# TRACE ELEMENT AND STABLE ISOTOPE VARIATIONS IN THREE COEVAL WEST VIRGINIA SPELEOTHEMS SPANNING THE LGM AND YOUNGER DRYAS

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# ABSTRACT

Three coeval stalagmites from Culverson Creek Cave, West Virginia, grew largely uninterrupted for approximately 15,000 years across the Last Glacial Maximum to early Holocene. Stable isotope carbon and oxygen and high resolution trace element (Sr/Ca) chronologies are supported by 63 Th-230 age dates. The timing of Heinrich events 1 and 2, LGM, B/A and YD are well-constrained by abrupt shifts in the highfrequency oscillations observed in both stable isotope and trace element analyses, providing a detailed paleohydrological chronology for the mid-Appalachian region during this time.

The δ18O curves attained for these speleothem is largely supported by GRIP and GISP2, as will be demonstrated by time-series comparison. The stable isotope chronology is, however, markedly different from many speleothem chronologies from other regions. We present a comparison of this mid-Appalachian record with those of other regions, as well as an interpretation of the various climatic mechanisms controlling speleothem deposition.

In addition to this chronology, we also present a new technique for trace element analysis (Sr/Ca) through μ-X Ray Fluorescence (μ-XRF). Trace element ratios in speleothems (Sr/Ca, Mg/Ca, Ba/Ca) have been used to interpret the hydrogeochemical processes in the epikarst zone as well as the partitioning that occurs at the calcite-water interface. During periods of low rainfall, trace element ratios generally increase as a result of the longer residence time of water in the soil and epikarst zones. High-resolution time series analyses of these elements in speleothems provide evidence for changing paleohydrological and geochemical condition addition to this chronology, we also present a new technique for trace element analysis (Sr/Ca) through µ-X Ray Fluorescence (µ-XRF). Trace element ratios in speleothems (Sr/Ca, Mg/Ca, Ba/Ca) have been used to interpret the hydrogeochemical processes in the epikarst zone as well as the partitioning that occurs at the calcite-water interface. During periods of low rainfall, trace element ratios generally increase as a result of the longer residence time of water in the soil and epikarst zones. Highresolution time series analyses of these elements in speleothems provide evidence for changing paleohydrological and geochemical conditions over time. This non-destructive and non-contact method could serve as a viable alternative to conventional methods and prove important in future paleoclimate research

# **STUDY AREA & SIGNIFICANCE OF LOCATION**



FIGURE 2 (right): Adapted from Hardt et al, 2010. The study location lies at a juncture of two primary moisture sources- the Northern Hemisphere Westerlies (NHW) and the Bermuda

FIGURE 1 (left): Speleothems for this study were collected from a humid cave passage, more than a kilometer from the closest known entrance in Culverson Creek Cave, in the Mississippian limestone of the Greenbrier Group in the Allegheny Mountains of southeastern West Virginia, USA.

Culverson Creek Cave is one of many caves in this region and is part of a broader study to establish a continuous chronology of speleothem paleoclimate records for the past 600 kyr for eastern North America.



# METHODS



FIGURE 3 (above): Speleothems CCC-001, 003, and 007 showing the stable isotope sampling axis (for 001 and 003) and the locations of samples taken for U-Th dating (for 007). Top and bottom dates for each stalagmite are shown with the location from which the powdered sample was taken.

The stalagmites- CCC-001, 003, and 007, respectively, were cut in half along the growth axes, polished, and drilled for powdered samples for stable isotope and dating analyses. Trace element data were obtained using the Artax µ-XRF.

Stable isotope samples were milled contiguously in sub-mm increments (in order to reduce any aliasing effects that may result from taking discrete samples) by a dental drill. The samples were then processed by a GasBench II coupled to a ThermoFinnigan Delta-**PlusXP IRMS and standardized to V-PDB.** 

Th-230 age-dating was performed at the University of Minnesota using a Finnigan-MAT Element IC-PMS with a single MasCom multiplier using the decay constants reported by Cheng et al. (2000). Figure 3 shows the location of the top and bottom ages obtained for each speleothem while Figures 4 & 5 show the age model constructed by linear interpolation between U/Th ages to create a radiometric timescale for  $\delta$ 18O and  $\delta$ 13C measurements. For age results. see Table 1.

Trace element data were obtained using the ARTAX µ-XRF systema motor-driven, tripod-supported, x-y-z axis with a spot size of 70 microns, and is equipped with an Rh tube and Al-Ti-Cu filter. The spatial sensitivity of the system allows for a minimum step increment of 30 microns, ultimately allowing for resolution down to spot-size overlap. Instrument settings for analyses of CCC speleothems was 50kV/500 µA with a count-time of 180 seconds.

# RESULTS

						U	Th	dati	ng						
CCC-	001														
Sample	238	T	232,	TL	234	ίπ.	1230 TL	/238	1230 TL	/232 Th 1		<b>A</b> and	234	T	4.00
Sample	nn	U h	- In		U measu	Uured	11 acti	ivitv	I I	l/ Inj	unco	Age		Uinitial rected	Age
	P. P		hhr		incas	incu			Руш						corrected
CCCIT	382.5	+0.8	928	+4	648.4	+3.2	0.0838063	+0.00132	570	+9	5678	+92	658.9	+3.2	5635 +97
CCC1-90	487.6	+0.9	170	+1	724.1	+3.1	0.1013625	$\pm 0.00132$ $\pm 0.00142$	4797	+75	6588	+96	737.7	+3.2	6583 +96
CCC1 181	402.0	+1.0	2/2	±1	724.1	+2.0	0.1013023	$\pm 0.00142$	4202	+52	8002	+06	805.1	+2.1	8085 ±06
CCC1 197	492.9	±1.0	245	±1	780.9	±3.0	0.120074	$\pm 0.00140$	4295	±33	0095	±90	705.2	±3.1	0003 ±90
CCC1 100 5	429.5	±0.8	3/3	±1	777.0	±2.9	0.1300/4	±0.00119	(125	±24	8233	±/9	795.5	±3.0	8241 ±80
0001-190.5	509.1	±1.0	1/5	±1	010.2	±3.0	0.12/6348	±0.00093	0125	±33	8118	±63	/90.2	±3.1	8112 ±03
CCC1-250	444.4	±0.8	169	±I	818.3	±3.1	0.1899237	±0.00140	8246	±/5	11948	±95	846.4	±3.2	11942 ±95
CCC1-260	438.0	±0.8	157	±l	808.4	±3.2	0.1975385	±0.00163	9107	±94	12524	±111	837.5	±3.3	12518 ±111
CCC1-280	434.8	±0.9	265	±1	833.5	±3.7	0.2050482	±0.00206	5546	±59	12836	±138	864.3	±3.9	12826 ±138
CCC1-300.5	603.6	±1.2	27	±1	826.0	±3.2	0.211811	±0.00170	78630	±2913	13341	±115	857.7	±3.3	13340 ±115
CCC1-330.5	559.3	±1.1	122	±1	806.1	±3.1	0.2160753	±0.00199	16328	±193	13784	±137	838.1	±3.3	13780 ±137
CCC1-375	508.1	±0.9	52	±1	746.4	±3.1	0.2245408	±0.00259	36365	±728	14882	±185	778.5	±3.3	14881 ±185
CCC1-465	641.6	±1.3	58	±1	788.7	±3.2	0.2531066	±0.00165	46522	±786	16476	±119	826.2	±3.3	16475 ±119
CCC1B	287.2	±0.7	4154	±15	807.2	±3.6	0.2818293	±0.00242	322	±3	18282	±174	849.4	±3.9	18054 ±237
000-	003														
Samela	238	1	232		230-, , 232		.234	230	238.	230	(	230		.234.	230
Number	(ppb)		(ppt)		Th atomic x10 <sup>-6</sup>	(me	(measured)		/ity)	Th Age (uncorrec	(yr) ted)	(corrected)	)	(corrected)	(corrected )
	(1-1/		AF 7			(		(				, ,			
CCC3-29	737.7 ±1.	1	13435 ±269		93 ±2	66	8.3 ±1.8	0.1023 =	±0.0004	6873 ±2	8	6558 ±225		681 ±2	6497 ±225
CCC3-30	1091.1 ±1.	8	709 ±15		3328 ±69	704	4.8 ±1.9	0.1312 =	±0.0004	8686 ±3	1	8675 ±32		722 ±2	8614 ±32
CCC3-1	$1143.8 \pm 2.2$ 770 3 +1 1		$639 \pm 13$		4801 ±99 6032 +130		094.8 ±2.2 718 0 +1 8		±0.0005	$11072 \pm 33$	5	$11063 \pm 36$		717 ±2	11003 ±36
CCC3-31 CCC3-32	$7/0.3 \pm 1.$	2	$35/\pm 8$ 684 +14		$6032 \pm 130$ 3272 $\pm 68$	72	$5.9 \pm 1.8$ 5.2 ± 1.9	0.1695 =	±0.0005 ±0.0005	$11240 \pm 3$ 11461 $\pm 4$	0	$11232 \pm 40$ 11446 $\pm 42$		$742 \pm 2$ 749 +2	$111/1 \pm 40$ 11385 $\pm 42$
CCC3-32	$512.3 \pm 0.1$	7	$103 \pm 3$		$15672 \pm 474$	80	$7.1 \pm 1.8$	0.1908 =	±0.0005	12071 ±4	1	$12068 \pm 41$		835 ±2	11303 ±42
CCC3-34	1175.1 ±2.	1	111 ±4		33017 ±1107	72	1.3 ±2.0	0.1894 =	±0.0006	12615 ±4	2	12613 ±42		747 ±2	12552 ±42
CCC3-3	970.1 ±1.	5	237 ±5		13278 ±309	72	0.3 ±1.8	0.1969 =	±0.0006	13145 ±4	3	13141 ±43		748 ±2	13080 ±43
CCC3-4A	1356.1 ±2.	2	34 ±2	1	40717 ±9030	76	5.7 ±2.1	0.2113 =	±0.0005	13766 ±3	9	13766 ±39		797 ±2	13705 ±39
CCC3-4B	1341.6 ±2.	4	36 ±3	1	30734 ±12107	76	$5.0 \pm 2.0$	0.2111 =	±0.0006	13763 ±4	7	13762 ±47		796 ±2	13701 ±47
CCC3-6	$1211.3 \pm 1.$ 942.8 ±1	8 5	$42 \pm 2$	1	$0/510 \pm 6232$ 81158 $\pm 4745$	83	$7.1 \pm 1.9$ 3.5 $\pm 2.2$	0.2256 =	±0.0005 ±0.0007	$14153 \pm 37$ $14561 \pm 47$	7	$14153 \pm 38$ $14560 \pm 47$		$\frac{8}{1} \pm 2$	$14092 \pm 38$ 14499 +47
CCC3-7	894.9 ±1.	4	$\frac{40 \pm 3}{25 \pm 3}$	1	49987 ±15354	94	$4.2 \pm 2.2$	0.2402 =	±0.0007	14983 ±4	5	14982 ±45		985 ±2	14921 ±45
CCC3-8	702.3 ±1.	1	118 ±4		25798 ±805	97.	3.0 ±2.1	0.2627 =	±0.0007	15403 ±4	8	15401 ±48		1016 ±2	15340 ±48
CCC3-9	1057.9 ±1.	8	121 ±4		38553 ±1190	96	5.4 ±2.3	0.2667 =	±0.0007	15712 ±4	9	15710 ±49		1010 ±2	15649 ±49
CCC3-10	857.6 ±1.	3	78 ±3		49226 ±1821	954	4.7 ±2.2	0.2699 =	±0.0007	16013 ±4	9	16012 ±49		999 ±2	15951 ±49
CCC3-11	$1161.1 \pm 2.1$	0	19 ±3	2	67668 ±37148	902	2.5 ±2.3	0.2657 =	±0.0007	16216 ±5	1	16216 ±51		945 ±2	16155 ±51
CCC3-12	$1252.8 \pm 2.$	2	$35 \pm 3$ 19 +3	1	97696 +29582	89. 96	$3.1 \pm 2.3$ $3.4 \pm 1.9$	0.2003 =	±0.0007 ±0.0008	$16342 \pm 5$ 16487 +5	1	$16342 \pm 50$ 16487 $\pm 51$		$935 \pm 2$ 1006 ± 2	$10281 \pm 50$ 16426 $\pm 51$
CCC3-14	1031.6 ±1.	6	$40 \pm 3$	1	19590 ±29582	89	$3.6 \pm 1.8$	0.2782 =	±0.0007	17082 ±52	2	$170407 \pm 51$ 17081 ±52		943 ±2	17020 ±52
CCC3-15	830.9 ±1.	3	81 ±3		49304 ±1752	914	4.9 ±2.3	0.2927 =	±0.0007	17860 ±52	2	17859 ±52		962 ±2	17798 ±52
CCC3-16	707.3 ±1.	1	170 ±4		20224 ±509	88	1.5 ±2.2	0.2944 =	±0.0007	18318 ±5	5	18314 ±55		928 ±2	18253 ±55
CCC3-17	570.8 ±0.	9	136 ±4		$21032 \pm 608$	89	5.5 ±2.1	0.3037 =	±0.0008	18779 ±6	1	18775 ±61		945 ±2	18714 ±61
CCC3-18 CCC3-19	$641.5 \pm 1.0$	7	$46 \pm 3$		$66367 \pm 4402$ $44387 \pm 2586$	73	/.8 ±1.9	0.2857 =	±0.0009	19342 ±6 19727 ±7	1	$19341 \pm 67$ 19725 $\pm 74$		779 ±2 781 ±2	$19280 \pm 67$ 19664 $\pm 74$
CCC3-20	408.0 ±0. 891.2 ±1	3	199 ±5		$21190 \pm 511$	68	$5.5 \pm 1.8$	0.2910 -	±0.0009	20151 ±5	9	20147 ±59		781 ±2 726 ±2	20086 ±59
CCC3-21	798.5 ±1.	3	134 ±4		29441 ±809	66	3.7 ±2.3	0.2992 =	±0.0008	21268 ±7	2	21265 ±72		710 ±2	21204 ±72
CCC3-22A	771.9 ±1.	1	261 ±6		15144 ±344	63:	5.5 ±1.7	0.3106 =	±0.0008	22660 ±7	0	22654 ±70		677 ±2	22593 ±70
CCC3-22B	595.6 ±0.	9	145 ±4		21195 ±600	64	1.7 ±1.9	0.3119 =	±0.0009	22667 ±7:	5	22663 ±75		684 ±2	22602 ±75
CCC3-23	799.7 ±1.	3	581 ±12		7193 ±150	61	$3.6 \pm 1.9$	0.3169 =	±0.0009	$23432 \pm 7$	7	$23419 \pm 77$		661 ±2	23358 ±77
CCC3-25A	785.9 ±1. 876.6 ±1.	4	$327 \pm 7$ 385 +8		13040 +277	65	$3.6 \pm 2.0$	0.3418 -	+0.0010	$24003 \pm 84$ 25287 +80	+	24596 ±84 25280 ±80		$718 \pm 2$ 702 +2	24555 ±84 25219 +80
CCC3-25B	925.7 ±1	6	382 ±8		$13822 \pm 300$	65	3.3 ±2.2	0.3461 =	±0.0010	25220 ±8	7	25213 ±87		701 ±2	25152 ±87
CCC3-26	745.5 ±1.	0	1693 ±34		2677 ±54	73	3.6 ±1.8	0.3687 =	±0.0009	25641 ±7	4	25604 ±78		789 ±2	25543 ±78
CCC3-2	765.0 ±1.	3	1376 ±28		3333 ±67	679	9.6 ±2.1	0.3637 =	±0.0009	26175 ±8	1	26145 ±84		732 ±2	26085 ±84
CCC3-27	901.6 ±1.	6	129 ±4		44762 ±1344	77	5.8 ±2.3	0.3890 =	±0.0010	26460 ±8	6	26458 ±86		837 ±3	26397 ±86
CCC3-28	1088.2 ±1.	8	2/3 ±0		20430 ±004	81.	5.7 ±2.0	0.4021 =	±0.0011	20820 ±8.	5	20822 ±85		878 ±2	20/01 ±85
CCC-(	007														
Sample	<sup>238</sup> U		<sup>232</sup> Th	2	<sup>30</sup> Th / <sup>232</sup> Th		l <sup>234</sup> U*	<sup>230</sup> Th /	<sup>238</sup> U	<sup>230</sup> Th Age	(yr)	<sup>230</sup> Th Age (yr	·)	d <sup>234</sup> U <sub>Initial</sub> **	<sup>230</sup> Th Age (yr BP)***
Number	(ppb)		(ppt)	(a	tomic x10 <sup>-6</sup> )	(me	asured)	(activ	rity)	(uncorrec	ted)	(corrected)		(corrected)	(corrected)
CCC7 1	370 / ±0 5		1612 -22		608 5 ±12 2	061	9 +2 2	0 1560	+0.0004	0000 - 2	7	8066 157		987 +2	8006 +52
CCC7-15	508.6 ±0.5	,	1929 ±39		776 ±16	901	$7.8 \pm 2.0$	0.1309 -	±0.0004	10345 +2	, 9	10289 ±49		986 ±2	10228 ±49
CCC7-16	462.5 ±0.6	i	403 ±8		3372 ±69	953	3.2 ±2.2	0.1783 =	±0.0004	10361 ±2	7	10349 ±29		981 ±2	10288 ±29
CCC7-5	542.6 ±0.7	,	3106 ±62		517 ±10	953	3.1 ±2.0	0.1797 =	±0.0005	10445 ±3	0	10361 ±67		981 ±2	10300 ±67
CCC7-6	612.4 ±0.9		235 ±5		8103 ±170	946	5.6 ±2.1	0.1888 =	±0.0006	11036 ±4	1	$11030 \pm 41$		977 ±2	10969 ±41
CCC7-7	472.2 ±0.7		320 ±7		5129 ±106	940	0.5 ±2.5	0.2111 =	±0.0006	12448 ±3	9	12438 ±40		974 ±3	12377 ±40
CCC7 0	$5/1.1 \pm 0.9$	,	200 ±4 722 ±15	1	10491 ±221 2840 ±57	950	$3.8 \pm 2.4$	0.2233 =	±0.0006	13128 ±3	9 7	13123 ±39 13750 ±20		987 ±3	13062 ±39
CCC7-10	546 9 +0 7	,	491 +10		4473 ±91	943		0.2551 =	±0.0005	13/19 ±3	9	14421 +40		$983 \pm 2$	14360 +40
CCC7-11	$510.9 \pm 0.7$ $510.9 \pm 0.7$	,	44 ±2	4	51734 ±1924	937	7.5 ±2.1	0.2704 =	±0.0006	16201 ±4	5	16200 ±45		981 ±2	16139 ±45
CCC7-12	388.9 ±0.5		137 ±3	1	13561 ±299	901	.7 ±2.0	0.2908 =	±0.0007	17865 ±4	9	17859 ±49		948 ±2	17798 ±49
CCC7-13	371.9 ±0.5		264 ±5		6820 ±141	774	4.8 ±2.0	0.2935 =	±0.0007	19456 ±5	4	19445 ±55		818 ±2	19384 ±55
			2270 1 (9		555 7 +11 2	713	15 +1 7	0 3366 -	+0.0008	22405 +6	5	22220 +122		762 12	23270 ±133

 

 TABLE 1 : Th-230 age dates obtained for CCC

speleothems. Corrected ages appear in blue.



FIGURE 6 (above): d13C records for the three CCC speleothems. Although these stalagmites grew over largely the same time period and in very close proximity to one another, significant variablity exists between these three records.

FIGURE 7 (right): d180 records for the three CCC speleothems. These records largely agree with one another.

200 CCC-001 - CCC-007 Age (kyrs BP) FIGURE 4 (above): Age Model for CCC Speleothems with uncertainties for individual ages shown as brackets.



CCC-003 illustrating the growth rate

### **INTRA-CAVE VARIABILITY**

Figures 6 and 7 serve to show the variability that can be seen between coeval speleothems from the same location. All were analysed using the same methods, so the variability seen is either a product of cave microclimate variability within a very small cave section, different isotope fractionation effects, or perhaps different vadose flow regimes and pore water residence time in the epikarst.

All of these factors could influence the preservation of the climate signal.









FIGURE 8: The CCC-003 stable isotope and Sr/Ca record as compared to the Sofular d18O record (Fleitmann et al., 2009), NGRIP 20-yr d18O record, Hulu PD/MSD d18O record (Wang et al., 2001), and the Dongge D4 d18O record (Dykoski et al., 2005). The various colored bars show the timing of major events within the records. Th-230 age dates with are shown as brackets.

### **TAKE-AWAY POINTS**

The high-resolution, absolutedated Culverson Creek speleothem record for West Virginia provides a unique opportunity to reconstruct the paleoclimate of eastern North America.

A new non-destructive method of obtaining trace metal results has allowed for repeatable analyses.

The timing of several climatic events as seen in other proxy records can be correlated with the CCC record.

The three CCC speleothems provide an opportunity to examine not only inter-cave variability but also intra-cave variability, which can lead to new insights on the preservation of climatic signals within speleothem calcite.

Future work includes timeseries analysis of records and understanding the global and regional environmental controls on speleothem proxies.

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