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Generation and dispersal of carbon dioxide in the caves and karst of Gibraltar

T. Atkinson (2), D. Mattey (1), J-P. Latin (3), M. Ainsworth (3), and R. Durell (3)

(1) Department of Earth Sciences, Royal Holloway University of London, UK, (2) Department of Earth Sciences, University College London, UK, (3) Gibraltar Cave Science Unit, GONHS, Jews Gate, Gibraltar

The gases in the soil, in caves and in the smaller voids of the vadose zone in karstic limestones are all generally enriched in CO_2 relative to open atmosphere. The concentrations and fluxes of CO_2 in cave air have a close relationship with the deposition of speleothem calcite but there are still very few detailed studies that trace the generation and dispersal of CO_2 in whole karst systems, $i.e.$ as a gas and in dissolved form within a linked system comprising soil, caves and the vadose zone. The Rock of Gibraltar forms a N-S trending ridge 2.5 km long within which solution caves are present at altitudes extending from below sea level to over 300m asl. Cave monitoring has been carried out since 2004 and focuses on two cave systems: St Michaels Cave (SMC) located near the top of the rock at 275m asl and Ragged Staff Cave located in the heart of the rock near sea level. Monthly sampling and analysis of air and water combined with continuous logging of temperature, humidity and drip discharge rates reveals the importance of density-driven seasonal ventilation which drives large-scale advection of CO_2-rich air though the cave systems. Advective flow is upwards during winter months, resulting in low pCO_2 at sea level and high pCO_2 in caves near the top of the rock and the flow reverses in summer, ventilating high-level caves and raising cave air pCO_2 at lower altitudes. In this talk we focus on geochemical tracing of CO_2 generation and dispersal using the abundance and carbon isotopic compositions of gaseous CO_2 and dissolved inorganic carbon (DIC). The results of a four-year study at SMC are not consistent with the generally accepted view that CO_2in cave air originates by degassing of dripwater that has acquired CO_2primarily from the soil zone. We demonstrate the importance of deep vadose zone air as a *source* of CO_2 in karst systems and show that in St. Michaels Cave the abundance and isotopic composition of CO_2 of the cave atmosphere is primarily controlled by mixing between a CO_2– rich vadose air component and background atmospheric air introduced into the cave by seasonal ventilation.