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# The stratigraphy,chronology and palaeoenvironment of The Pleistocene Cave Fill, Gladysvale Cave, South Africa

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# CHAPTER TWO
# MATERIALS AND METHODS

## 2.1 Sedimentology

### 2.1.1 Mapping

At the beginning of the study the ~250 ka (Curnoe, 1999; Schmid, 2002) upper fan surface of the internal deposits at Gladysvale Cave was covered by miners' rubble, consisting predominantly of fragmented speleothem. This rubble was carefully cleared to the level of the uppermost flowstone capping.

### 2.1.2 Three-dimensional sedimentological logging

The best exposed sequences of the fan were logged as detailed stratigraphic sections. Terminology and methodology used was that of Moriarty *et al.* (2000), in which clastic units are defined by lower and upper confining flowstone layers, forming flowstone bounded units (FBU). Figure 2.1 is a sketch of the cave in plan view showing the locations of the major features of the deposit. Within FBU sedimentary facies were identified, along the lines of those in Kos (2001). Facies colours were assigned using a standard Munsell colour chart. The measured stratigraphic sections and vertical and lateral arrangement of facies were combined to investigate the three-dimensional sedimentary architecture of the cave fill fan (e.g. Miall, 1985).

### 2.1.3 Sampling

FBU and flowstones from the best preserved and calcified sections were sampled with a hand held diamond drill, for petrographic analysis. Only sections 3 and 4 of the western face of the Eastern Lobe, and the Peabody Chamber, fulfilled these specifications (Figure 2.1). Some thin sections from previous work on the Peabody Chamber (Pickering, 2002) were included.

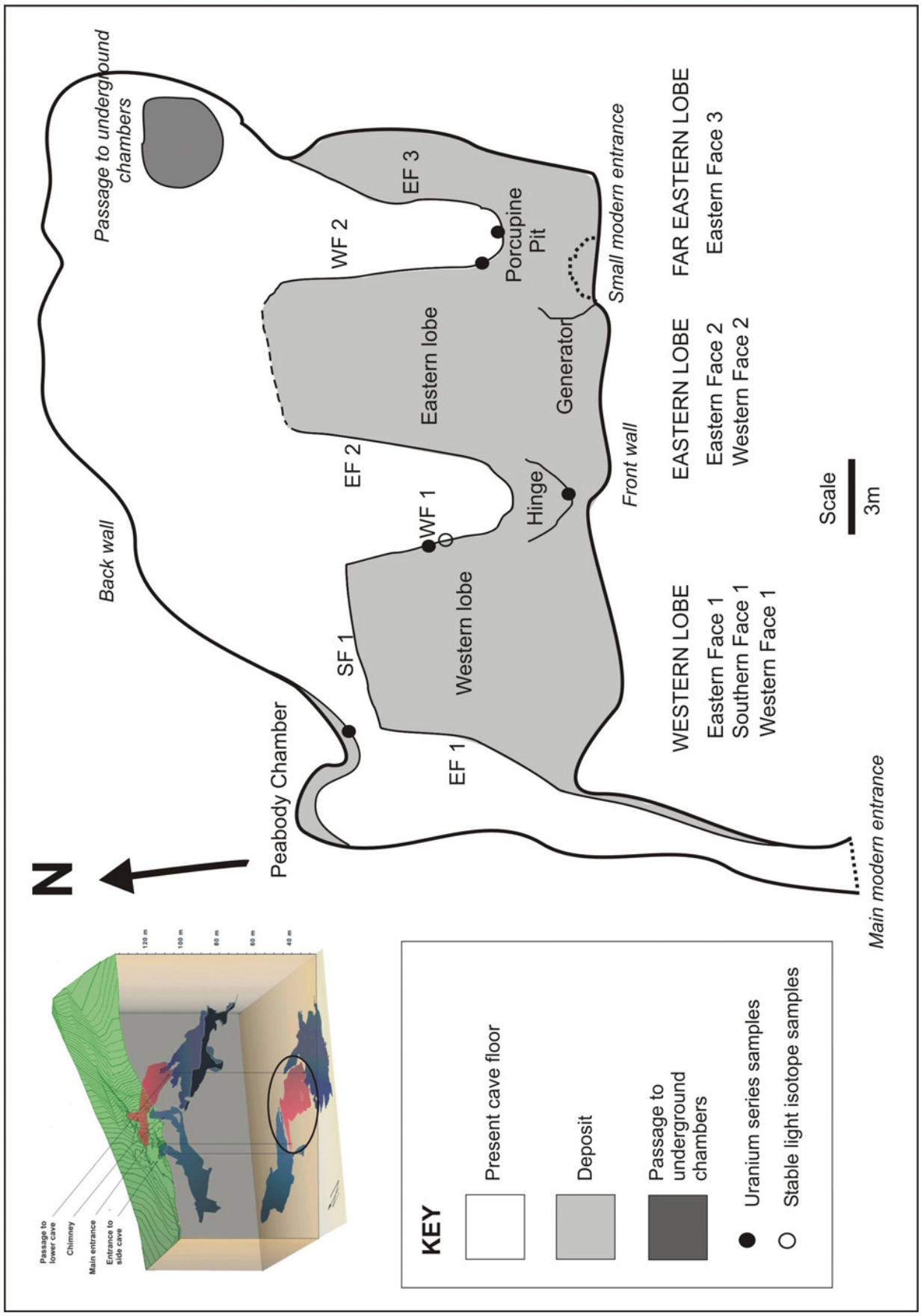



Figure 2.1. Plan view of the upper chamber at Gladysvale Cave showing the areas of the deposit, section names and U-series and stable light isotope sample locations (Note: one open circle represents several samples for stable light isotope analysis).

## 2.2 Uranium series dating

Uranium series dating and laser ablation were undertaken in the Earth Environment Group (EEG) laboratories in the Research School of Earth Sciences (RSES) at the Australian National University (ANU), Canberra, Australia. The RSES MAT Finnigan 'Neptune' Multi-Collector Inductively-Coupled-Plasma Mass Spectrometer (MC-ICP-MS) was used for background U levels pre-screening and dating. Laser ablation was done using the He ablation cell of the laser ablation system coupled to the ICP 20P VG Plasmaquad XR Mass Spectrometer.

### 2.2.1 Sampling

The National Speleological Society (USA) Code of Conduct states that sampling of speleothems should be 'professional, selective and minimal'. *A priori* considerations to sampling for U-series dating of speleothems are outlined by Richards & Dorale (2003). The most useful speleothems for dating are the common forms: stalagmites, stalactites and flowstones. The best samples are taken from deep within the cave, where the humidity is high and the air circulation low to non-existent, where speleothems have grown slowly and consist of dense calcite and are free from detritus (Richards & Dorale, 2003). The suitability of speleothems for dating analysis is determined by their mineralogy and fabric. An unaltered or primary fabric, consisting of coarse columnar or palisade calcite, equant calcite or microcrystalline calcite is best. Thin section analysis of samples is important in revealing the extent of porosity, primary fabric, contaminants and diagenetic history (Railsback, 2000; Richards & Dorale, 2003).

With these *a priori* conditions in mind, samples were taken from the large stalagmite at the base of the sequence, and from five intercalated flowstone horizons above this, as well as a small stalagmite growing on top of one of the flowstones, exposed in the Western face, (Figure 2.2). These sections are well preserved and well calcified. Other samples were taken from the top flowstone on the eastern lobe of the fan, the top of the Peabody Chamber and the top and bottom of the western lobe sequence exposed in the Porcupine Pit (Figure 2.1). Samples were also taken from the top and bottom of the two major lobes of the deposit, from each intercalated flowstone on the Western Face 1 where the deposit is well preserved, and from the most proximal and distal reaches of the deposit (Figure 2.1). Some samples were taken with a hand held diamond drill, but the drill used is designed to work in a vertical

position, not a horizontal one, so the majority of samples were taken with a geopick. Any obvious dirt covering samples was washed off with tap water, but no other preparation was done at the University of the Witwatersrand.

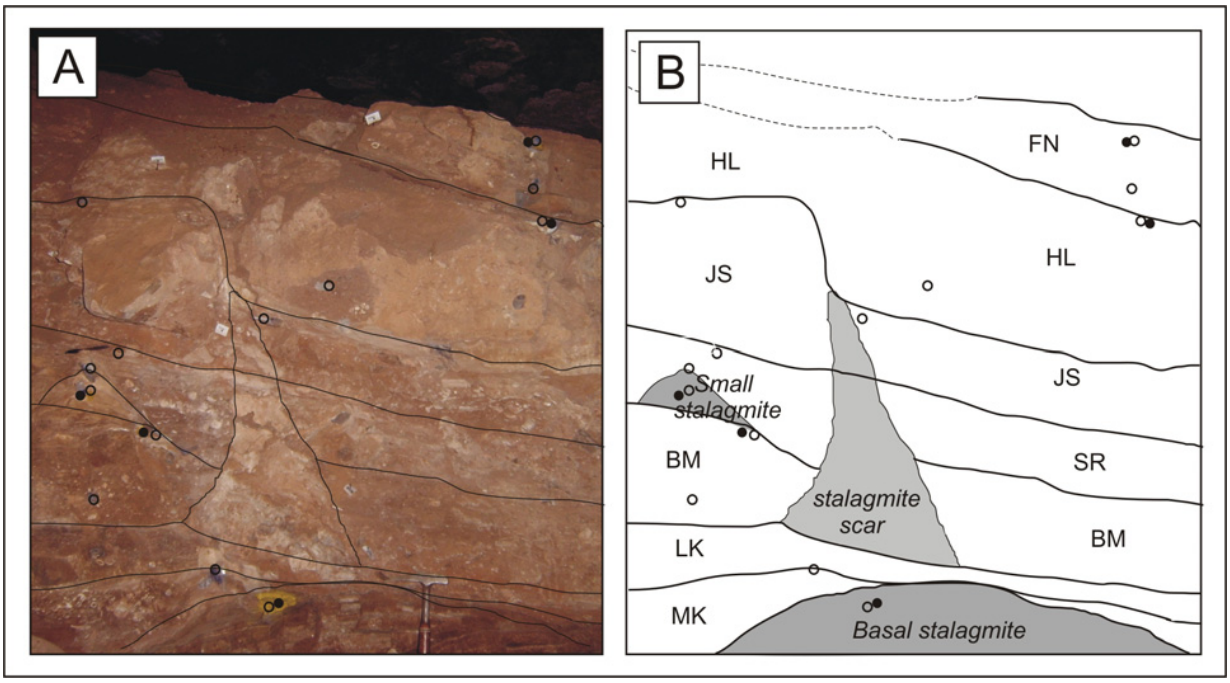



Figure 2.2. Photograph and line drawing of U-series (black circles) and stable light isotope (open circles) sample locations in the Western Face 1 (30cm geopick for scale).

At the Australian National University samples were re-assessed and two with obvious detrital contamination were excluded, leaving the ten samples shown in Table 2.1. The flowstone capping the western lobe of the fan above the Porcupine Pit (PP) (Figure 2.1) was sampled twice to include the top and bottom layers of flowstone, in order to access flowstone growth rates.

| Number | Description | Provenance |
|---|---|---|
| RP 001 | Stalagmite, cleanish calcite with some layering | Porcupine Pit |
| RP 002 | Layered flowstone with some clean calcite | Porcupine Pit |
| RP 003 | Layered flowstone with some clean calcite | Porcupine Pit |
| RP 004 | Layered stalagmite with some visibly clean layers | Section 3/4 Western Face 1 |
| RP 005 | Flowstone, cleanish calcite | Section 3/4 Western Face 1 |
| RP 006 | Flowstone, cleanish calcite | Peabody Chamber |
| RP 007 | Layered flowstone, few clean layers | Section 3/4 Western Face 1 |
| RP 008 | Flowstone, very clean, creamy calcite | Section 3/4 Western Face 1 |
| RP 009 | Very clean, creamy stalagmite calcite | Section 3/4 Western face 1 |
| RP 010 | Layered flowstone with very clean layers | Section 3/4 Western face 1 |

Table 2.1. Names, numbers, descriptions and provenance of ten U-series flowstone samples.

### 2.2.2 Background U levels screening

Background U concentrations in samples were measured to pre-screen samples and establish uranium and thorium concentrations, and to determine samples and spike weights needed to produce optimum uranium levels. Uranium levels of speleothems within a single cave system may vary by orders of magnitude.

Representative amounts of each flowstone sample were collected with a small diamond tipped burr, weighed and dissolved in 2% $HNO_3$. A 2% $HNO_3$ blank was put through the 'Neptune' MC-ICP-MS first to establish machine baseline measurements. Then a wash cycle of 2% $HNO_3$, with added 0.05N HF and trace Triton detergent, was initiated; washes were also used between samples.

Sample solutions were then put through the Neptune and $^{238}U$, $^{235}U$, $^{233}U$ and $^{232}Th$ concentrations were measured in the Multi-Collector's alternating set up of Faraday cups and Secondary Electron Multiplier (SEM). The SEM registers a pulse of secondary electrons cascading through a set of plates (or dynodes) within the multiplier, where the secondary electrons are produced by the arrival at the first plate (or dynode) of a positive ion, and is a more sensitive receptor than the Faraday cups. Each sample cycled through the sequence of Faraday cups and SEM ten times in order to measure each isotope in the SEM adequately.

Results were captured into a Microsoft Excel spreadsheet, and sample weights and spike weights calculated from $^{238}U$ concentrations.

### 2.2.3 Laser ablation

Six flowstone samples were selected to undergo laser ablation, in order to determine which layers within the flowstones had the lowest and highest concentrations of Th and U respectively. Major elements (Mg and Ca) and trace elements (Sr and Ba) were also determined.

Flowstone samples were cut into one inch width slices with a diamond rock saw, polished using a range of wet and dry papers (grit 280 – 1000) and given an ultra-sonic bath in Milli-Q water. Sliced samples were then loaded into the 10x10 cm dead-space free He

ablation cell of the laser ablation system coupled to the ICP 20P VG Plasmaquad XR Mass Spectrometer. An ANU standard of synthetic glass containing over 40 elements was used to calibrate the Mass Spectrometer. The laser runs on an automated system, which was set up before ablation. Each sample was analysed down the central axis, with an initial pre-ablation at 5 microns/second to clean off any surface contamination. Even the cleanest samples have some contamination from the act of loading them in the laser cell. Each sample is then lasered at 100 microns/second, with a one minute break between samples and a return to the standard before each new sample.

Results were captured in a Microsoft Excel spreadsheet and normalised against the Ca values, which remain constant throughout the samples.

### 2.2.4 Dating

*Mechanical preparation:*

Clean or creamy layers of flowstone, identified through the laser ablation to be high in U and low in Th, were mechanically separated using a small diamond-wheel saw. Samples were then cleaned in an ultrasonic bath in a solution of Milli-Q water, and between 3g and 5g of each sample weighed out.

*Chemical preparation:*

Chemical preparation was undertaken according to the method set out in Stirling *et al*. (1995) and in the internal EGG Th U Sample Preparation guidelines (Mortimer, 2003). Weighed samples were gradually dissolved in concentrated $HNO_3$ in PFA vials. Samples were centrifuged to remove visible organic matter.

The "U-2 dil" mixed spike of $^{233}U/^{229}Th$ was weighed out for each sample (aiming for a $^{233}U/^{235}U$ mix of ~0.2) and ~5 drops of concentrated $HNO_3$ were then added. Spikes were then evaporated to dryness on a low temperature hot plate to drive off any excess HF. The spike was then redissolved in ~0.5 ml 2N $HNO_3$ and added to the sample. The spiked samples were then evaporated to a minimum volume on the low temperature hot plate and with a heat lamp. A few drops of $H_2O_2$ were added to remove any residual organic matter.

Samples were then redissolved in 2N $HNO_3$ ready for TRU ion exchange column chemistry. TRU ion exchange columns were set up with some Pre-filter resin and TRU resin, and washed with 0.1N HCl/0.3N HF. Samples were loaded onto columns 3-5ml at a time. Uranium and thorium was then collected off the columns using 0.1N HCL/0.3N HF. The Th-U fraction was then evaporated with a drop of dilute $H_3PO_4$ added, and then redissolved in ~4 ml of 2% $HNO_3$, and diluted to produce expected yields of uranium in the Neptune. Finally samples were put through the Neptune by the aspiration of dilute solutions into high temperature (~7000 K) plasma, which produces an almost 100% atomisation and ionisation of Th and U.

*Data capture and correction*

Data was captured in a Microsoft Excel spreadsheet and transferred to a Monte Carlo Simulation Excel spreadsheet, such as the one used by Hellstrom (1998). Monte Carlo strategies consist of a Microsoft Excel spreadsheet into which the ion and activity ratios from the Neptune output, corrected by its online software for mass fractionation, and according to the spike isotope ratios, are entered. Ages are calculated by solving the U-series disequilibrium equation and errors are then calculated by randomising each input variable, such that after iterations its means and standard deviation correspond to its reported value and reported error respectively (Hellstrom, 1998).

## 2.3 Stable light isotopes

Stable light isotope analysis was undertaken in the Stable Light Isotope Facility, of the Archaeology Department, University of Cape Town (UCT).

### 2.3.1 Sampling

Samples of breccia and flowstone were selected from the best preserved and calcified sections (sections 3 and 4 of the Western Face 1, Figure 2.1). Drilled samples were taken from each FBU and intercalated flowstone, and where possible the same flowstone samples that were used for U-series dating were chosen. Several samples were analysed more than once to determine if the isotopic fractionation was in equilibrium, and to establish the contribution of kinetic fractionation to the isotope values.

In order to build up a background picture of stable light isotope distribution at Gladysvale, modern flowstones currently growing on the upper cave floor, recent stalactites and the dolomitic cave roof were also sampled. The recent stalactites have growth on the stumps of larger stalactites, broken during the blasting activity of the lime miners. The stalactites are about 5cm in length, and must have grown in the period between the cessation of mining in 1928 and the present. Three stalactites were sampled from the roof from the area of massive stalactite development above the Porcupine Pit (Figure 2.2). The dolomite sample was taken from the hillside above the cave. As 2004 was a drought year, there were no drip waters in the upper cave to sample.

All samples were powdered using a hand-held drill with a diamond-tipped burr. Approximately 0.075mg of each sample was weighed out. This value was later increased to 0.085mg as the yields were too low otherwise.

### 2.3.2 Standards and calibration

International Standard NBS 18 and internal laboratory standards Cavendish Marble and Cararra Z were used to determine correction factors. The expected values of these standards are listed in the Table 2.2.

| **Material** | **δ $^{13}$C PDB** | **δ $^{18}$O PDB** |
|---|---|---|
| NBS 18 | -5.05 | -23.03 |
| Cavendish Marble | 0.34 | -8.95 |
| Cararra Z | 2.25 | -1.27 |

Table 2.2. δ $^{13}$C and δ $^{18}$O (w.r.t to PDB) values for known standards (UCT Archaeology Department).

These standards were chosen as they provide a range of positive and negative values for carbon, and a large range of negative values for oxygen. This range of values is important in the calibration of the samples, as the results from the standards are used to draw a graph of the raw data from the standards versus the known values for each standard. The trend line of these three points was then used to calibrate the samples, and for this line to be meaningful the values of the standards need to cover a wide amplitude of values.

### 2.3.3. Analysis

Samples were analysed via a Kiel autocarbonate online preparation system coupled to a Finnigan Mat 252 Mass Spectrometer. Within the Kiel device samples are loaded into glass vials held in a revolving carousel. The entire unit is housed in an insulated casing and is kept at 70°C. The mechanisation of the device is remotely controlled through a computer, and a pre-written program is selected, depending on the sample types, which controls the various mechanisms of the device. Phosphoric acid is dropped via a capillary tube and a dropper into each vial, and allowed to react with the sample for a controlled period of time. Vacuum pumps are then used to pump off the gas released by the sample. A series of valves and heated and cooled chambers are used to separate the carbon and oxygen gases, which are then sent through to the mass spectrometer, where they are measured against a standard gas.

The Kiel autocarbonate carousel holds 24 glass sample vials. The first one is always left blank, so 23 samples can be loaded at a time. The first three vials are loaded with standards, with samples filling the rest, with further standards positioned every five to six samples. Five runs were needed to process the 38 Gladysvale samples. Some breccia samples had to be re-sampled and re-run, as they produced very low voltages, which affect the oxygen isotopes in particular.

Data was captured in a Microsoft Excel spreadsheet, and results are reported in relation to PeeDee Belemnite (PDB).

### 2.3.4 Correction of samples

As already discussed, the results from the standards and the expected values of the standards are graphed against each other to produce a trend line. The formula of this line is used to correct the raw sample data.