

T.E. Horsfield\* (1), M. Rogerson (1), G.M. Henderson (2), E.J. Rohling (3), A. Mihevc (4), M. Budja (5), M. Prelovsek (4), T.J. Coulthard (1), G.M. Greenway (6)

\*Corresponding Author ✉: t.e.horsfield@2006.hull.ac.uk (1) Department of Geography, University of Hull, Cottingham Road, Hull, UK (2) Department of Earth Sciences, University of Oxford, Oxford, UK (3) National Oceanography Centre, Southampton, University of Southampton, Southampton, UK (4) Karst Research Institute, ZRC-SAZU, Postojna, Slovenia, (5) Department of Archaeology, University of Ljubljana, Ljubljana, Slovenia (6) Department of Chemistry, University of Hull, Hull, UK

## Introduction

Two stalagmites, SLO-1 and SLO-2, were collected from Jazbina cave, Slovenia.

Samples were extracted from deep within the cave, minimising the effects of fluctuating temperature and air ventilation.

Both show very high growth rates ( $\sim 0.28\text{mmyr}^{-1}$ ).

SLO-1 measures 2.2m (2200mm) and SLO-2 measures 1.38m (1380mm).

Within the stalagmites, there is an overlapping period between  $\sim 4.5$  and  $\sim 9.1\text{ka}$  which allows cross-validation of two records.

The large ( $\sim 6\%$ ) seasonal variation in  $\delta^{18}\text{O}$  allows for the opportunity to differentiate between summer and winter precipitation.

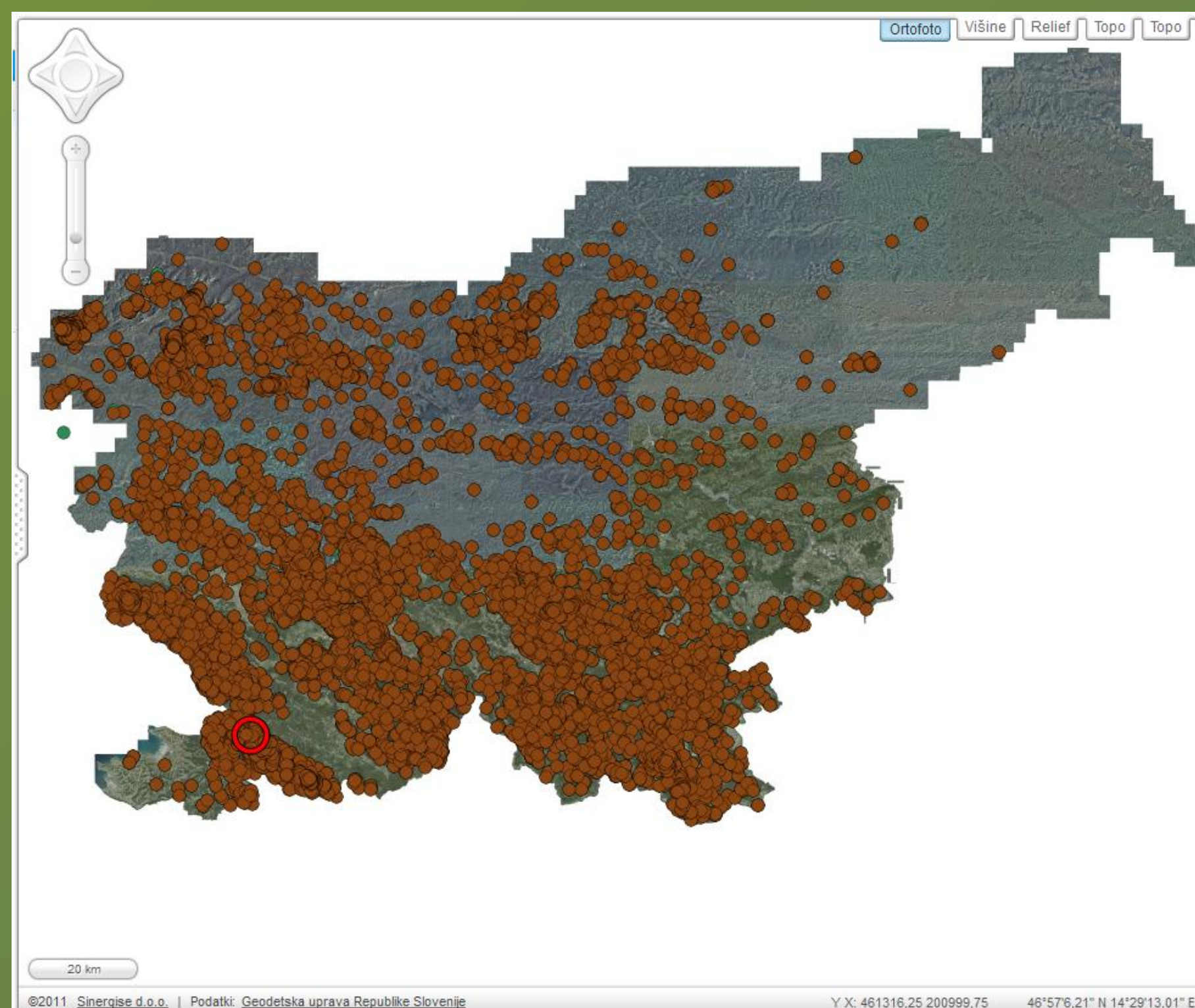


Figure 1: Map of Slovenia showing the location of caves. The red circle shows the location of Jazbina cave, from where SLO-1 and SLO-2 were extracted.

Routine chemical analyses have been carried out on the material in these stalagmites in order to produce a climate record for the Late Holocene in the Central Northern Mediterranean.

This record is presented below along with a calibration of two techniques used for trace element analysis: inductively coupled plasma optical emission spectrometry (ICP-OES) and X-ray fluorescence (XRF).

## Stable Isotope Climate Record

The upper 554mm of SLO-2 has been sampled at 1-mm ( $\sim 3\text{-}4\text{years}$ ) resolution, yielding a stable isotope climate record which covers the period  $\sim 2.1\text{-}0.6\text{ka BP}$  at high resolution.

Drilled samples from close to the growth axis were analysed for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  using Stable Isotope Mass Spectrometry at the National Oceanography Centre, Southampton.

The record is constrained by U-series dating of four samples from down the length of the stalagmite, analysed by inductively coupled plasma mass spectrometry (ICP-MS) at the University of Oxford. Additional samples are currently being analysed to improve the age model further.

Hendy Tests (*not shown*) show no significant kinetic fractionation effects ( $R < 0.3$ ).

The record (*see Figure 2*) shows obvious short-term (annual to decadal) variability in addition to longer term variation, in line with well-documented climate fluctuations, indicated by periods of glacier advance.

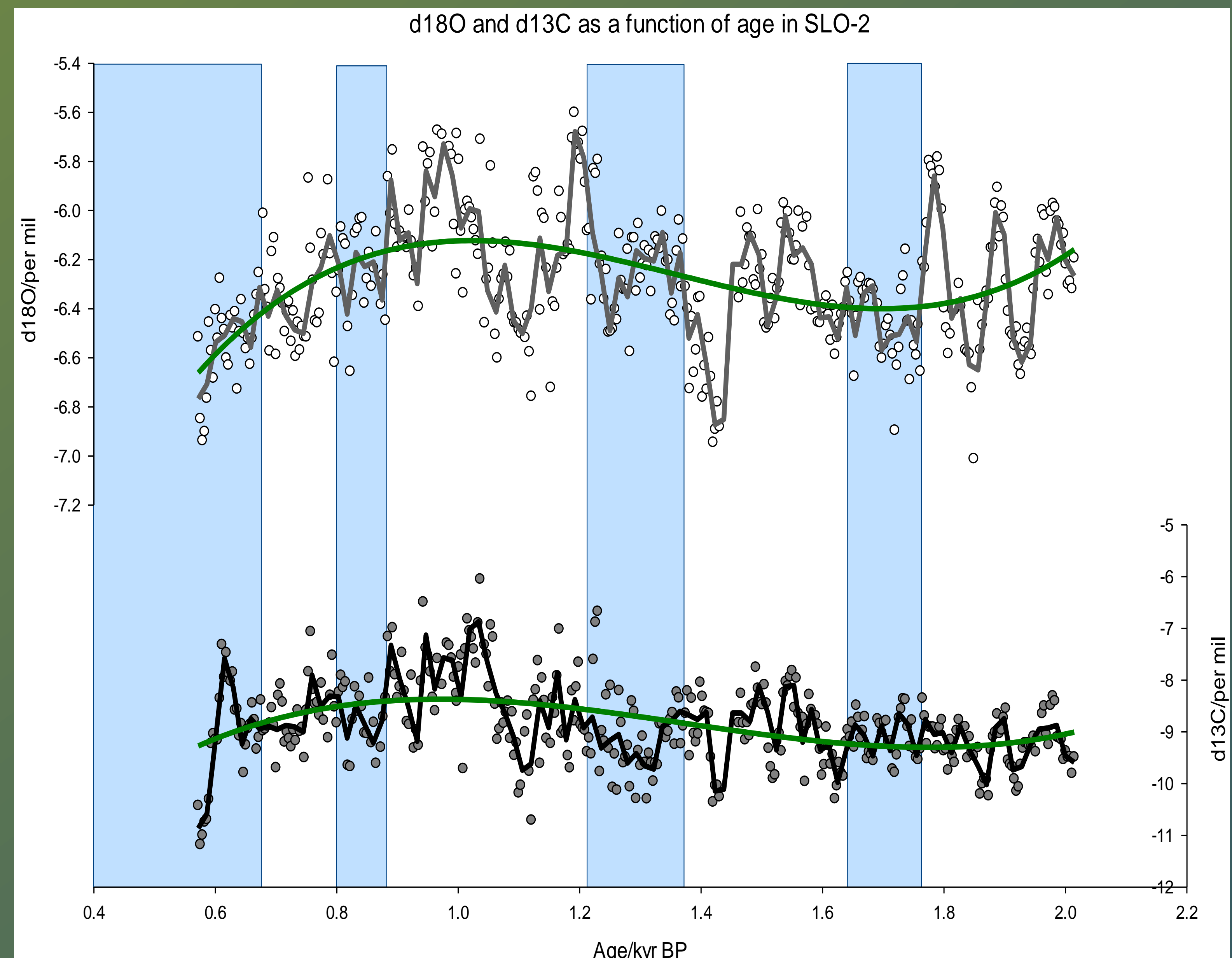
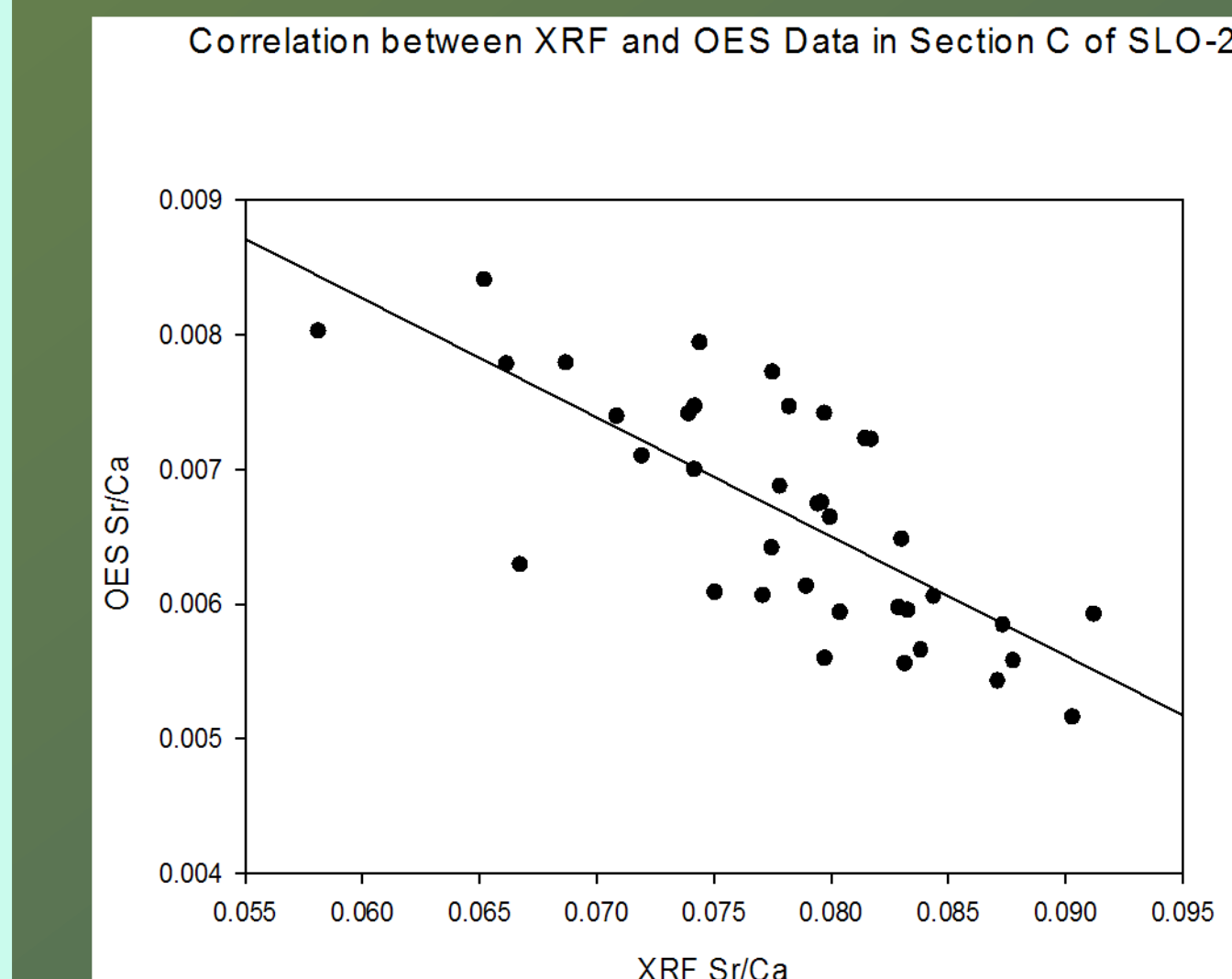


Figure 2: Stable isotope record obtained from SLO-2. Grey symbols represent  $\delta^{13}\text{C}$ , white symbols represent  $\delta^{18}\text{O}$ . Black and grey lines represent moving averages (Sampling Interval = 0.01) for  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ , respectively. The green lines show a trinomial best fit through the datasets. Blue blocks represent periods of glacier advance in Switzerland (Holzhauser et al., 2005)

## Calibration of ICP-OES and XRF Techniques for Trace Element Determination

ICP-OES is a commonly used technique for determining trace element concentrations.



XRF offers several advantages over OES, including faster sample throughput, minimal preparation and non-destructive analysis, but suffers from lower resolution and poorer characterisation.

Figure 3: Scatter plot comparing the Sr/Ca results of the XRF analyses against the OES analyses in Section C. The correlation is fairly strong ( $R^2 = 0.5508$ ) and statistically significant ( $p < 0.01$ )

Three sections of SLO-2 (labelled A, B and C) which had been analysed by both techniques were tested for significant correlation between the two techniques using Spearman Rank Correlation Analysis. The measured Sr/Ca ratios for each technique were compared.

Section C was found to show very strong significance ( $p < 0.01$ ), whilst neither Section A or B were statistically significant ( $p > 0.05$ ). However, the strong significance of Section C was sufficient to make comparisons across all three sections statistically significant.

This vast difference in applicability may be due to self-absorption effects due to varying calcite density in different parts of the stalagmite.

Further samples from a different stalagmite are currently being investigated to further explore this issue.

## Conclusions

SLO-2 provides good material for climate reconstruction, with little kinetic fractionation.

The stable isotope record collected so far shows good correlation with known climate variations during the Late Holocene.

Short term (sub-decadal) variation has been observed, in spite of a well-mixed aquifer. This may be due to cave ventilation effects.

A significant correlation has been observed between the OES and XRF techniques for trace element analysis, though material composition appears to have an as-yet-unknown effect on this.

## References

Hendy, C. H. 1971. Isotopic Geochemistry of Speleothems .1. Calculation of Effects of Different Modes of Formation on Isotopic Composition of Speleothems and their Applicability as Palaeoclimatic Indicators. *Geochimica et Cosmochimica Acta*, 35, 801-8.

IAEA/WMO (2006). Global Network of Isotopes in Precipitation. The GNIP Database. Accessible at: <http://www.iaea.org/water>

Bambynek, W., Crasemann, B., Fink, R. W., Freund, H.-U., Mark, H., Swift, C. D., Price, R. E. & Venugopala Rao, P., 1972. X-ray Fluorescence Yields, Auger and Coster-Kronig Transition Probabilities. *Reviews of Modern Physics*, 44, 716-813

Holzhauser, H., Magny, M., Zumbühl, H. J., 2005. Glacier and lake-level variations in west-central Europe over the last 3500 years. *The Holocene*, 15, 789-801

