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Mapping the Evolution of Diagenetic Fluids using LA-ICPMS of Carbonate Cements and Implications for Redox-Sensitive Metals

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Carbonate cements can be used to constrain the history of pore fluids from the seafloor to later burial. Reed and Wallace (2001 and 2004) documented a consistent cathodoluminescence paragenesis for the Waulsortian Limestone in Ireland: 1) early, non-luminescent, Mn-Fe-poor cement, 2) a bright luminescent, Mn-rich cement, and, finally, 3) dull-luminescent, Mn- and Fe-rich cement. This paragenesis represents a progression from near surface oxidized conditions to reduced burial conditions (Barnaby and Rimstidt, 1989). With LA-ICPMS, it is now possible to determine the trace element composition that occurs with this transition and, therefore, the evolution of diagenetic fluids. Here, we present new LA-ICPMS data from two localities in Ireland.

At Ballinalack, MVT-style Zn-Pb mineralization occurs synchronous with bright luminescent cements. A second locality 15 km west is barren with no known mineralization but preserves the same calcite cement paragenesis.

Both localities record similar Mn and Fe profiles that correlate with the non-bright-dull cement generations consistent with a transition to reduced burial conditions. A difference is that the Fe profile is more depressed relative to Mn at Ballinalack.

The Mg profile shows a decrease at the beginning of the bright luminescent cement. This is consistent with the relative timing of the regional dolomite as constrained by previous paragenetic studies (Reed and Wallace, 2001, 2004). This trend is most pronounced at the unmineralized locality.

The concentration of Zn also decreases to near zero coincident with the bright luminescent cement. This is consistent with the initiation of Zn-Pb mineralization. While the Zn profiles are similar for both localities, the dull-luminescent cement shows more metal variability after the main mineralization event at Ballinalack.

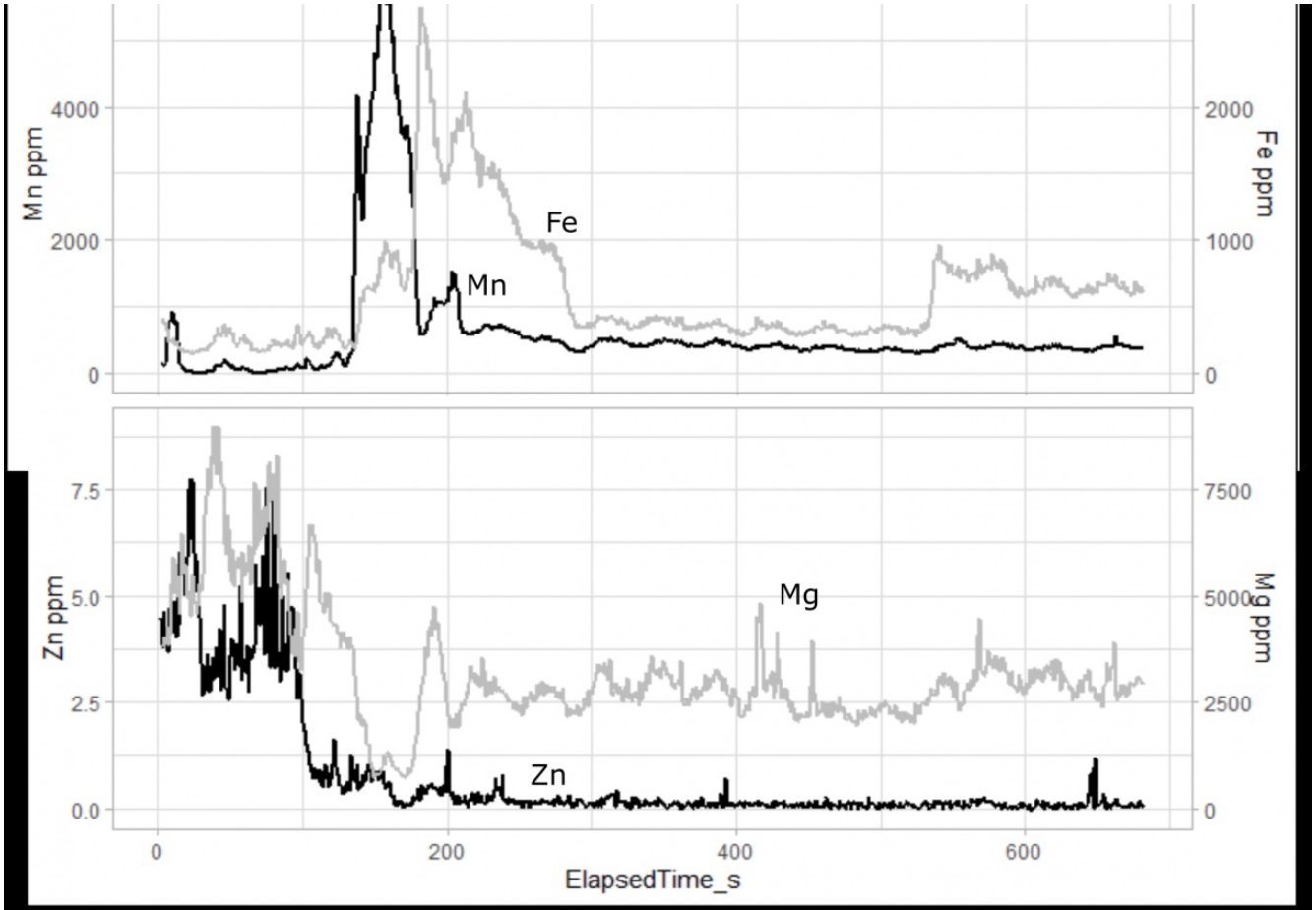
Zinc and Fe have a high affinity for reduced sulfur and will form sulfides in the presence of even small concentrations (Jacobs et al., 1987). The reduction in Zn and Fe during mineralization suggests that sulfur has been introduced into the system, causing sulfide precipitation.

We suggest the period of mineralization records the transition to reduced conditions and the availability of reduced sulfur, triggering the formation of Zn-Pb-Fe sulfides. This event is coeval with dolomitization, which is fueled by the drawdown of Mg from pore fluids. The lack of any significant increase in metals (or Mg) prior to this event and the relatively early timing of the sulfide precipitation suggest that regional subsurface fluids are involved in supplying metals. There is evidence for continued influx of metalliferous fluids during the dull-luminescent cement stage, however, this postdates the mineralization event.

This work also demonstrates the application of LA-ICPMS for constraining the nature of burial fluids within carbonate cements.

Figure

(A) Barren locality and (B) Ballinalack Deposit. For each locality, the cathodoluminescence traverse (top), Mn-Fe profile (middle), and Mg-Zn profile (bottom) are shown. The x-axis is presented as time along the traverse and the y-axis as element concentration.


Mn ppm
Fe ppm
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Mg ppm
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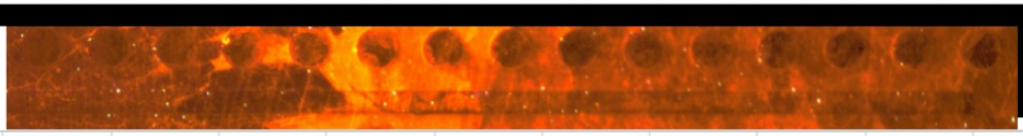

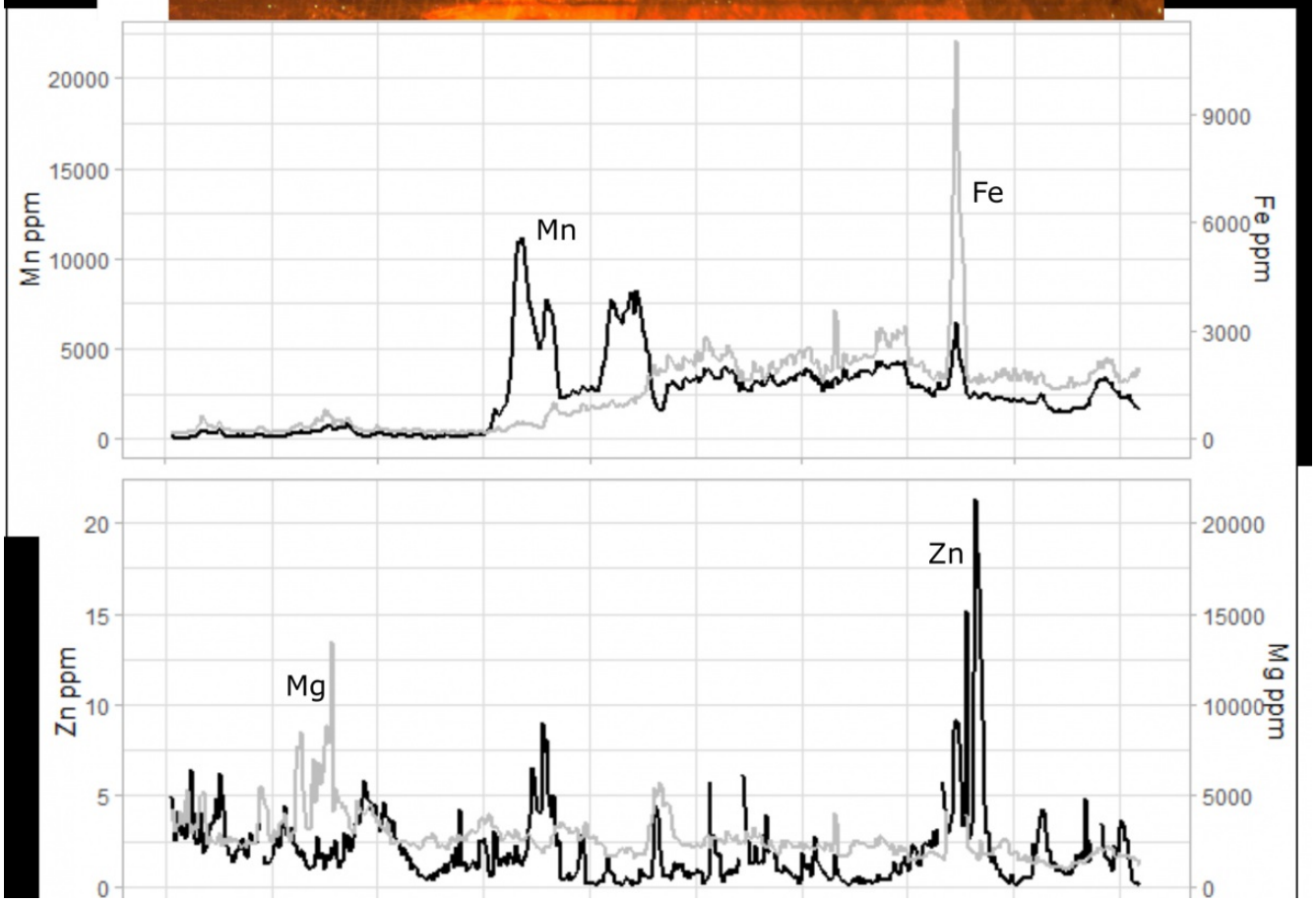
Mn ppm
Fe ppm
Mn
Fe
Zn ppm
Mg ppm
Mg
Zn


0
100
200
300
400
ElapsedTime_s