

## METHODS

### Analytical methods

#### X-ray diffraction

X-ray diffraction of the boxwork samples was performed using a Rigaku Miniflex 200sc101 powder X-ray diffractometer, CuK<sub>α</sub> radiation, kV = 30, Ma = 15 at Hartwick College, Oneonta, New York, U.S.A.

#### Carbon-13 and Oxygen-18 analysis of carbonate samples

The carbonate samples were analyzed in duplicate by Iso-Analytical Limited (United Kingdom). The average value is reported in delta notation. Two milligrams of fine dry powder of each sample was placed in clean glass septum capped vials. The vials were then sealed and their headspaces flushed with pure helium (99.995%). After flushing, ~0.5 mL of pure phosphoric acid, prepared according to Coplen et al. (1983), was injected into the vials and mixed with the sample powder. The samples were left to react for a period of not less than 36 hours to ensure complete conversion of carbonate to carbon dioxide for analysis. Standard reference materials were prepared in the same manner as the samples.

The CO<sub>2</sub> gas was then analyzed by continuous flow isotope ratio mass spectrometry. The CO<sub>2</sub> is flushed from the septum vial using a double holed needle and resolved on a packed column gas chromatograph. The carbon dioxide then enters the ion source of a Europa Scientific 20-20 IRMS and is ionized and accelerated. Here, gas species of different mass are separated in a magnetic field then simultaneously measured using a Faraday cup collector array at m/z 44, 45, and 46.

The reference material used for this analysis was the laboratory's calcium carbonate standard IA-R022 ( $\delta^{13}\text{C}_{\text{V-PDB}} -28.63\text{‰}$  and  $\delta^{18}\text{O}_{\text{V-PDB}} -22.69\text{‰}$ ), which is traceable to NBS-19 Limestone ( $\delta^{13}\text{C}_{\text{V-PDB}} +1.95\text{‰}$  and  $\delta^{18}\text{O}_{\text{V-PDB}} -2.2\text{‰}$ ). During analysis, NBS-18 calcite ( $\delta^{13}\text{C}_{\text{V-PDB}} -5.00\text{‰}$  and  $\delta^{18}\text{O}_{\text{V-PDB}} -23.00\text{‰}$ ), NBS-

19 limestone and IA-R022 were analyzed as check samples.

#### Sulphur-34 analysis of sulfate samples

Sulfur isotopic compositions in cave samples were determined by a helium gas continuous flow isotope ratio mass spectrometer (CF-IR-MS; ISOPRIME-EA; Isoprime Ltd., UK) at the University of Tsukuba (Ikehata and Maruoka, 2016). The sulfur isotopic compositions are expressed in terms of  $\delta^{34}\text{S}$  (‰) relative to the V-CDT (Vienna-Canyon-Diablo-Troilite) standard. The results of three IAEA (International Atomic Energy Agency) silver sulfide standards (IAEA-S-1, -0.3‰; IAEA-S-2, +21.80‰; IAEA-S-3, -31.95‰; Mayer and Krouse, 2004) were compared to constrain the  $\delta^{34}\text{S}$  values. The isotopic compositions of sulfur were determined to a precision of  $\pm 0.1\text{‰}$  (1 $\sigma$ ), the precision being reached by combining the standard deviations for repeated analyses of samples and standards (Maruoka et al., 2003).

## SUPPLEMENTARY REFERENCES

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