Title
Modern systematics and environmental significance of stable isotopic variations in Wanxiang Cave, Wudu, Gansu, China

Journal
Chinese Science Bulletin, 49(15)

ISSN
1001-6538

Authors
ZHANG, Ping zhong
Johnson, Kathleen R
Chen, Yimeng
et al.

Publication Date
2004

DOI
10.1360/03wd0382

Chinese Science Bulletin 2004 Vol. 49 No. 15 1649—1652

Modern systematics and environmental significance of stable isotopic variations in Wanxiang Cave, Wudu, Gansu, China

ZHANG Pingzhong[1], Kathleen R. Johnson[2], CHEN Yimeng[1], CHEN Fahu[1], Lynn Ingram[2], ZHANG Xinli[3], ZHANG Chengjun[1], WANG Sumin[4], PANG Fushun[5] & LONG Lude[5]

1. Center for Arid Environment and Paleoclimate Research (CAEP) and Key Laboratory of Western China's Environmental Systems, Ministry of Education, College of Earth and Environment Sciences, Lanzhou University, Lanzhou 730000, China;
2. Department of Earth and Planetary Sciences, University of California, Berkeley, CA, USA;
3. The Scientific Information Center for Resources and Environment, Chinese Academy of Sciences, Lanzhou 730000, China;
4. Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, China;
5. Wudu Administration Unit of Wanxiang Cave, Wudu 746000, China

Correspondence should be addressed to Zhang Pingzhong (e-mail: pzzhang@lzu.edu.cn)

Abstract **This paper presents the stable isotopic compositions from the cave dripwater and actively forming soda straw stalactites collected from Wanxiang Cave, Wudu, Gansu, located on the Qinghai-Tibetan Plateau and Loess Plateau transition zone, China. The $\delta^{18}O_{dw}$ and δD_{dw} of dripwater samples in the cave plot directly on the local MWL, constructed by using GNIP data from 3 sites surrounding the cave regions (Lanzhou, Xi'an, and Chengdu), the nearest site to the cave, suggesting that there is a close relationship between the $\delta^{18}O_{dw}$ of the cave water and the $\delta^{18}O$ of the precipitations. Using the measured $\delta^{18}O_{dw}$ and $\delta^{18}O_{mc}$ values from the mid-farthest parts from the cave entrance and the carbonate paleotemperature equation, the calculated temperatures range from 8.9 to 12.4℃, with the mean value of 10.7℃ and the temperature calculated at 8 locations in the farthest part of the cave is in the range of 10.1—12.4℃, with the mean value of 11.5℃, being consistent with the survey value(10.99℃)in the cave, slightly lower than the mean annual temperature (14.4℃) in Wudu. This suggests that modern speleothems are forming under isotopic equilibrium and their isotopic composition accurately reflects the mean annual temperature at the surface, indicating that the isotopic composition of the modern speleothems records local temperature change with credibility.**

Keywords: cave dripwater, hydrogen and oxygen Isotopes, speleothem, Qinghai-Tibetan Plateau and Loess Plateau, China.

DOI: 10.1360/03wd0382

At present, cave precipitates have presented huge potential in the study of past climatic change, e.g. precise dating of Dansgaard-Oeschger climate oscillations during the last glacial period[1], the variation of the East Asian Monsoon intensity[2,3] and close relationship between solar variability and the monsoon intensity[4]. But there are multi-answers in explaining oxygen isotopic compositions of the speleothems from different regions, e.g. $\delta^{18}Oc$ of speleothem calcite indicating the temperature effect dominant in Norway[5] and France[1], which is negatively related to the temperature in Israel[6], representing the amount of the precipitation; the $\delta^{18}Oc$ from the region influenced dramatically by monsoon is more complex[2–4], indicating the change of the monsoon intensity. Therefore, in order to interpret past stable isotope variations in speleothems, it is necessary to perform a thorough study of the modern carbonate-water system in the cave where they were formed[7,8]. Under equilibrium conditions, the $\delta^{18}O$ of calcite is a function of the $\delta^{18}O_{dw}$ (dripwater) and temperature[9]. If the $\delta^{18}O$ of both calcite and dripwater can be determined, the cave temperature can be obtained[10], which has been shown to approximate the mean annual surface temperature[11]. The $\delta^{18}O$ of cave water has, in general, been shown to be slightly enriched in ^{18}O relative to precipitation above the cave. The isotopic composition of cave waters, however, may exhibit complex variations on seasonal or even longer time scales, that is related to changes in annual precipitation amount, recharge rates, storm tracks, and evaporation in the epikarst[12]. To interpret $\delta^{18}O$ variations in fossil speleothems, we must show (ⅰ) the $\delta^{18}O$ of modern speleothems reflects the $\delta^{18}O$ of modern dripwater, and hence, modern precipitation, and (ⅱ) the speleothem calcite was formed in isotopic equilibrium with the water. Therefore, the aim of this paper is to determine the principle controls on the calcite isotopic composition, by studying the stable isotopic compositions between the cave dripwater and actively forming soda straw stalactites collected from Wanxiang Cave, Wudu, Gansu, for obtaining the past climatic and environmental information from cave precipitates in the long period of time.

1 Sampling and experimental

(ⅰ) Geographic environment and site. The study sites are located in the Qinghai-Tibetan Plateau and Loess Plateau transition zone, China, a key geographic location on the eastern edge of the Qinghai-Tibetan Plateau and the southwest edge of the Loess Plateau (Fig. 1), near the modern limit of the summer monsoon, being very sensitive to monsoon change. Therefore, close relationships between cave precipitates and climate will be considered to be more significant in study.

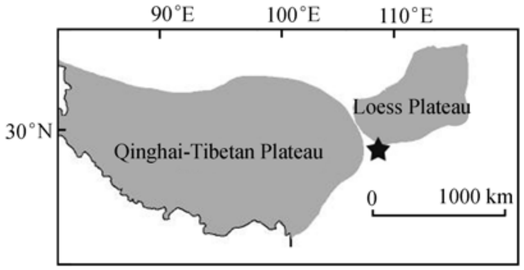

Fig. 1. Geographic location of the study region and Wanxiang Cave (ξ).

Wanxiang Cave (33°19′N, 105°00′E, 1200 m a.s.l.) in Wudu, Gansu, one of the largest caves in the northern China, is formed primarily in the Silurian limestone, and cave precipitates are shown by the way of large and various type of stalagmites and stalactite and stone-column etc., presenting a splendid sight. Loess deposits consist of the overlying soil outside cave. Therefore, it is of ideal conditions and advantageous geographic site in study of modern and past climatic changes.

(ii) Samples collecting and cave detecting. We systematically collected some samples of cave dripwater from entrance to the end of the cave during the fall (October) of 1999, at the same time some actively dripping, fine, un-consolidated and/or un-crystal growing soda straw stalactites were collected, sagged from the coping of the cave. And several glass slides were also put in the cave at the dripping location. The data-logger for detecting the temperature and relative humidity was set in the farthest site from the entrance.

(iii) Analytical method. Isotopic compositions of all samples were completed in the Center of Isotope Geochemistry, University of California, Berkeley. The δ notation represents hydrogen, oxygen data,

$$\delta = [(R_{sample}/R_{std}) - 1] \times 1000,$$

R is D/H and $^{18}O/^{16}O$, respectively.

(1) $\delta^{18}O$ and δD analysis of the water samples. $\delta^{18}O$ of cave dripwater samples was measured by the equilibrium method between water CO_2 Vacutainers; δD of all water samples will be measured using the method described by Venneman and O'Neil[13], and analyzed with a VG Prism II isotope ratio mass spectrometer. $\delta^{18}O$ and δD values will be reported relative to VSMOW. The precision for each analysis is ±0.01‰ for $\delta^{18}O$ and ±0.1‰ for δD.

(2) $\delta^{18}O$ analysis of the carbonate. 0.1 mm thickness of down-edge calcite scraped from un-consolidated and/or un-crystal growing soda straw stalactites with knife-blade was put into the preparation system——an Isocarb automated carbonate device attached to a mass spectrometer, reacted with 100% of phosphoric acid (following the method of McCrea[14]), and CO_2 produced was measured by an Optima mass spectrometer. Oxygen isotopic data are relative to the VPDB standard for carbonate samples, and the precision for each analysis is ± 0.1‰ for oxygen.

2 Results and discussion

(i) The local meteoric water line (LMWL). To characterized approximately modern precipitation, we are utilizing data from the last 15 years, obtained from the WMO/IAEA Global Network for Isotopes in Precipitation (GNIP)[15], from 3 sites surrounding the cave region, Lanzhou (36°N, 104°E, 1517 m a.s.l.), Xi'an (34°03 N, 108°93 E, 397 m a.s.l.), and Chengdu (31°N, 104°E, 506 m a.s.l.), to construct a local meteoric water line (Fig. 2). The weighted mean annual $\delta^{18}O$ values of precipitation are −7.2 ‰ in Xi'an, −5.7‰ in Chengdu and −7.1‰ in Lanzhou.

The local δD-$\delta^{18}O$ relationship differs slightly from the Global Meteoric Water Line (GMWL) of Craig[16] and from the Meteoric Water Line in China[17], with close slope and very different interceptors.

The δD and $\delta^{18}O$ values of the dripwater samples collected in the cave during 1999 plot directly on the local MWL (Fig. 2), suggesting that the cave water has not been significantly affected by evaporative processes in the epikarst[18]. Therefore, this result indicates that the isotopic

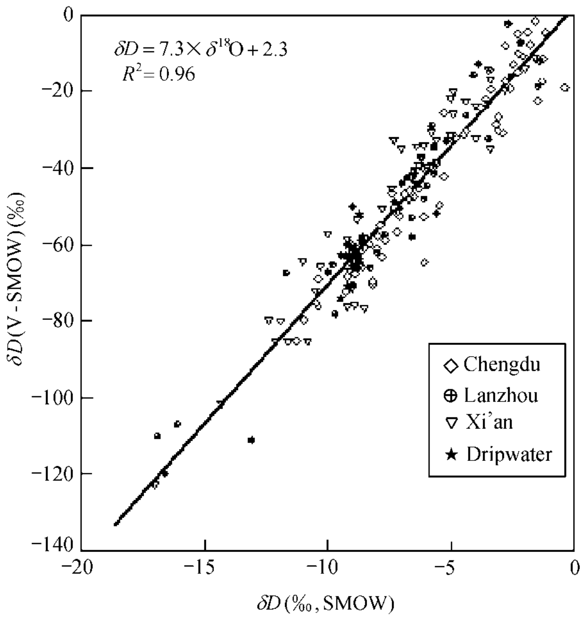

Fig. 2. The local Meteoric Water Line around Wanxiang Cave, Wudu, Gansu.

composition of dripwater in the cave reflects the isotopic composition of precipitation in the overlying cave at the surface. There is, however, a trend towards heavier dripwater δD_{dw} and $\delta^{18}O_{dw}$ values from the end of the cave towards the entrance of the cave. The $\delta^{18}O_{dw}$ value in Wanxiang Cave, based on 34 cave water samples collected in October 19th—23th, 1999, is ranged from –8.6‰ to –9.5‰ (mean –9.0‰), and the δD_{dw} is between –52‰ and –74.2‰ (mean –62.0‰, $n = 20$).

The smaller depletion of $\delta^{18}O_{dw}$ in the dripwater from Wanxiang cave relative to the precipitation in Xi'an and Lanzhou (ca. 2‰) reflects either a seasonal bias in the drip composition, the depletion of local precipitation relative to Xi'an and Lanzhou due to local topographic variations, or a combination of these factors, and the bigger depletion relative to the precipitation in Chengdu (ca. 3.3‰) results from the altitude effect, i.e. δD and $\delta^{18}O$ values of precipitation decline with the increase of the altitude[19], except for the depletion caused by either a seasonal bias in the dripwater composition, or the depletion of local precipitation.

(ii) The relationship between dripwater and oxygen isotope of modern soda straw stalactite. The $\delta^{18}O$ of the modern soda straw stalactite ranges from –6.4‰ to –8.4‰ (PDB), with the most enriched values found being towards the entrance, consistent with an enriched trend dripwater δD and $\delta^{18}O$ values in the cave, indicating evaporation near the cave entrance. Due to the close relationship between dripwater and local precipitation, using the measured $\delta^{18}O_{dw}$ and $\delta^{18}O_{mc}$ (modern calcite) values from 28 locations from mid to the farthest parts of the cave, and the carbonate paleotemperature equation[9,10]:

$$T = 16.9 - 4.2(\delta c - \delta w) + 0.13(\delta c - \delta w)^2,$$

the calculated temperatures (T) range from 8.9 to 12.4℃ (mean value of 10.7℃), and T from the 8 locations in the farthest part of the cave ranges from 10.1 to 12.4℃with the mean value of 11.5℃. The $\delta^{18}O_{mc}$ values of the received modern carbonate from two glasses of slides between September, 2001 and May, 2002 are –6.9‰ and –7.6‰ (PDB), respectively, in the range of $\delta^{18}O_{mc}$ values from the modern soda straw stalactites, indicating that modern dripwater is in situation of the supersaturation; and data logger presents unchanged temperature of 10.99 ℃ and relative humidity of 100% during August, 2001—January, 2003, supporting the above results from other ways. The data from TIMS U-series dating in the fossil stalagmites (unpublished data) indicate that there is a very high sediment ratio during the last interglacial (mean 0.045 mm/a), the $\delta^{18}O_{mc}$ values of 0.1 mm thickness of soda straw stalactites is an average of $\delta^{18}O_{mc}$ values deposited during 2.2 a by the calculation, i.e. the dating of the down-part calcite is less than 2 a, and carbonate formed during 1—2 a. Therefore, our results are exactly reflecting the isotopic system in modern water-carbonate of Wanxiang Cave.

Furthermore, according to the fractionation condition between the system of actively forming carbonate and liquid of the Hendy and Wilson[20], the isotopic equilibrium was formed in the stalagmite from the Wanxiang Cave, and its isotopic composition could indicate the annual average temperature outside the cave closely, being slightly lower than the annual average temperature (14.4℃) during 1961—1990 (the data from the weather station of Wudu, Gansu).

3 Conclusion

There is a close relationship between the δD_{dw} and $\delta^{18}O_{dw}$ values of the dripwater in Wanxiang Cave and local precipitation, indicating that the isotopic composition of the local precipitation has been influenced weakly on the cave dripwater by the overlying limestone and surface overlying soil. And the data from the $\delta^{18}O_{dw}$ of the dripwater and the $\delta^{18}O_{mc}$ of the down part in modern soda straw stalactite are closely related to the mean annual temperature outside cave, suggesting that modern speleothems are forming under isotopic equilibrium with water.

Acknowledgements The authors thank Kathryn Trueheart, Doug LaRowe and Cliff Riebe, Zhang Hong, He Jian, Wang Yongli, Wei Linjun for their help in doing fieldwork and analysis. This work was supported financially by the National Natural Science Foundation of China (Grant No. 40173010), the National Natural Science Foundation of China for Excellent Younger People (Grant No. 40125001), the National "973" Project (Grant No. 2002CB714004) and US Natural Science Foundation and National Geographic Society of US.

References

1. Genty, D., Blamart, D., Ouahdi, R. et al., Precise dating of Dansgaard-Oeschger climate oscillations in western Europe from stalagmite data, Nature, 2003, 421: 833—837. [DOI]
2. Wang, Y. J., Cheng, H., Edwards, R. L. et al., A high-resolution absolute-dated late Pleistocene monsoon record from Hulu cave, China, Science, 2001, 294: 2345—2348. [DOI]
3. Tan, M., Liu, D. S., Zhong, H. et al., Preliminary study on climatic signals of stable isotopes from Holocene speleothems under monsoon condition, Chinese Science Bulletin, 1998, 43(6): 506—509.
4. Neff, U., Burns, S. J., Mangini, A. et al, Strong coherence between solar variability and the monsoon in Oman between 9 and 6 kyr ago, Nature, 2001, 411: 290—293. [DOI]
5. Lauritzen, S. E., High-resolution paleotemperature proxy record for the last interglaciation based on Norwegian speleothems, Quaternary Research, 1995, 43: 133—146. [DOI]

6. Bar-Matthews, M., Ayalon, A., Kaufman, A., Late Quaternary paleoclimate in the eastern Mediterranean region from stable isotope analysis of speleothems at Soreq Cave, Israel, Quaternary Research, 1997, 47(2): 155—168. [DOI]
7. Hendy, C. H., The isotopic geochemistry of speleothems-Ⅰ, The calculation of the effects of different model of formation on the isotopic composition of speleothems and their applicability as paleoclimatic indicators, Geochimica et Cosmochimica Acta, 1971, 35: 801—824.
8. Li, B., Yuan, D. X., Lin, Y. S. et al., Oxygen and carbon isotopic characteristic of rainwater, drip water and present speleothems in a cave in Guilin area, and their environmental meanings, Science in China, Ser. D, 2000, 43(3): 277—285.
9. O'Neil, J. R., Clayton, R. N., Mayeda, T., Oxygen isotope fractionation in divalent metal carbonates, Journal of Chemical Physics, 1969, 51: 5547—5558.
10. Epstein, S., Mayeda, T., Variation of 18O content of waters from natural sources, Geochimica et Cosmochimica Acta, 1953, 4: 213—224.
11. Wigley, T. M. L., Brown, M. C., The physics of caves, in The Science of Speleology (eds. Ford, T. D., Cullingford, C. H. D.), London: Academic Press, 1976, 329—358.
12. Bar-Matthews, M., Ayalon, A., Matthews, A. et al., Carbon and oxygen isotope study of the active water-carbonate system in a karstic Mediterranean cave: Implications for paleoclimate research in semi-arid regions, Geochimica et Cosmochimica Acta, 1996, 60: 337—347. [DOI]
13. Venneman, T. W., O'Neil, J. R., A simple and inexpensive method of hydrogen isotope and water analyses of minerals and rocks based on zinc reahent, Chemical Geology, 1993, 103: 227—234. [DOI]
14. McCrea, J. M., On the isotopic chemistry of carbonates and a paleotemperatures scale, Journal of Chemical Physics, 1950, 18: 849—857.
15. IAEA/WMO, Global Network of Isotopes in Precipitation, The GNIP Database, 2003 (GNIP/isohis.iaea.org).
16. Craig, H., Isotopic variations in meteoric waters, Science, 1961, 133: 1702—1703.
17. Zheng, S. H., Hou, F. G., Ni, B. L., Study for hydrogen and oxygen of the precipitation in China, Chinese Science Bulletin (in Chinese), 1983, 13: 801—806.
18. Gat, J. R., Oxygen and hydrogen isotopes in the hydrologic cycle, Annual Reviews of Earth and Planetary Science, 1996, 24: 225—262. [DOI]
19. Yu, J. S., Yu, F. J., Liu, D. P., Hydrogen and oxygen isotopic compositions in meteoric water from eastern China, Geochemica (in Chinese), 1987, 16(1): 22—26.
20. Hendy, C. H., Wilson, A. T., Palaeoclimatic data from speleothem, Nature, 1968, 219: 48—51.

(Received February 11, 2004; accepted March 22, 2004)