Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 184 (2016) 88–113

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Carbon dioxide, ground air and carbon cycling in Gibraltar karst

D.P. Mattey [a,*], T.C. Atkinson [b], J.A. Barker [c], R. Fisher [a], J.-P. Latin [d], R. Durrell [d], M. Ainsworth [d]

[a] Department of Earth Sciences, Royal Holloway, University of London, Egham, Surrey TW20 0EX, UK
[b] Department of Earth Sciences, University College London, WC1E 6BT, UK
[c] School of Engineering and the Environment, University of Southampton, Southampton SO17 1BJ, UK
[d] Gibraltar Cave Science Unit, Gibraltar Ornithological and Natural History Society, Jews Gate, Gibraltar

Received 16 October 2015; accepted in revised form 31 January 2016; available online 8 February 2016

Abstract

We put forward a general conceptual model of CO_2 behaviour in the vadose zone of karst aquifers, based on physical principles of air flow through porous media and caves, combined with a geochemical interpretation of cave monitoring data. This 'Gibraltar model' links fluxes of water, air and carbon through the soil with the porosity of the vadose zone, the circulation of ground air and the ventilation of caves. Gibraltar hosts many natural caves whose locations span the full length and vertical range of the Rock. We report results of an 8-year monitoring study of carbon in soil organic matter and bedrock carbonate, dissolved inorganic carbon in vadose waters, and gaseous CO_2 in soil, cave and ground air. Results show that the regime of cave air CO_2 results from the interaction of cave ventilation with a reservoir of CO_2-enriched ground air held within the smaller voids of the bedrock. The pCO_2 of ground air, and of vadose waters that have been in close contact with it, are determined by multiple factors that include recharge patterns, vegetation productivity and root respiration, and conversion of organic matter to CO_2 within the soil, the epikarst and the whole vadose zone. Mathematical modelling and field observations show that ground air is subject to a density-driven circulation that reverses seasonally, as the difference between surface and underground temperatures reverses in sign. The Gibraltar model suggests that cave air pCO_2 is not directly related to CO_2 generated in the soil or the epikarstic zone, as is often assumed. Ground air CO_2 formed by the decay of organic matter (OM) washed down into the deeper unsaturated zone is an important additional source of pCO_2. In Gibraltar the addition of OM-derived CO_2 is the dominant control on the pCO_2 of ground air and the Ca-hardness of waters within the deep vadose zone. The seasonal regime of CO_2 in cave air depends on the position of a cave in relation to the density-driven ground air circulation pattern which is itself determined by the topography, as well as by the high-permeability conduits for air movement provided by caves themselves. In the steep topography of Gibraltar, caves in the lower part of the Rock act as outflow conduits for descending ground air in summer, and so have higher pCO_2 in that season. Caves in the upper Rock have high pCO_2 in winter, when they act as outflow conduits for rising currents of CO_2-enriched ground air. Understanding seasonal flows of ground air in the vadose zone, together with the origins and seasonal regimes of CO_2 in cave air underpins robust interpretation of speleothem-based climate proxy records.

* Corresponding author.
E-mail address: mattey@gl.rhul.ac.uk (D.P. Mattey).

http://dx.doi.org/10.1016/j.gca.2016.01.041
0016-7037/

1. INTRODUCTION

The gases in the soil, in caves and in the smaller voids of the vadose zone in karstic limestones are generally all enriched in CO_2 relative to open atmosphere (Atkinson, 1977a; Baldini et al., 2006a; Baldini, 2010; Benavente et al., 2010; Bourges et al., 2001, 2014; Breecker et al., 2012; Ek and Gewelt, 1985; Ford and Williams, 2007; Wood and Petraitis, 1984). The concentrations and fluxes of CO_2 in cave air have a close relationship with the deposition of speleothem calcite and the way that chemical proxies for palaeoclimate are recorded and interpreted from cave deposits (Baldini, 2010; Banner et al., 2007; Breecker et al., 2012; Cosford et al., 2009; Frisia et al., 2000, 2011; Mattey et al., 2010; Spotl et al., 2005), but there are still few studies that trace the generation and dispersal of CO_2 in deep karst systems, *i.e.* as a gas and in dissolved form within a linked system comprising soil, caves and the vadose zone. Our previous publications on Gibraltar caves have described the relationships between the surface and cave microclimates, hydrology, fabrics and chemistry of modern speleothem in New St. Michaels Cave (Mattey et al., 2008, 2010, 2013). In this paper we report results of a monitoring program carried out in Gibraltar from 2004 to 2012. Using field observations of airflow patterns, measurements of seasonal variations in the abundance and $\delta^{13}C$ of CO_2 in soil, cave and vadose air, and geochemical modelling, we show that seasonal patterns in cave air CO_2 concentrations are explained by advection of CO_2-rich vadose zone air (or 'ground air') within the Rock of Gibraltar. Our results are not consistent with the generally accepted view that CO_2 in cave air originates only from the soil zone and we show that 'ground air' is an internally generated *source* of CO_2 in karst systems (*cf.* Atkinson, 1977a; Wood and Petraitis, 1984; Wood, 1985; Wood et al., 1993). The abundance and isotopic composition of CO_2 of cave atmospheres are primarily controlled by mixing between a CO_2 – rich ground air component and background atmospheric air introduced into the cave by seasonal ventilation. We put forward a general conceptual model of CO_2 behaviour in the vadose zone of karst aquifers based on physical principles of air flow through caves and porous media, combined with a geochemical interpretation of our monitoring data. The model links fluxes of water, air and carbon through the soil with the porosity of the vadose zone and ventilation of caves (Fig. 1). We show that ground air circulation is driven by density differences between underground and outside air, in patterns that depend on the locations of caves in relation to the overall topography.

Caves act as sources and/or sinks for ground air circulation and the seasonal contrasts in CO_2 concentrations observed in many cave atmospheres result from varying mixtures of CO_2 – rich ground air with low CO_2 air from the external atmosphere. Soil gas CO_2 undoubtedly contributes indirectly to cave air and to the dissolved DIC of vadose groundwaters but in both of these phases it is supplemented to a greater or lesser extent by CO_2 derived from the decay of organic matter that is washed down into the karst by infiltrating water. We show through geochemical modelling that CO_2 formed internally within the karst environment tends to acquire a distinctive isotopic composition, typically in the modelled range −20‰ to −22‰, and similar to values observed in direct measurements of ground air in Gibraltar and at Nerja Cave in Spain (Benavente et al., 2010). The 'standard' model in which soil gas is seen as the primary source of CO_2 in both vadose waters and cave air is therefore a special case of the more general model we propose on the basis of the evidence from Gibraltar.

1.1. The role of CO_2 in speleothem growth

Speleothems (especially stalagmites and flowstones formed of calcium carbonate precipitated from groundwater percolating into caves) are widely used to reconstruct oxygen isotope records of palaeoclimate and atmospheric processes across the continents (*e.g.* McDermott, 2004; Fairchild et al., 2006; Ford and Williams, 2007; Lachniet, 2009). The 'standard model' of speleothem deposition in the interior parts of caves (Ford and Williams, 2007; Holland et al., 1964; Roques, 1956, 1969; Smith and Mead, 1962; White, 1988) envisages that infiltrating waters acquire high pCO_2 as they react with the CO_2-enriched gases in the soil. The water then passes through the vadose zone to the point where it enters a cave, having dissolved $CaCO_3$ from bedrock during its passage. If pCO_2 of the cave atmosphere is less than the value possessed by the water, degassing of CO_2 from water to cave air ensues and causes the precipitation of a $CaCO_3$ mineral, usually calcite. Fig. 1 illustrates the pathways between CO_2 reservoirs in atmosphere, soil and karst associated with vadose groundwater movement and limestone dissolution and the formation of cave air. The route of CO_2 fluxes in the 'standard model' is indicated by the grey arrow linking soil air via groundwater to cave air, which is enriched in CO_2 relative to background atmosphere as a result of degassing. The gases contained in the fissures, fractures and pore-spaces of rock in the vadose zone have little part to play in the standard model, but in this study we show that microbial decay of organic matter, washed into this environment from the soil zone, is capable of generating extremely high pCO_2 in ground air with associated $\delta^{13}C$ values that may be diagnostic of this process (*cf.* Atkinson, 1977a; Wood and Petraitis, 1984).

The CO_2 content of cave air exerts a strong influence on speleothem deposition through its control on the rate at which drip-water solutions degas after entering a cave (Banner et al., 2007; Dreybrodt, 2008, 2011; Mattey et al., 2010). Other factors aside, degassing depends on the difference between the pCO_2 of cave air and the partial pressure of CO_2 with which the solution is in equilibrium. Degassing rates will be greatest when cave air pCO_2 is lowest, and may vary seasonally if the cave air CO_2 displays seasonal variations, as is the case in Gibraltar (Mattey et al., 2010). The rate of degassing is normally much faster than the rate of calcite nucleation, so the degree of supersaturation exhibited by cave waters is strongly influenced by ambient cave air CO_2. Supersaturation in turn controls the rate of calcite precipitation (Dreybrodt, 1988, 2008; Plummer et al., 1979) the type of fabric formed, and the capture of trace elements