Chemostratigraphic trends of the Middle Devonian Marcellus Shale, Appalachian Basin; Preliminary Observations

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Trace element and metals abundances have been used to elucidate the hydrography of silled basins as well as watermass chemistry and deep-water residence times. The database of our preliminary study of the Middle Devonian Marcellus Shale comprises chemostratigraphic (X-ray fluorescence) elemental concentrations determined from cores recovered from eastern New York, southwest Pennsylvania and northern West Virginia. Regional covariance trends of authigenic molybdenum (Mo_{auth}) and uranium (U_{auth}) and their respective enrichment factors (EFs) define a uniform $(Mo/U)_{auth}$ ratio of ≈ 2 - 3 times the Mo/U molar ratio of seawater. Mo_{auth} is enriched relative to U_{auth} by a factor of 5:1 to 10:1 suggesting accelerated transport of Mo to the seafloor by a particulate (Mn) transport mechanism that would have required frequent fluctuations between suboxic and moderately sulfidic water column conditions. Indeed, the relationship of total organic carbon and Mo(ppm) in eastern New York suggests water renewal times on the order of several hundred years. A data subset defined by diminishing Mo_{auth} and U_{auth} EFs at reduced aqueous Mo/U ratios may reflect the preferential uptake of U under largely suboxic conditions. Moreover, data from a well in northern West Virginia defines Mo_{auth} and U_{auth} values typical of bottom water depleted in Mo (Mo/U = 0.1 - 0.3 x seawater) and $(Mo/U)_{auth}$ ratios of ≈ 1:1. Thus, whereas the Marcellus basin may have experienced frequent episodes of suboxic to sulfidic conditions that accelerated Mo enrichment, local hydrographic conditions (i.e., stronger degree of water column stratification) appear to have favored Mo drawdown in bottom water. Equally intriguing is the regional concentration of barium in the upper part of the Marcellus, which may reflect an episode of enhanced paleoproductivity at this time. Further, chloride and strontium are especially concentrated in transgresive systems tract deposits perhaps reflecting salinity excursions that could have enhanced the preservation of organic matter in these intervals.