

The Impact and Implications of Aragonite-to-calcite Transformation on Speleothem Trace Element Composition

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Speleothems play a key role in studying past climate change, benefitting mainly from their accurate and precise U-series chronology [1-3]. Trace elements in cave carbonates (both calcite and aragonite) considered as major proxies provided our main entry into reconstructing paleo-hydroclimate history [4]. However, their imprints in authigenic minerals might be altered by neomorphic processes (e.g., aragonite-to-calcite transformation), biasing resulting environmental reconstruction [5,6]. Therefore, it is crucial to understand the impacts of neomorphism on the trace element compositions of secondary calcite and understand the mechanisms of trace elements redistribution during neomorphic processes. In this study, we obtained two aragonite stalagmites (SN3 and SN15) from Shennong Cave, part of which were transformed into calcite. Then we observed their morphologies and microstructures using polarizing microscope and scanning electron microscopy (SEM). We further measured trace element geochemistry by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), and acquired Mg compositional mapping using energy dispersive spectrometer (EDS). The results show that (1) the aragonite-to-calcite transformation in SN3 and SN15 occurs by a dissolution-precipitation mechanism, and is influenced by several factors, including internal fluid compositions, microstructure (such as porosity and permeability) of the parent material, and crystal defects. (2) The primary aragonite is enriched in Sr but depleted in Mg compared with secondary calcite because of the crystallographic disparity. The nonequilibrium absorption of Mg and slow diffusive element transport may contribute to the extremely high Mg/Ca ratios in secondary calcite near the mineral phase boundary. Incorporation competition among trace elements also plays an important role in affecting the distribution of Sr and Mg in neomorphic calcite. Considering the previous study on the alteration of stable oxygen and carbon isotopes associated with the aragonite-to-calcite transformation^[7], we propose that intervening fluids play an important role in altering the secondary calcite oxygen isotopic composition and Mg/Ca ratio, while the composition of primary aragonite dictates the secondary calcite carbon isotopic composition and Sr/Ca ratio, provided that the transformation of aragonite to calcite caused by a dissolution–reprecipitation process occurring in trapped pore water. These results highlight the indispensability of petrographic analysis of speleothem specimens before using trace elements and isotopes for paleoclimate research [8].

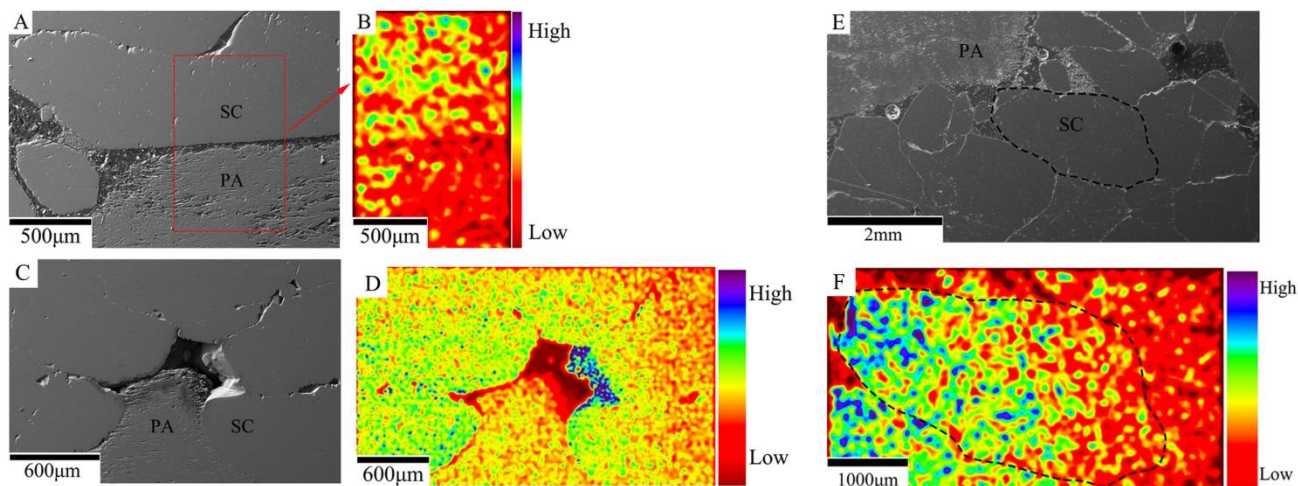


Figure 1. The composition map for Mg is analyzed by the EDS system from sections of SN15 and SN3, including both aragonite and calcite. (A) An SEM image of the selected area in SN3. (B) The Mg composition map (red rectangle in panel A). (C) An SEM image of the selected area in SN15. (D) Mg composition map. (E) An SEM image of the transformation front in SN3. (F) The Mg composition map of a selected area in E (black dashed circle). (SC = secondary calcite; PA = primary aragonite).

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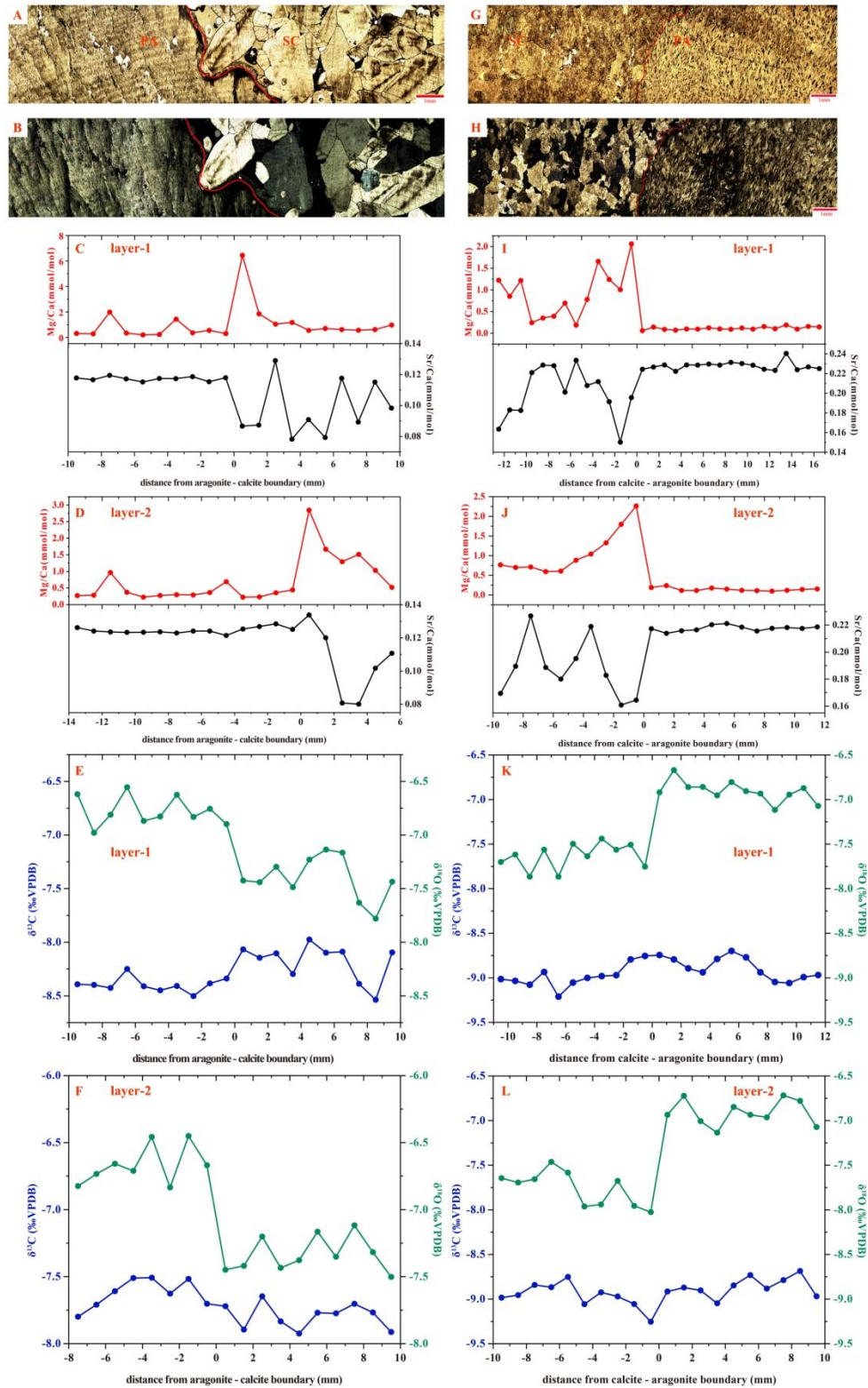


Figure 2. Variations of trace element (Mg/Ca, Sr/Ca) and isotopic compositions ($\delta^{18}\text{O}$, $\delta^{13}\text{C}$) along the same growth layers in SN3 (A, B, C, D, E, F) and SN15 (G, H, I, J, K, L). (SC=secondary calcite; PA = primary aragonite).