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Deciphering annual and long term trace element cycles in speleothems using cave monitoring and simple models

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Routine very high resolution trace element analysis using LA-ICPMS methods reveals seasonal scale trace element variation in many speleothems. However interpretation of these cycles are complex. Caves located in the same region, which experience the same seasonal climatic oscillations in temperature and precipitation, nonetheless show significant differences in relationship of different elements at seasonal scales. For example stalagmites from one cave show sympathetic seasonal cycles in Mg and Sr, whereas in another Mg and Sr are out of phase. The caves feature important differences in degree of ventilation, with some caves showing strong summer stratification and CO_2 buildup but others maintaining atmospheric CO_2 levels year round. We develop a simple geochemical model of dripwater chemistry and element partitioning in which three fit parameters – driprate, initial dripwater Ca concentration, and Ca concentration in equilibrium with cave atmosphere – are allowed to temporally vary to simulate the observed elemental profiles in the stalagmites. Prior calcite precipitation as a function of driprate, and known kinetic effects on partitioning which covary with dripwater saturation state are included. We compare the coherence between modeled processes and observed differences in cave hydrology and parameters. We also use the model to explore potential explanations for long term variations in trace element content in recent and fossil speleothems from the same caves. We find that a highly condensed interval corresponding with the H1 Mystery Interval in a speleothem from NW Spain was likely triggered first by a strong drop in dripwater saturation state, likely due to reduction in soil CO_2 from cold temperatures, and subsequently by dry conditions and lower driprates. On long timescales, we identify precessional cycles in saturation state independent of prior calcite precipitation. These trace-element inferred changes in dripwater saturation state suggest that at least part of the precessional variations in oxygen isotopic composition may be attributed to kinetic saturation state effects.