

# Sulphur isotope evidence for the origin of cave evaporites in Ogof y Daren Cilau, south Wales

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## Abstract

Gypsum evaporites are forming under desiccating conditions in relict cave passages in Mynydd Llangattwg, south Wales. Sulphur isotope compositions of these sulphates indicate that oxidation of diagenetic pyrite in the overlying Millstone Grit is the source of sulphate solutions, rather than dissolution of evaporitic sulphate in the limestones.

**KEYWORDS:** gypsum, evaporites, sulphur isotopes, caves, Wales.

## Introduction

THE Carboniferous limestone escarpment of Mynydd Llangattwg, on the south side of the Usk valley in south Wales, contains several miles of relict cave passage of substantial dimensions (Smart and Gardener, 1989), mainly in the caves of Agen Allwed and Ogof y Daren Cilau. These caves are often partially infilled with boulder collapse and/or inwashed sediment and in several areas crystals of gypsum grow on the surface of sediment infill, boulders and cave walls. These crystals are generally small, mostly less than 5 mm maximum length, and acicular or bladed in form, though fibrous masses and thin crusts are also found. More rarely, larger bladed crystals, up to 25 cm long, grow upwards from mud banks.

These gypsum deposits appear to form by evaporation of solutions rich in calcium sulphate under the relatively dry conditions in the relict passages (desiccation cracks are common in the finer-grained sediment banks). What is less certain is the origin of the calcium-sulphate-rich solutions from which the gypsum crystallizes and it is this problem which is addressed in this paper. In the case of the Mynydd Llangattwg caves, two hypotheses may be advanced for the source of sulphate in the gypsum-forming solutions. Sulphate may be produced by oxidation of diagenetic pyrite in the Millstone Grit overlying the limestones (Smart and Gardener, 1989). An alternative sulphate source is dissolution of evaporite minerals in the limestones by groundwaters. The limestones are known to have been emergent at times during their deposition (Wright, 1982; Smart and Gardener, 1989) and

sulphate minerals formed in the limestones from seawater sulphate (Lowe, 1989). These two sulphate sources have distinct sulphur isotope signatures which should persist in the gypsum cave deposits (see discussion below) and thus provide a means of distinguishing the origin of the sulphate solution.

## Sampling and analytical details

Small samples (20–30 mg) of gypsum crystals were taken at three localities in Ogof y Daren Cilau (NGR SO 2051 1529). At one site in Antler Passage two samples of crystals on a limestone face were taken and in Epocalypse Way one sample of similar crystals and a sample of a gypsum crust were taken. Each sample was dissolved in 0.05 M HCl and filtered prior to precipitation of sulphate as BaSO<sub>4</sub>. Sulphur dioxide for isotopic analysis was prepared from the BaSO<sub>4</sub> using the method of Halas *et al.* (1982) and analysed on a VG SIRA 10 gas source, dual inlet mass spectrometer. Data were corrected using standard procedures (e.g. Coleman, 1980). Errors estimated from four analyses of international standard OGS-1 run with the samples are  $\pm 0.17\%$  (2 sigma).

## Results and discussion

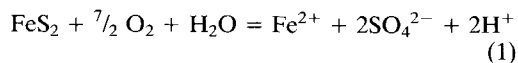
All of the gypsum samples have relatively light sulphur isotope compositions ( $-26.3$  to  $-33.3\%$  CDT, Table 1). These compositions are most likely to result from sulphate formed by oxidation of diagenetic pyrite in the Millstone Grit which

Table 1. Sulphur isotopic compositions of gypsum from Ogof y Daren Cilau.

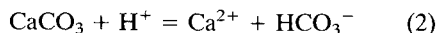
Sample No.	Description	$\delta^{34}\text{S}$ CDT ‰
DC-1	Crystals, Antler Passage	-30.3
DC-2	Crystals, Antler Passage	-31.6
DC-3	Crystals, Epocalypse Way	-33.3
DC-4	Crust on boulder, Epocalypse Way	-26.3

will have a similar light sulphur isotopic composition (Schwartz and Burnie, 1971; Goldhaber and Kaplan, 1980). Since oxidation of sulphide involves little isotopic fractionation (Nakai and Jensen, 1964) this light signature will also be characteristic of the resulting sulphate. Evaporitic sulphate in the limestone would have a far heavier 'seawater' signature (+15 to +20‰ CDT for Carboniferous seawater; Claypool *et al.*, 1980) which would characterize sulphate solutions resulting from its dissolution by percolating groundwater.

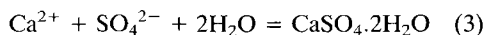
Oxidation of pyrite in the Millstone Grit will give rise to acidic sulphate solutions,



On percolating into the underlying limestones this acidity would be neutralized by dissolution of calcite,



producing a neutral to alkaline calcium sulphate solution. Concentration by evaporation in the desiccating environment of the relict cave passage can then lead to supersaturation and precipitation of gypsum



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