Sedimentary evolution of the Dawan travertines and their geological environmental significance, Huanglong, China

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Abstract
The Huanglong travertine landscape, which is located on the eastern edge of the Qinghai-Tibet Plateau, is a World Natural Heritage Site with important tourism, aesthetic and scientific research value. However, no convincing travertine sedimentary age data have been reported for this area, and these late Cenozoic terrestrial carbonates have not been effectively included in studies of the Qinghai-Tibet Plateau geological environment. In this study, U-series dating of the travertines was carried out using a multi-collector inductively coupled plasma mass spectrometer to determine a time series for travertine deposition in the Dawan Valley (only a mountain away from Huanglong). The analyses of the processes operating during travertine deposition as the trench system evolved are performed based on a comprehensive study of the geological setting, structure and glacial landforms. The results suggest that travertine deposition in the Dawan Valley started at ca. 13 ka and had begun to wane by the early Holocene (ca. 7 ka). At the same time, the Huanglong Valley travertines began to be deposited on a large scale in response to a hydrological transition event. This event might reflect tectonic activity in particular, or possibly earthquakes or glacial retreat caused by climate warming. The findings reported here provide age data for late Cenozoic geological and environmental events such as climate variations and continental activity on the eastern margin of the Qinghai-Tibet Plateau. It also presents new insights for research on glaciation, tectonic activity and seismicity; however, depositional breaks and forcing factors need to be explored further.

KEYWORDS
Alpine karst, eastern margin Qinghai-Tibet Plateau, glaciation, Huanglong travertine, uranium series

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1 INTRODUCTION

Travertine/tufa, despite its controversial nomenclature, is a type of non-marine carbonate rock produced by structural factors, volcanism and karstification (Capezzuoli et al., 2014 and references therein). Laminated travertines are high-resolution geological information carriers that have received widespread academic attention (Ihlenfeld et al., 2003; Kele et al., 2008; Mangini et al., 2005; Pentecost, 2005). In recent years, travertine research has mainly focused on its influencing factors and mechanisms of formation; climate and environmental changes affect travertine deposition in such a way that it can be used as an indicator for reconstructing palaeoenvironment and palaeoclimate (Ghannem et al., 2020; Matsuoka et al., 2001; Priestley et al., 2017; Wang et al., 2020). Another aspect of innovative research involves the ‘travitonics’ proposed by Hancock et al. (1999), which is based on late Quaternary thermogenic travertine research in Turkey, the Aegean region of Greece, the Apennines in northern Italy and the basin-mountain region of the United States. Such research has greatly expanded and has been applied to the study of structural records in travertines from Europe, the USA and West Asia (Brogi et al., 2020; Mesci et al., 2008). In China, Liu et al. (2009b) and Wang et al. (2014) determined that travertine can be used as a palaeoclimate and environmental record and can constrain this information better than other approaches. There has been additional research on palaeoclimate and the carbon cycle in Huanglong, Jiuzhaigou, Baishuitai, Libo and other places in China (Liu et al., 2014; Wang et al., 2014; Yan et al., 2020). However, research on travertines in alpine karst areas (called the alpine type here, e.g. in the Huanglong region) remains insufficient, and more research is needed. There are basic issues that are poorly known, such as the start and end of travertine deposition in the Dawan Valley and the factors controlling its development.

A precise timescale is helpful to understand these issues. Various travertine dating methods have been used, including $^{14}$C (Srdoč et al., 1983), optically stimulated luminescence (OSL) (Zhang & Li, 2002), thermoluminescence (TL) (Engin & Güven, 1997), electron spin resonance (ESR) (Engin et al., 1999; Grün et al., 1988) and U-series disequilibrium dating methods (Harmon et al., 1980; Schwarcz, 2007; Srdoč et al., 1994; Sturchio et al., 1994). With continuous progress in dating techniques and multidisciplinary research, radioisotope systems such as $^{14}$C, OSL and ESR have become popular methods for dating physical chronology since the 1980s. However, Wang et al. (2004) and Liu (2014) observed that the carbon in travertine systems, especially endogene/thermogene travertines, does not contain $^{14}$C and is not suitable for dating by the $^{14}$C method. When analysing travertine samples from the Dawan Valley, Wang et al. (2006) also observed that the proportion of dead carbon added between different sampled layers was not constant in the case of an open carbon system, which may lead to $^{14}$C dating errors. Although the reliability of dating by OSL has been confirmed (Huntley & Prescott, 2001; Lai et al., 2014; Zhou et al., 2005), direct dating of carbonate rocks in this area is not applicable because the dating minerals used by OSL are quartz or feldspar. If obtaining the indirect depositional age of travertine is limited to measuring the marine debris in the area, this method is relatively simple, but improper sampling or incomplete protection from light reduces the intensity of the luminescence signal of the sampled quartz and affects the dating results (Chen, 2013; Mi & Zhou, 2012). The ESR method, which has the advantage of a large dating range, is not suitable for travertine because it requires complicated dating procedures and is affected by acid-insoluble impurities (Wang, 2005; Xue et al., 2003).

Throughout the development of travertine dating in the Huanglong area, the depositional times have been estimated based on laminae counts or chemical equilibrium calculations and $^{14}$C age profiles (Jiang, 1990; Zhu & Zhou, 1990). For example, the starting time of travertine deposition in the Huanglong valley can be roughly estimated by the depositional rate of sediment that covered the tower (Chi: Shita Zhenhai), that is, the thickness of the current tower covering divided by the tower construction time. Alternatively, other Quaternary geo-chronological methods (such as $^{14}$C and ESR spectroscopy) have been applied to constrain travertine ages in the Huanglong area (Cao et al., 2009; SGMBGST, 2001; Wang et al., 2010; Zhou & Li, 2004; Zhu & Zhou, 1990). Travertine deposition in this area is generally accepted to be roughly divided into different stages from 0.898 Myr to the early Holocene.

Although chronological studies have been conducted in the Huanglong area, the overlapping or disordered timescales obtained make it difficult to determine the relationship between travertines from the Dawan Valley and those in the Huanglong Valley. By adopting the latest multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) U-series chronological methods, a different understanding might be obtained. This study discusses the evolutionary characteristics of travertines in the Dawan Valley through U-series chronology, which is combined with information on the geological background and travertine sedimentology. These findings are important in understanding the dynamics of alpine karst on the eastern edge of the Qinghai-Tibet Plateau and provide guidance for the protection and sustainable development of the Huanglong World Natural Heritage travertine landscape.
2 | GEOLOGICAL BACKGROUND

Huanglong is located approximately 400 km from Chengdu in the northern Sichuan Basin in south-west China (Figure 1). Geomorphologically, it is located in the transition zone between the Qinghai-Tibet Plateau and the Sichuan Basin. Travertine is produced in several U-shaped glacial valleys, one of which is the Huanglong Valley. Due to the Wangxiangtai Fault (Figure 1), several springs with high calcium ion concentrations are exposed. The spring water extends for 3.6 km and forms pools, beach lands, waterfalls and caves and eventually discharges into the Fujiang River (a tributary of the Yangtze River).

Structurally, the study area is located at the contact zone of the Motianling block in the West Qinling orogenic belt and the Danba-Wenchuan structural rock slice in the Songpan-Garzê orogenic belt (Figure 1). Tectonic lines extend from east to west and include, from south to north, the Tanzigou Fault, Wangxiangtai Fault and Xueshan Fault (Cao et al., 2009; Wang et al., 2007). Bounded by the Wangxiangtai Fault, the southern
region mainly exposes Devonian to Permian soluble rocks such as limestones, dolomitic limestones and bioclastic limestones (Figure 1). The region exhibits strong tectonic effects, with fractured rocks and the development of joints, fissures and karst, which are conducive to the influx of rainwater and glacial meltwater. The karst water in the area migrates to the low-potential points of the deep topography and structure in the north, and the Wangxiangtai Fault prevents water from rising to form a transformation spring, which is a travertine source spring supply area. On the northern side of the Wangxiangtai Fault, there are insoluble rock groups, such as Triassic sandy slate, which is intercalated with limestone, and Silurian (north of the Xueshan Fault) slate, which is intercalated with thin limestone (Figure 1). The water-bearing capacity is poor, and this is a relatively water-resistant area. This layer is a runoff drainage area (Guo et al., 2002; Jiang et al., 2007, 2008; Wan et al., 2010). The northern Wangxiangtai Fault is conducive to spring water upwelling, and travertine is vigorously deposited.

3 | CHARACTERISTICS OF TRAVERTINE DEPOSITS IN THE HUANGLONG REGION

Huanglong is a typical alpine-travertine depositional system found on the eastern edge of the Qinghai-Tibet Plateau. However, with the development of tourism in the Huanglong area (Figure 2A,B) and with uplift and tectonic activity on the eastern margin of the Qinghai-Tibet Plateau, as well as climate warming, spring supplies and travertine deposition have decreased (Liu et al., 2009a; Qiao, 2008), which has led to travertine weathering, denudation, blackening and desertification (Figure 2C,D). The study of travertine evolution in the Huanglong area, especially comparisons of ancient and modern travertines from different valleys, is helpful for understanding the geological and environmental changes that have occurred in the area since the late Cenozoic. The direction of travertine evolution can serve as a reference for future evolutionary trends of travertines in the Huanglong Valley and thus provide theoretical support for the sustainability of this natural heritage area.

FIGURE 2 Field photographs of the Huanglong Scenic Area. (A) Colour pools, (B) Waterfall landscape, (C) Blackening of a fossil travertine beach and (D) Desertification of colour pools
The Dawan Valley is separated from the Huanglong Valley by only a single mountain (Figures 1 and 3). Springs also flowed along the eastward extension of the Wangxiangtai Fault during historical geological periods but did not form a continuous, well-developed travertine landscape similar to that seen in the Huanglong Valley. Travertines are exposed only in the upper and lower trenches of the Dawan Valley, while travertine deposits are absent in the middle part. No spring water is exposed at present, and only snow meltwater flows in the valley, which contains ancient travertines whose deposition has ceased.

The Dawan Valley is a typical ancient glacial valley with a length of approximately 5 km (Figure 3). The cross-section of the valley is V-shaped due to glacial activity in the Quaternary Period. Three travertine terraces are exposed from south to north along the valley (Figure 4).

Travertine platform 1 (32°43′20.60″N, 103°52′0.97″E) is located 3,666 m above sea level and north of the Wangxiangtai Fault below the outcrop position (Figure 4). Travertine was deposited along the slope in a nearly triangular travertine platform (Figure 5A). A section was exposed after erosion by surface water (Figure 5B). It is approximately 7 m high and consists of laminated travertines with obvious parallel bedding with layer thicknesses ranging from 1 to 3 cm. Overall, the thickness of the profile increases with depth, and the bottom is not reached. The ancient spring mouth is concealed by later residual slope accumulations.

Travertine platform 2 (32°43′42.2″N, 103°52′01.1″E) is located 3,448 m above sea level and situated approximately 4 km from the mouth of the Dawan Valley (Figure 4). Due to deep down-cutting by flowing water, the travertine body has dissolved and collapsed. The bottom boundary and stratification are clear. There is a complete longitudinal section of travertine in these travertine deposits (Figure 6A). Due to weathering and biological effects, the colours of this section are mixed, and the travertine varies in hardness and porosity. Some sections have brown-white interphase mixed laminae and show a clear contact relationship with the bottom bedrock (Wang et al., 2007). The travertine outcrop thickness is approximately 26.3 m, and the underlying Triassic Zagashan sandstone is in unconformable contact with the travertine (Figure 6A). The profile, from top to bottom, is (a) light yellow, yellow and horizontally laminated travertine with grey-white and brown-grey weathered surfaces (thickness = 5.80 m); (b) yellow-grey, light yellow and horizontally laminated travertine with a brown-grey weathered surface (thickness = 5.46 m); (c) yellow, yellow-white, wavy, curved and laminated travertine containing plant fossils with
weathered grey-white and brown-black surfaces (thickness = 8.83 m); and (d) yellow-grey, wavy, curved, layer-stratified travertine with a gravel layer lens containing plant fossils (thickness = 6.21 m).

Travertine platform 3 is located at the mouth of the Dawan Valley (32°45′36.36″N, 103°52′7.30″E) at an elevation of 2,959 m (Figure 4). It is a fan-shaped platform with a thickness of approximately 3–10 m and an area of approximately 59,000 m². The fan is approximately 235 m long, and 3–4 m laminated travertines with plant debris are exposed (Figure 6B). The middle of the platform is covered by slope debris on both sides, and locations near the fan tail are eroded by running water. The height of the exposed slope is greater than 5 m, and a laminated tree hole has developed.

4 | SAMPLING AND TESTING

Samples were collected from a typical section of the Dawan Valley (platform 2) and its mouth and tail (platforms 1 and 3) (Figures 4 through 6). Samples from the bottom of Huanglong Cave and the mouth of Huanglong Valley were powdered and sent to Xi’an Jiaotong University to measure U-Th compositions. Sample pre-treatments followed those of Edwards et al. (1987).

All test samples were obtained using microdrills to extract the white laminae (Figures 4 through 6). Powder samples were placed in small, clean Teflon beakers. Sufficient quantities of ultrapure water were added to submerge the samples. The powder samples were dissolved with 14 N HNO₃. After the sample reaction stopped with no further emergence of bubbles, a mixture of the ²²⁹Th-²³⁵U-²³⁶U spike of known composition was added along with HClO₄. After capping the reflux for approximately 2 hr, the samples were placed on an electric hotplate to fume to dryness to honeycomb shapes. The residue was dissolved in a solution of 2 N HCl and transferred to centrifuge tubes with a drop of FeCl₃ solution. The small beakers were washed again with 2 N HCl, transferred to centrifuge tubes and shaken well. Thick ammonia water drops were added to the centrifuge tubes until flocculent precipitation (Fe-U-Th coprecipitation) occurred. The tubes were centrifuged at 3,500 rpm for 7 min, and the supernatants were discarded. Ultrapure water was used to clean the precipitate, which was then
centrifuged and washed twice more. After the third washing, the supernatant was poured out; the precipitate was dissolved in 7 N HNO₃ and transferred to small, clean Teflon beakers. The insoluble silicate portion was dissolved with a HF-HClO₄-HNO₃ acid solution and transferred into beakers. The centrifuge tubes were washed with ultrapure water, and the water was transferred to the beakers. More HClO₄ was added, and the beaker was placed on an electric plate to evaporate to dryness. After drying, 14 N HNO₃ was added and evaporated several times to remove HF. The residue was dissolved in 7 N HNO₃, and transferred to a prepared anion exchange column for U–Th separation. The iron ions in the solution were removed with 7 N HNO₃; then, 6 N HCl was added, and U was collected with ultrapure water. HClO₄ was then added to the dissolved samples with collected U and Th; then, 14 N HNO₃ was added and evaporated twice, and the samples were dissolved with 1% HNO₃ (with a small amount of HF) and transferred to sample bottles for testing.

The U and Th solutions that were separated by the above method were subjected to isotope composition determinations using a Neptune MC-ICP-MS system. The detailed analytical procedures followed those of Cheng et al. (2013).

5 | RESULTS

The U and Th contents, activity ratios and chronological measurements are shown in Table 1. All samples have $^{238}$U contents of 91–2,470 ppb, with the vast majority >300 ppb. The contents of the $^{238}$U samples on platform 2 are nearly unchanged and range between 311 and 331 ppb, and the $^{232}$Th contents are relatively low at 4–13 ppb. The $^{232}$Th content of platform 3 is 24 ± 0.03 ppb, and the $^{232}$-
contents of the samples from platform 1 have anomalous characteristics that may be related to the samples themselves, but a reliable age was still obtained after correction. A similar sample is HLD-10, which is listed for reference only.

It is often believed that when $^{230}$Th/$^{232}$Th activity ratios are $<$20, the samples must be corrected for debris contamination. The $^{230}$Th/$^{232}$Th atomic ratios of the samples analysed in this article are between 41 and 237 (Table 1), and the activity ratios of some samples are $<$20. However, according to current global testing levels and instrumental accuracy limitations, these data are still acceptable. The age of the bottom of platform 1 is 11.25 ± 0.50 ka, the age of the travertine samples on platform 3 is ca 6.5 ± 0.65 ka, and the average age of the travertines in the nine samples from platform 2 is 12.97 ± 0.11 ka (mean squared weighted deviation [MSWD] = 0.50). The measured ages of the three powder samples that were drilled in the same layer, from bottom to top, are 13.04 ± 0.21 ka (MSWD = 0.80), 12.96 ± 0.14 ka (MSWD = 0.14) and 12.93 ± 0.28 ka (MSWD = 0.80). These measured ages are consistent with continuous travertine deposition. That is, from bottom to top, the travertine ages vary from older to younger in a continuous manner. The age measured at the bottom of Huanglong Cave is 5.75 ± 0.21, which is consistent with the data (6.11 ka) reported by Liu et al. (2009a) within the error range.

### TABLE 1 Age determination of travertine samples by MC-ICP-MS ($\pm 2\sigma$)

| No. | Sample  | $^{238}$U/ ($10^{-9}$) | $^{232}$Th/ ($10^{-12}$) | $^{230}$Th/$^{232}$Th (AT$\times 10^6$) | $\delta^{234}$U | $^{230}$Th Age (yr) (corrected) | $^{230}$Th Age (yr) (uncorrected) |
|-----|---------|-----------------------|--------------------------|---------------------------------|--------------|---------------------------------|---------------------------------|
| 1   | ZJ1-9   | 90.8 ± 3.4            | 89,557 ± 1797            | 107 ± 2                         | 62,787.1 ± 1,820.2 | 6.3994 ± 0.2410 | 11,453 ± 564                   |
| 2   | XK3-1   | 326.8 ± 0.5           | 11,472 ± 230             | 85 ± 2                          | 520.0 ± 2.1   | 0.1813 ± 0.0004 | 13,751 ± 38                    |
| 3   | XK3-2   | 323.2 ± 0.6           | 10,617 ± 213             | 88 ± 2                          | 499.6 ± 2.3   | 0.1746 ± 0.0004 | 13,413 ± 43                    |
| 4   | XK3-3   | 310.8 ± 0.4           | 13,365 ± 268             | 70 ± 1                          | 501.3 ± 1.9   | 0.1825 ± 0.0005 | 14,035 ± 45                    |
| 5   | XK2-1   | 321.6 ± 0.4           | 7,865 ± 158              | 120 ± 2                         | 510.1 ± 1.7   | 0.1777 ± 0.0003 | 13,560 ± 32                    |
| 6   | XK2-2   | 318.4 ± 0.4           | 8,795 ± 176              | 107 ± 2                         | 516.0 ± 1.8   | 0.1785 ± 0.0004 | 13,571 ± 36                    |
| 7   | XK2-3   | 330.8 ± 0.6           | 4,051 ± 81               | 237 ± 5                         | 528.9 ± 2.4   | 0.1758 ± 0.0004 | 13,229 ± 42                    |
| 8   | XK1-1   | 318.1 ± 0.6           | 12,143 ± 244             | 78 ± 2                          | 503.2 ± 2.7   | 0.1812 ± 0.0007 | 13,909 ± 64                    |
| 9   | XK1-2   | 324.8 ± 0.7           | 10,335 ± 208             | 91 ± 2                          | 502.9 ± 2.8   | 0.1758 ± 0.0005 | 13,470 ± 48                    |
| 10  | XK1-3   | 325.7 ± 0.4           | 6,215 ± 125              | 153 ± 3                         | 506.0 ± 1.9   | 0.1769 ± 0.0004 | 13,535 ± 37                    |
| 11  | ZJK-7   | 350.8 ± 0.2           | 22,169 ± 43              | 29 ± 1                          | 314.2 ± 1.3   | 0.1230 ± 0.0004 | 7,140 ± 33                     |
| 12  | ZJK-10  | 1,694.6 ± 2.3         | 278,011 ± 5,571          | 10 ± 0                          | 356.2 ± 1.9   | 0.1001 ± 0.0005 | 8,336 ± 46                     |
| 13  | HLD-1   | 228.7 ± 0.5           | 3,120 ± 63               | 105 ± 3                         | 602.3 ± 4.7   | 0.0829 ± 0.0015 | 6,059 ± 111                   |
| 14  | HLD-10  | 2,470.1 ± 3.8         | 52,863 ± 1,060           | 14 ± 0                          | 485.8 ± 2.1   | 0.0181 ± 0.0003 | 1,335 ± 25                     |
| 15  | LZH-1   | —                     | —                        | —                               | —             | —                               | —                               |

Note: Sample numbers 2–10 are from Wang et al. (2018a, 2018b).

### DISCUSSION

#### 6.1 Significance of U-$^{230}$Th estimates of travertine age in the Dawan Valley

Deposition of travertine in this area can be roughly divided into four stages (Table 2): (a) approximately 78,000 years; (b) 22,000–35,000 years; (c) 13,000–16,300 years (all deposited during the late Pleistocene); and (d) 0.898 Myr to Holocene accumulation. The most reliable data are the U-series dates first reported by Liu et al. (2009a). The travertine at the bottom of Huanglong Cave is believed to be 6,110 years old although it was largely deposited by 9,870 years ago, an age determined by high-precision uranium-thorium isotope dating at the University of Minnesota, USA (Liu et al., 2009a). However, a detailed datum isotope composition is not provided in their article. Based on these dating results, the times of travertine deposition in different valleys can be repeated and disordered. Within the same section of the same valley, travertine deposition ages may also be discontinuous, and there is no temporal continuity that reflects environmental changes.

This paper uses the most suitable U-$^{230}$Th dating method to redefine the oldest travertine age in the Dawan Valley. Initial deposition of the travertine in platform 2 was approximately 13 ka (Table 1). The ages of both travertine platforms 1 and 3 are younger than the initial
deposition age of travertine from platform 2. This is because, on the one hand, surface water had not eroded the base for platforms 1 and 3, while on the other hand, their samples were collected only from the lowest parts of their respective profiles (Figures 4 through 6).

6.2 | Time series of travertine sedimentary evolution in the Dawan Valley

Due to the strong late Indosinian orogeny triggering north-south and east-west compressional stresses (SGMBGST, 2001), the Triassic and earlier strata/rocks in the Motianling area were strongly fractured and deformed (Figure 1). At this stage, strong deformation shear folds and regional shear cleavage with excellent penetration were initially formed, which created preliminary spatial conditions for the migration of karst water (Xu et al., 1992). By the Early Cretaceous, the magma in the Earth’s crust exhibited a large overall increase, and then in the early Pleistocene, the south-eastern edge of the Motianling region pushed from north to south with the late Himalayan tectonic movement. Due to a large-scale thrust nappe structure, the crust was strongly uplifted (Chen, 1998). Therefore, the region experienced at least two compression-uplift cycles (SGMBGST, 2001). The tectonic activity associated with block extrusion and uplift provided favourable conditions for the formation of alpine karst in this area. Similar mechanisms are prominent in tectonically active regions around the world. For example, from a study of travertines in the eastern foothills of the Precordillera in Argentina, Sanchez et al. (2020) reported that active faults are usually contemporaneous with travertine deposits in karst development areas. Based on a study of travertines along the Gedez River, Turkey, climate and structure were reported to be the key driving forces of travertine landscape evolution, while underground fissures and faults act as pipelines for groundwater

### TABLE 1

| No. Sample  | 238U/235U (10−9) | 232Th/238U (activity) | 230Th/232Th (AT×10−6) | δ234U | 230Th/238U (corrected) | δ234Uini | 230Th Age (yr) (corrected) |
|-------------|-----------------|----------------------|----------------------|-------|-------------------------|---------|--------------------------|
| 1 ZJ1-9     | 90.8 ± 3.4      | 107 ± 2              | 62,787.1 ± 1,820.2    | 6.3994 ± 0.2410 | 11,251 ± 503 | 11,012 ± 626 |
| 2 XK3-1     | 326.8 ± 0.5     | 85 ± 2               | 520.0 ± 2.1           | 0.1813 ± 0.0004 | 13,751 ± 38 | 13,086 ± 472 |
| 3 XK3-2     | 323.2 ± 0.6     | 88 ± 2               | 499.6 ± 2.3           | 0.1746 ± 0.0004 | 13,413 ± 43 | 12,781 ± 449 |
| 4 XK3-3     | 310.8 ± 0.4     | 70 ± 1               | 501.3 ± 1.9           | 0.1825 ± 0.0005 | 14,035 ± 45 | 13,209 ± 529 |
| 5 XK2-1     | 321.6 ± 0.4     | 120 ± 2              | 510.1 ± 1.7           | 0.1777 ± 0.0003 | 13,560 ± 32 | 13,094 ± 331 |
| 6 XK2-2     | 318.4 ± 0.4     | 107 ± 2              | 516.0 ± 1.8           | 0.1785 ± 0.0004 | 13,571 ± 36 | 12,980 ± 373 |
| 7 XK2-3     | 330.8 ± 0.6     | 237 ± 5              | 528.9 ± 2.4           | 0.1758 ± 0.0004 | 13,229 ± 42 | 12,932 ± 168 |
| 8 XK1-1     | 318.1 ± 0.6     | 78 ± 2               | 503.2 ± 2.7           | 0.1812 ± 0.0007 | 13,909 ± 64 | 13,177 ± 522 |
| 9 XK1-2     | 324.8 ± 0.7     | 91 ± 2               | 502.9 ± 2.8           | 0.1758 ± 0.0005 | 13,470 ± 48 | 12,794 ± 449 |
| 10 XK1-3    | 325.7 ± 0.4     | 153 ± 3              | 506.0 ± 1.9           | 0.1769 ± 0.0004 | 13,535 ± 37 | 13,143 ± 586 |
| 11 ZJK-7    | 350.8 ± 0.2     | 29 ± 1               | 314.2 ± 1.3           | 0.1230 ± 0.0004 | 7,140 ± 33 | 7,128 ± 659 |
| 12 ZJK-10   | 1,694.6 ± 2.3   | 10 ± 0               | 356.2 ± 1.9           | 0.1001 ± 0.0005 | 8,336 ± 46 | 4,775 ± 2,523 |
| 13 HLD-1    | 228.7 ± 0.5     | 105 ± 3              | 502.3 ± 4.7           | 0.0829 ± 0.0015 | 6,059 ± 111 | 5,812 ± 207 |
| 14 HLD-10   | 2,470.1 ± 3.8   | 14 ± 0               | 485.8 ± 2.1           | 0.0181 ± 0.0003 | 1,335 ± 25 | 915 ± 298 |
| 15 LZH-1    | —                | —                   | —                    | —     | —                       | —       | 6,110 |

### TABLE 2

| Valley | Sampling location | Method | stage | Age (Ka) | Reference |
|--------|-------------------|--------|-------|----------|-----------|
| Dawan Valley | Travertine platform 2 | 14C+ESR | 1 | 40–78 | SGMBGST (2001) and references therein; Wang et al. (2007) |
| | | | 2 | 22–35 | |
| | | | 3 | 13–16 | |
| | | | 4 | ca 89 | |
upwelling (Maddy et al., 2020). Brogi et al. (2020) studied travertine in the Apennine Mountains, Italy, and reported that travertine deposition can be enhanced by faulting and associated seismicity. It is not difficult to observe that faults, climate and tectonic activity are closely related to travertine deposition.

Among the fossil travertines in the Dawan Valley, platform 2 is the most complete at present. The travertine samples collected at the sandstone unconformity can best represent the age of the initial travertine deposition in the trench system. The weighted average age is 12.97 ± 0.11 ka, older than the travertine ages observed at platform 1 and younger than the 14C ages determined by previous studies (Wang et al., 2006). Considering that direct determination of travertine ages via 14C produces a ‘dead carbon effect’ (Liu, 2014; Wang et al., 2004), the ages determined in this paper are more reliable. Additionally, the initial deposition age of travertine in the Huanglong area is not as old as previously reported but is within the late Pleistocene (ca 13 ka). The measured age of the middle section of platform 1 is 11.3 ka (Table 1), while the initial deposition age of platform 2 is from the late Pleistocene (ca 13 ka) to the early Holocene. These ages indicate a vigorous period of travertine deposition in this trench system. The travertine sample from platform 3 was collected from the edge of the platform and represents the period of waning travertine deposition. Its actual age is 6.5 ka (Table 1), which indicates that the travertine in the trench system gradually atrophied and was deposited during the early-mid Holocene.

The reasons for the absence of travertine deposits between platforms 2 and 3 are as follows. (a) This section is flat (Figure 2), and the substrate is mainly formed of highly permeable debris deposits, which might cause the formation of subsurface instead of surface stream water; hence, there is less surface sediment. (b) The mountains on both sides of the gully are fairly steep, and the residual slope that formed in the gully also covers the fossil travertines. Additionally, the alluvial-proluvial products carried by surface water in the later stage also played a role in submergence. (c) Platform 3 might represent an individual system because there may have been ancient springs on platform 3, and the satellite map shows obvious fault triangles (blue lines in Figure 2). This has been confirmed on the Huanglong ecological and geological map drawn by the regional geological survey team of the Sichuan Geological and Mineral Exploration and Development Bureau (SGMBGST, 2001). It is speculated that springs were exposed to the same fault for platforms 1 and 2, which is independent of platform 3, and that the spring water of platform 3 was mixed with traces of waters from the other two platforms.

### 6.3 Travertine deposition conversion between the Dawan and Huanglong valleys

In this study, the cessation of travertine deposition (6.5 ± 0.65 ka) measured on platform 3 from the Dawan Valley is consistent with the age (6.1 ka) measured by Liu et al. (2009a) and others at the bottom of Huanglong Cave using the same method. However, the age of platform 3 determined in this paper is older than the Huanglong Cave bottom age (5.7 ± 0.21 ka) (Table 1). This suggests that the period of spring activity from the Dawan Valley to the Huanglong Valley may have been ca 7.0 ka (middle Holocene) based on these reliable U-series age data. This is probably related to glacial retreat and tectonic activity, although other controlling factors may have been involved.

Stratigraphically, the rocks occurring to the north of the fault are inverted strata (Figure 7), consisting of sandstones and relatively impermeable strata. In contrast, the strata to the south of the Wangxiangtai Fault are carbonate rocks, which are relatively permeable. A syncline axis (see tendency of attitude and axis symbol in Figure 7) notably developed on the western side of the Huanglong Valley with a nearly north–south axis that dips to the south. Syncline development played a role in collecting water. Both the Huanglong and Dawan valleys are located on the eastern flank of the syncline axis and groundwater flows through the two systems. The difference is that the Huanglong Valley is closer to the syncline axis and is more conducive to water collection; that is, no fault causes groundwater to suddenly emerge in the Dawan Valley, by contrast, the groundwater there would tend to move towards the syncline axis in the direction of the Huanglong Valley. Such geological conditions determine the conversion relationship between the two drainage systems; that is, groundwater is more likely to migrate in the direction of the Huanglong Valley.

Based on this information combined with the ages of the two valleys (from the above analysis and Table 1), hydrological conversion occurred in the early Holocene (ca 7 ka), and travertine deposition in the Dawan Valley gradually waned, while that in the Huanglong Valley began across a large area. There are two reasons for this result, tectonic activity and climate change.

The Huanglong Valley travertines were influenced by tectonic activity. This area is located in China’s ‘North-South Seismic Zone’. Earthquakes can promote fluid circulation by creating new conduits and enhancing substrate permeability (Brogi & Capezzuoli, 2014). Springs in both the Dawan and Huanglong valleys are exposed along the same fault (Wangxiangtai Fault) at the same elevation (Figures 4 and 7); however, due to the existence of the syncline, groundwater associated with an earthquake
may migrate to the Huanglong Valley. This was shown by Liu et al. (2011), who studied the impact of the Wenchuan earthquake on Huanglong springs. They found that the great earthquake had a significant influence on the hydrogeochemistry of the source springs, which recharge the travertine-deposition stream. There are reports of level changes or even disappearances of groundwater in tectonically active regions due to earthquakes (Hosono et al., 2019; Ichiyanagi et al., 2020; Muir Wood & King, 1993), suggesting that hydrological changes and depositional breaks in travertine in this area may also be caused by earthquakes. Although seismites have not yet been identified, the tectonic activity in this area suggests that the transfer of groundwater may be related to earthquakes. There have been 20 large and small earthquakes in the area (SGMBGST, 2001), such as the recent magnitude 7.0 earthquake that occurred in Jiuzhaigou County, northern Sichuan Province, on August 8, 2017.

The warm period of the early Holocene led to glacial retreat and hydrological changes. The Younger Dryas cold reversal event has been well-studied on the eastern margin of the Tibetan Plateau (Wang et al., 2018), and its duration is consistent with the lowest boundary age (average age is 12.97 ± 0.11 ka) determined for the travertine in this study. Kaufman et al. (2020) collected and sorted 679 various proxy data extending over at least 4 kyr from around the world and concluded that the temperature increased before 7 ka in the Holocene. However, a multiproxy approach from lake and sediment cores indicated that a generally warmer period occurred between ca 8,500 and ca 6,000 cal yr BP, even ca 5,000 cal yr BP (Opitz et al., 2015; Zhang et al., 2017). The warm climate was conducive to the melting of glaciers and promoted the circulation of groundwater to karst water during that period.

According to the path of glacial retreat (Figure 8), glacial deposits in the Dawan Valley travertine depositional area are not developed, so travertine was deposited directly on sandstone (Figure 6). In contrast, travertine was generally deposited on the penultimate moraine in the Huanglong Valley (Figure 8). A typical terminal moraine developed on the upper edge of the coloured pool, and at least two moraines formed towards the tail of the gully. These characteristics indicate that the glacier was shrinking and that groundwater was gradually converted into subsurface flow of snow meltwater and rain, which accelerated the transfer of the groundwater system to the Huanglong Valley.

Glacial retreat was encouraged as the terrain in the snow area of the Dawan Valley formed a slope to the east where the snow was irradiated by the sun for a long time. The resulting snow meltwater formed surface runoff rather than infiltrating and forming karst water (Figure 8). In contrast, the landforms in the snow-covered area of Huanglonggou are relatively gentle and located on the shady side of Xuebaodong Mountain (Figures 3 and 8). The snow retention time here is long, which is more

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**FIGURE 7** Hydrological transformation map of Huanglong area (modified from SGMBGST, 2001)
conducive to the slow infiltration of snow meltwater and the formation of karst water. Therefore, the spring waters of Huanglonggou have continued developing to the present day.

In summary, after the last glacial period, travertine was deposited at the end of the Dawan Valley at 13 ka, with the main body deposited on platforms 1 and 2. Most of the spring water flowed downstream and entered the subsurface flow. The travertine deposits gradually decreased and reappeared on platform 3 and were mixed with new spring waters to be deposited again. That is, the amount of travertine deposited in the Dawan Valley in the current period was similar to that of the Huanglong Valley. Travertine was deposited from the spring outcrop to the gully mouth, but there was less travertine in the middle section. Tectonic activity and glacial retreat caused the groundwater to gradually migrate towards the Huanglong Valley in the early Holocene (ca 7 ka) so that the spring waters of the Dawan Valley gradually subsided while the travertine in the Huanglong Valley was still being deposited.

**FIGURE 8** Glacial landforms in Huanglong area
7 | CONCLUSIONS

1. Using the MC-ICP-MS U-series dating method, the travertine deposition time series in the Huanglong area was redetermined. Travertine deposition in the Dawan Valley began ca 13 ka with deposition gradually waning in the early Holocene (ca 7 ka). At this time, the Huanglong Valley travertine began to be deposited on a large scale.

2. The Dawan and Huanglong valleys directly underwent a hydrological transition in the early Holocene (ca 7 ka), which led to the gradual withdrawal of travertine deposits in the Dawan Valley, while the Huanglong Valley began to receive travertine deposits on a large scale. Hydrological transition events are induced by tectonic activity or earthquakes, as well as glacial retreat caused by climate warming.

3. The establishment of a travertine deposition time series in the study area provides an age reference for late Cenozoic geological and environmental events at the eastern margin of the Qinghai-Tibet Plateau. These data also provide new information for glacial, tectonic and seismic research; however, depositional breaks and forcing factors need to be further explored.

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