

**Phosphorus  
variability in  
speleothems**

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# A re-evaluation of the palaeoclimatic significance of phosphorus variability in speleothems revealed by high-resolution synchrotron micro XRF mapping

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## Abstract

The distribution of phosphorous (P) in one modern and two Early Pliocene speleothems formed in low-lying, Christmas Island and the coastal Nullarbor caves wet settings in Australia is here investigated by microscopy and ultra-high resolution chemical mapping. Monitoring data in the modern setting suggest that co-precipitation of P with calcite occurs when the drip rate decreases, the aquifer is progressively drained and microbial mats possibly aid in the formation of concentrating phosphates. A bulk partition coefficient is proposed, which indicates that the P enrichment in the speleothem could be accounted for by inorganic processes. Our interpretation of the hydrological significance of P incorporation in wet, tropical speleothems is then used to interpret P peaks associated with micritic and stromatolithic layers in the two Early Pliocene stalagmites from the Nullarbor. From these observations it is speculated that dry periods may have interrupted the wet climate regime at ca. 4 Myr ago, hinting at a possible early onset of the Pleistocene climate mode.

## 1 Introduction

Speleothem-based palaeoclimate research, to date, capitalizes on models and experiments targeting stable isotope fractionation under a wide spectrum of environmental parameters (Scholz et al., 2009; Tremaine et al., 2011; Dreybrodt and Scholz, 2011). By contrast, the study of environmentally significant trace elements incorporation in speleothems has only recently gained momentum, although trace element variability provides robustness to palaeoclimate and ecosystem process reconstructions (e.g. Griffiths et al., 2010; Lewis et al., 2011; Borsato et al., 2007). The incorporation of trace elements in cave calcite is related to the composition of the parent fluid (cf. Fairchild and Baker, 2012), crystal surface processes and complex interactions between crystal surfaces and microbes (Banfield and Neelson, 1997). The latter is the

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most controversial (cf. Jones, 2010), because bacteria may drive non-equilibrium partitioning (Warren et al., 2001).

Direct and indirect evidence of microbial influence on calcite precipitation has been frequently documented (Cañaveras et al., 1999; Castanier et al., 2000; Jones, 2001; Braissant et al., 2003; Cacchio et al., 2004; Barton and Northup, 2007), to the point that the assumption that speleothem calcite forms through pure abiogenic processes has been challenged (Jones, 2009, 2010). Stromatolite morphologies typical of calcite precipitation associated with bacterial action, such as filaments, rods and layered micrite have been reported in flowstones and stalagmites from caves in the Italian Alps (Borsato et al., 2000; Frisia and Borsato, 2010), and organic compounds extracted from the same speleothems have been related to bacteria (Blyth and Frisia, 2008). Whether the microbes had been transported from the soil or had been living in-situ remains unclear. Cave dwelling chemolithotrophs, however, were inferred to be responsible for the formation of fossil stromatolites in the deep, dark interior of a cave in Spain (Rossi et al., 2010). Still, despite growing evidence, biomediation has been largely neglected in speleothem-based palaeoclimate research because its products “*have chemical properties within the range of laboratory precipitated inorganic crystals*” (Fairchild and Baker, 2012). Controversy has recently focused on the palaeoclimatic significance of phosphorus (P) concentration variability in speleothems.

A study on P variability in a modern speleothem from Western Australia suggested a link between increase in rainfall and increase in the speleothem P/Ca ratio (Treble et al., 2003). P concentration maps generated by Synchrotron Radiation-based micro X-Ray Fluorescence (SR- $\mu$ XRF) of annually layered speleothems from the Alps also revealed a connection between higher infiltration and P peaks (Borsato et al., 2007). The P/Ca ratio in stalagmites, thus, has become a proxy for seasonal hydrological variability and ecosystem processes (Lewis et al., 2011). Nuclear Magnetic Resonance, however, reveals that P is not only present as adsorbed phosphate incorporated into the calcite lattice, but also as crystalline, phosphate phases co-precipitated with the calcite (Mason et al., 2007). Critically, P peaks in Alpine speleothems were

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also associated with UV-fluorescent layers, where fluorescence is commonly activated by organic molecules (cf. Borsato et al., 2007). There was, thus, a potential relation between bacteria and P-rich phases, which became subject of controversy when Jones (2009) concluded that caution should be taken in considering speleothem P/Ca ratio as palaeoclimate proxy. The argument is based on observation of microbes and P-rich phases in speleothems from Great Cayman (Caribbean), where high concentration of P was interpreted to be the result of microbially-related processes. The P-rich, crystalline phases were observed to form in condensation-corrosion microcavities occupied by microbial mats and mark periods when active calcite growth apparently stopped (Jones, 2009). In their extensive summary of speleothem research, Fairchild and Baker (2012) seem to dismiss the Grand Cayman microbial hypothesis, and advocate the common interpretation that increased P/Ca ratio in stalagmites is a proxy for high infiltration. The controversy, however, highlights a lack of knowledge regarding P in speleothems and its palaeoclimatic significance. To a certain degree, part of the problem is the avoidance of microscopy, based on the tacit assumption that such method is useful only to discern recrystallization phenomena; petrographic observation, however, should allow recognition of bacterially related morphologies. Another critical issue is the selection of the analytical methods, which understandably favors time- and cost-efficient Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). Climate-important trace elements such as Strontium, Phosphorus and Silicon may form distinct co-precipitated phases or be associated with micro-detrital inclusions, all of which are potentially averaged in LA-ICP-MS analyses which may encompass areas up to a few hundred square microns. By contrast, microfluorescence mapping allows resolution of element concentrations at the scale of 1 to 2  $\mu\text{m}$ , which can be easily related to fabrics, and potentially highlight if tracers are in lattice or extra-lattice sites.

Here, we focus on the palaeoclimatic significance of P by using a combination of techniques, from standard petrographic observations to LA-ICP-MS and SR- $\mu$ XRF mapping. We selected a modern speleothem from a low lying, insular cave, not

dissimilar to Great Cayman, to elucidate mechanisms of P incorporation in warm and wet coastal setting speleothems, and then applied the results to Early Pliocene stalagmites formed in a cave near the Southern Australian coast to gain information on processes which may provide insight on both timing and nature of Pliocene climate switch from a dominant El Niño-like state (cf. Steph et al., 2010). Our study confirms that P concentration variability is a powerful climate proxy, but in our speleothems P peaks appear not be related to an increase in colloidal transport from the soil, but to complex interactions between microbial and hydrological processes.

## 2 Samples, settings and analytical methods

### 2.1 Speleothem geographic, climate and geologic settings

The studied speleothems come from coastal caves at Christmas Island in the Indian Ocean (105°40' E and 10°30' S) and in the Nullarbor Plain in Southern Australia (at ca. 127°8' E and 31°9' S), and were originally collected for palaeoclimate studies. The Tertiary host rocks are shallow marine carbonates which have not been modified in the deep burial diagenetic environment (>200 m to 4 km deep). The Christmas Island and Nullarbor limestones are relatively rich in phosphates (Grimes, 2001 and our data), as are most Cainozoic carbonates of the Indo Pacific region (Ayliffe et al., 1992).

An actively forming stalagmite (SC4) was collected from the coastal Smiths Cave, located on the NW part of Christmas Island, in 2004 as part of a study of recent monsoon history. The climate of the island is monsoonal, with a mean annual rainfall range of 900 to 3700 mm. During the wet season, from December to May, the NW monsoon results in mean monthly rainfall amounts between 200 and 300 mm. The driest months on average are August to October, with mean monthly values of 50–60 mm. However, the seasonal rainfall pattern evident in the mean monthly data masks significant year-to-year variability, with coefficients of variation ranging between 60% for January to

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174% for September. By contrast, temperature is relatively constant throughout the year (22 to 27 °C).

Drip waters feeding SC4 were collected on a monthly basis for two years (Drysdale unpublished data) and show the following mean values ( $\pm 1$  SD) for a suite of elements which are most commonly used for speleothem palaeoclimate reconstructions: Ca:  $103 \pm 10.8$  ppm; Mg:  $4.24 \pm 0.22$  ppm; P:  $0.28 \pm 0.09$  ppm; Sr:  $0.48 \pm 0.02$  ppb; Ba:  $2.13 \pm 0.34$  ppb; and U:  $0.063 \pm 0.005$  ppb. Silicon was not measured. The high concentration in P in the dripwaters likely derives from dissolution of phosphates that are present in the rock, most commonly as hydroxylapatite and chlorapatite (our data).

Initial attempts to date SC4 by uranium-thorium methods were unsuccessful due to possible multiple sources of non-authigenic thorium. More recently, an age model has been developed based on radiocarbon dating, which indicates it commenced growing at ca. 600–700 yr ago (Hua et al., 2012). A characteristic revealed from LA-ICP-MS trace element analyses of SC4 is the recurrence of layers containing P concentrations in excess of 10 000 ppm, which is relative to the parent water. Petrographic observations and chemical mapping for the present study consequently focused on the regions where P-peaked in the cycles. The synchrotron sample was cut from the top 3 cm and encompasses the last ca. 100 yr (mean age at ca. 30 mm is between 1871 and 1894 AD).

Speleothems 645-FS04 and 645-MO1 were collected within the framework of a study on Pliocene climate in Australia (Woodhead et al., 2006) and have ages of 4.3 and 3.9 Myr, respectively (Woodhead, preliminary data). Cave 645 is a coastal cave in the Nullarbor Plain (SW Australia) where, today, the only forming speleothems mostly consist of evaporites. The Nullarbor caves developed in Tertiary limestones (late Eocene to middle Miocene) which did not undergo burial diagenesis (Miller et al., 2012). Today, surface temperature may reach values as high as 35 °C in summer and as low as 5 °C in winter, and rainfall of up to 400 mm yr<sup>-1</sup> occurs in wet years, with a potential evaporation in summer of 2000 mm. This results in either no infiltration, or infiltration by waters strongly modified by evaporation. Existing data indicate that present-day drip-

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and pool-waters have chemistry similar to that of seawater (Turin and Webb, 2002), and are unlikely to be representative of drip waters in the Early Pliocene, when wetter climate allowed speleothem formation (Miller et al., 2012). Soil today is extremely thin and there is scanty vegetation (Webb and James, 2006), but in the Pliocene humid climate conditions a C3 vegetation cover probably existed (Miller et al., 2012). Phosphorous is present in the Nullarbor Limestone in concentration ranging from 20 to 50 ppm (LA-ICP-MS analyses, this work) and appears to be associated with bioclasts.

The fabrics of 645-FS04 and 645-MO1 stalagmites are typical of at least other 50 specimens of Pliocene stalagmites and flowstones collected from different caves in the Nullarbor Plain and consist of elongated columnar, Mg-rich (up to 4 mole %  $\text{CaCO}_3$ ), dark calcite crystals with visible lamination highlighted by subtle changes in colour. Changes in stalagmite morphology (such as a diminution or increase in diameter, or a slight shift in growth axis), are marked by light colored, mm-thick, opaque, microsparite layers showing irregular, stromatolite-like lamination. These microsparite layers are not a unique, exceptional occurrence, as at least 6 are present in the ca. 10 cm long 645-FS04 and 645-MO1 and they have been observed in many other hand specimens from the Nullarbor. Because of their similarity to stromatolites, we focused P-mapping on the microsparite layers, which suggest microbial laminites.

## 2.2 Methods

All samples had been analysed prior to this study for stable carbon and oxygen isotope ratios, and cave monitoring data were collected for the active Smiths cave. For the Nullarbor, the general absence of infiltration as well as the remoteness of the area prevented a monitoring program. Petrographic observations were carried out in thin sections by optical microscopy, and micromorphological characteristics of crystals were investigated by Scanning Electron Microscopy (SEM). Rapid, in-situ qualitative composition was carried out during SEM observations using EDAX mapping. Mineral phases were identified by X-Ray diffraction on both powdered (to avoid the effects of preferential fabric orientation) and polished samples using  $2\theta$  range from 5 to 80 degrees,

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with acquisition time up to 10 h. When necessary, Raman microspectroscopy phase recognition was carried out on the polished samples used for synchrotron mapping. Micrometer-scale trace-element distributions were mapped at high resolution (2  $\mu$ m-steps) on polished, free-standing thick sections by using synchrotron-radiation micro X-ray fluorescence (SR  $\mu$ XRF) at beamlines ID21 of the European Synchrotron Radiation Facility (ESRF). Instrumental settings and procedures were as described in Frisia et al. (2005) and Borsato et al. (2007). Polished thick sections, ca. 20 mm long, were ultrasonically cleaned, washed with deionised water, air-dried and handled with sterile gloves prior to insertion in the sample chamber to avoid contamination. Trace element concentrations were obtained as counts (cts). Quantitative concentrations of trace elements were then obtained on the synchrotron samples by LA-ICP-MS calibrated using the NIST SRM612 glass reference material and the stoichiometric abundance of Ca in calcium carbonate. Samples were preablated and a laser spot size of 71  $\mu$ m was used. Instrumental drift was monitored using the  $^{43}\text{Ca}$  channel. Raw mass spectrometry data were reduced using the software lolite (Paton et al., 2011) at the School of Earth Sciences, the University of Melbourne. Christmas Island drip waters were collected in acid-washed, deionised-water-rinsed glass vials from the stalactite feeding SC4 at mostly monthly intervals from July 2005 to April 2007. Drip counts were taken using a stop watch during each of the cave visits. Drip waters were analysed using a Varian Quadrupole ICP-MS at the University of Melbourne.

### 3 Results and discussion

#### 3.1 Phosphorus significance in modern Christmas Island stalagmite

The SR  $\mu$ XRF elemental mapping in the top part of SC4 was carried out across dark, 0.01 to 0.2 mm thick, irregular layers which, when observed by optical and electron microscopy, show corroded crystal surfaces (Fig. 1a, b), where globular, tabular and lamellar P-rich phases are nested (Fig. 1a). Their morphologies are comparable



to biogenic stable amorphous carbonates known to contain P (Addadi et al., 2003) and Octacalcium Phosphate (OCT) crystals precipitated in the presence of proteins (Combes and Rey, 2002), but dissimilar to those of the P-rich phases associated with mineralization of actinomycetes in Great Cayman stalagmites. By contrast, the micro cavities hosting P-rich phases resemble the corrosion discontinuities colonized by microbes in the speleothems from Great Cayman, which had been interpreted as being formed by condensation-corrosion, or dissolution (Jones, 2009). In SC4, micro cavities are lined by amorphous sheaths (Fig. 1a) similar to the exopolysaccharides illustrated by Jones (2009), which suggests that the corrosion of crystal surfaces may have been mediated by biological oxydation processes (Frisia, 1996).

The XRD pattern did not match any known Ca-phosphate with the exception of ardealite, a phosphate typical of dry, slightly acidic environments, whose presence corroborates our hypothesis of dissolution as by-product of organic matter oxydation. Preliminary NMR analyses suggest that the unknown P-rich phases are similar to those reported by Mason et al. (2007) in annually laminated Alpine speleothems (B. Phillips, 2010, personal communication).

The Synchrotron  $\mu$ XRF maps clearly show that P highest concentration coincides with corroded crystal surfaces and crystal boundaries (Fig. 1c). The map highlights also a similar distribution for Si. By contrast, Mg is dispersed within columnar crystals, probably substituting Ca in the lattice. Smiths cave drip water analyses show a strong positive correlation between P and Ca ( $r^2 = 0.84$ ) and anticorrelation between P and Mg/Ca ratio (Fig. 2a). The supply of P and Ca is likely to be, therefore, from the same source.

To date, the most important source of speleothem P is believed to be the soil zone, from which P transported chelated to organic acids (Treble et al., 2003). P in a tropical island would be released under reduced pH produced by soil respiration, more likely during the wet monsoon season, but this P is probably taken up by plant roots and P retention in the soil zone is very likely to occur (Filippelli, 2002; Sørensen et al., 2011). The most probable source of P for SC4 is likely to be dissolved orthophosphate from weathering

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of hydroxylapatite and chlorapatite in the host rock, which explains the good correlation between P and Ca. The anticorrelation between P and the Mg/Ca ratio suggests either Prior Calcite Precipitation (PCP) (Huang et al., 2001) or an increase in rock/water interaction, given that the parent rock contains dolomite. Critically, the drip rate does not show a good correlation with P concentration. It is commonly assumed that PCP is a phenomenon related to lower infiltration, air-filled voids and degassing of the infiltration water prior to reaching the cave, and we should, thus, expect a positive correlation between P and Ca concentration and drip rate. As it is not the case in Smiths cave, we favour the hypothesis of higher P concentration in dripwater as related to water/rock interaction. During decreasing drip regime, the dissolved P in the waters is concentrated at speleothem surface, with a “bulk” partition coefficient ( $K_{P\text{-bulk}}$ ) between speleothem and water of 7.3, if we consider a mean P concentration in the P-rich stalagmite layers of 8000 ppm and a mean dissolved P in the dripwater of 0.28 ppm (Fig. 2b). The  $K_{P\text{-bulk}}$  accounts for the fact that P may be present in the speleothem as discrete phosphate phases co-precipitated with calcite, and not only incorporated in its lattice, which is in agreement with experimental data (House and Donaldson, 1985). Critically, as P and calcium concentration in the dripwaters co-vary, phosphates coprecipitate with calcite when the dissolved calcium in the parent fluid is also high (up to 120 ppm), which has been predicted by coprecipitation experiments in purely inorganic conditions (Ishikawa and Ichikuni, 1981). In practice, the presence of microbial mats associated with P-rich phases, and suspect biomediation in SC4 does not seem to result in a sensible enrichment in P incorporation relative to inorganic processes. Probably, the high  $K_{P\text{-bulk}}$  observed in SC4 results from the fact that Smiths cave drips have  $>80\text{ mg l}^{-1}$  calcium in solution (cf. Ishikawa and Ichikuni, 1981).

This mechanism of P incorporation in SC4 is different from that hypothesized for the annual layers in the Alpine Grotta di Ernesto stalagmites, where a large proportion of P is associated with colloiddally transported orthophosphate, which is adsorbed on the speleothem surface at a time when the pH of the film of fluid is low and the drip rate is high at the end of the warm season (Borsato et al., 2007). At this critical time, given that

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the  $\text{Ca}^{2+}$  in solution in the drips is about  $53 \text{ mg l}^{-1}$  (Borsato et al., 2007), the expected theoretical partition coefficient  $K_P$  should be less than 1 (Ishigawa and Ichikuni, 1981), but the calculated  $K_{P\text{-bulk}}$  is 3. The discrepancy is well explained by an increase in colloiddally transported P at a time of reduced calcite precipitation related to seasonal ventilation patterns driven by temperature contrast (Borsato et al., 2007; Miorandi et al., 2010). Thus, we can reasonably hypothesize that in speleothems from Tropical warm and wet settings, peaks in P concentration do not mark seasonal vegetation decay (Treble et al., 2003) or soil moisture (Borsato et al., 2007), but hydrological processes within the aquifer controlled by the effective infiltration. Although there are P peaks associated with the drip rate peaks at the beginning of each summer (Fig. 2b), which may be related to a piston effect, most of the dissolved P peaks between January and March and is likely due to the progressive drainage of the aquifer, which yields high Ca and P in solution in the pores. This is probably the major annual event recorded by P concentration variability in SC4.

Further information on P significance in SC4 is gained from the synchrotron  $\mu\text{XRF}$  maps, which show an increase in silicon (Si) concentration coinciding with the P-rich layers. Higher Si/Ca ratios in speleothems have been commonly related to low rainfall (Polyak and Güven, 2004; Hou et al., 2007), although it is also known that bacteria may precipitate silica from groundwaters (Nash and Ulliyott, 2007). It stands then to reason that Si also derives from the long water-rock interaction in the aquifer during periods of infiltration decrease.

We believe that, in the case of Smiths Cave, and probably of other Tropical caves where dripwaters have high calcium concentration, P is directly related to Ca and, apart from short-lived fast infiltration (Fig. 2), its concentration becomes higher during seasonal low effective infiltration. Contrary to what concluded by Jones (2009), we support the significance of P concentration variability as palaeoclimate proxy, and we here hypothesize that microbes may only slightly enhance inorganic processes, as already implied by Fairchild and Baker (2012).

## 3.2 Application to the Nullarbor speleothems: insight on climate ca. 4 Myr ago

The understanding of the processes of P incorporation in SC4 can now be used to interpret the palaeoclimatic significance of P concentration increase at micritic and stromatolite-like layers within the ca. 4 Myr old stalagmites from the Nullarbor (Figs. 3 and 4). The compact elongated columnar fabric of MO1-645 and FS04-645 (Fig. 3) is indicative of formation under relatively constant drip rates and supersaturation (Frisia and Borsato, 2010). Contrary to SC4, thus, the Early Pliocene examples do not provide petrographic evidence of seasonal drip rate variability. Rather, their fabrics imply formation under conditions of constant recharge (cf. Frisia et al., 2000). The internal stratigraphy of the two speleothems, however, shows mm-scale white laminae, where stromatolite-like structure, or irregular crystals riminescent of the corrosion surfaces in SC4, are visible even on the polished surface (Fig. 3). These white laminae (at least 4 in less than 10 cm) mark the end of periods when the internal morphology show decreases in the stalagmite diameter, and are characterized by distinctive P peaks (Fig. 3). In the stromatolite-like laminae of FS04, marked as Phase 2 in Fig. 3, the concentration of P is 12 times higher relative to the baseline. The concentration of the divalent cation  $Mg^{2+}$  in Phase 2 is within the mean values of Phases 1 and 3 (Figs. 3 and 4), whereas  $Sr^{2+}$  and  $Ba^{2+}$  concentrations are within the mean for Phase 3, and the decrease in their concentration relative to Phase 1 occurs before the onset of Phase 2 (Figs. 3). A similar behavior for  $Mg^{2+}$ ,  $Sr^{2+}$  and  $Ba^{2+}$  has been commonly interpreted as being sensitive to PCP (Treble et al., 2003), which would suggest that the stromatolite-like layer was preceded by a relatively dry episode, when the three divalent cations peak, followed by recharge and then a period when the aquifer was drained and Phase 2 developed. The decrease in U concentration in Phase 2 relative to phases 1 and 3 (Figs. 3 and 4) corroborates this hypothesis, as it is the opposite to what it would be expected if P and U were related to higher infiltration during seasonal vegetation decay (Treble et al., 2003). It can be argued, then, that P in the Nullarbor

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Pliocene samples derived from host rock dissolution similarly to SC4, and not from soil-sourced chelates.

As Early Pliocene drip water chemistry is unknown, we reconstructed an “empirical enrichment factor” by comparing the concentration of trace elements in the host rock and in the speleothems. Although we are aware that the host rock composition is probably variable and one cave is not representative of all sites, and that one or two Early Pliocene speleothems are not representative of all the ca. 4 Myr old stalagmites from the Nullarbor, we still believe that our approach can be used to understand processes of trace element incorporation in these specimens from the deep past. Phase 2 in 645-FS04 is enriched in P, Al, Si and Mg relative to the host rock and in Y, Mn, P, Al, Fe and Si relative to phases 1 and 3 (Figs. 3 and 5). By contrast, U in the columnar calcite has the same concentration as the host rock, but is depleted in Phase 2. One possible explanation is that Phase 2 is detritus-rich, which may be the case for a portion of Si as highlighted in the SR  $\mu$ XRF map, but P is not detrital, because its distribution mimics crystal tips and microlaminates (Fig. 6). A portion of Si is also unlikely to be related to detritus, as it follows the same micromorphology of P and Raman spectroscopy has revealed the presence of an amorphous Silica phase. In analogy to what concluded for SC4, we propose that the enrichment in trace elements relative to the host rock and the elongated columnar calcite may be related to microbial processes. In support of our hypothesis is the UV fluorescence associated with the laminae, which suggests the presence of organic compounds (Fig. 4) as well as the overall fabric. The implication is that the association of microbial laminae and amorphous silica indicates a low drip rate relative to the columnar calcite, when bacterial colonization of the speleothem surface was possible. The high concentration of sulphur (S) as sulphate, confirmed by XRD as being related to gypsum, particularly above the P-rich laminae in Phase 2 may be indicative of precipitation by evaporated waters.

At few tens of  $\mu$ m-scale the SR  $\mu$ XRF maps also show that P concentration is highest when Mg concentration is lowest (Fig. 4), which may be explained as competition

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between Mg and P for kink sites, and/or the effect of Mg reducing adsorption of phosphate (House et al., 1986).

Another analogy with SC4 is the occurrence of corrosion and micritization, which are clear in 645-MO1 (Fig. 6). The SR  $\mu$ XRF maps of the corroded crystals highlight the association of P with Si, and S as sulphate as revealed by XANES spectra.

It stands, therefore, to reason that peaks in P concentration associated with micrite and stromatolite-like fabrics in the two Early Pliocene speleothems from cave 645 mark periods of aquifer drainage, possibly following a major recharge, but at a different time scale relative to SC4, a scale which we are unable to quantify because of the age errors of the samples. We can only speculate that several tens of thousand of years relatively separated each relatively dry period on the basis of the number of micrite and stromatolite-like layers and the mean age of the two samples. A climate scenario with a regime of relatively constant recharge within predominant humid climate conditions (Miller et al., 2012) punctuated by “recurrent” relatively dry periods at millennial time-scale, emerges from cave 645. Then, if our palaeoclimate implications based on the Christmas Island model interpretation of the significance of speleothem P holds true, our proxy data corroborate the hypothesis for an early start of the Eastern Equatorial Pacific (EEP) at ca. 4.3 and 4.0 Myr ago as shown by Steph et al (2010), which argued that the gradual closure of the Central American Seaway had an influence on global climate.

Thus P concentration variability in Ealy Pliocene Nullarbor speleothems may reveal itself as a powerful proxy to unravel climate change in a key period of the deep past, when mean global surface temperatures were at least 3 °C higher than today, and atmospheric carbon dioxide concentrations close to Present values, but there are uncertainties in the palaeodata which still prevent our full understanding of the Plicene to Pleistocene climate mode transition (Brierley and Fedorov, 2010).

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## 4 Conclusions

The palaeoclimatic significance of P concentration variability in speleothems is complex, because its pattern of incorporation depends on the source, the calcium concentration in the dripwater, the climate regime and the presence of microbial activity.

Our study indicates that in wet, tropical speleothems from cave cut in Tertiary limestones, the likely source of P is the host rock. Synchrotron radiation based high-resolution chemical mapping coupled with petrography has shown that discrete P-rich phases coprecipitate with calcite preferentially in corrosion pores colonised by microbial mats. The co-precipitation of P-rich phases with calcite seems to occur when the drip rate decreases as a result of the aquifer progressive drainage. We provide a bulk partition coefficient, which suggests that the P enrichment in the speleothem may still be described through inorganic processes, thus, we concur with Fairchild and Baker (2012) in their assertion that the properties of speleothem crystals precipitated via biomediation or inorganically may be very similar. The most important finding is that, contrary to P incorporation in speleothems from regions characterized by strong seasonality (in rainfall or temperature), our example suggests that P peaks in stalagmites from predominantly wet climate regimes may mark a decrease in effective infiltration.

This interpretation of P significance was applied to explain P concentration peaks in stromatolite-like and micrite layers of two ca. 4 million year old stalagmites from the Nullarbor. It is here speculated that relatively dry periods may have interrupted the Early Pliocene wet regime, at unknown time intervals, but possibly spaced apart several tens of thousands of years. The implication is that there is potential to use trace elements, such as P, to complement and refine climate information from the Nullarbor speleothems to shed light on the onset of the EEP.

Finally, our study demonstrates that any accurate palaeoclimate interpretation of trace elements variability in speleothems needs to be based on petrographic and chemical mapping, which should become desirable routine (cf. Fairchild and Baker, 2012).

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*Acknowledgement.* Nullarbor results were obtained within the framework of an ARC Discovery project. We thank J. Woodhead for allowing us to use unpublished ages for the Nullarbor stalagmites. ESRF is acknowledged for provision of synchrotron radiation facilities. Vincent De Andrade and Murielle Salome assisted at ID21. S. Frisia and B. Paul are grateful to the Australian Synchrotron for the Grant AS\_IA104\_ESRF\_EC794. Microscopy and XRD were carried out at the Electron Microscopy and X-ray Unit facility of the University of Newcastle. Maurizio Mattarelli helped with Raman spectroscopy at the University of Trento, Italy. Brian Phillips (SUNY at Stony Brook, USA) provided preliminary data on NMR analyses. Vanessa Johnston (Museo delle Scienze, Trento, Italy) helped processing synchrotron maps. We are deeply grateful to Mr. Mick Jeffery (Parks Australia North) for the dripwater monitoring at Christmas Island.

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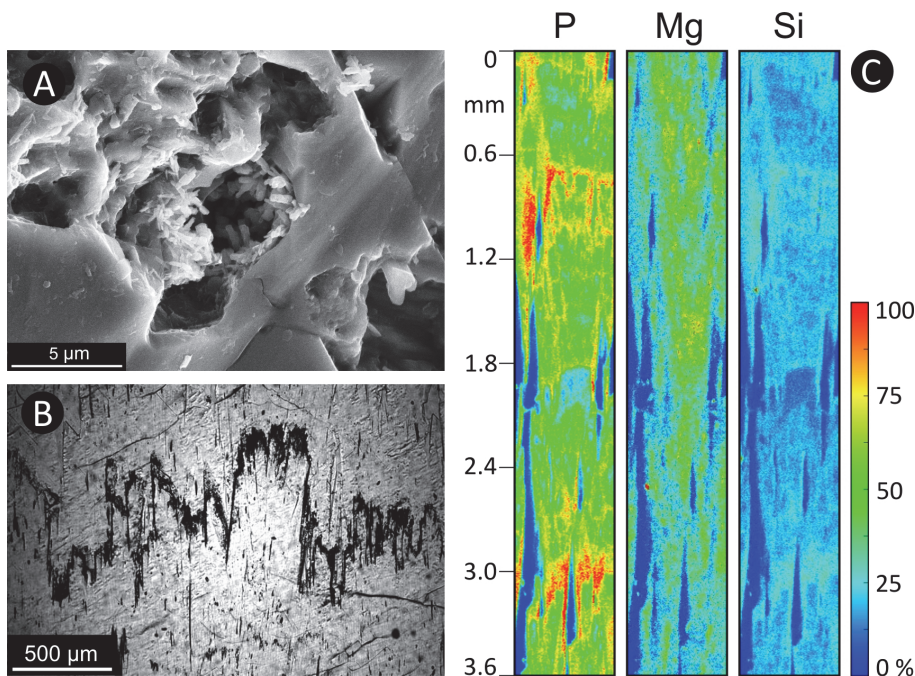
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**Fig. 1.** Christmas Island stalagmite SC4 from Smiths Cave. **(A)** Scanning electron microscope image showing microcavities where globular, tabular and lamellar P-rich phases are nested. **(B)** Thin section showing corroded crystal surfaces (polarised light). **(C)** Synchrotron Radiation micro XRF maps ( $600 \times 3600 \mu\text{m}$ , pixel size  $6 \mu\text{m}$ ) showing P, Mg and Si concentration. All linear scales are normalized to the minimum and maximum counts for each element: P = 10 to 185 cts; Mg = 0 to 60 cts; Si = 0 to 195 cts.

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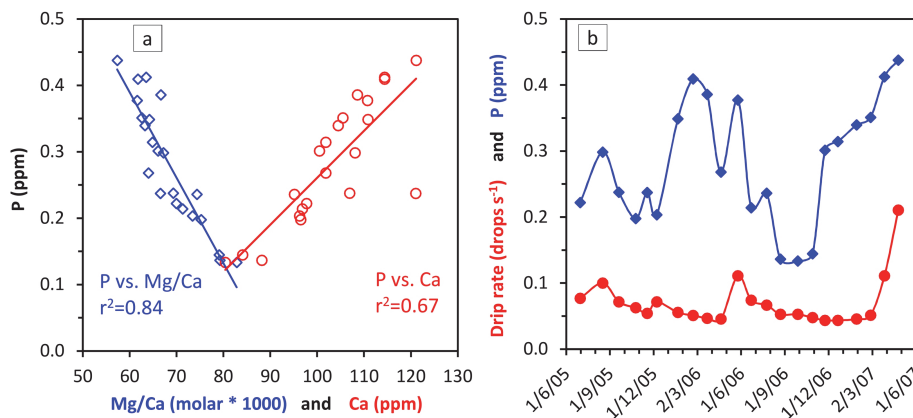
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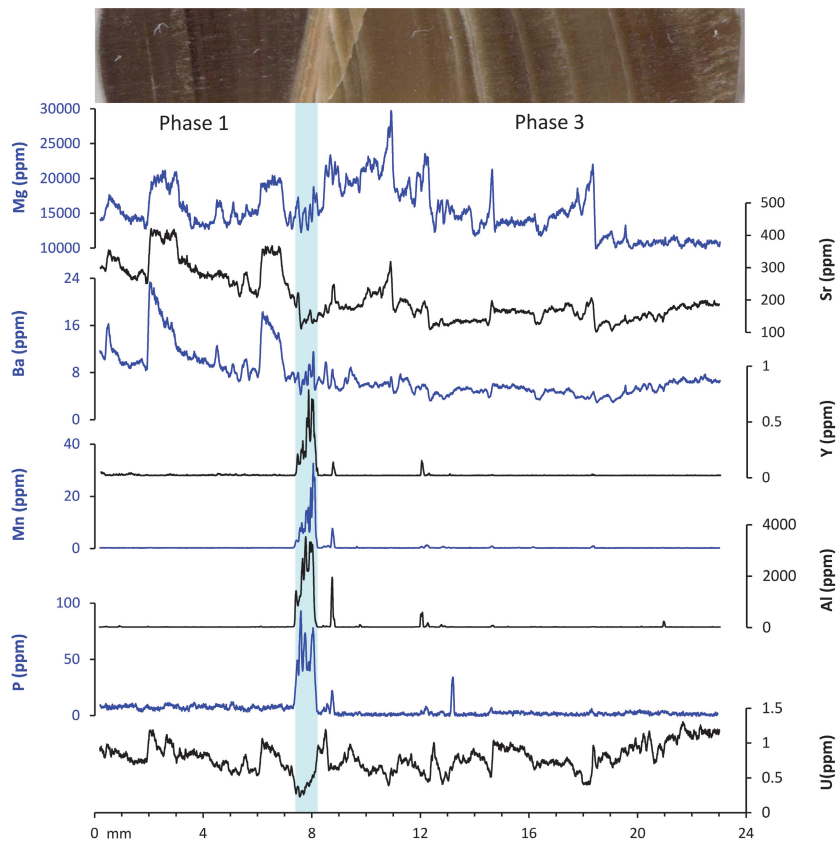
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**Fig. 2.** Dripwater from Smiths Cave, Christmas Island. **(a)** Correlations between P and Mg/Ca (diamonds) and between P and Ca (circles) based on a 22 monthly samples collected between July 2005 and April 2007. **(b)** Concentration in P (diamonds) and drip rate (circles) between July 2005 and April 2007.

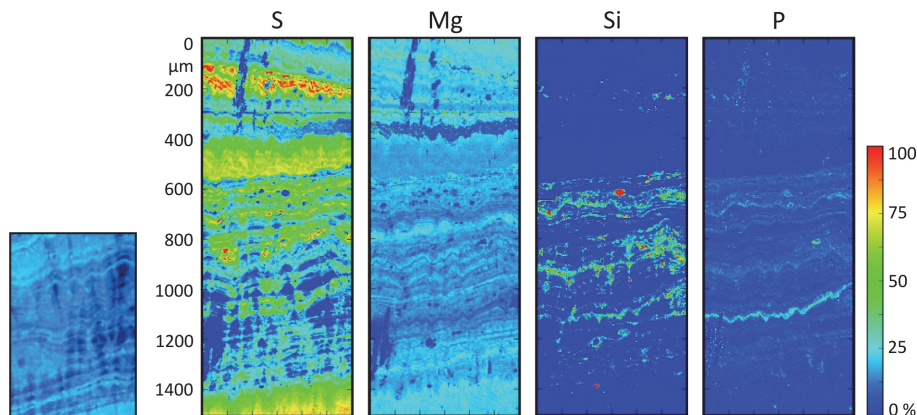
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**Fig. 3.** Nullarbor stalagmite 645-FS04. LA-ICP-MS scan of central part of the sample (growth direction from left to right). All the elemental scans are averaged with a 15 points running mean corresponding to a width of 25  $\mu\text{m}$ . The pale blue bar corresponds to the stromatolithic layer (phase 2).

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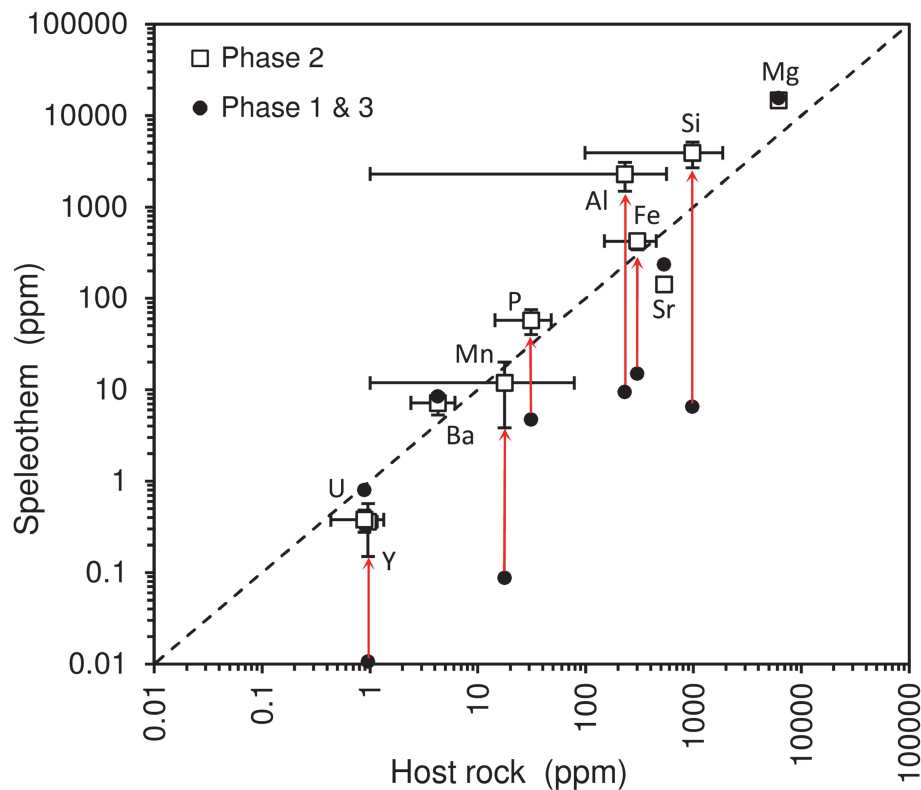
**Fig. 4.** Nullarbor stalagmite 645-FS04. Right: Synchrotron Radiation micro XRF maps ( $600 \times 1500 \mu\text{m}$ , pixel size  $2 \mu\text{m}$ ) across the stromatolithic layer (phase 2 in Fig. 3) showing S, Mg, Si and P concentration. All linear scales are normalized to the minimum and maximum counts for each element: S = 0 to 180 cts; Mg = 0 to 210 cts; Si = 0 to 550 cts; P = 0 to 35 cts. Left: UV-fluorescent thin section micrograph corresponding to the bottom part of the synchrotron maps (same scale).

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**Fig. 5.** Comparison of major and trace elements composition between the Nullarbor Limestone host rock and the Nullarbor stalagmite 645-FS04. The data and the three stalagmite growth phases correspond to the ones in Fig. 3. The red arrows visualize the elemental enrichment between the average values of phases 1 and 3 with respect to phase 2 (stromatolitic layer). Error bars (1SD) are shown for phase 2 only.

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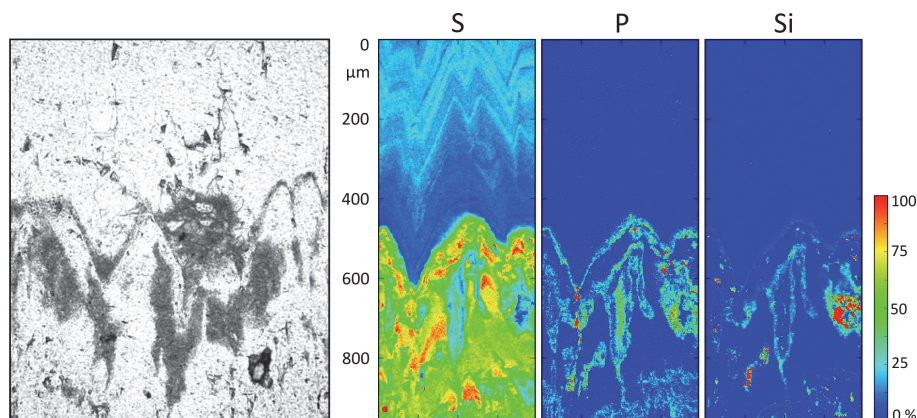
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**Fig. 6.** Nullarbor stalagmite 645-MO1. Right: synchrotron radiation micro XRF maps ( $400 \times 950 \mu\text{m}$ , pixel size  $2 \mu\text{m}$ ) showing S, P, and Si concentration. All linear scales are normalized to the minimum and maximum counts for each element: S = 0 to 240 cts; P = 0 to 32 cts; Si = 0 to 195 cts. Left: Thin section micrograph made in the same region of the synchrotron maps (same scale).

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