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Field Trip 1

Geochemistry of Waipuna Cave

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Note: Cover photo shows karst landscape on limestone west of Waitomo (from Edbrooke 2005).

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GEOCHEMISTRY OF WAIPUNA CAVE

Introduction to Waipuna Cave

Fig. 1. Elemental and isotopic sample collection at Waipuna Cave (Blogs 2019).

Waipuna Cave is the subject of a multi-year cave monitoring programme, which focusses on the development of novel quantitative proxies for palaeoclimatology. The parameters measured in the cave are the elemental and isotopic composition of drips, electrical conductivity, drip rate and temperature (Fig. 1). These results are compared to the meteorological records in order to calibrate proxies for quantitative climate reconstruction. The larger purpose of this data collection is to understand the dynamics of the El Niño-Southern Oscillation with the southern westerlies and the local response to changes in their interplay (Blogs 2019).

Waipuna Cave is a non-commercial cave jointly managed between landowners and the Department of Conservation. This cave is 3560 m long (New Zealand Speleological Society 2018) and 20 m deep from the entrance point. Waipuna is subject to a temperate climate because of its geographical location at latitude 38° 15S' and longitude 175° 06'E. The cave is 214 km south of Auckland (Fig. 2) and the annual mean air temperature in the Waitomo region varies between 12–13 C° with a minimum of 4–5 C° during winter and a maxima between 22–23 C° during summer months (Chappell 2013). The mean annual rainfall at Waitomo is between the 1,600 and 1,800 mm, but the ranges to the west receive over 2,000 mm since most of the rainfall is carried by westerly winds (Chappell 2013). The oldest records found in this cave date to 35,000 BP (B. Ward, personal communication, November 7, 2019) although there is undoubtedly older material, and speleothems are still actively growing.

Geological context

Waipuna Cave is located on an unnamed northeast trending fault west of the southern end of the Hikurangi Fault (Nelson 1973, 1978; Edbrooke 2005). Faults are permeable pathways to focus water flow into karstic landscapes, with these widening over time. To the west of the karst landscape is the Herangi Range, a thrusted block of greywacke basement corresponding to the Murihiku Terrane. This range protrudes 180–240 m above sea level (Nelson 1973).

Fig. 2. Google Earth satellite image of study sites in relation to Auckland and Hamilton (White 2019).

Most of the Waipuna Cave bedrock is composed of Otorohanga Limestone. This limestone formed between 37.8 and 28.1 million years ago in subtidal seaways at 40 to 60 m depth in <20˚C waters. The Otorohanga Limestone is composed of erect robust and delicate branching bryozoans, echinoderm fragments and large benthic foraminifers (Anastas et al. 2006). However, further upstream in Waipuna cave, the bedrock changes to a yellow-brown very fine grained sandstone, which Nelson (1973) has described as the Aotea Sandstone.

Principles of karst geochemistry

Plants expire large quantities of CO_2 from their roots and soil microorganisms also respire CO_2 into the soil pore space. Thus, biological processes act to raise the ${}_{P}CO_2$ of the soil atmosphere to several percent of an atmosphere. Water passing down through the soil will dissolve this CO_2

$$H_2O + CO_2 \quad = \quad HCO_3^- + H^+$$

When this solution comes into contact with the limestone, the hydrogen ions attack the carbonates

$$H^+ + CaCO_3 \quad = \quad Ca^{2+} + HCO_3^-$$

which results in solution of calcium ions and a disturbance of the chain of equilibria:

$$\begin{aligned} H_2O + CO_2 &= HCO_3^- + H^+ \\ HCO_3^- &= CO_3^- + H^+ \\ CO_3^{2-} + Ca^{2+} &= CaCO_3 \end{aligned}$$

If the soils are shallow, as CO_2 is removed from solution through attack on $CaCO_3$, more CO_2 is replaced from the soil atmosphere (OPEN SYSTEM). However, if the soils are deep and plant roots are isolated from the limestone, the ${}_{P}CO_2$ will drop substantially, and the pH will rise as the water passes into the limestone (CLOSED SYSTEM).

When the solution reemerges in a cave the ${}_{P}CO_2$ will readjust to achieve equilibrium with the cave air. If it is higher than the cave air, CO_2 will be lost from solution, forcing carbonates to be precipitated.

$$Ca^{2+} + 2HCO_3^- = CaCO_{3(\text{calcite})} + H_2O + CO_2$$

But if it is lower than the cave atmosphere the reverse will occur and further solution of calcium carbonate will take place. Where calcium carbonate is precipitated formations known as “speleothems” will be deposited. These include stalactites, stalagmites and flowstone. You can find both of these effects in Waipuna Cave. A special problem can arise when large numbers of people occupy small or poorly ventilated caves. As people respire CO_2 the partial pressure rises in the cave atmosphere and can exceed that of the drip waters causing speleothems to redissolve (Figure 3). Other deposits can also occur as a result of the loss of CO_2 (and rise in pH). Look for deposits of black MnO_2 (pyrolusite) in the form of cave varnish on stones, and “cave leather”. These are precipitated by:-

$$Mn^{2+} + H_2O + {}^{1}/{}_{2}O_2 + MnO_{2(\text{pyrolusite})} + 2H^+$$

as the pH rises and oxygen is readily available. Evaporation also causes precipitation of carbonates and sulphates.

$$Ca^{2+} + SO_4^{2-} = CaSO_4.2H_2O_{(\text{gypsum})}$$

Measure the pH of the solutions and decide the extent of the access of soil CO_2 to the limestone in various cave and karst waters.

A supplementary diagram of cave processes in provided in Fig. 3.

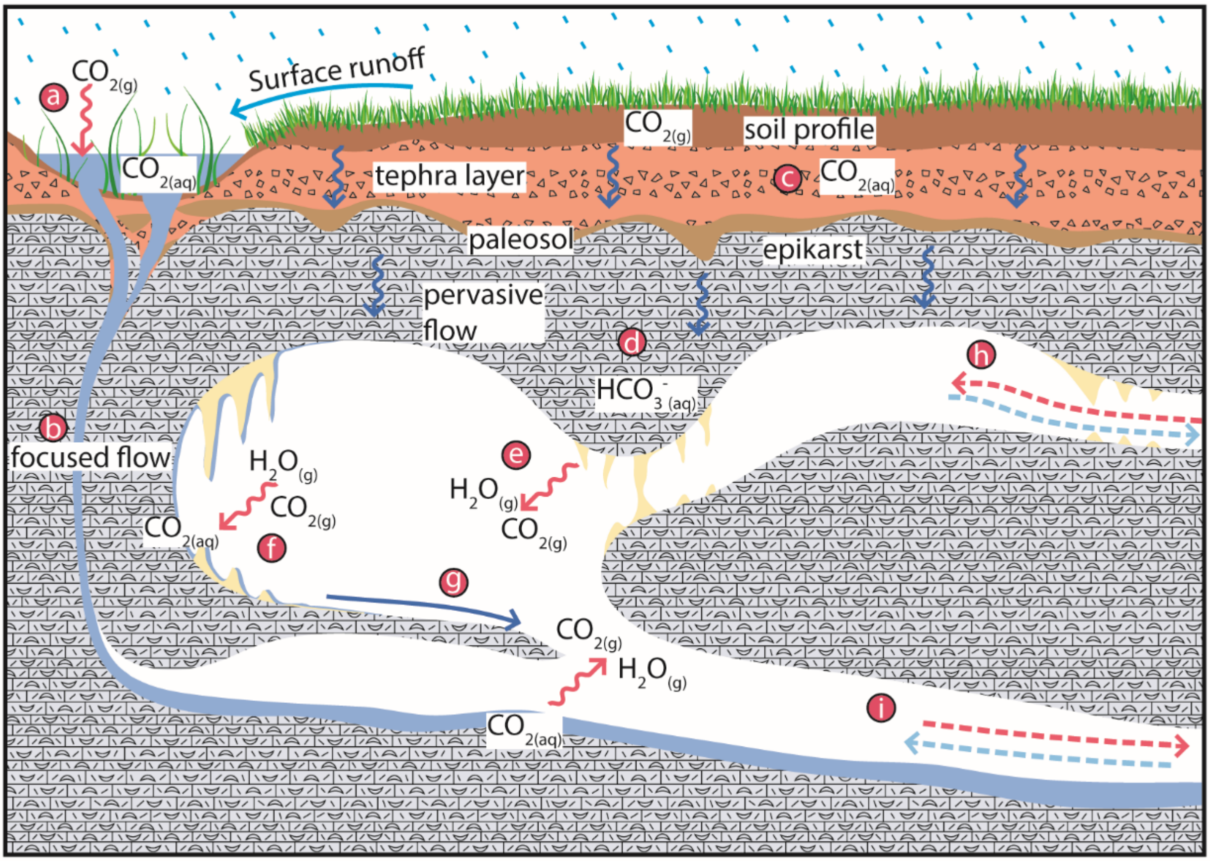

Fig. 3. Summary of cave processes in the Waitomo region with relevance to condensation corrosion. (a) Diffusion of atmospheric CO_2(g) into surface water. (b) Focused (channelized) flow catch surface and groundwater flow into open spaces (Ague 2014), which flow through karst. (c) Diffusion of CO_2(g)¬ from soil respiration (microbial and plant contributions) into percolating water due to the partial pressure gradient between reservoirs (Ford and Williams 2007). The partial pressure of CO_2(g) in percolating water is atmospheric (≈405 ppm, NOAA 2018) while the contribution from soil respiration is in the range between 1,000 ppm and 60,000 ppm this temperate region (Ford and Williams 2007). (d) Once percolation waters pass through the soil horizon, they become more corrosive with the additional dissolved CO_2 contributed by soil respiration. These corrosive groundwaters flow through tephra and reach limestone where calcium carbonate is dissolved between the shell-derived grains (pervasive flow, Ague 2014) and can later find preferential flow paths in fractures. (e) As pervasive flows enter the cave, the groundwater releases CO_2(g) due to the partial pressure difference between cave atmospheric CO_2(g) and the groundwater. This release results in calcite precipitation and the formation of speleothems. (f) Condensation films form on speleothems and cave walls depending on the cave atmospheric conditions. CO_2(g) in the cave atmosphere diffuses into and out of theses condensate films which dissolve or precipitate calcite, respectively. (g) When condensation forms a film thick enough, it will flow, transporting dissolved Ca^{2+}(aq) and CO_3^{2-}(aq) ions with it. (h) The red dashed arrow indicates the direction of air flow during summer in a dual entrance cave. Air enters from the top entrance as the cave air is cooler and therefore denser. (i) In contrast, the blue dashed arrows indicate the airflow direction in winter; when the cave air is warmer (less dense) than the air outside. Figure taken from White (2019).

Monitoring of Waipuna Cave dripwaters for climate signals

Cave microclimatic and geochemical monitoring is essential for correct interpretations of proxy time series from speleothems with regard to past climatic and environmental dynamics. A complex cave monitoring programme has been undertaken in Waipuna Cave over the last three years. The caves' location in the North Island of New Zealand provides the opportunity to study the past expression of the southern westerlies and the El Niño-Southern Oscillation (ENSO). Our work aims to characterize the hydrological response of Waipuna Cave to atmospheric circulation dynamics in the southwestern Pacific region in order to improve the interpretation of palaeo-environmental reconstructions from this cave.

Cave air temperature and CO_2, water isotopes ($\delta^{18}O$, δD, $D\text{-}_{excess}$, $^{17}O_{excess}$) and trace elements (Mg/Ca, Sr/Ca), drip rates, and water temperatures are collected continuously and at monthly intervals from 10 drip sites inside Waipuna Cave. Based on the drip response dynamics to rainfall and other characteristics we identify three hydrological pathways in Waipuna Cave: diffuse flow, combined flow, and fracture flow. Water isotopes do not reveal seasonal variability, but show higher values during severe drought. Dripwater $\delta^{18}O$ values are very narrow and reflect the mean isotopic signature of precipitation (Fig. 4), testifying to rapid and thorough buffering in the epikarst. Mg/Ca and Sr/Ca in dripwaters are predominantly controlled by prior calcite precipitation (PCP): PCP is strongest during austral summer (December-February), reflecting drier conditions and lack of effective infiltration; and is weakest during the wet austral winter (July-September). These elemental ratios are particularly sensitive to ENSO conditions because of the interplay of congruent/incongruent host-rock dissolution, becoming manifest in lower Sr/Ca in above-average warmer and wetter (La Niña-like) conditions. Our microclimatic observations at Waipuna Cave therefore provide valuable baseline data for the interpretation of speleothem proxy records with a view to the past expression of Pacific climate modes.

Unpublished data from dripwater monitoring in Waipuna Cave are provided in Figs. 4 and 5. The hydrological significance of these data will be discussed during the field trip.

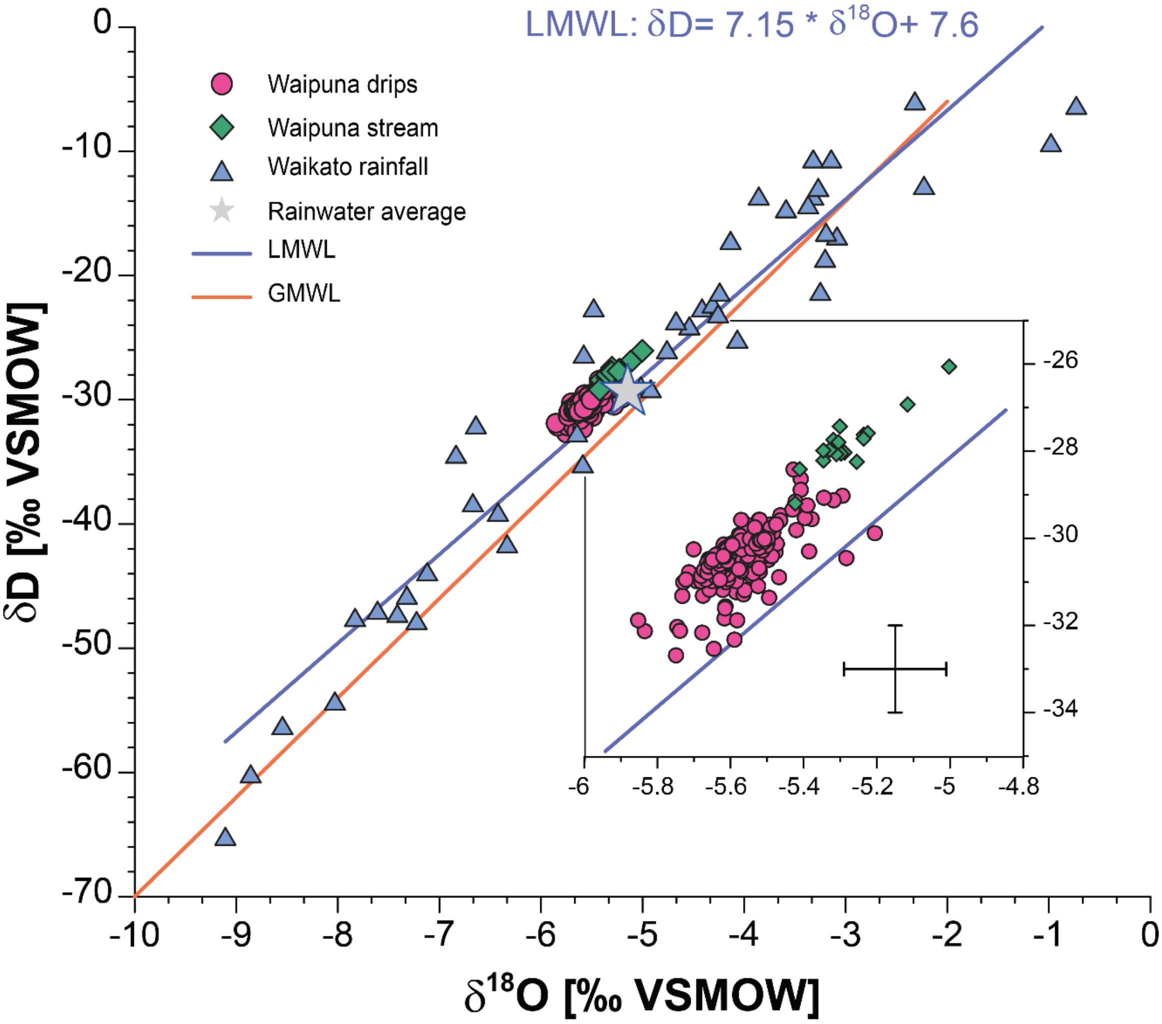

Fig. 4. Cross-plot of δD versus δ18O in dripwater (pink circles), the Waikato region precipitation (blue triangles), and Waipuna stream (green diamonds). All cave waters fall in a very narrow range (inset) on the Local Meteoric Water Line (blue line). The cross in the inset shows the 2σ uncertainties for δ18O and δD.

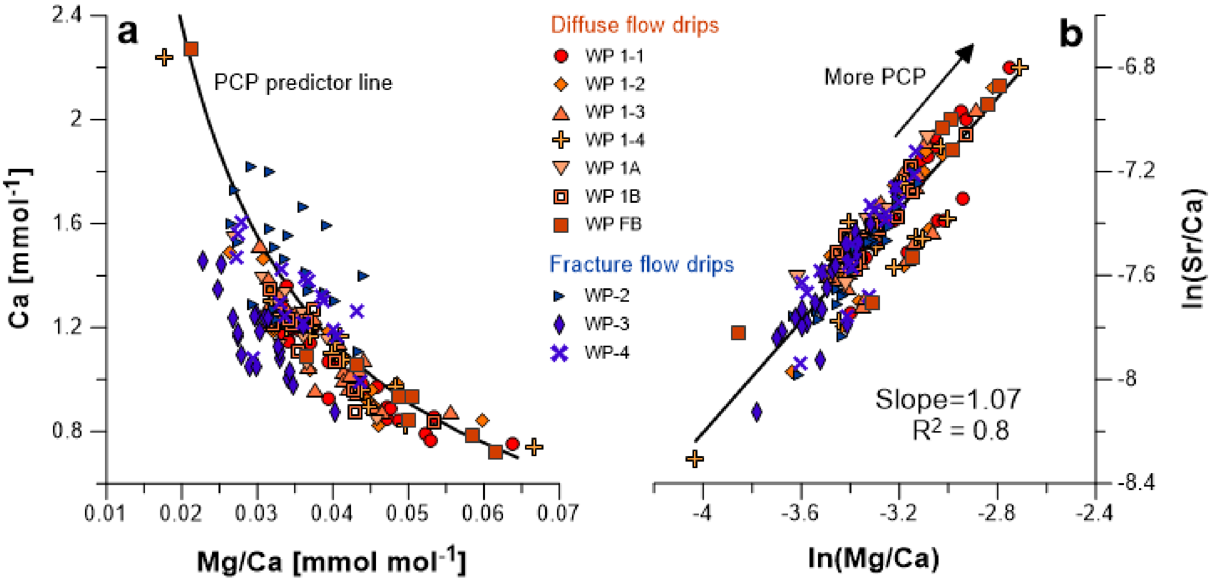

Fig. 5. (a) Ca concentration vs. Mg/Ca, and (b) Sr/Ca vs. Mg/Ca ratios for all Waipuna Cave waters sampled during the monitoring period October 2016 to January 2019. The orange symbols correspond to diffuse flow drip sites and blue symbols signify fracture flow drip sites.

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