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 high-frequency 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 conditionn 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 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

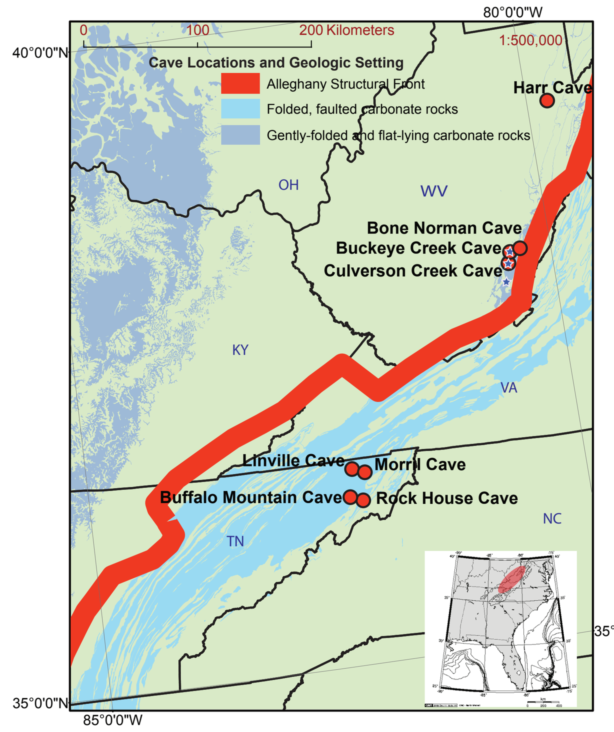

FIGURE 1 (left): Speleothems for this study were collected from a humid cave passage, more than a kilometer from the closest known entrance in Culverson Creek Cave, in the Mississippian limestone of the Greenbrier Group in the Allegheny Mountains of southeastern West Virginia, USA.

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.

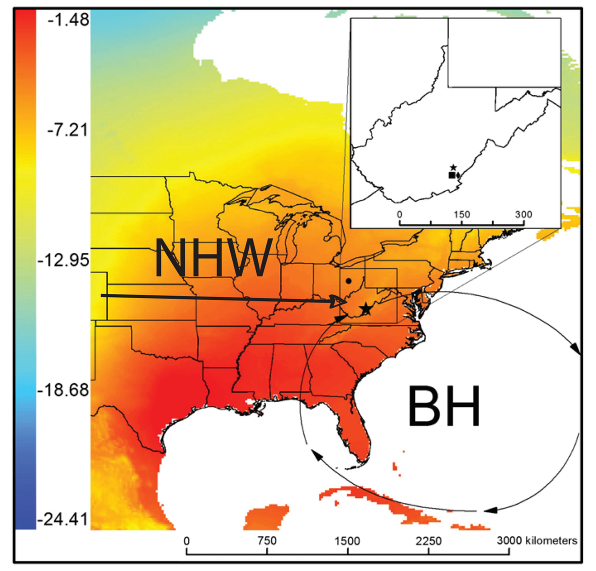

FIGURE 2 (right): Adapted from Hardt et al, 2010. The study location lies at a juncture of two primary moisture sources- the Northern Hemisphere Westerlies (NHW) and the Bermuda High (BH).

METHODS

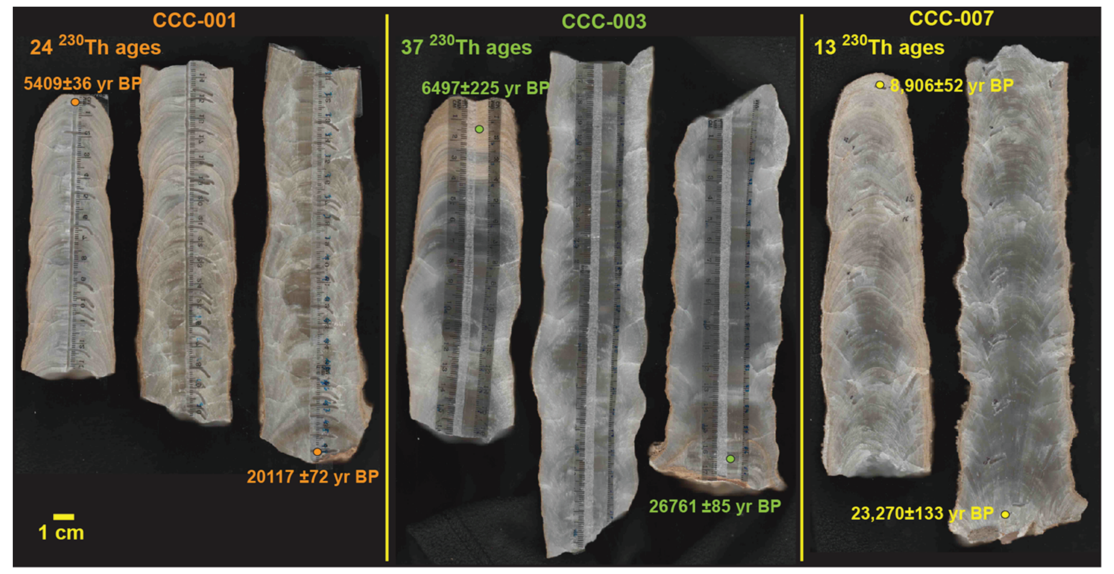

FIGURE 3 (above): Speleothems CCC-001, 003, and 007 showing the stable isotope sampling axis (for 001 and 003) and the locations of samples taken for U-Th dating (for 007). Top and bottom dates for each stalagmite are shown with the location from which the powdered sample was taken.

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 δ18O and δ13C measurements. For age results, see Table 1.

Trace element data were obtained using the ARTAX µ-XRF system- a 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.

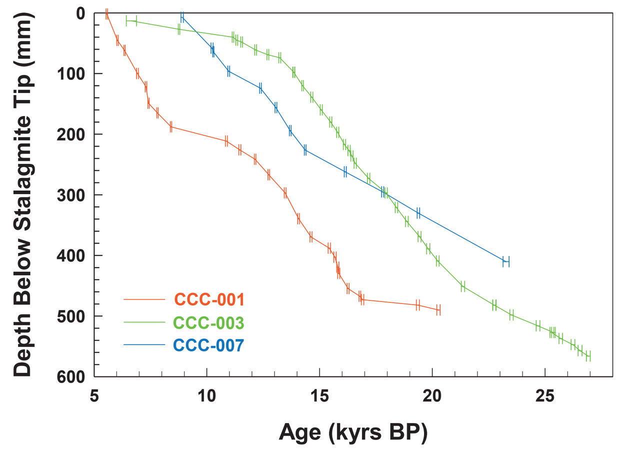

FIGURE 4 (above): Age Model for CCC Speleothems with uncertainties for individual ages shown as brackets.

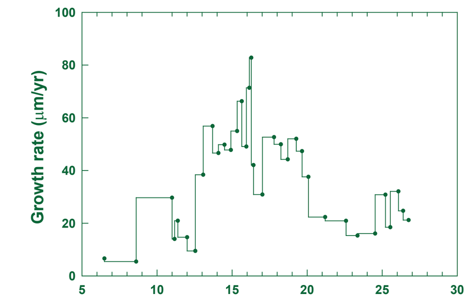

FIGURE 5 (above): Age model for CCC-003 illustrating the growth rate

RESULTS IN GLOBAL CONTEXT

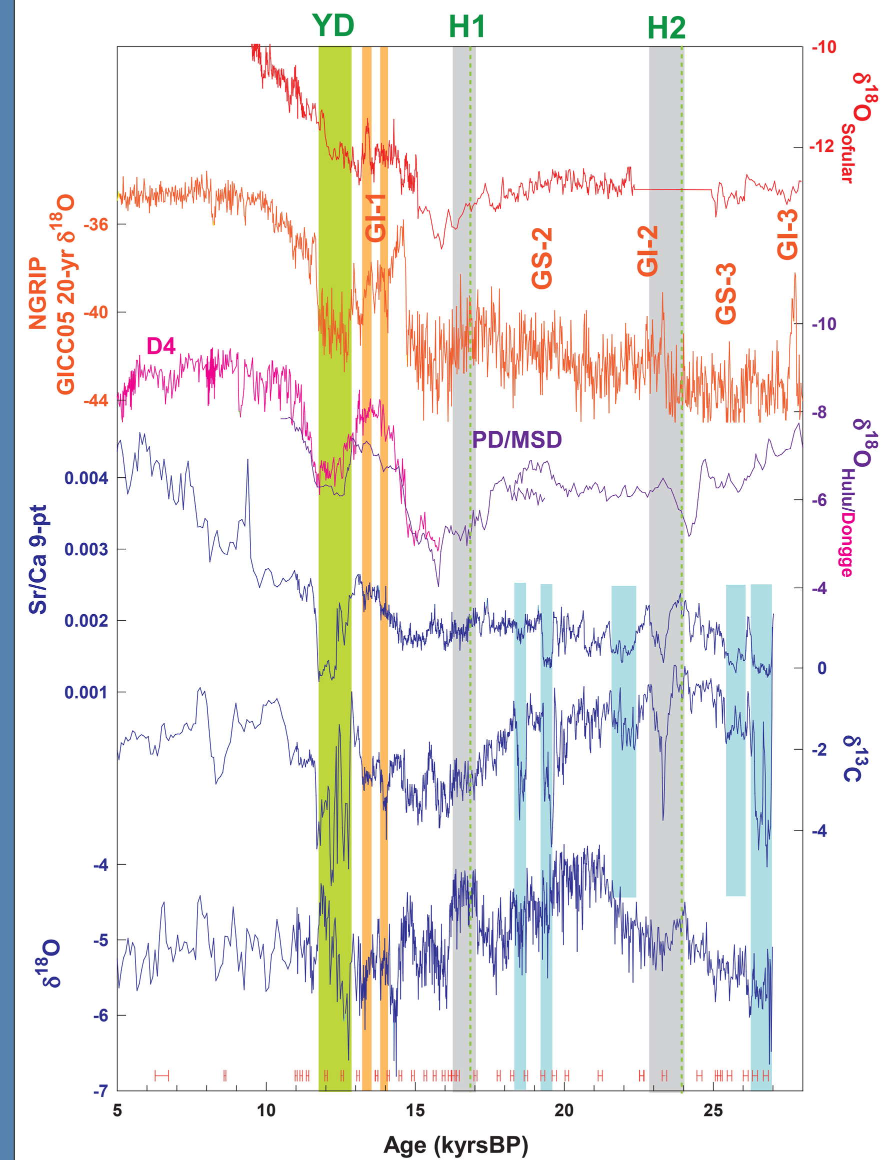

FIGURE 8: The CCC-003 stable isotope and Sr/Ca record as compared to the Sofular d18O record (Fleitmann et al., 2009), NGRIP 20-yr d18O record, Hulu PD/MSD d18O record (Wang et al., 2001), and the Dongge D4 d18O record (Dykoski et al., 2005). The various colored bars show the timing of major events within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

TAKE-AWAY POINTS

The high-resolution, absolute-dated 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 time-series analysis of records and understanding the global and regional environmental controls on speleothem proxies.

RESULTS

U-Th dating

CCC-001

Sample ID	^{238}U ppb		^{232}Th ppt		$d^{234}U$ measured		$[^{230}Th/^{238}U]$ activity		$[^{230}Th/^{232}Th]$ ppm		Age uncorrected		$d^{234}U_{initial}$ corrected		Age corrected	
CCC1T	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	±0.00142	4797	±75	6588	±96	737.7	±3.2	6583	±96
CCC1-181	492.9	±1.0	243	±1	786.9	±3.0	0.1283186	±0.00146	4293	±53	8093	±96	805.1	±3.1	8085	±96
CCC1-187	429.5	±0.8	375	±1	777.0	±2.9	0.130074	±0.00119	2457	±24	8255	±79	795.3	±3.0	8241	±80
CCC1-190.5	509.1	±1.0	175	±1	772.3	±3.0	0.1276348	±0.00093	6125	±53	8118	±63	790.2	±3.1	8112	±63
CCC1-250	444.4	±0.8	169	±1	818.3	±3.1	0.1899237	±0.00140	8246	±75	11948	±95	846.4	±3.2	11942	±95
CCC1-260	438.0	±0.8	157	±1	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

CCC-003

Sample Number	^{238}U (ppb)		^{232}Th (ppt)		$^{230}Th/^{232}Th$ (atomic x10^{-6})		$d^{234}U$* (measured)		$^{230}Th/^{238}U$ (activity)		^{230}Th Age (yr) (uncorrected)		^{230}Th Age (yr) (corrected)		$d^{234}U_{Initial}$** (corrected)		^{230}Th Age (yr BP)*** (corrected)	
CCC3-29	737.7	±1.1	13435	±269	93	±2	668.3	±1.8	0.1023	±0.0004	6873	±28	6558	±225	681	±2	6497	±225
CCC3-30	1091.1	±1.8	709	±15	3328	±69	704.8	±1.9	0.1312	±0.0004	8686	±31	8675	±32	722	±2	8614	±32
CCC3-1	1143.8	±2.2	639	±13	4861	±99	694.8	±2.2	0.1647	±0.0005	11072	±35	11063	±36	717	±2	11003	±36
CCC3-31	770.3	±1.1	357	±8	6032	±130	718.9	±1.8	0.1695	±0.0005	11240	±39	11232	±40	742	±2	11171	±40
CCC3-32	783.6	±1.2	684	±14	3272	±68	725.2	±1.9	0.1733	±0.0005	11461	±40	11446	±42	749	±2	11385	±42
CCC3-33	512.3	±0.7	103	±3	15672	±474	807.1	±1.8	0.1908	±0.0006	12071	±41	12068	±41	835	±2	12007	±41
CCC3-34	1175.1	±2.1	111	±4	33017	±1107	721.3	±2.0	0.1894	±0.0006	12615	±42	12613	±42	747	±2	12552	±42
CCC3-3	970.1	±1.5	237	±5	13278	±309	720.3	±1.8	0.1969	±0.0006	13145	±43	13141	±43	748	±2	13080	±43
CCC3-4A	1356.1	±2.2	34	±2	140717	±9030	766.7	±2.1	0.2113	±0.0005	13766	±39	13766	±39	797	±2	13705	±39
CCC3-4B	1341.6	±2.4	36	±3	130734	±12107	766.0	±2.0	0.2111	±0.0006	13763	±47	13762	±47	796	±2	13701	±47
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CCC-007

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TABLE 1 : Th-230 age dates obtained for CCC speleothems. Corrected ages appear in blue.

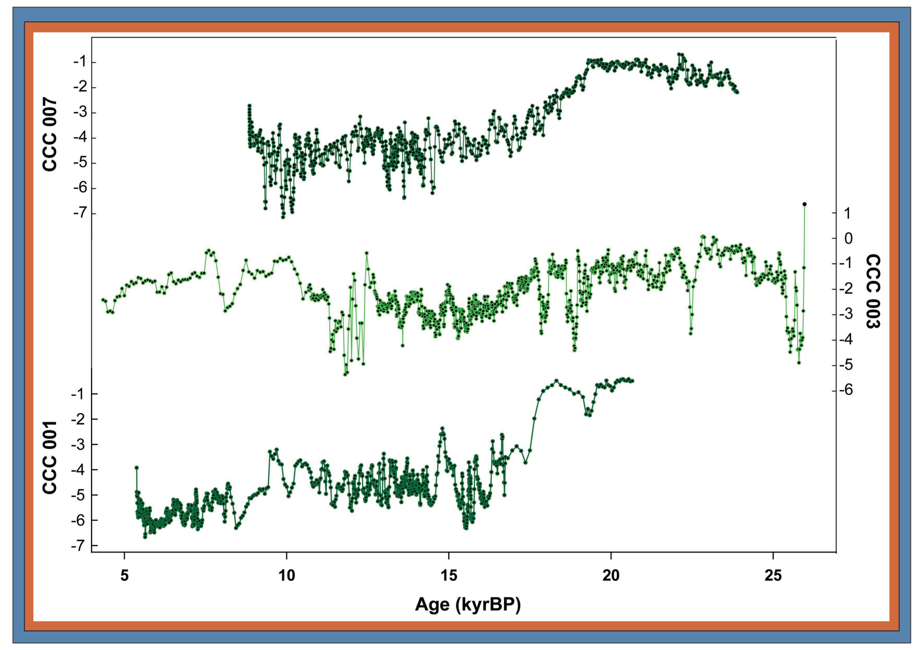


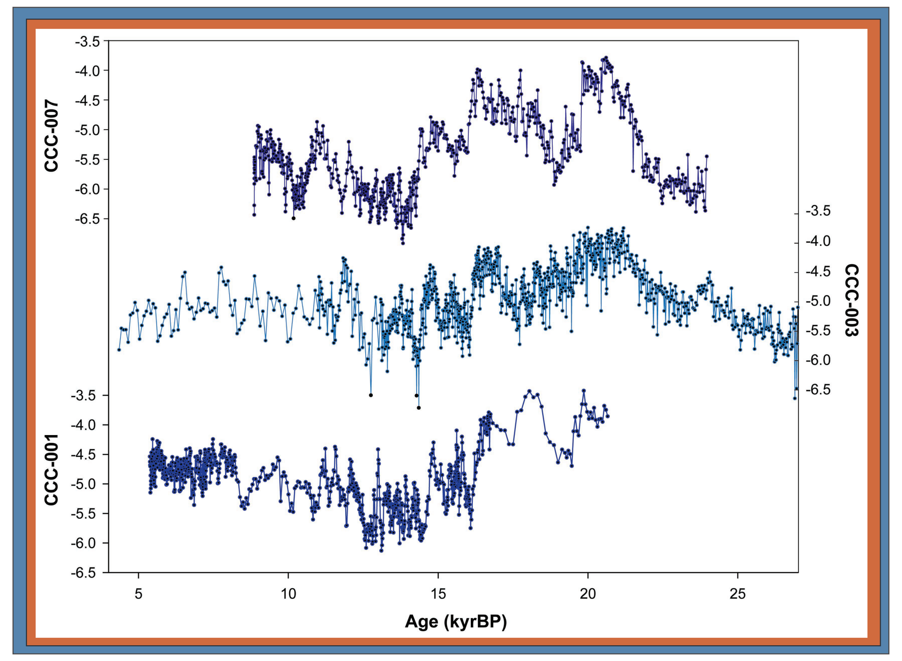
FIGURE 6 (above): d13C records for the three CCC speleothems. Although these stalagmites grew over largely the same time period and in very close proximity to one another, significant variablity exists between these three records.

FIGURE 7 (right): d18O records for the three CCC speleothems. These records largely agree with one another.

INTRA-CAVE VARIABILITY

Figures 6 and 7 serve to show the variability that can be seen between cave 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.



ACKNOWLEDGEMENTS

Funding for this work was awarded through NSF-P2C2 grant (#0903071), entitled *"Global Change and the Terrestrial Paleoclimate Record from Eastern North America: 600,000 years BP to Present"*. We acknowledge the generous instrument support and technical interaction provided by Brüker AXS, and especially, the kind, respectful interaction with Dr. Bruce Kaiser.

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