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Kinetic factors control trace element and isotope zoning in Archean pyrite corona nodules

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Pyrite corona nodules from the ~2.7 Ga Kapai Slate, a thin, sulfidic carbonaceous shale horizon interbedded with plume-associated basaltic lava flows in the Yilgarn Craton, Western Australia, have compositional and isotopic zoning with distinctive textural differences between cores and mantles. A striking feature is that both compatible (Ni, As, Ag, Te, Sb, Bi and Pb) and incompatible (Mo and Tl) elements are linearly correlated (Fig. 1), with correlation coefficients as high as 0.99. A marked drop in concentration of compatible elements and an increase in incompatible elements at the core-mantle boundary is attributed to a sudden change in the nodule growth rate produced by eruption of the voluminous overlying Paringa Basalt. The weight of basalt produced sudden compaction of the unconsolidated clays below resulting in upward advection of pore fluid, which thinned the boundary layer around the growing nodules, leading to a marked increase in growth rate (Fig. 2). Rapid pyrite growth led to a dramatic depletion in compatible elements, and a build-up in incompatible elements, in the boundary layers, which resulted in extreme depletion of compatible elements, and enrichment of incompatible elements, in the nodule mantles. The corona nodules are also isotopically zoned, with cores having higher $\delta^{34}S$ and less positive $\Delta^{33}S$ than mantles. The $\Delta^{33}S$ increase towards the rims is attributed to S_8 being advected to the growing mantles by upward fluid movement during sudden compaction, and the $\delta^{34}S$ decrease to the lighter S isotope, with its higher reactivity and diffusivity, being preferentially incorporated into the fast-growing pyrite mantle.

The extreme changes in the growth rates of these corona nodules provide a new constraint on the partition coefficients of the trace elements between Archean ocean water and sedimentary pyrite. The compatibility of the trace elements decreases in the order Bi > Te > Sb > Ag > Cu > Pb > Ni ≈ As > (Co, Zn, Se, Cd, Mn, W) > Tl > Mo, consistent with the order obtained from modern sedimentary pyrites, except for the redox-sensitive elements Mn, Tl and Mo. These differences are attributed to the lower oxygen content of the Archean atmosphere and oceans.

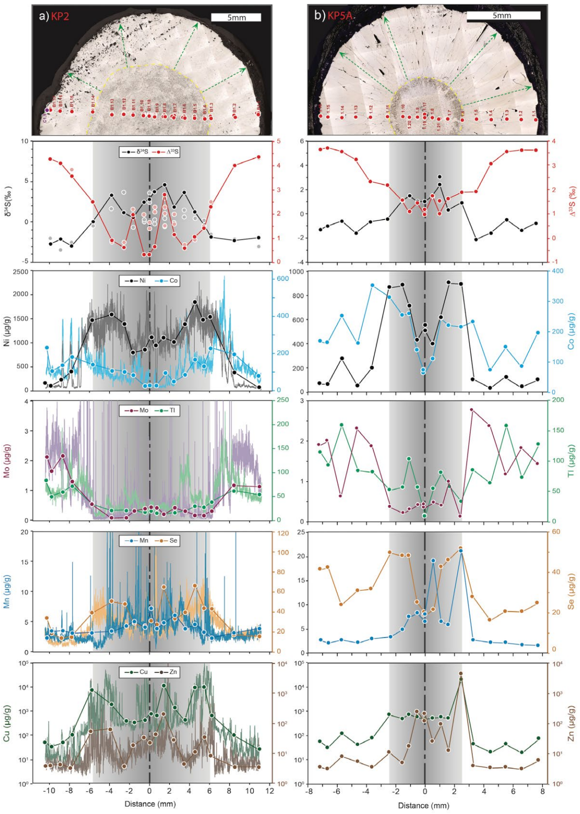

Fig. 1 Traverses across Kapai Slate pyrite corona nodules showing variations in $\delta^{34}S$, $\Delta^{33}S$ and representative trace elements. Grey horizontal dashed lines mark the nodule centre, and grey shaded areas represent cores.

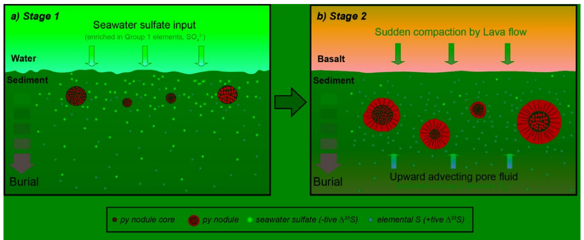

Fig. 2. Diagrammatic representation of the two-stage corona nodule growth model as described in the text.a) slow formation of nodule core near the sediment-water interface from pore fluid rich in sulfate and compatible Group1 elements; b) fast growth of the nodule mantle from an upward flux of pore fluid, which enriched in elemental S, following the eruption of the Paringa Basalt.