**Assessing the palaeoenvironmental potential of Pliocene to Holocene tufa deposits along the Ghaap Plateau escarpment (South Africa) using stable isotopes**

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**Supplementary Materials and Methods**

*Geochronology*

Radiocarbon samples were prepared for AMS radiocarbon assay and measured on the 2 MV HVEE “STAR” accelerator following the methods described in Hua et al.(2001) in the Institute for Environmental Research at the Australian Nuclear Science and Technology Organisation (ANSTO) (Fink et al., 2004). Samples were cut to size using a rotary diamond tipped blade, ultrasonically cleaned in milli-Q high-purity water, and dried overnight. For AMS 14C measurement, ~20 mg sized pieces were then partially etched for 20 minutes using 2 ml 85% H3PO4 and the evolved CO2 discarded. The remaining sample was then completely dissolved in the H3PO4 and the evolved CO2 converted to graphite using H2 and an Fe catalyst. The graphite was subsequently rear-pressed into 1.60-mm-diameter recess aluminium cathodes. The technical aspects of these pre-treatment methods are described in Hua et al.(2001). Cathodes were generally measured for ~30 minutes in total giving around 80,000 counts of 14C and a statistical uncertainty <0.4%. Interspersed were measurements of oxalic acid I and II (HOxI and HOxII) normalisation standards, IAEA C1 marble procedural blank, and unprocessed commercial graphite (spectroscopic grade powdered graphite from Union Carbide Corporation) for assessing machine background (>55,000 yrs). δ13C for correction of the 14C/12C ratio was measured on portions of the same graphite using an Elemental Analyser-Isotope Ratio Mass Spectrometer (EA-IRMS) at ANSTO. The results from analyses on three modern tufa samples (GOR-08a, GOR-11a, GOR-11b) collected from a tufa-depositing stream at the Gorrokop site were used to assess the effects of a Dead Carbon Fraction (DCF) from dissolution of the dolomite (Supplementary Table 1). Measured AMS 14C/13C ratios were converted to conventional radiocarbon ages after background subtraction and 13C fractional correction. A correction was then made for the DCF. All radiocarbon ages were converted to calibrated calendar ages BP (before present, 1950) using the OXCAL 4.1 calibration software and the ShCal13 data sets (Hogg et al., 2013).

Densely laminated fossil tufa specimens were selected for uranium-thorium (U-Th) dating. Cleaned subsamples were prepared and measured at the University of Melbourne Earth Science Laboratories following the protocols of Cheng et al. (2000) and Hellstrom (2003, 2006). Samples of 10 to 50 mg were chemically separated using Eichrom TRU resin. U and Th activity ratios determined simultaneously by parallel ion counting using a Nu Plasma Multi-collector ICP-MS. U-Th dating of tufa can potentially be problematic due to mobility of U within the porous tufa material, in which case the most likely bulk effect would be U loss. As such U-Th age determinations on tufa might overestimate the true sample age where porous material is used. Another consideration is the effect of incorporation of detrital Th at time of sample formation. This can be corrected for but can have the effect of greatly increasing age uncertainty for some samples (Hellstrom, 2006). Based on previous experience with porous speleothems at the site of Buffalo Cave (Herries et al., 2006) and Pinnacle Point (Pickering et al., 2013), samples were chosen that consisted of dense laminations rather than the more porous, vegetation rich layers due to the high likelihood of detrital thorium contamination in these latter specimens, as also noted by Morinaga et al. (2010).

Palaeomagnetic methods follow protocols set out in Herries and Shaw (2011). All samples were oriented in the field using a Suunto Compass and Clinometer and final directions were corrected for local secular variation using the 11th generation International Geomagnetic Reference Field Model (IGRF: http://www.geomag.bgs.ac.uk/data\_service/models\_compass/igrf.html). Directions were determined using principal component analysis (Kirschvink, 1980) and final polarities based on Palaeolatitude (<+/-60o = intermediate) defined from Fisher (1953) statistics. Samples were primarily subjected to alternating field demagnetisation (AFd; Molspin AF demagnetiser) because of the expansion and cracking of tufa at higher temperatures. However, some samples were also subjected to comparative 11-point thermal demagnetisation (THd; Magnetic Measurements MMTD80A thermal demagnetiser) and a hybrid demagnetisation method (AF-THd) aimed at isolating the primary remnant at lower temperatures. This involved the AFd of the samples to 10mT followed by THd in 50-degree steps up to at least 400°C. All samples were measured on an AGICO JR6 magnetometer.

*Micromorphology*

Thin sections were made using cut blocks taken from hand specimens. These were mounted on glass slides, ground to a thickness of ~30 μm, and analysed under a polarizing microscope in Birkbeck College’s Department of Earth Sciences.

X-ray diffraction (XRD) was carried out on seven Ulco tufa specimens from Groot Kloof and Malony’s Kloof (GKD\_UTH\_01, GKDPM2, GKD\_UTH\_08, GKD\_UTH\_04, GKD\_C14\_04, MKPM1, MKA\_03) to quantitatively determine the mineralogy. Powder samples were drilled parallel to the growth banding at an average interval of ~1.5 cm down the length of each specimen, which generated up to 300mg of powder to allow for aliquots of each to be used in stable isotope analysis. The powder samples for XRD were ground using an agate pestle and mortar until they passed a 210 μm sieve, liquefied with distilled water, pipetted onto a glass slide, and left to air dry. Analysis was conducted using a Philips PW1710 diffractometer with a PW 1730 generator and PC-APD software in the School of Earth Sciences at Birkbeck College. Machine conditions were as follows: 40 kV voltage, 30 mA current, Copper K alpha radiation source, .5° divergent and scatter slits, 0.2 mm receiving slit, scan range, from 2θ 18° to 50° scan range, and 0.5° 2θ/ min scan speed.

*Stable Isotopes*

Powder samples were drilled parallel to growth banding, predominantly on the white layers, at an average interval of ~1.5 cm using a 2 mm-diameter diamond-tipped drill bit. Additional samples were also drilled along a single growth layer on six stromatolitic tufas (GKD\_UTH\_01, GKDPM2, GKD\_UTH\_08, GKD\_UTH\_04, GKD\_C14\_04, MKA\_03) in order to test for kinetic fractionation using the correlation criterion (Hendy, 1971). Standard and powder samples were loaded into glass vials, methanol rinsed, and left overnight in an oven at 70°C. Each vial was then manually acidified with 100% Phosphoric acid (0.1 ml) using a syringe injection via the screw cap septa. Geochemical analysis was conducted on a total of 65 samples in the Bloomsbury Environmental Isotope Facility at University College London on a ThermoFinnigan DeltaPLUS XP stable isotope mass spectrometer attached to a ThermoScientific Gas Bench II device with errors of 0.03‰ at 1 standard deviation. 13C/12C and 18O/16O ratios are expressed in the delta notation (δ) notation in parts per mil (‰) relative to that of the Pee Dee Belemite (PDB) standard.

**Supplementary Results**

*Dating results*

Accurate tufa ages will be key for reconstructing the palaeoenvironmental history of the Ghaap Plateau escarpment sites. Dating of tufa deposits by 14C methods requires a correction for the 14C free carbon dissolved from the carbonate host rock (the DCF). In order to assess the suitability of 14C dating for tufa, we have dated modern, actively forming tufa deposits to calculate the offset due to old or dead carbon. The DCF is the ratio between the measured radiocarbon concentration (percent modern carbon – pMC) in the tufa and the atmospheric 14C concentration at a particular time. Effectively, DCF is equivalent to the proportion of carbon incorporated into the tufa from limestone bedrock and ancient soil organic matter (SOM), assuming these sources contribute negligible 14C. It can be calculated using the following formula:



[1]

Calculating and using the correct DCF value for tufa is vital. Horvatinčić et al. (2003) measured tufa DCF as around 10-30%, using a number of different methods, with a final assumed value of around 15%, similar to that for speleothems. However, in addition to having very few measured values for tufa, the Eastern European origin of the samples used in the Horvatinčić et al. (2003) study imply differences in temperature and vegetation type, which likely influence the amount of dead carbon incorporated into the tufa, as they do for speleothems (Genty et al., 2001). In the current study, three different tufas from Gorrokop yielded similar, low DCF values between 3.9% and 6.1% (Supplementary Table 1). We are more confident in relying on these locally derived values for DCF of fossil tufas than to use eastern European derived DCF values to correct our South African samples. The DCF for tufa in the current study was calculated to be 5.3 ± 1.2%, equivalent to a 437 ± 103 year offset.

*Micromorphology Results*

While XRD analysis identified calcite and quartz as the primary phases of the Ghaap Plateau escarpment, the occurrence of aragonite in GKD\_UTH\_08 suggests deposition under conditions favouring this mineral over calcite, which have been linked toevaporatively enriched waters (Deocampo, 2010). The preservation of this meta-stable mineral phase may be indicative surface aridity following the original deposition (e.g. Johnson et al., 2009).

Thabaseek Tufas

The Thabaseek Tufas studied (TDPC 2, 7, 16, 26) can all be classified as phytoherm boundstones (Pedley, 1990) or as microphytic thrombolitic tufa (Carthew et. al., 2006). The fabric overall appears peloidal, although rather than being truly peloidal deposits, the Thabaseek Tufa thin sections represent a thrombolitic texture in three dimensions. Thrombolites are microbial carbonates that lack lamination and form clotted centimetre-scale patches, which are, in turn, formed of smaller clots internally. In thin section, the Thabaseek Tufa specimens consist of micrite, peloids, fenestral pores, and phytomoulds of hydrophytic plant stems encrusted by fringes of calcite cement (Fig. 2a). All Thabaseek thin sections contain a fenestral porosity, but in TDPC 7, 16, and 26 this porosity is often associated with branching, bifurcating networks of subvertical casts of hydrophytic plant stems (2 to 4 mm in cross-section of hand specimens). An isopachous, radial spar cement envelope precipitated around filaments, which subsequently decayed leaving a cavity that was later filled in by micrite. This suggests that the initial stage of precipitation created a calcite rind, likely a biofilm that trapped detrital micrite forming a carbonate envelope (Pedley, 1992) around the plant stem, and was subsequently infilled with micrite upon the plant’s decay. Numerous sections also cut across higher plant leaves, some with remnant structure preserved. In TDPC 16, a thrombolitic texture is superimposed upon a framework of near-vertical stalks of algal thalli, or possibly slightly curved bryophyte stems. While the original stems are not preserved, the prevalence of hydrophilic plants in the form of these mouldic pores filled by alternating envelopes of spar and micrite suggests that these deposits formed subaqueously, in the vicinity of a palustrine environment, in a position peripheral to a flowing channel or on the margins of the slow-flowing and pooled areas where hydrophilic vegetation would have grown thickly and encrusting biofilms were protected (Vazquez-Urbez et al., 2012). The USGS Classification of Wetlands and Deepwater Habitats of the United States categorises the depth of water in which hydrophytes are found as < 2m (Cowardin et al., 1979). At times when the water level was higher, the encrusted stems may have become fragmented and accumulated with others that maintained their upright position (Vàzquez-Urbez et al., 2012). Interpretation as phytoherm tufas in a subaqueous, dominantly sluggish water pool environment, probably at the margins of ponded areas behind barriers (Arenas et al., 2007) is reinforced by a number of observations. The detrital component is very low, never exceeding 1% of a thin section (mainly quartz grains), and very few intervals can be considered to be phytoclastic. Oncoids (with one possible exception) are absent and no bryophytes have been confidently identified. A subaqueous setting is also indicated by the presence of ostracodes in most sections. Collectively, this petrographic evidence suggests that the Thabaseek Tufa in the vicinity of the Dart and Hrdlička Pinnacles was formed in sluggish flowing waters marginal to a shallow pool or small lake.

Ulco Tufas

In contrast to the Thabaseek Tufa, the Ulco specimens were collected from various parts of multiple cascade and barrage formations at both sites, which are a combination of the phytoherm framestone and phytoherm boundstone deposits (Pedley, 1990), characterised largely by stromatolitic facies. Only GKD\_UTH\_08, which samples a barrage in the middle of the T3 formation (Fig. 1c), displays an unlaminated facies consisting of a highly porous, spongy framework of bryophyte encrustations; voids formed following decay of the biological material has remained uncemented. The stromatolitic facies of the other Ulco tufas is represented by centimeter-thick, tabular to undulatory and hemidomic layers of microbial boundstones. In thin section, the laminar structure appears as cryptalgal and bacterial structures embedded in a dense, whitish, micrite groundmass forming millimeter-thick planar to wavy stromatolithic laminae containing calcified algal filaments and fan-shaped branching algae. While no depositional structures were observed in the stratified muds, calcite tubes preserved within the light spar laminae reflect the filamentous micro-organisms that acted as templates, sometimes producing characteristic growth patterns such as the wavy lamination of bush-like microbial bodies (Andrews and Brasier, 2005). The decay of organic inclusions has also generated void space, which has either remained empty or secondarily in-filled by micrite, isopachous rim cement, sparry calcite, and drusy mosaic cements. All of the thin sections of the Ulco tufa deposits are cemented to some degree, yet those sampling ancient formations at Groot Kloof and Malony’s Kloof (GKD\_UTH\_01, GKDPM2, MKPM1, MKA\_03) exhibit more complete cementation relative to those from modern deposits (GKD\_UTH\_04, GKD\_C14\_04). Notably, the upper ~1-2 cm sections of the ancient tufa specimens, GKD\_UTH\_01 and MKA\_03, display macro- and micromorphological features distinct from those characterizing the respective basal portions of each sample. In hand specimen, the tops GKD\_UTH\_01 and MKA\_03 are largely brown in colour indicative of a higher organic content. In thin section, the uppermost layers of GKD\_UTH\_01 and MKA\_03 evince a notable increase in void space and open fenestral porosity comparable to that of the younger Ulco deposits that contrasts the high degree of cementation in the basal sections that typifies the ancient deposits. The lower degree of porosity typifying the more ancient deposits is primarily due to the filling of voids by sparry calcite cementation of void space, a common diagenetic feature of tufas (eg. Nicoll et al., 1999). While all of the Ghaap Plateau escarpment tufa thin sections contain evidence of cementation and/or aggrading neomorphism, which can occur very early after deposition (Arenas-Abad et al., 2010; Lojen et al., 2004), no evidence of recrystallization was detected in any of the deposits.

**Supplementary Table 1**

AMS 14C data from modern tufa. Percent modern carbon (pMC) corrected for blank and d13C normalisation. DCF calculated relative to 2006 mustard seed oil (106.51 pMC).

|  |  |  |  |
| --- | --- | --- | --- |
| **ANSTO Code** | **Sample Name** | **Corrected pMC** | **Calculated DCF** |
| OZJ944 | GOR-08a Tufa | 102.40 | 3.854846 |
| OZJ945 | GOR-11a Tufa | 100.31 | 5.819098 |
| OZJ946 | GOR-11b Tufa | 100.03 | 6.086193 |

**Supplementary Table 2**

Complete stable isotope analysis results.

|  |  |  |
| --- | --- | --- |
| **Sample Name** | **δ13C** (**‰ PDB)** | **δ18O (‰ PDB)** |
| Taung\_TDPC\_2\_Sample01 | -6.7 | -6.5 |
| Taung\_TDPC\_2\_Sample02 | -6.7 | -6.5 |
| Taung\_TDPC\_2\_Sample03 | -6.5 | -6.1 |
| Taung\_TDPC\_7\_Sample01 | -6.7 | -5.8 |
| Taung\_TDPC\_7\_Sample02 | -6.8 | -5.9 |
| Taung\_TDPC\_7\_Sample03 | -7.0 | -6.0 |
| Taung\_TDPC\_16\_Sample01 | -5.4 | -5.7 |
| Taung\_TDPC\_16\_Sample02 | -5.9 | -5.9 |
| Taung\_TDPC\_16\_Sample03 | -5.6 | -5.7 |
| Taung\_TDPC\_26\_Sample01 | -6.8 | -5.9 |
| Taung\_TDPC\_26\_Sample02 | -6.6 | -5.9 |
| Taung\_TDPC\_26\_Sample03 | -6.7 | -6.0 |
| Malony’s Kloof\_MKPM1\_Sample01 | -7.5 | -5.3 |
| Malony’s Kloof\_MKPM1\_Sample02 | -7.5 | -5.1 |
| Malony’s Kloof\_MKPM1\_Sample03 | -7.6 | -5.1 |
| Malony’s Kloof\_MKA\_03\_Sample01 | 1.9 | -1.9 |
| Malony’s Kloof\_MKA\_03\_Sample02 | -7.6 | -5.5 |
| Malony’s Kloof\_MKA\_03\_Sample03 | -7.8 | -5.4 |
| Malony’s Kloof\_MKA\_03\_Sample04 | -7.7 | -5.5 |
| Malony’s Kloof\_MKA\_03\_Sample05 | -7.6 | -4.9 |
| Malony’s Kloof\_MKA\_03\_Sample06 | -7.8 | -5.2 |
| Malony’s Kloof\_MKA\_03\_HendyTest01 | -7.6 | -5.2 |
| Malony’s Kloof\_MKA\_03\_HendyTest02 | -7.3 | -5.2 |
| Malony’s Kloof\_MKA\_03\_HendyTest03 | -7.8 | -5.4 |
| Groot Kloof\_GKD\_UTH\_01\_Sample01 | -1.5 | -2.0 |
| Groot Kloof\_GKD\_UTH\_01\_Sample02 | -2.9 | -2.5 |
| Groot Kloof\_GKD\_UTH\_01\_Sample03 | -3.1 | -3.7 |
| Groot Kloof\_GKD\_UTH\_01\_Sample04 | -3.3 | -3.4 |
| Groot Kloof\_GKD\_UTH\_01\_Sample05 | -3.7 | -3.8 |
| Groot Kloof\_GKD\_UTH\_01\_HendyTest01 | -3.7 | -3.5 |
| Groot Kloof\_GKD\_UTH\_01\_HendyTest02 | -3.5 | -3.1 |
| Groot Kloof\_GKDPM2\_Sample01 | -3.6 | -3.7 |
| Groot Kloof\_GKDPM2\_Sample02 | -5.1 | -4.7 |
| Groot Kloof\_GKDPM2\_Sample03 | -3.8 | -3.8 |
| Groot Kloof\_GKDPM2\_Sample04 | -3.9 | -4.0 |
| Groot Kloof\_GKDPM2\_Sample05 | -4.1 | -3.9 |
| Groot Kloof\_GKDPM2\_Sample06 | -3.8 | -3.8 |
| Groot Kloof\_GKDPM2\_Sample07 | -3.8 | -4.0 |
| Groot Kloof\_GKDPM2\_Sample08 | -3.7 | -4.0 |
| Groot Kloof\_GKDPM2\_Sample09 | -3.6 | -3.6 |
| Groot Kloof\_GKDPM2\_Sample10 | -3.3 | -3.5 |
| Groot Kloof\_GKDPM2\_Sample11 | -3.0 | -3.5 |
| Groot Kloof\_GKDPM2\_Sample12 | -3.2 | -3.6 |
| Groot Kloof\_GKDPM2\_HendyTest01 | -4.0 | -3.9 |
| Groot Kloof\_GKDPM2\_HendyTest02 | -4.0 | -3.7 |
| Groot Kloof\_GKDPM2\_HendyTest03 | -3.4 | -3.7 |
| Groot Kloof\_GKDPM2\_HendyTest04 | -3.8 | -3.5 |
| Groot Kloof\_GKDPM2\_HendyTest05 | -3.6 | -3.6 |
| Groot Kloof\_GKD\_UTH\_08\_Sample01 | -1.1 | -2.8 |
| Groot Kloof\_GKD\_UTH\_08\_Sample02 | -1.3 | -3.2 |
| Groot Kloof\_GKD\_UTH\_08\_Sample03 | -0.5 | -1.9 |
| Groot Kloof\_GKD\_UTH\_08\_Sample04 | -1.6 | -3.2 |
| Groot Kloof\_GKD\_UTH\_08\_HendyTest01 | -1.7 | -3.2 |
| Groot Kloof\_GKD\_UTH\_08\_HendyTest02 | -1.9 | -3.4 |
| Groot Kloof\_GKD\_UTH\_04\_Sample01 | 1.2 | -1.6 |
| Groot Kloof\_GKD\_UTH\_04\_Sample02 | 1.0 | -2.3 |
| Groot Kloof\_GKD\_UTH\_04\_Sample03 | 0.3 | -2.6 |
| Groot Kloof\_GKD\_UTH\_04\_Sample04 | 1.0 | -2.2 |
| Groot Kloof\_GKD\_UTH\_04\_HendyTest01 | 0.8 | -1.3 |
| Groot Kloof\_GKD\_UTH\_04\_HendyTest02 | 1.0 | -2.3 |
| Groot Kloof\_GKD\_C14\_04\_Sample01 | 0.9 | -0.4 |
| Groot Kloof\_GKD\_C14\_04\_Sample02 | -0.4 | -2.8 |
| Groot Kloof\_GKD\_C14\_04\_Sample03 | 1.4 | -0.9 |
| Groot Kloof\_GKD\_C14\_04\_HendyTest01 | 0.6 | -2.9 |
| Groot Kloof\_GKD\_C14\_04\_HendyTest02 | 0.7 | -2.3 |