

Uranium in shales as a proxy for the evolution of surficial redox conditions

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Redox-sensitive trace elements in the rock record are a reliable indicator of the evolution of surficial redox conditions through geologic time. The redox-sensitive element, uranium, is released from continental rocks having an average U concentration of 2.8 p.p.m. during oxidative weathering, and delivered in the mobile hexavalent form (U^{6+}) via rivers to the ocean. In oxic seawater, U is conservative, accumulating to the present-day concentration of 14 nM (Ku *et al.*, 1977) with an oceanic residence time of 400,000 yr (Klinkhammer and Palmer, 1991). In reducing marine conditions, U^{6+} is reduced to the immobile tetravalent state (U^{4+}), and preserved in black shales. U^{6+} may also be adsorbed to iron oxides, and preserved in iron formations or altered basalts. Today, this sink represents less than 10-20% of total U delivery to the ocean, whereas suboxic and anoxic continental margin sediments represent the remaining 40-70% (Klinkhammer and Palmer, 1991; Dunk *et al.*, 2006). As riverine delivery represents the only significant source of U to the oceans, and reducing marine sediments represent the most significant sink, the secular changes in concentration of U in marine sediments through time provides constraints on the strength of oxidative continental weathering, and the extent of reducing conditions in the ocean.

Here we present a record of secular changes in the authigenic component of the redox-sensitive element uranium in black shales and iron formations. Changes in the concentrations of uranium in black shales can be attributed to two first-order controls: 1) variable delivery of riverine uranium to the ocean, a reflection of levels of oxygen in the atmosphere, and 2) the extent of ocean anoxic conditions. A marked change in the uranium concentration of both black shales and iron formations is apparent across the Great Oxidation Event (GOE). Pre-GOE concentrations of uranium reflect near to crustal concentrations under prevailing anoxic surficial conditions. Post-GOE concentrations of uranium show significant authigenic uranium enrichments, demonstrating the strength of the oxidative weathering cycle to carry soluble U^{6+} to the oceans, and the ability of anoxic bottom water conditions to reduce and immobilize this uranium. Authigenic uranium enrichments reaching concentrations of up to 440 p.p.m. in the Phanerozoic align with ocean anoxic events, and reflect an increasing oceanic reservoir of uranium. Comparatively muted enrichments in the Proterozoic demonstrate less intense weathering and a lower concentration of uranium in the oceans. There is, however, a decreasing trend of uranium concentration from the GOE through the Mesoproterozoic, reflecting perhaps a progressive increase in the extent of ocean anoxic conditions, or a decline in atmospheric oxygen. The Neoproterozoic record marks a return to significant authigenic uranium enrichments in black shales, in conjunction with environmental changes documented during that time. Thus, the marine cycle of uranium, sensitive to fluctuations in ocean chemistry, can provide constraints on past surficial redox conditions, particularly across the GOE.

References

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