

## **Early diagenetic high-magnesium calcite and dolomite indicate that coal balls formed in marine or brackish water: Stratigraphic and paleoclimatic implications**

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Coal balls are carbonate and pyrite permineralizations of peat that contain three-dimensional plant fossils preserved at the cellular level. Coal balls, which occur in Pennsylvanian and earliest Permian equatorial coals, provide a detailed record of terrestrial ecology and tropical climate during the Late Paleozoic Ice Age; yet their depositional environment remains controversial. The exquisite preservation of some coal-ball fossils, e.g. pollen with pollen tubes and leaves with mesophyll, indicates rapid formation. The presence of abundant, cement-filled, void spaces within and between the plant debris in most coal balls indicates that they formed in uncompacted peat, near the surface of the mire.

Botanical, taphonomic and isotopic evidence point to a freshwater origin for coal balls. The nearest living relatives of coal ball plants (modern lycopsids, sphenopsids, marattialean ferns and conifers) grow in fresh water. Coal-ball peat contains a high percentage of aerial debris, similar to modern freshwater peat. The stable oxygen isotopes of coal-ball carbonate ( $\delta^{18}\text{O} = 16$  to 3 per mil) suggest a freshwater origin. However, the widespread occurrence of marine invertebrates and early diagenetic framboidal pyrite in coal balls suggests that many formed in close proximity to marine water. Indeed, carbonate petrology points to a marine or brackish water origin for the first-formed carbonate cements in coal balls. Petrographic and geochemical (microprobe) analysis of coal-ball carbonates in Pennsylvanian coals from the midcontinent of North America (Western Interior Basin, West Pangaea) and the Ruhr and Donets Basins (East Pangaea) indicate that the first formed carbonate is either radaxial, nonstoichiometric dolomite or high magnesium calcite (9 – 17 mol %  $\text{MgCO}_3$ , indicating precipitation in marine or brackish water. Although both primary dolomite and high magnesium calcite can form in lacustrine settings, the lakes in which these minerals form occur in carbonate terranes and experience significant evaporation. Paleotropical coals with coal balls are under- and overlain by siliciclastic sediments, and, if fresh, would have required ever-wet climatic conditions for peat to accumulate.

Pervasive freshwater diagenesis, with low magnesium calcite enveloping individual grains of high-magnesium calcite, results in most coal-ball carbonates having a freshwater or mixed isotopic signature. In some coal balls, cell walls in the root cortex (a soft tissue) separate carbonate of differing magnesium content, resulting in cells filled with low-magnesium (freshwater) calcite adjacent to cells filled with high-magnesium (marine) calcite, suggesting that these cements formed in recently dead or dying roots. The juxtaposition of high-magnesium (marine) calcite and low-magnesium (freshwater) calcite in coal balls suggests that they formed at the marine/freshwater interface in mires that contained salt-tolerant plants.

This model of coal-ball formation suggests that coals bearing coal balls accumulated early in marine transgression as glaciers melted and sea level rose. In modern coastal mires, tidal incursion of salt water can maintain high freshwater tables, enabling domed freshwater peat to form in climates that normally would be too dry for tropical freshwater peat accumulation. Peat accumulation in these mires may be due to marine transgression rather than the ever-wet paleoclimates.