Variation in weight percent organic carbon versus depth for weathering profiles developed on black shales. (A) Devonian black shales from central/eastern USA; (B) other shales from western USA.

profile experiences significant change in composition and structure as a result of weathering. Kerogen initially dominated by predominantly straight-chain aliphatic material becomes progressively enriched in alkyl aromatic-, hydroxyl- and carbonyl-rich structural elements as weathering progresses. These observations are supported FT-IR spectroscopy as well as bulk elemental (CHNS/O) analysis of the kerogen. Both selective enrichment of initially present resistant structural elements as well as the formation of more oxidized components were found to accompany progressive weathering.

Discussion

Weathering of ancient sedimentary organic matter results in removal of organic carbon from the original rock, as well as chemical alteration of the remaining material. The specific shape of an TOC profile at any site results from a balance between physical and chemical erosive processes. The presence of residual organic carbon at the surface of weathered shale indicates that physical transport supplies incompletely oxidized organic matter to downstream sediments. However, detailed structural analyses reveal that this material is not representative of the bulk, unaltered organic matter composition, but instead reflects more oxidized forms of organic carbon. A rough estimate of the rate of SOM weathering is provided by comparison of the Marcellus and New Albany profiles, which have developed in regions of similar climate and on shales of similar organic matter type, and exhibit very similarly shaped weathering profiles. The Marcellus sampling site was glaciated as recently at 18 kya. If this profile is taken to be at erosive steady state (reasonable because of the similarity with the New Albany profiles) then at a maximum, as span on the order of 10-20 ky was required to develop this profile. However, once steady state has been reached (as in the New Albany sites), gradual denudation and erosion of the landscape is likely to limit the rate of weathering of sedimentary organic matter.

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