

## **Co-variation of U and Mo in Pennsylvanian and Devonian black shales in the Illinois Basin**

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U and Mo are redox-sensitive trace elements in black shales. Geochemical proxies based on these two elements, such as U/Th and Mo/Al, have been used as indicators of bottom-water redox conditions during black shale deposition. U and Mo are generally thought to become enriched in black shales under reducing conditions during the early diagenetic stage. Geochemical data from 44 Devonian New Albany Shale samples and 85 Pennsylvanian black shales in the eastern part of the Illinois Basin show that U and Mo exhibit co-variation characteristics ( $R^2= 0.80$  and  $0.78$ , respectively). The average U content of the Devonian New Albany Shale and Pennsylvanian black shales is 24.20 ppm and 59.81 ppm, respectively, with the highest value up to 63.88 ppm for the New Albany Shale and 269 ppm for Pennsylvanian black shales. The average Mo content of the Devonian New Albany Shale and Pennsylvanian black shales is 52.59 ppm (maximum 201.48 ppm) and 364.40 ppm (maximum 1620 ppm), respectively. Both the Devonian New Albany Shale and Pennsylvanian black shales were deposited in epicontinental seas. The Devonian New Albany Shale is a normal marine black shale, with total organic carbon (TOC) content ranging from 0.18 to 16.29% (average 6.53%) and organic matter type I/II kerogen. In comparison, the Pennsylvanian black shales (TOC 0.42 to 41.35%, average 12.82%, and organic matter a mixture of type I, II, and III kerogen) are interbedded with coal seams and were deposited during transgression when epeiric seas inundated peat swamps. The Pennsylvanian black shales were likely deposited in shallower water compared to the Devonian New Albany Shale, but they have higher U and Mo concentrations. This contradicts the general understanding of U and Mo enrichment in marine sediments, i.e., the deeper the water, the more reducing conditions and higher U and Mo contents. High organic matter content likely consumed dissolved oxygen in pore water and contributed to the formation of reducing conditions and reduction of U and Mo in the Pennsylvanian black shales. Other factors such as pH conditions and adsorption by terrestrial organic matter likely contributed to the enrichment of U and Mo.