Biotic and abiotic controls on black shale diagenesis and redistribution of trace elements

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The Llanvirn-Llandeilo/Caradoc black shales of southwest Wales, U.K. have undergone a multi-stage diagenetic history (Lev *et al.*, 1998). The paragenetic sequence from these rocks requires early and late diagenetic events that have redistributed trace and major elements and left an overprint on the Sm-Nd and U-Pb whole rock isotopic systems. The types of reactions essential to produce these mineralogic and geochemical changes require both biotic and late abiotic processes. The relative importance and timing of these processes can be evaluated by examining their net effect on the mineralogy and geochemistry of the whole rock

Paragenetic sequence of the Llanvirn-Llandeilo\Caradoc black shales

The order of diagenetic mineral appearance in the Llanvirn-Llandeilo\Caradoc black shales is as follows: 1) pyrite formation, 2) apatite in the form of rims and small grains, 3) finely crystalline calcite, 4) apatite nodules, 5) monazite replacing apatite and forming in the shale matrix and 6) late calcite replacing earlier-formed carbonate. This sequence begins at or near the sediment-water interface during bacterial sulphate reduction (BSR) and continues into the realm of thermal sulphate reduction (TSR) (Fig. 1).

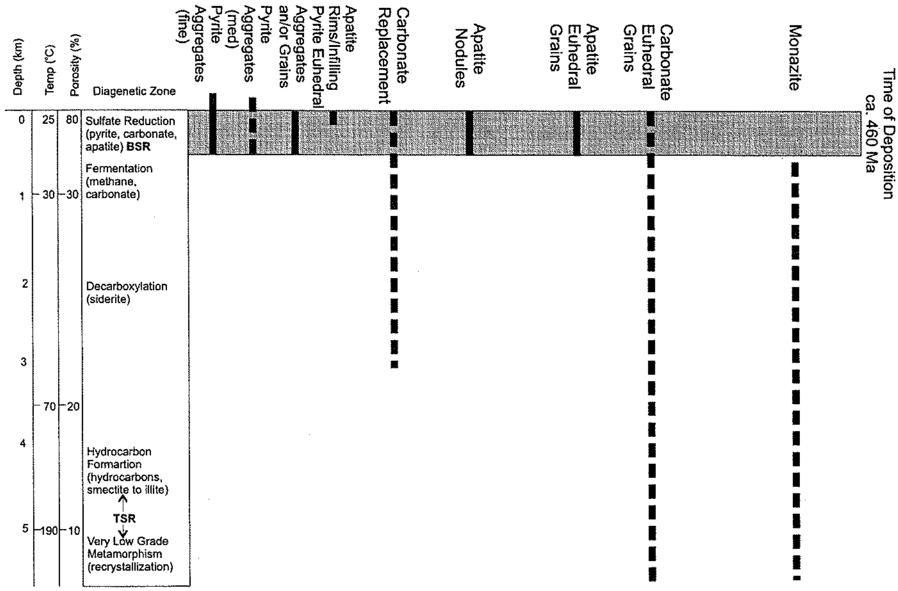

FIG. 1. Typical black shale diagenetic conditions (after Berner, 1980 and Curtis, 1977; 1980) as compared to the observed parageneisis in the Llanvirn-Llandeilo\Caradoc black shales (after Lev *et al.*, 1998).

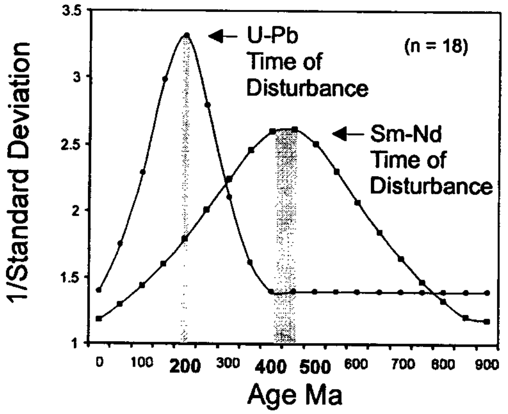

FIG. 2. The point of minimum variation in whole rock (n = 18) isotopic compositions of 206Pb/204Pb and 143Nd/144Nd is equal to the age of disturbance in each isotopic system.

The presence of early diagenetic pyrite, apatite and carbonate, suggests that Fe, Ca and P as well as rare earth elements (*REE*) and U were being redistributed at or near the time of sedimentation during BSR. Monazite, observed in the Llandeilo\Caradoc black shales is texturally a late diagenetic phase (Fig. 1). The formation of monazite involves the breakdown of early diagenetic apatite to form late monazite. The formation of monazite at the cost of apatite again requires that Ca, P, *REE* and U are redistributed.

Timing and relative importance of biotic *vs* abiotic trace element redistribution

The Llandeilo\Caradoc black shales record considerable *REE* and U redistribution as well as an isotopic disturbance in both the Sm-Nd and U-Pb systems. The Sm-Nd system appears to be reset at about 460 Ma, which is about the time of sedimentation (Fig. 2). This disturbance requires, at least in part, a biotic control in that the timing of the event coincides with BSR, early diagenesis and the formation of apatite. The U-Pb system records a disturbance at about 250 Ma (Fig. 2). The timing of this event coincides with late diagenesis and TSR. The mineral most closely associated with this period of disturbance is U-rich monazite. The late formation of monazite is almost certainly an inorganic process however, the early disturbance related to the presence of apatite is more complicated. In order to account for the deviation of *REE*s in the Llandeilo\Caradoc shales from typical *REE* shale values and from the expected isotopic composition, the loss of some monazite is required. This can occur by the formation of early apatite and later dissolution and loss of *LREE* with a pattern equivalent to that of monazite, or by the formation of an early monazite pre-cursor, rhabdophane (($LREE$)$PO_4 \cdot H_2O$), and later loss due to the metastable nature of monazite under 400°C.

The formation of early diagenetic phases and initial element redistribution coincides with BSR. However, the trace element signature and isotopic disturbance recorded by the Llanvirn-Llandeilo\Caradoc black shales is ultimately associated with TSR and late diagenesis.

References

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