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Ranges (amplitudes) of isotopic ratios in speleothems, with particular reference to samples from the centre of North America.

DEREK FORD

School of Geography and Geology, McMaster University, Hamilton, ON L8S 4K1, Canada.
E-mail: dford@mcmaster.ca

ABSTRACT:

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This paper compares unstable and stable isotope ratios measured in a speleothem core from the Nevada desert (the well-known DH 11) with speleothems at the centre of the continent in the Black Hills of South Dakota. All samples grew over most of the past 500,000 y.

The thermal calcite in the large Nevadan desert basin displays a range of the initial U ratio ($^{234}U/^{238}U_0$) of only 0.25 and is much enriched in ^{234}U, reflecting selective leaching in a very low energy weathering environment. Similar thermal calcite from a much smaller basin the Black Hills (Wind Cave) is less homogenised (U/U_0 range is ~0.5) and less enriched as a consequence of its more vigorous sem-arid weathering environment. Both display glacial-interglacial cyclicity in the ratio. A vadose speleothem from Jewel Cave, Black Hills, has a U/U_0 range of 0.75 and many erratic features attributable to rapidly changing local conditions in the overlying tall grass- coniferous forest vegetal transition.

O and C stable isotopes are again homogenised in the large Nevada basin: the range is 2.8 ‰ ^{18}O and 1.2 ‰ ^{13}C, encompassing all glacial-interglacial cyclicity. In the Wind Cave thermal calcites the range again is roughly double, an effect of lesser homogenisation taking place in the smaller aquifer. There is also a perturbation of the signals of ~100 ky duration that may have been caused by release of deep CO_2. ^{18}O and ^{13}C measurements in the Jewel Cave vadose sample form a broad envelope that encloses the Black Hills thermal calcite data, indicating that the full range, glacial – interglacial, of speleothem ^{18}O was probably 10 ‰ here in the centre of the continent, which may be compared to 1.2 ‰ estimated at the sources of the precipitation in the Gulf and Caribbean. ^{13}C of the vadose speleothem ranged 7.0 ‰ in the Black Hills, oscillating between moderate and very low (desert-like) levels of soil CO_2 activity.

Key words: Thermal water speleothems, Vadose speleothems, Uranium isotope ratios, Oxygen and carbon isotope ratios.

INTRODUCTION

Analyses of the changes with time of the ratios of some unstable (^{14}C, U, Th) and stable (O, C) isotopes in calcite speleothems are the fundamental tools of speleothem paleoenvironmental reconstruction. Attention is customarily focussed upon the details of changes in the $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios as paleoclimate indicators in a sample, measuring the passage of time by U series (or more rarely, by $^{14}C/^{12}C$) methods. There has been less discussion on the more general topic of the ranges of variation seen in the various ratios, the comparison of ranges in different types of samples in a given geographical area, or between comparable samples from different areas. This paper comments on ranges in thermal phreatic and meteoric vadose speleothems from South Dakota, in the centre of the North American continent, and compares them to the well-known Devil's Hole 11 (DH 11; WINOGRAD & *al.* 1992) sample from the Nevada Desert, 1250 km to the SSW. It concludes with a brief comparison with ranges of ratios in the Gulf of Mexico/Caribbean region, the chief source area of the precipitation falling on South Dakota.

Jewel Cave and Wind Cave, Black Hills, South Dakota, are drained thermal water caves with subaqueous calcite precipitates exposed on their walls, plus a few modem grottos with conventional vadose speleothems (BAKALOWICZ & *al.* 1987; FORD & *al.* 1993). Jewel Cave is between 1500-1650 m above sea level and Wind Cave at 1000-1250 m asl. The modem regional climate is at the temperate sub-humid to semi-arid boundary, with open pinon forest above Jewel Cave and grassland over Wind Cave. For lengthy periods both caves were backwaters accreting calcite in thermal water aquifers having catchment basins of intermediate scale, probably a few hundred square km. The Devil's Hole samples are extracted from below the modem waterline in a backwater location in a large thermal aquifer (>12,000 km^2) beneath a temperate desert.

U SERIES RANGES

The speleothem samples are dated by the ^{230}Th/^{234}U/^{238}U method in which ^{234}U and ^{238}U are incorporated at the time of calcite deposition, and the ^{230}Th accretes subsequently from their decay (IVANOVICH & HARMON 1992). ^{234}U/^{238}U$_0$, the ratio at time of deposition, can be an intriguing indicator of the environmental conditions prevailing when weathering liberates these two isotopes from their sources in older rocks or soils drained into the aquifer. As ^{238}U is the parent isotope, a large excess of "daughter" ^{234}U points to a very selective weathering environment, one in which this slightly more detachable product is preferentially taken into solution.

The DH 11 thermal calcite grew slowly from >500,000 years BP until 60,000 years ago (LUDWIG & *al.* 1992). During that great span of time its ^{234}U/^{238}U$_0$ was between approximately 2.75 and 3.00, a range of 0.25. The variation appears systematic over time, suggesting that this is a signal varying roughly with the 100,000 year glacial cycle. This enrichment of the daughter isotope is more substantial than tends to be found in most speleothems and so suggests that the desert environment has favoured very selective, slow weathering. In the smaller Wind Cave basin ^{234}U/^{238}U$_0$ varies between 1.05 and 2.5 in a large sample of its thermal precipitates that grew between 450,000 years BP and the present. This is a significantly larger range than in the single core of Devil's Hole, which indicates that less homogenizing is taking place in the smaller basin. However, most Wind Cave values are very close to the mean of 2.0, varying about it in phase with the glacial cycles. Like Devil's Hole, the enrichment of the daughter isotope may be interpreted as an indication of sustained selective weathering due to quite dry (or "low energy") conditions.

The thermal calcite precipitates in Jewel Cave are too old to be dated by U series methods. Interest there has focussed on a vadose stalagmite boss, JC 11, which grew in a grotto ~80 m beneath the forest. Growth was intermittent from >450,000 years until about 90,000 years BP, when it fell and shattered. The hiatuses are closely correlated with the coldest parts of glacial cycles. The ^{234}U/^{238}U$_0$ ratios in the top one third of the sample range between 1.225 (youngest) and 1.555 (oldest, ~400,000 years BP) to suggest that there was an approximately linear decline towards 1.0 over the period. When this linear relation is extrapolated to the lowest one third of the sample ("RUBE" dating; see FORD & WILLIAMS 1989, p 359) it produces reasonable calculated initial ratios between 1.8 and 2.0, from which reasonable age estimates may also be derived; the base of the stalagmite may be about 800,000 years in age. The middle one third of the specimen yields irrational ages for all likely U/U$_0$ ratios between 1.5 and 2.0. It is concluded that, when deposition commenced, the U/U$_0$ ratio was similar to that of Wind Cave but in the more "energetic" forest weathering environment above Jewel Cave the ratio declined towards 1.0. This single site thus experienced a range of ~0.8 over a timespan of about 700,000 years. The ratio varied in a highly erratic manner during the middle period of the accumulation, demonstrating that too much trust should not be placed on paleoenvironmental interpretations of ^{234}U/^{238}U$_0$ ratios in vadose speleothems.

O AND C ISOTOPIC RANGES

Where the calcite is deposited in equilibrium with the thermodynamic environment, the ^{18}O/^{16}O ratio in a speleothem may vary with the temperature of the cave or with the isotopic composition of the rainfall (itself a temperature-dependent variable). The ^{13}C/^{12}C ratio is believed to vary with the abundance of ^{13}C-depleted CO_2 in the soil in a similar manner. Both ratios may be distorted by kinetic processes, chiefly evaporation. The thermal water calcites of Devil's Hole and Wind Cave both accumulated very slowly in nearly static water bodies and so can be presumed to be equilibrium deposits. This cannot be so certain in the Jewel Cave vadose stalagmite but it also grew very slowly, in a cave that is cool (8°C) and very humid in today's interglacial conditions, suggesting that there can be little deviation from equilibrium. It passes the Hendy & Wilson (1969) test for equilibrium conditions.

In the large Devil's Hole basin $\delta^{18}O$ displays a range of only 2.8‰ (–15.5 to –18.3 VPDB) during its >500,000 years of deposition, becoming enriched ("heavier") in interglacials. $\delta^{13}C$ varies between –1.5 and –2.7 ‰ VPDB, which is within the 0+/–5‰ range characteristic of marine limestones themselves, indicating that there is very little effect of soil CO_2 in this arid region. However, the ^{13}C becomes depleted in each interglacial, probably pointing to slightly increased rainfall supporting more vegetation then.

Most of the Wind Cave thermal crust samples were too thin for sequential measurements of O and C isotope ratios. Single measurements on 60 different fragments ranging from ~450,000 years to modem in age gave a $\delta^{18}O$ range from –14 to –19.5‰, roughly double that of DH 11 and neatly encompassing its range. This can be interpreted as a consequence of the lesser homogenization (damping) of signal variation in a smaller basin. del ^{13}C varied between –5 and –7.5‰, again approximately double the DH 11 range; its distribution centres around –6‰, indicating some weak effect of soil P_{CO_2}. One sample, WCMAJ, was thick enough for multiple measurements. Its upper half displays climatically-driven swings of $\delta^{18}O$ between –15 and –18.7‰ over the warmer 75% of a glacial cycle. In the lower half the climatic signal is erased; ^{18}O and ^{13}C are both constant at enriched levels although the $^{234}U/^{238}U_0$ ratio continues to shift with the glacial cycle. This marks the intrusion of some other CO_2 effect (a deep thermal release of gas?), warning us that thermal water calcites may not be wholly controlled by basin-wide climatic effects.

The $\delta^{18}O$ and ^{13}C measurements in the vadose speleothem, JC 11, form a broad envelope that encloses all of the Wind Cave thermal results if the $\delta^{18}O$ values of the latter are slightly adjusted (enriched) to eliminate the effect of deposition from warm waters. It is the least damped (i.e. most sensitive) paleo-environmental indicator. The $\delta^{18}O$ range is 7.0 ‰, from –11.5 to –18.5‰; from the U series dating this represents the warmer 70-80% of each glacial cycle because growth ceased during the coldest parts. The ^{13}C range is the same, 7.0 ‰ between –2.0 and –9.0‰, although most data are below –3.5‰.This suggests soil CO_2 oscillating between moderate and very low (cool desert) values, though changes from C3 to C4 vegetation and back again could also play a role at this forest-grassland transitional site.

The general conclusions are that at the sub-humid centre of the North American continent the potential amplitude of ^{18}O variation over a complete glacial cycle in vadose cave deposits is probably as great as 10‰, and that of ^{13}C can be at least 5-6‰. These ranges are reduced to approximately one half in phreatic deposits which integrate the signals in medium-sized thermal water basins. There is a further reduction to about 25% in the big, arid Ash Meadows (DH 11) basin in the western deserts.

Jewel and Wind Caves in the Black Hills receive the bulk of their precipitation from the warm seas of the Gulf of Mexico and the Caribbean. It is interesting to consider isotopic conditions in these source areas. Vadose speleothems in warm tropical caves are often subject to evaporation, which enriches the ^{18}O and ^{13}C proportions by kinetic fractionation. However, recent studies of speleothems from ancient marine mixing zone caves in raised cliffs on Mona Island, Puerto Rico, and Cayman Brac, Caymans, have provided some insight (Tarhule-Lips 1999). All of the caves were eroded back by cliff recession during the marine stage 5e high sea level ~125,000 years BP, which introduced entrance zone, highly evaporitic conditions into cave chambers that were previously interior and more humid. Speleothems older than 125,000 years in a given cave display significantly smaller ranges of ^{18}O and ^{13}C than those that are younger, allowing the evaporative fractionation effects to be estimated and partly discounted. It appears that the amplitude of the glacial cycle effect on $\delta^{18}O$ in speleothems was 1.2‰, the same amount (and with the same trend) as is measured in *foraminifera* in tropical oceans. In transit to the Black Hills in the dry interior of the continent the trend is reversed and the range of ^{18}O variation is increased by about one order of magnitude.

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