Revision 3

Origin of gem-quality turquoise associated with quartz-barite veins in western Hubei Province, China: constraints from mineralogical, fluid inclusion, and C-O-H isotopic data

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ABSTRACT

Two types of turquoise, including homogeneous Cu-rich turquoise and oscillatory zoned turquoise-planerite series, are recognized in association with quartz-barite veins hosted by Cambrian carbonaceous slates from western Hubei Province of China. Combined fluid inclusion and Raman microspectroscopic data reveal that turquoise-bearing barite-quartz veins contain three types of fluid inclusions (pure CH₄-N₂, carbonic-aqueous, and aqueous), suggesting the responsible fluid is of carbonic-aqueous composition with low oxygen fugacity. Pressure-corrected homogenization temperatures in quartz and barite show a range from 325 °C to 485 °C and 186 °C to 391 °C, respectively. Carbon, oxygen and hydrogen isotopic data suggest that the mineral-forming fluids have a mixed
metamorphic-organic affinity, in which the fluids have $\delta^{18}$O and $\delta$D values of 15.0 to 18.8 ‰ and -111 to
-93 ‰, respectively. Generally, the formation of quartz-barite-turquoise veins could be triggered by prior
metamorphic devolatilization, followed by the interaction of fluids with country rocks enriched in
carbonaceous material, which resulted in the leaching of Cu, Fe, P and Al from chalcopyrite, pyrite,
magnetite, monazite, xenotime, apatite, feldspar and muscovite in the wall rocks. Decomposition of the
organic matter in the carbonaceous slates, caused by regional metamorphism and deformation, could also
promote the concentration and transportation of necessary metals for the turquoise. Thus, we propose a
new model and suggest that the turquoise gem deposits in western Hubei Province of China belong to the
non-magmatic hydrothermal vein type deposit, not the previously proposed supergene origin. The
turquoise-forming fluids were characterized by the coexistence of two immiscible fluids of non-magmatic
affinity (i.e., moderate to high temperature and low salinity aqueous fluid and pure CH$_4$-N$_2$ fluid formed
by interaction with carbonaceous slates). The bluish green homogeneous turquoise in the metamorphic
quartz-barite-turquoise veins evolved towards the turquoise-planerite solid solution series as the
metal-leaching capability of the aqueous fluids decreased.

**Keywords**: turquoise, fluid inclusions, H-O-C isotopes, metamorphic hydrothermal origin, western Hubei
Province

**INTRODUCTION**

The name turquoise is derived either from the French *Turquois* for Turkish, or possibly from the
French *pierre turquin* (King, 2002). Turquoise is a hydrated copper aluminum phosphate and belongs to
the turquoise group, consisting of akeylite, chalcosiderite, faustite, planerite and turquoise. All of them
crystallize in triclinic system with the general formula $A_0.1B_0.4(PO_4)_{4.8}OH_{8}4H_2O$, where $Zn^{2+}$, $Cu^{2+}$, and $Fe^{2+}$ occur at the A site and $Al^{3+}$, $Fe^{3+}$, and $Cr^{3+}$ replace each other at the B site (Abdu et al., 2011; Jomeh et al., 2020). Turquoise is well known as a valuable gemstone for its impressive color and thus used for rituals, demonstrating social status and adornments (Fritsch et al., 1999). The oldest turquoise deposit has a history going back 70 centuries to ancient Egypt (Fritsch et al., 1999) and for now commercial sources of this gemstone are mainly exploited from Iran, United States, Egypt, Russia, Chile, South Africa, and China. Several minerals may resemble turquoise and are commonly known as semi-precious turquoise simulants. These include malachite ($Cu_2(OH)_2CO_3$) and a fairly unusual, green variety of lazulite ($MgAl_2(PO_4)_2OH_2$) (King, 2002). Chrysocolla ($Cu_2Al_2Si_2O_5(OH)_4\cdot nH_2O$) and dyed howlite ($Ca_2B_5SiO_9(OH)_5$) have also been used to imitate turquoise (Bernardino et al., 2016). Finally, amazonite ($KAlSi_3O_8$), a variety of microcline, can also be used to forge turquoise (Kile and Eberl, 1999; Bernardino et al., 2016).

Comprehensive research has concentrated on the mineralogy of the turquoise-group minerals (Fritsch et al., 1999; Taghipour and Mackizadeh, 2014; Dumanska-Slowik et al., 2020). Their compositional evolution during the ore-forming process, although critical for commercial exploitation, has rarely been studied in detail. Gem-quality turquoise of uncertain origin has been reported by Chen et al. (2012), Cejka et al. (2015), Rossi et al. (2017) and Dumanska-Slowik et al. (2020) from Iran, the United States and China. Previous researchers have suggested that this gemstone originates, in general, from: (1) supergene processes (meteoric water migrates along crack and fractures, leaching mineral-forming elements; Qin et al., 2015; Chen et al., 2012; Shi and Cai, 2011); (2) hydrothermal processes; and (3) hydrothermal-metasomatic processes. The hydrothermal turquoise (Type 2) precipitates from fluids which are enriched in Cu, Fe, Al and P from magmatic fluids, such as those from
porphyry intrusions. This type of turquoise can occur as nodules and veinlets in fractures, or in the cavities of quartz in the intrusive and volcanic rocks (Disbrow and Stoll, 1957; Szakáll et al., 2012). The generation of the hydrothermal-metasomatic turquoise (Type 3) could be linked to the interactions between hydrothermal fluids and wall rocks containing copper-bearing phases. Such a type of turquoise can also form as a result of the neoformation from preexisting minerals during reaction between phosphates (e.g., montebrasite) and copper-bearing fluid (Pirard et al., 2007; Ribeiro et al., 2021).

Turquoise deposits in western Hubei Province of China, which occur mainly in Lower Cambrian carbonaceous slates, are regarded as a significant gem source with superior quality. These account for the majority of China’s total turquoise production. However, the mineralogical evolution, derivation, and characteristics of the fluids that control the crystallization of gem turquoise remain open questions.

The representative turquoise deposit within the carbonaceous slates studied here is located at Zhushan County of western Hubei Province, which shows gem-level quality and has over 800 t ore reserves with an annual production from 50 to 129 t (Chen et al., 2012). In this paper, we present the geological, electron probe micro-analysis and laser ablation (LA) ICP-MS imaging analysis on the turquoise-group minerals combined with the fluid inclusions and stable isotope (H-O-C) data of the co-existing gangue minerals including barite and quartz, to better understand the formation of gem turquoise. Previous research speculated that the formation of the turquoise in Zhushan County can be ascribed to supergene processes involving the circulation of meteoric water along the fractures and fissures, followed by leaching the mineral-forming elements (i.e., Cu, P, and Al) from the host rocks (Jiang et al., 1983; Tu, 1996, 1997; Qin et al., 2015; Liu et al., 2020). Our results reconsider the turquoise as a non-magmatic hydrothermal mineral which is most likely formed by the interaction of metamorphic fluids, characterized by low salinity and moderate to high temperature, with organic matter.
from wall rocks. The results allow us to propose a new genetic type named the non-magmatic hydrothermal quartz-vein type turquoise deposit worldwide.

**REGIONAL AND DEPOSIT GEOLOGY**

The Qinling orogenic belt is distributed in the central segment of the Central China Orogenic Belt which was formed by the late Triassic collision of the North China Block (NCB) and the Yangtze Block (YB) (Fig. 1a; Chen et al., 2009). The Qinling orogenic belt, separated by the San-Bao Fault to the north and the Longmenshan Fault to the south, can be further subdivided into: (1) the Huaxiong Block as the southern margin of the NCB; (2) the north Qinling accretionary belt; (3) the south Qinling orogenic belt; and (4) the northern margin of the YB or the Songpan fold belt by the Luanchuan Fault, the Shang-Dan Fault and the Mian-Lue Fault from north to south (Fig. 1b; Li et al., 2015).

The Zhushan turquoise deposit studied here is located in the southwestern fragment of the Wudang Block which is one of the Precambrian crystalline basements of the south Qinling orogenic belt (Zhang et al., 1995). The Wudang Block is mainly composed of the Neoproterozoic Wudangshan Group which is unconformably overlain by the early Neoproterozoic Yaolinghe Group, late Neoproterozoic Doushantuo and Dengying Formations, and Paleozoic sedimentary rocks (Fig. 1c; Ling et al., 2002; Yue et al., 2014). The Wudangshan Group comprises a suite of greenschist facies metamorphosed volcanic-sedimentary rocks (Zhang et al., 2002). The early Neoproterozoic Yaolinghe Group occurs along the western edge of the Wudang Block and contains greenschist facies metamorphosed quartz-keratophyre tuff and pebbly tuff (Zhang et al., 2001). The late Neoproterozoic Doushantuo and Dengying Formations contain limestone, dolomite, sericite schist, and phyllite (Yue et al., 2014).

The Wudang Block has undergone multiple deformation events, leading to the formation of NNW-
trending folds and faults followed by the nearly EW- and NW-trending faults, produced by continental collision between the NCB and YB and local extension in the Early Paleozoic and Jurassic-Early Cretaceous (Hu et al., 2002; Zhang et al., 2019). Felsic intrusions are rarely observed in the region, while mafic dykes emplace into the Wudang Group along the NNW- and NW-trending faults and have undergone greenschist facies metamorphism as the result of continental collision (Zhou et al., 1998; Ling et al., 2007; Li and Zhao, 2016; Nie et al., 2016).

The turquoise deposits in the western Hubei Province are currently divided into three ore belts, where turquoise deposit in Zhushan County belongs to the south one (Fig. 1c; Tu, 1996). Lin et al. (2006) delineated the Cu-Ag-turquoise prospective districts in the north of the Fangshan-Zhushan Fault on the basis of the metallogenic geological conditions. They also linked the Ag-Cu-Zn geochemical anomalies to the regional dynamic metamorphism contributing the enrichment of copper, silver and ore-forming elements. Moreover, the Fangshan-Zhushan Fault was thought to significantly facilitate the migration of ore-forming fluids as conduits (Fig. 1c).

In particular, the distributions of the turquoise deposits are controlled by the strata of the Lower Cambrian Shuigoukou Formation (Fig. 1c). The Lower Cambrian Shuigoukou Formation is subdivided into two lithologic members. The lower part is composed of sericite quartz schist and siliceous rock interbedded with the carbonaceous slate with phosphatic nodules. The upper lithologic member is dominated by the limestone, interbedded with a small amount of mudstone (Li et al, 2012; Zhang et al., 2019). The majority of turquoise ores mainly distribute in the carbonaceous slates with phosphate nodules in the lower part of the Shuigoukou Formation.

The turquoise ore bodies occur in 20 to 100 m length and 1 to 25 m width in the carbonaceous slate layers, and the largest one is about 250-m-long and 10-m-wide. Turquoise in Zhushan County has two
occurrences: (1) quartz-barite vein, and (2) disseminated in the carbonaceous slates. The former mineralization (1) is typically hosted in continuous quartz-barite veins controlled by the faults and fractures along or cross-cutting the bedding planes of the carbonaceous slates, showing sharp contact between the veins and the wall rocks (Fig. 2a). The quartz-barite-turquoise associations not only occur as elongated lenses and/or veins, but also remain in concordance with the foliations of the carbonaceous slates (Fig. 2b), suggesting a ductile deformation regime during the coeval precipitation of quartz, barite and turquoise (Li et al., 2014). The disseminated turquoise (2) is characterized by massive structure and occurs as the block-shaped aggregates outside of the quartz-barite veins, of which synchronous ductile deformation is also noticed accompanied with the mineralization (Fig. 2c, d).

METHODS

Scanning electron microscope

A JEOL JCM-7000 environmental scanning electron microscope (SEM) fitted with an energy dispersive spectrometer (EDS) system was used to identify textural and compositional features of the carbonaceous siliceous slate and turquoise at the Collaborative Innovation Center for Exploration of Strategic Mineral Resources (CIC-ESMR), China University of Geosciences (Wuhan). Back-scattered electron (BSE) images were taken to distinguish compositional zonation of turquoise and mineral assemblages in the carbonaceous slates.

Electron probe microanalysis

Major element measurements of the turquoise group minerals were carried out at the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan) (GPMR-CUG), with a JEOL JXA-8100 Electron Probe Micro Analyzer (EPMA) equipped with four wavelength-dispersive spectrometers (WDS). Standards and samples were analyzed by 20 µm spot size
at an accelerating voltage of 20 kV and a beam current of 5 nA. Data were corrected on-line using a ZAF (atomic number, absorption, fluorescence) correction procedure. H2O contents were calculated by difference of analytical total to the 100 wt.% and then incorporated into the ZAF correction procedure. The peak counting time was 10 s for Al, P, Si, C, Cu, Fe, K and 20 s for Zn, Sr, Cr, Ti, V, Ti, Y, U and Ba. The background counting time was one-half of the peak counting time on the high- and low-energy background positions. The peak overlap of Ti Kβ on V Kα and V Kβ on Cr Kα was corrected by the interference correction program provided by the Japan Electron Optics Laboratory (JEOL) during the analysis. The following standards were used: pyrope garnet (Fe, Al), apatite (Ca, P), sphalerite (Zn), olivine (Si), barite (S), copper (V), sanidine (K), chromium (Cr), vanadium (V), rutile (Ti), barium fluoride (Ba), uranium (U). The calculation of their crystal-chemical formula was based on the 11 cations following the general formula from Foord and Taggart (1998).

**LA-ICP-MS mapping**

LA-ICP-MS analysis was undertaken at the CIC-ESMR, China University of Geosciences (Wuhan), using NWR 193 HE laser ablation system and He-Ar carrier gas (ca. 1.2 L min⁻¹ He and ca. 0.9 L min⁻¹ Ar) coupled to an Agilent 7900 single quadrupole ICP mass spectrometer. A trace element map was constructed from the sequential line analyses under the following conditions: laser beam size (Øspot) of 5 μm, scan speed (Vscan) of 17 μm/s, repetition rate of 20 Hz, and the total dwell time (Tacq) of 147 ms, corresponding a high X-spatial resolution of 7.5 μm calculated from the following equation:

\[
X_{\text{resolution}} = \sqrt{\text{Øspot}^2 + V_{\text{scan}}^2 \times T_{\text{acq}}} 
\]  

(1)

Each line analysis was composed of 10 s for background signal acquisition before the line ablation and 10 s for washout after the line analysis on the basis of a fast washout system (70% signal reduction in...
less than 0.4 s). Further detailed analytical processes are similar to those described by Ubide et al. (2015). NIST 610 glass was used as a calibration standard which was determined twice at the beginning, middle and end of the analysis under the same parameters relative to the 84 unknown lines for the entire mapping. Data reduction of trace elements distribution map was carried out by software Iolite v2.5 under semi-quantitative mode, using NIST 610 as the external standard.

**Fluid inclusion analysis**

Microthermometric determinations on a total of 134 fluid inclusions were carried out on doubly polished 100-μm-thick sections, using a Linkham THMS-600 Heating-Freezing Systems (from -196 °C to 550 °C) attached with a Zeiss AX-1 microscope at the CIC-ESMR, China University of Geosciences (Wuhan). The stage was calibrated with synthetic fluid inclusions at -56.6 °C, 0.0 °C and 374.1 °C supplied by SYN FLINC. The accuracy of the systems was ± 2.0 °C for homogenization temperatures and ± 0.2 °C during the freezing cycle.

Laser Raman spectroscopic analyses of the individual inclusion were performed on a Renishaw RM-1000 Raman spectrometer attached with a 514.5-nm Ar ion laser operating at 5mW as the source of excitation at the GPMR-CUG. The analysis of the inclusions was undertaken by the spectra from 1200 to 3800 cm⁻¹ with an accumulation time of 30 s per scan and a spectral resolution of 1 to 2 cm⁻¹. The longpass Rayleigh filter was 785 nm. All spectra were collected with the 1800 groove/mm grating, and a 20× objective or a 50× long working distance objective. Raman data were processed using the Labspec6 software (Horiba Jobin Yvon). The baseline subtraction was first operated automatically at the degree of 5-8 in the Labspec6 software. Peaks were then searched and fitted using Gaussian-Lorentzian functions with the level of 10 and the size of 30 according to the spectroscopic half width and peak intensity. The
laser beam size was 1 μm in diameter. Raman spectra and particular band assignments of individual fluid inclusion as well as relevant references were listed in the Table 3.

Stable isotope analysis

Oxygen isotopic compositions of quartz and hydrogen and carbon isotopic compositions of the fluid inclusions in quartz were determined at the analytical laboratory of Beijing Research Institute of Uranium Geology (BRIUG), China, using a MAT253 mass spectrometer. Two QtzI samples dominated by the primary and pseudosecondary type I and type II inclusions and one QtzII sample dominated by the type II and III inclusions were picked out from hand specimens and ground to about 60 mesh. Separated quartz grains were cleaned by pure 6 N nitric acid to remove other minerals and organic matter and were rinsed with deionized water. Oxygen was liberated from quartz by quantitatively reacting with pure BrF5 and heating with a CO2 laser, following the method of Clayton and Mayeda (1963). For H and C isotope analysis of fluid inclusions in quartz, grains were first heated at 150 °C for over 4 h to remove surface water and water from the secondary fluid inclusions. Then, mixed gases were released and collected under vacuum after the decrepitation of heated quartz above 550 °C; H2 was obtained from the reaction of H2O and zinc at 800 °C. Mixed CO2 and CH4 were also collected, frozen by liquid nitrogen, and separated by adsorbed materials for δ13C measurement using the method of Jin et al. (2021). The H-O isotope data were reported relative to Vienna-Standard Mean Ocean Water (V-SMOW) with internal precisions of better than 1 ‰ for δD and 0.2 ‰ for δ18O of a single analysis. Oxygen isotopic compositions in hydrothermal fluids were calculated following the equation:

\[ 1000 \times \ln \alpha_{\text{quartz-water}} = 3.38 \times \left(10^6 \times T^{-2}\right) - 3.40 \]  \hspace{1cm} (2)

where T in Kelvin (K) is the average pressure-corrected homogenization temperature from fluid
inclusion measurement as shown in Table 4, and $\alpha$ represents the equilibrium constant between the quartz and fluid at a given temperature.

RESULTS

Sample characterization

Disseminated turquoise occurring as blocks and anhedral masses in the country rocks has bluish green color and shows a waxy luster (Fig. 3a). On the other hand, turquoise distributed in the metamorphic quartz-barite veins along or cross-cutting stratigraphic horizons is characterized by either bluish green (Fig. 3b) or light green color (Fig. 3c, d) as well as vitreous and waxy luster. At the microscale, two types of turquoise were further recognized in the transmitted-light photomicrographs (Fig. 4a). The quartz-barite-turquoise veins and carbonaceous slates comprise the homogeneous bluish green turquoise (TrqI) in 3-5 mm which is mostly intergrown with euhedral barite (BrtI), surrounded by quartz (QtzI) (Fig. 4a). Additionally, quartz-barite veins contain light-green TrqII, characterized by more transparent crystal surface. TrqII replaces the TrqI along the crystal margin and is cut by fine-grained irregular (anhedral) barite veins (BrtII) as shown in Fig. 4a, suggesting both TrqII and BrtII are paragenetically later. Even though QtzI and QtzII show less variations in terms of their textures, they could be successfully distinguished according to the characteristics of the enclosed fluid inclusions as described later. Back-scattered electron (BSE) images of the bluish green turquoise in the country rocks and veins (Fig. 3a, b) show that all the TrqI samples are non-turbid, homogeneous, and mineral inclusions free (Fig. 4b). The TrqI intimately contacts with the QtzI and BrtI grains along smooth, wave-like boundaries, and there is no cross-cutting, alteration or dissolution observed in their contact zones. Light green TrqII (Fig. 3c, d) in quartz veins shows well defined oscillatory zonation and coexists
with Qtz, which is filled with anhedral Brt according to the BSE images (Fig. 4c).

In petrographic observations of the thin sections, the carbonaceous slate is composed of micro-fine to fine-grained quartz and muscovite, and medium-grained magnetite and pyrite (Fig. 4d-h). The deformed carbonaceous slate presents a lamination determined by quartz and muscovite framework with a strongly-developed foliation defined by alignment of elongated magnetite and fine-grained muscovite (Fig. 4d, e). The mineralogy of the carbonaceous slates includes quartz, anhedral coarse-grained barite, and apatite, with subordinate muscovite, distributed as fine flakes in the quartz (Fig. 4f, g).

Medium-grained pyrite occurs as disseminated euhedral to subhedral grains in the quartz or is overprinted by the medium to coarse-grained magnetite and barite (Fig. 4f). Monazite, rutile and xenotime are common but less abundant in the carbonaceous slate (Fig. 4h). Rock-Eval pyrolysis and the separation of soluble organic compounds of the carbonaceous slates have been conducted by Wang (2009) which illustrated that the carbonaceous matter is mainly composed of kerogen with a small amount of the hydrocarbons from the kerogen decomposition due to the thermal evolution. Yields of extractable soluble organic matter in the host rocks are fairly low in the range of 15.0 and 142.0 mg/g, which might be attributed to the high thermal maturity of the organic matter in these rocks (Hu et al., 2000).

Chemical compositions

Detailed EPMA compositional determination and the unit formula (apfu) of the turquoise group minerals are summarized in Table 1. Major element analysis of samples collected from Zhushan County indicates they belong to turquoise-planerite solid solution series.

Trq within the carbonaceous slate and the quartz-barite veins display similar chemical
compositions with an average calculated formula of

(Cu_{0.81}Fe_{0.08}Zn_{0.01}K_{0.01}Ca_{0.01})_{\Sigma 0.92}(Al_{6.05})_{\Sigma 6.05}(P_{1.01}O_{4})_{\Sigma 7.13} \cdot 4H_{2}O 

and

(Cu_{0.82}Fe_{0.07}Zn_{0.01}K_{0.01}Ca_{0.01})_{\Sigma 0.92}(Al_{6.05})_{\Sigma 6.05}(P_{1.03}O_{4})_{\Sigma 7.92} \cdot 4H_{2}O,

respectively. Generally, Trq\textsuperscript{I}
displays higher CuO, FeO\textsuperscript{T} and Cr\textsubscript{2}O\textsubscript{3} but lower Al\textsubscript{2}O\textsubscript{3} and ZnO contents than those of Trq\textsuperscript{II} (Fig. 5).

Trq\textsuperscript{I} shows a narrow range of CuO, FeO\textsuperscript{T} and Cr\textsubscript{2}O\textsubscript{3} contents of 7.69-8.35 wt\%, 0.57-0.74 wt\% and 0.11-0.19 wt\%, respectively. The Al\textsubscript{2}O\textsubscript{3} and ZnO concentrations of Trq\textsuperscript{I} are 37.01 to 37.98 wt\% and 0.07 to 0.10 wt\%, respectively. The Trq\textsuperscript{I} has a site of 0.88-0.97 apfu that is mainly occupied by Cu (0.78-0.84 apfu) and minor Ba and Ca (up to 0.01). Such invariable compositions of Trq\textsuperscript{I} are consistent with their homogeneity in BSE images (Fig. 4b). In the case of Trq\textsuperscript{II}, compositional differences are determined from the core to rim which show gradually depletion of CuO, FeO and Cr\textsubscript{2}O\textsubscript{3} and enrichment of Al\textsubscript{2}O\textsubscript{3} and ZnO contents (Fig. 5b-f), accompanied by cation deficiency in the A site and increase of H\textsubscript{2}O contents (Fig. 6). Correspondingly, the unit formula of Trq\textsuperscript{II} shows a relatively large compositional range of (Cu_{0.31-0.82}Fe_{0.03-0.07}Zn_{0.01-0.03}K_{0.01-0.02}Ca_{0.01})_{\Sigma 0.37-0.93}(Al_{5.92-6.37})_{\Sigma 5.92-6.37}(P_{1.03-1.07}O_{4})_{\Sigma 6.84-7.43} \cdot 4H_{2}O.

LA-ICP-MS elemental mapping

As shown in Fig. 7a, two types of turquoise are recognized. Anhedral Trq\textsuperscript{I} has compositional homogeneity and displays higher concentrations of Cu, Fe and Ti, evidenced on trace element maps (Fig. 7b-d). Elemental mapping of Trq\textsuperscript{II} reveals more pronounced laminations of concentric geometry. Both the core and rim of Trq\textsuperscript{II} grain share an enrichment of Zn and U in comparison with Trq\textsuperscript{I} (Fig. 7e, f). The core shows slightly higher Cu, Fe, Ti and Zn concentrations with a decrease trend towards the outer zones. Zhou et al. (2017) interpreted analogous zonation to an environment of changing chemical and/or physical conditions. Noticeably, Trq\textsuperscript{I} and Trq\textsuperscript{II} are overprinted by a thin vein enriched in Sr and La along
the turquoise-quartz contact (Fig. 7g, h).

**Fluid inclusion data**

Fluid inclusions in quartz and barite that coexisted with TrqI and TrqII are identified as fluid inclusion assemblages (FIA) according to their textural characteristics, illustrating groups of coeval inclusions (Goldstein and Reynolds, 1994). Primary inclusions were entrapped on the growing faces of the quartz during its precipitation, and the pseudosecondary inclusions were entrapped in fractures during the growth of the quartz which were commonly overgrown by a layer of the host minerals (Roedder, 1984). Accordingly, isolated fluid inclusions and FIA entrapped along the growing face of the mineral grain are presumed to be most likely primary (Fig. 8a-c). Intra-crystal FIA within the barite and quartz that stop at the grain boundary are assumed to be pseudosecondary (Fig. 8d-f).

Microthermometric measurements were conducted on the primary and pseudosecondary inclusions as shown in Table 2. Bulk density of fluid inclusions were calculated using the Flincor software (Brown, 1989) and the computer program from Bakker (1997, 2003).

Three primary types of fluid inclusions are identified according to the phase relations at room temperature and compositional data revealed by Raman spectroscopic analysis, including: aqueous-carbonic (Type I), carbonic (Type II) and aqueous-salt (Type III) inclusions. Type I inclusions have two phases at room temperature in which the liquid phase consists of C₃H₆, C₂H₆, and H₂O (Fig. 9a), whilst the vapor phase, occupying 5-90 percent of the total volume of the inclusion, is composed of CH₄ and N₂ (Table 3; Fig. 9b). The Type I inclusions could be further subdivided into two types on the basis of the degree of filling (F): Type Iₐ is vapor-rich (F > 0.6) and Type Iₘ is liquid-rich (F = 0.1-0.4). They are mainly found in the QtzI, coexisting with Type II inclusions as fluid inclusion assemblages.
(FIA) along the growing face of Qtz\(^I\), exemplified as a group of primary inclusions trapped coevally
(Roedder, 1984; Fig. 8b, c).

Accurate estimation of salinities of Type I inclusions is prevented because the melting temperatures
of clathrates are no longer a function of salinity as a result of the addition of the CH\(_4\) and N\(_2\) (Jia et al.,
2000). Thus, the simplified NaCl-H\(_2\)O system may be acceptable for the maximum salinity calculation
(Collins, 1979). In Qtz\(^I\), Type I\(_a\) inclusions have final ice melting temperatures (T\(_{m,\text{ice}}\)) ranging from -6.6
to -2.5 °C, corresponding to low salinities of 4.4 to 11.9 wt% NaCl equiv., with calculated densities of
0.36-0.58 g/cm\(^3\) (Davis et al., 1990). The total homogenization temperatures (T\(_h\)) of the Type I\(_a\)
inclusions range from 357 to 455 °C. Type I\(_b\) inclusions yield lower T\(_h\) of 217 to 340 °C and show
similar T\(_{m,\text{ice}}\) of -5.5 to -1.4 °C to those of Type I\(_a\) inclusions, equivalent to a salinity of 2.5 to 9.9 wt%
NaCl equiv., resulting in the density of 0.68 to 0.95 g/cm\(^3\). Some of Type I inclusions display clathrate
melting temperatures (T\(_{m,\text{clath}}\)) of 12 to 17 °C.

Type II inclusions are dominant in Qtz\(^I\) and Brt\(^I\) as individual or coexisting with Type I inclusions
along trails, and their abundances decrease in Qtz\(^II\). They are 10 to 20 μm in diameter and composed of a
single phase (liquid CH\(_4\)-N\(_2\) or vapor CH\(_4\)-N\(_2\); Table 3) at room temperature, which develop into
two-phase inclusions on cooling to < 90 °C. Estimations of initial ice melting temperatures (T\(_m\)) failed
because phase changes were invisible below -120 °C. Generally, they homogenized into the liquid phase
at temperatures between -145 and -127 °C and partly into vapor phase at -144 to -136 °C, which are
much lower than the critical point of pure CH\(_4\)(-82.6 °C), suggesting the addition of dissolved N\(_2\), which
is also evidenced by laser Raman analysis (Fig. 9c).

Type III inclusions mainly occur in Qtz\(^II\), Brt\(^II\) and Brt\(^I\) as isolated two-phase inclusions or
randomly coexisting with Type II inclusions, consisting of 5-25 vol% vapor and 75-95 vol% liquid.
Raman spectra of vapor and liquid phases from Type III inclusions show narrower and more symmetrical bands (Fig. 9d) than those from the pure water showing relatively broad signal, with a shoulder situated in lower wavenumbers, indicating the addition of salts (Lawler and Crawford, 1983; Mernagh and Wilde, 1989). Moreover, measurements of initial ice melting temperatures ($T_m$) for Type III inclusions are -24.2 to -21.3 °C, implying the NaCl is dominant among the dissolved salts (Davis et al., 1990). Based on the equations of Davis et al. (1990), aqueous fluids of Qtz II show relatively broad range of 1.6-9.3 wt.% NaCl equiv., whereas those from Brt I and Brt II fall into 1.2-4.1 and 1.8-6.6 wt.% NaCl equiv., respectively (Table 2). Type III inclusions in Brt I, Qtz II and Brt II homogenized into the liquid phase at temperatures of 195-355 °C, 136-315 °C and 222-341 °C (Table 2). As shown in the Fig. 10c and g, the $T_h$ of the Type III inclusions follow the unimodal distributions and decrease in the order of the Brt I, Qtz II and Brt II, displaying the mean values of 292 ± 43 °C, 239 ± 40 °C and 238 ± 11 °C, respectively. From the estimations of $T_h$ and salinity, the bulk density of Type III fluid inclusions in Brt I, Qtz II and Brt II are calculated as 0.60-0.81 g/cm³, 0.78-0.91 g/cm³ and 0.62-0.86 g/cm³, respectively.

Since the homogenization temperatures of fluid inclusions may not represent the actual trapping temperatures for the fluids, pressure correction is conducted followed the iterative method of Roedder (1984) and Fan et al. (2003). Isochores are obtained for the Type Ib CH₄-NaCl-H₂O inclusions and Type III NaCl-H₂O inclusions to constrain the pressure and temperature of the fluids, using Flincor software and the computer program of Bakker (2003) (Shepherd, 1986; Brown, 1989). For Type Ib CH₄-NaCl-H₂O inclusions in the Qtz I, the homogenization temperatures are 217 °C to 340 °C. The preliminary pressure is about 150 MPa from Fig. 11. Accordingly, the pressure correction at 150 MPa is about +130 °C (Roedder, 1984). Therefore, the trapping temperature for Type Ib inclusions is from 347 °C to 470 °C and the recalculated trapping pressure from Fig. 11 is greater than 300 MPa.
For Type III NaCl-H₂O inclusions in the BrtI, QtzII and BrtII, the analyzed homogenization temperatures are 195-355°C, 136-315 °C and 222-341 °C, corresponding to the low minimum pressure estimations of 50-150 MPa from Fig. 11. At such pressure, the corresponding temperature correction would be +130 °C in BrtI and +50 °C in QtzII and BrtII (Roedder, 1984). Thus, estimated entrapping temperatures for Type III inclusions in BrtI, QtzII and BrtII are 325-485 °C, 186-365 °C and 272-391 °C, and the recalculated trapping pressure is 150-250 MPa.

H-O-C isotope data

Hydrogen, oxygen and carbon isotope data were determined and listed in Table 4. The measured δ¹⁸O values of QtzI range from 20.9 to 22.4 ‰, and that of QtzII is 22.6 ‰. Hydrothermal fluids in equilibrium with QtzI have the calculated oxygen isotopic compositions of 17.3 to 18.8 ‰, using the quartz-water fractionation equation of Clayton et al. (1972) and the average pressure-corrected homogenization temperature of 422 °C. Calculated oxygen isotopic composition of hydrothermal fluids equilibrated with QtzII is relatively lower at 15.0 ‰ on the basis of the lower pressure-corrected homogenization temperature of 282 °C. The measured δD values of fluid inclusions in QtzI and QtzII are extremely negative and range from -111 to -93 ‰. Measured δ¹³C values of CO₂ and CH₄ in quartz fluid inclusions range from -27.6 to -22.5 ‰ and -40.8 to -30.3 ‰, respectively.

DISCUSSION

Mineralogy of the turquoise occurrence

On the basis of SEM-BSE images and EPMA data, two types of gemstone turquoise could be distinguished: TrqI and TrqII. TrqI appears homogeneous in SEM-BSE images, mainly comprises of turquoise endmember as shown by relatively high Cu (apfu) at A site (up to 0.84 apfu), low A-site...
vacancy and calculated water content (Table 1; Foord and Taggart, 1998). TrqII with oscillatory zoning
texture consists of turquoise endmember at the core and gradually evolves to the planerite endmember
towards the rim as a result of the decreasing A site occupancy, accompanied by increasing water content
(Fig. 6; Rossi et al., 2017; Jomeh et al., 2020). Of note, TrqII contains anomalous concentrations of Cr,
Zn, U, Pb and Sr, which are obviously discriminated from those of TrqI. Such compositional and textual
distinctions could be explained by different properties of non-magmatic hydrothermal fluids and
changing physicochemical conditions when TrqI and TrqII precipitated.

Source and evolution of mineralizing fluids

Microthermometric data combined with laser Raman spectroscopic analysis reveal that there are
three types of fluid inclusions in the quartz and barite associated with the formation of TrqI and TrqII: the
carbonic-aqueous fluid inclusion (Type I), pure CH$_4$-N$_2$ fluid inclusion (Type II), and the aqueous-salt
fluid inclusion (Type III), from which the presence of pure CH$_4$-N$_2$ fluids is significantly distinct from
the meteoric water that is represented by the H$_2$O-CO$_2$-NaCl system (Jenkin et al., 1994; Menzies et al.,
2014).

Coexistences of pure CH$_4$-N$_2$ inclusions (type II) and carbonic-aqueous inclusions (type I) within
trails along the quartz growth zones form distinct primary FIA in the QtzI (Fig. 8b, c), reflecting they
were trapped coevally (Roedder, 1984). Of particular note is that Type I$_a$ and I$_b$ inclusions with various
ratios of vapor to liquid display a large range of homogenization temperatures to both vapor and liquid
(Fig. 8c and 10c), which could be ascribed to various molar volumes of inclusions due to the randomly
mixtures of two phases in fluids resulted from the heterogeneous trapping of the immiscible fluids
(Ramboz et al., 1982). The Type II fluid inclusions represent the pure CH$_4$-N$_2$ fluids, and the Type I$_a$ and
fluid inclusions with various V/L ratios reflect the heterogeneous trapping of the aqueous fluids and pure CH$_4$-N$_2$ fluids. The coexistence of such three types of fluid inclusions is the most direct evidence of fluid immiscibility in which CH$_4$-N$_2$ might be exsolved from aqueous fluids due to the low CH$_4$-N$_2$ solubility limits (Ramboz et al., 1982; Xu, 1998; Chi et al., 2021). For such case, Type I$_a$ inclusions with higher vapor volumes commonly homogenize at temperatures far above the actual trapping temperatures, which are supposed to be geologically meaningless. Hence, Type I$_b$ inclusions with the lowest V/L ratios are thought to most likely represent the primary free liquid, and their molar volumes and homogenization temperature are taken to be the best estimations of those of the original liquid (Roedder, 1984).

In summary, the earlier turquoise-forming fluids contain all of three types of fluids, while later ones were primarily aqueous fluids with smaller CH$_4$-N$_2$ components, promoting higher salinity with less proportions of CH$_4$ and N$_2$ (Fig. 12a, b). Non-magmatic hydrothermal fluids in Qtz$^I$ and Brt$^I$ associated with Trq$^I$ were characterized by relatively high proportions of CH$_4$ and N$_2$, low salinities of 1.2-9.9 wt.% NaCl equiv. with most values lying between 6-8 wt.% NaCl equiv., and fairly high homogeneous temperature ($T_h$) of 325-485 °C (Table 2; Fig. 12a-c). On the contrary, the fluids responsible for the formation of Qtz$^{II}$ and Brt$^{II}$ coexisting with Trq$^{II}$ are devoid of CH$_4$ and N$_2$, but show similar salinities of 1.6-9.3 and 1.8-6.6 wt.% NaCl equiv. and lower average $T_h$ of 289 ± 40 °C and 288 ± 11 °C, respectively (Table. 2; Fig. 12a, b and d). In either case, the homogenization temperatures of the fluid inclusions are pronouncedly higher than those of the meteoric waters ranging from 17 to 35 °C (Shi and Cai, 2011), implying a much more differentiated source.

The main stage of fluid immiscibility events mainly occurred during the formation of the homogeneous Trq$^I$ (Fig. 12c). The immiscible fluids of two endmembers, namely pure CH$_4$-N$_2$ fluids
and aqueous fluids, have been rarely documented in the context of gem turquoise mineralization. Cox et al. (1995), Jia et al. (2000) and Fu et al. (2014) have attributed the presence of CH$_4$ to the interaction of magmatic and/or metamorphic fluids with carbonaceous slates during the metamorphism. As for the production of N$_2$ in fluids, previous studies confirmed that the release of NH$_3$ from wall rocks is a significant source of nitrogen following the equation at 600 K and 1.8 kbar (Bottrell and Miller, 1990; Shepherd et al., 1991; Andersen et al., 1993; Berwick et al., 2007):

$$3C+4NH_3 = 3CH_4 + 2N_2$$

Therefore, we speculate that the methane and nitrogen were leached into fluids as a consequence of extensive fluid-rock interaction.

This hypothesis is also confirmed by the stable isotopic compositions. Turquoise-forming fluids in equilibrium with quartz have δ$^{18}$O values of 15.0-18.8 ‰, showing a great affinity to those of metamorphic water (Fig. 13a; Taylor, 1974). Also, the absence of simultaneous magmatic activity in the study area precludes a magmatic origin for the fluids (Fig. 1; Zhang et al., 2019). Consequently, it is suggested that the turquoise-forming fluids are mainly metamorphic fluids.

Sedimentary rocks are generally composed of hydrous phyllosilicates, quartz, feldspars, carbonates and organic matter. Increasing temperature and pressure during prograde metamorphism will lead to the dehydration and decarbonation of the metasedimentary rocks, thus defining the nature of coexisting metamorphic fluids (Yardley, 1989; Ague, 2003; Stepanov, 2021). Besides, semi-quantitative calculation suggested that the devolatilization of a rock pile could form 2-5 wt.% aqueous fluids around the greenschist to amphibolite facies transition, indicative of a large volume of fluids (Phillips and Powell, 2010). Therefore, evidence above permits the quartz veins to be an end product of metamorphic devolatilization. Breakdown of chlorite, probably derived from the schist in the Lower Cambrian
Shuigoukou Formation (Zhao et al., 2017; Zhang et al., 2019), likely accounted for the generation of metamorphic fluids during the regional low greenschist facies metamorphism in the turquoise deposit following the reaction (Bebout and Fogel, 1992; Wang et al., 2019):

$$2 \text{Phengite} + \text{Chlorite} = \text{Muscovite} + \text{Biotite} + \text{Quartz} + 4\text{H}_2\text{O} \quad (4)$$

Such fluids, mainly distributed in situ at the grain-scale level throughout the rock, further promote the reactions with rocks and minerals, which eventually lead to the enrichment of elements in the fluids (Stepanov, 2021). With regard to the fluid compositions, they depend predominantly on the primary mineralogy of the source rocks (Yardley and Graham, 2002). The lack of minerals containing chlorine in the slates leads to the low salinity of the turquoise-forming metamorphic fluids.

Notably, the metamorphic fluids are characterized by significantly depleted δD values similar to those from waters that have reacted with organic matter (Fig. 13a; Taylor, 1974; Sheppard, 1986). The oxidation of CH$_4$ into CO$_2$ due to increasing fO$_2$ could dramatically deplete deuterium in fluids (Fu et al., 1991; Tarantola et al., 2007), while an increase of CO$_2$ contents is not observed in metamorphic fluids by microthermometry. Thus, possible interpretation of such low δD values might be the interaction between metamorphic fluids and organic materials (Kesler et al., 1997). Carbon isotope data are also useful for the determination of the potential sources in ore deposits (Fig. 13b; Hu et al., 2021; Ma et al., 2021; Niu et al., 2022): a marine carbonate source with δ$^{13}$C values of 0‰; an organic matter source with δ$^{13}$C value from -35‰ to -15‰ and a magmatic source with δ$^{13}$C values of -9‰ to -3‰. The carbon isotope compositions of CO$_2$ in the turquoise-forming system display obviously sedimentary organic carbon characteristics (-27.6 to -22.5‰; Fig. 13b). During the oxidation or hydrolysis of organic matter (i.e., graphite) at the temperature around 500 °C, strong carbon isotope fractionation occurs between the released gaseous CO$_2$ phase and the source rocks. The former prefers to be enriched
in $^{13}$C, leading to an increase of the $\delta^{13}$C values by almost +10 ‰ than those of the source rocks (Bottinga, 1968). Thus, the $\delta^{13}$C values of potential source rocks for the gaseous CO$_2$ are likely more negative as the measured $\delta^{13}$C$_{CO_2}$ values from fluid inclusions and cover the range of the reported bulk carbon isotope compositions of the Lower Cambrian Shuigoukou Formation (-35 ‰ to -15 ‰; Hou, 2008). Moreover, the measured $\delta^{13}$C values of methane from fluid inclusions between -40.8 ‰ and -30.3 ‰ are typically consistent with those produced by primary cracking of kerogen within the range of -45 ‰ to -31 ‰ (Schoell, 1980; Lueders et al., 2012). All these observations described above imply CO$_2$ and CH$_4$ in the turquoise-forming fluids were predominantly derived from the organic carbon coming from the carbonaceous slates by fluid-rock interaction.

Such unusual characteristics of C-H-O isotope compositions have been widely recognized regarding the formation of Pb-Zn-Mo-Au deposits, illustrating the interaction between ore-forming fluids and organic matter in the host rocks (e.g., Kelser et al., 1997; Xia et al., 2013; Zhou et al., 2015; Ma et al., 2021; Niu et al., 2022). Low $\delta$D values of fluid inclusions have been reported by Kelser et al. (1997) in the Mississippi Valley type (MVT)-forming brines, of which hydrogen and oxygen isotopes of fluids plot along the meteoric water line with $\delta^{18}$O and $\delta$D values of 2 ‰ and -41 ‰ and then evolved to the very low $\delta$D values of -87 ‰. Combined with the depleted $\delta^{13}$C values of CH$_4$ of inclusions, the mineralizing brines in the MVT deposits were identified as seawater that was modified by interaction with organic matter in the host rocks. Moreover, Niu et al. (2022) interpreted H-O isotope compositions of ore-forming fluids ranging from -111.2 ‰ to -85.5 ‰ and +9.0 ‰ to +11.5 ‰ as mixtures of magmatic fluids with the organic-containing water in the Suixian Mo deposit. The presence of CH$_4$ and the depleted $\delta^{13}$C values of CO$_2$ in the fluid inclusions also pointed to the thermochemical reaction between the magmatic fluids and organic matter from hosted metamorphic rocks.
In this regard, fluid evolution could be reconstructed for the turquoise deposit in Zhushan County. The turquoise-forming fluid system in the Zhushan County was initially CH$_4$-N$_2$-rich, high temperature (325–485 °C), low salinity (1.2-9.9 wt.% NaCl equiv.), and had low CO$_2$/CH$_4$ ratios, coexisting with immiscible CH$_4$-N$_2$ fluids. With decreasing temperature (186-391°C), fluids progressively evolved to become CH$_4$-N$_2$-poor, with lower salinity (1.6-6.6 wt.% NaCl equiv.) (Fig. 12). Throughout this process, metamorphic fluids locally interacted with organic matter from wall rocks, modifying fluid C-H-O isotope compositions.

The source of metals

Previous studies proposed that the turquoise deposits were sourced from the Lower Cambrian Shuigoukou Formation by weathering and leaching of the low-temperature oxidized surface water in a supergene environment (Tu et al., 1996, 1997; Qin et al., 2015; Liu et al., 2020). We agree with the general view that the turquoise-forming elements were sourced from the Cambrian carbonaceous slates. However, as discussed above, the Zhushan turquoise displays characteristics best explained by derivation from metamorphic fluids: high temperature, high contents of CH$_4$ and N$_2$, and H-O isotopic compositions distinct from meteoric water. Considering the above-mentioned features, the following discussion will concentrate on the essential origin of Cu, Fe, P and Al to form turquoise.

According to the previous geochemical analysis of the Shuigoukou Formation, the black slates contain appreciable amounts of Cu in the range of 10-1907 ppm (Wang, 2009; You et al., 2018), supporting the source bed for the turquoise mineralization. SEM results illustrate that the slate mainly consists of quartz, apatite, barite, muscovite, magnetite and pyrite with minor amounts of monazite, rutile and xenotime. Electron probe micro-analysis (EPMA) and X-ray diffraction (XRD) analysis have
also been carried out by Wang (2016), You et al. (2018) and Liu et al. (2021), which further refined the mineralogy of the carbonaceous slates with the presence of clay minerals including kaolinite and illite, and non-clay mineral assemblages of chalcopyrite, feldspar, calcite, dolomite and siderite in wall rocks.

As has been noted, minerals above are randomly dispersed in the carbonaceous slates, thus insufficient enriching Cu, Fe, Al and P to the economic value in the absence of remobilization as a result of weathering-leaching process, igneous intrusion, or metamorphic activity (Chen et al., 1990; Wang, 2009). Turquoise mixed with goethite, alunite, and jarosite in veins hosted in a shale unit have been attributed to a supergene origin at low temperatures (Crook and Lueth, 2014). Previous studies elucidated the oxidizing acid aqueous fluid, formed by the oxidation of pyrite and transformation of clay minerals in supergene environments, could promote the chemical reactions and ore metal transportations which further facilitated the formation of the turquoise (Crook and Lueth, 2014; Li et al., 2022).

Nevertheless, the absence of oxidized minerals such as malachite and hematite, coexistence of turquoise with quartz and barite, and high CH$_4$/CO$_2$ ratios in fluids of Zhushan turquoise preclude a supergene environment of formation. Moreover, no magmatic activity has been observed in the region (Fig. 1; Zhang et al., 2019). Therefore, we argue that metamorphic fluids generated from the dehydration and devolatilization of the carbonaceous slates produced the quartz-barite veins that deformed synchronously with wall rocks (Fig. 2, 4; Wang, 2009). In this process, we suggest that Cu, Fe, Ba, U, Ti, Al and P were remobilized from apatite, feldspar, barite, muscovite, chalcopyrite, magnetite, pyrite, rutile, monazite and xenotime in the slates during water-rock interaction, and transferred into fluids as chloride complexes in the function of the saline metamorphic fluids, ultimately to precipitate as gem turquoise in tectonically favorable sites (Chen et al., 1990; Yardley and Graham, 2002).

We interpret the compositional changes from turquoise (Trq) to turquoise-planerite solid solution
(TrqII) reflect evolution of the metamorphic fluids during the process of fluid-rock interaction. The fluid-rock interaction process was recorded by the evolution of fluid inclusions throughout the different stages. Legros et al. (2020) argued that the primary fluids from the intrusion in the Cantung tungsten deposit are CO2-rich which indicate their primary magmatic source, while fluids that interacted intensely with the surrounding limestone are CH4-rich. Correspondingly, carbonic-aqueous fluids with immiscible CH4-N2 fluids in TrqI-related samples (Fig. 12c) likely represent the initial fluids that underwent extensive interaction with surrounding carbonaceous slates, increasing the turquoise-forming elements in water. In contrast, the fluids related to the TrqII are CH4-N2-poor (Fig. 12d) and suggest the decreasing reactivity of fluids with the wall rocks, inducing the decrease of necessary metals for the turquoise (Table 1; Fig. 8).

Alternatively, such a pattern might be explained by the changing elemental partition behaviors during the precipitation of the turquoise. The uncertainties regarding fluid-rock and fluid-turquoise partitioning hinder the understanding of this mechanism. According to Skora et al. (2006), the decrease of Cu and Fe contents in the oscillatory zoning TrqII could also be interpreted by the transient matrix diffusion model that the TrqII have crystallized in the depleted matrix where Cu, Fe and other elements uptake were restricted by diffusion in the matrix surrounding the crystals. Nevertheless, neither explanation could account for the significantly decreasing CH4-N2 contents in the TrqII-forming fluids. Thus, we favor our interpretation that the decline of interaction between metamorphic fluid and metasedimentary rocks drove the geochemical evolution from homogeneous turquoise in TrqI towards turquoise-planerite solid solution in TrqII.

Another possible metal source (Cu, Fe, V, Zn and U) is envisioned on the basis of large amount of organic carbon in the Shuigoukou Formation, as indicated by the high total organic carbon (TOC)
content ranging from 0.46 to 2.43 % (Wang, 2009; You et al., 2018). Previous organic geochemical studies have confirmed there is a certain positive correlation between the metal contents (V, Ni, Zn, Cu, Os, Rh, Pt, Pd, Ir, Ru, Ag and U) and the total organic carbon content (TOC) in the Lower Cambrian Shuigoukou Formation (You et al. 2018). Such correlations have been reported in other carbonaceous rock-hosted Au-V-U ore deposits (Hu et al., 2000; Hou, 2008; Wang, 2009; Wang, 2016). Metals could be absorbed on organic matter before generating primary sulfides by the action of H₂S under reducing conditions (Chen et al., 1990). Moreover, experimental studies proved that gold-metallogenic elements could strongly combine with immature and low-maturity organic matter due to the action of chelation (Hu et al., 1993). Thus, organic-rich carbonaceous formations are supposed to highly promote the primary accumulation of metallogenic elements as the metal sources.

We interpret that the evolution of organic matter in the carbonaceous slates could facilitate the migration of metals in the aqueous fluids. Decomposition of organic matter would lead to the transformation from the organic carbon into gaseous H₂O, N₂, H₂S and hydrocarbon compounds (e.g., CH₄) which could self-extract metals or combine with metals as metal-organic complexes, promoting the release of metals from slates into fluids and their transportation in aqueous fluids (Breit and Wanty, 1991; Wang, 2009; Wang, 2016). Moreover, degradation and oxidation of organic matter could produce the organic acids, which are mainly composed of the negatively charged hydroxyl group, carboxy group and other function groups. Such groups have been assumed to significantly enhance the combination, adsorption and chelation of the metal ions, allowing soluble metals to migrate over long distances in aqueous fluids (Leventhal and Giordano, 1997; Hu et al., 2000; Qin and Zhou, 2009; Wang, 2009). Metal complexes will then break down from the metamorphic fluids owing to changes in pressure, temperature, and acidity in fluids, resulting in the formation of gem turquoise.
The turquoise deposit in Zhushan County, western Hubei Province, China, consists of turquoise-quartz-barite veins occurring along or cutting the bedding of the carbonaceous slates. New fluid inclusion and stable isotope data, combined with geological and geochemical evidence, substantiate a new genetic model for gem turquoise worldwide, termed the metamorphic quartz-vein type turquoise deposit. Devolatilization of Lower Cambrian carbonaceous slates transpired during regional metamorphism and deformation, and generated turquoise-forming metamorphic fluids characterized by low salinities (6-8 wt.% NaCl equiv.) at moderate to high temperatures (up to 450 °C).

Further support for this model comes from the δ¹⁸O values of turquoise-forming fluids (20.9-22.6 ‰), which are consistent with metamorphic fluids. The presence of CH₄-N₂ fluid inclusions, the remarkably depleted δ¹³C values of CO₂ and CH₄ in fluid inclusions from quartz (-27.6 to -22.5 ‰ and -40.8 to -30.3 ‰) and the extremely low δD values of turquoise-forming fluids (-111 to -93 ‰), suggest the intense interaction between the metamorphic fluids and the carbonaceous siliceous slates, leading to immiscibility between pure CH₄-N₂ and carbonic-aqueous fluids during the formation of the homogeneous turquoise. As temperature and reactivity with wall rocks decreased, so did the CH₄ and N₂ contents of fluids. Concurrently, the A site deficiency in the turquoise group minerals became more dominant, leading to the transition from gem turquoise to Cu-bearing planerite solid solutions.

Turquoise-forming metals (e.g., Cu, Fe, Ba, U, Ti, Al and P) are assumed to be sourced from the dissolving of various minerals (e.g., apatite, feldspar, barite, muscovite, chalcopyrite, magnetite, pyrite, rutile, monazite and xenotime) in the carbonaceous slates caused by the fluid-rock interaction. Moreover, decomposition of the organic carbon from the Shuigoukou carbonaceous slates might also contribute to the extraction and the transportation of the metals responsible for the formation of turquoise.
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**Figure captions**

**Fig. 1.** (a) A tectonic map of China showing the location of the Qinling Orogen (red square); (b) Tectonic subdivision of the Qinling Orogen comprising the Wudang Block (red square) where occur the turquoise deposits; (c) Geological map of the turquoise deposits in Zhushan County, western Hubei Province of China (modified after Yue et al., 2014; Zhang et al., 2019) (YB: Yangtze Block, NCB: North China Block).

**Fig. 2.** Photographs representing typical field occurrence of turquoise-bearing veins from Zhushan County. (a) Quartz-barite-turquoise vein as fracture infillings along or cross-cutting the beddings of the black carbonaceous slate; (b) coexisting turquoise and quartz as elongated lenses in the ductile deformed veins; (c, d) massive turquoise aggregates in the black carbonaceous slates show synchronous ductile deformation with wall rocks (Trq: turquoise, Qtz: quartz, Brt: barite, red lines outlining the elongated lens-shaped quartz, barite and turquoise, rock hammer as scale bar is approximately 13 cm in width).

**Fig. 3.** Photographs of turquoise from Zhushan County. (a) Massive bluish green turquoise in black slate; (b, c, d) Vein specimens consisting of quartz, barite and turquoise in different colors, i.e. bluish-green (b) and light-green (c, d) (Trq: turquoise, Qtz: quartz, Brt: barite).

**Fig. 4.** Transmitted- (a, d), reflected-light (e) and back scattered electron (BSE) images (b-c, f-h), showing representative mineralogical and textural features observed in hydrothermal veins and wall rocks: (a) oscillatory zoned turquoise (Trq\(^{\text{II}}\)) replacing homogeneous turquoise (Trq\(^{\text{I}}\)) along the margin, all included in quartz (Qtz\(^{\text{I}}\)) and cut by irregular barite vein (Brt\(^{\text{II}}\)); (b) quartz (Qtz\(^{\text{I}}\)) intergrowth with homogeneous turquoise (Trq\(^{\text{I}}\)) and euhedral barite (Brt\(^{\text{I}}\)); (e) oscillatory zoned turquoise (Trq\(^{\text{II}}\)) filled by anhedral barite (Brt\(^{\text{II}}\)) in quartz vein (Qtz\(^{\text{II}}\)); (d) preferred orientation of fine-grained quartz defining the foliations of the carbonaceous slate, showing typical rotational porphyroclast system; (e) intense...
foliation defined by alignment of elongated coarse-grained magnetite and fine-grained muscovite in the deformed carbonaceous slate; (f-h) medium to coarse-grained pyrite, magnetite, apatite, monazite, rutile and xenotime surrounded by quartz and muscovite (Trq: turquoise, Qtz: quartz, Brt: barite; Ms: muscovite, Ap: apatite, Mag: magnetite, Py: pyrite, Rt: rutile, Mnz: monazite, Xtm: xenotime).

Fig. 5. BSE image and characteristic chemical compositions collected from homogeneous turquoise (TrqI) and oscillatory zoned turquoise (Trq II) in from the rim to core: (a) BSE image; (b-f) major element compositions of turquoise-group minerals, where blue circles represent the compositions of TrqI, and dark green to light green circles refer to the various compositions of Trq II from the core to rim. EPMA data and corresponding unit formula (apfu) are from Table 1 (Trq: turquoise, Qtz: quartz).

Fig. 6. (a) Cu (apfu) versus A site (apfu); (b) Water contents (wt.%) versus A site (apfu) of all EPMA data of turquoise-group minerals from Table 1 (modified after Foord and Taggart, 1998).

Fig. 7. BSE image coupled with LA-ICP-MS elemental maps of a turquoise grain. (Trq: turquoise, Qtz: quartz).

Fig. 8. Photomicrographs of different types of fluid inclusions in quartz and barite: (a) Type I aqueous-carbonic fluid inclusion; (b, c) primary fluid inclusion trail containing Type I and II fluid inclusions with various vapor/liquid ratios along the growth faces of quartz; (d) pseudosecondary fluid inclusion assemblage consisting of Type II and III fluid inclusions in barite; (e, f) pseudosecondary fluid inclusion assemblage consisting of Type II inclusions at +23 °C and -190 °C in quartz. (Qtz: quartz, Brt: barite, S: solid phase in fluid inclusion as daughter mineral or accidently trapped solid).

Fig. 9. Laser Raman spectra of representative fluid inclusions in quartz and barite: (a) Raman spectrum of the aqueous phase in Type I fluid inclusion showing peaks of propane (2886 cm⁻¹), ethane (2943 cm⁻¹), and H₂O (3419 cm⁻¹); (b) Raman spectrum of vapor phase in Type I inclusion, showing significant contents of N₂ (2327 cm⁻¹) and CH₄ (2917 cm⁻¹); (c) Raman spectrum for Type II pure carbonic fluid inclusions, showing typical peaks of N₂ (2327 cm⁻¹) and CH₄ (2917 cm⁻¹); (d) Raman spectra for vapor and liquid phases of Type III aqueous-salt fluid inclusions, showing the narrower and more symmetrical water peaks.

Fig. 10. Histograms of (a, e) final ice melting temperature (Tm, sce), (b, f) salinity, (c, g) total homogenization temperature (Tb), (d, h) total homogenization temperature after pressure correction (Pressure-corrected Tb) of Type Ib, Type II and Type III fluid inclusions in quartz and barite. Average values with standard deviations are sourced from Table 2. (Qtz: quartz, Brt: barite).

Fig. 11. Isochore plots calculated from Type Ib H₂O-CH₄-NaCl and Type III H₂O-NaCl fluid inclusions identified in the quartz-barite-turquoise vein from Zhushan County, western Hubei Province of China.

Fig. 12. Paragenetic diagram and simplified sketch drawings showing the turquoise-related minerals and their enclosed fluid inclusions: (a) diagram showing relative timing of minerals associated with turquoise; (b) microthermometric charts showing ranges of pressure-corrected homogenization temperatures (Tb) and salinity, where fluid inclusions of different types are labelled with various colors, the same as Fig. 10;
(c, d) drawings showing the distributions of fluid inclusions of various types enclosed in the quartz and barite at room temperature. (Trq: turquoise, Qtz: quartz, Brt: barite, Fls: fluid inclusions).

Fig. 13. (a) Hydrogen versus calculated oxygen isotopic compositions diagram indicating ore fluid compositions from the turquoise deposit in Zhushan County, western Hubei Province of China. Also shown are fields for metamorphic fluids (Taylor, 1974), magmatic water (Hedenquist and Lowenstein, 1994), and organic water (Sheppard, 1986); (b) comparison of carbon isotopic compositions of CO₂ in the quartz fluid inclusions with data for various carbon sources (data after Veizer et al., 1980; Taylor, 1986; Ohmoto, 1972; Hou, 2008).

Table captions

Table 1. EPMA data (wt%) and calculated unit formula (apfu), based on 11 cations, for turquoise-group minerals from Zhushan County.

Table 2. Summary of microthermometric data of fluid inclusions from the quartz-barite-turquoise vein in Zhushan County.

Table 3. Raman spectra and band assignment of the individual fluid inclusion.

Table 4. Hydrogen, oxygen and carbon isotope analyses of quartz and fluid inclusions from the quartz-barite-turquoise vein in Zhushan County.

CRediT authorship contribution statement

WTL: Methodology, Formal analysis, Investigation, Writing - Original Draft; SYJ: Conceptualization, Resources, Supervision, Funding acquisition, Writing - Review & Editing; HZ and PLC: Methodology, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data and materials availability

All the data used in this paper are listed as Tables 1-4 within this paper, and are also available from the corresponding author on reasonable request.
Table 1

EPMA data (wt%) and unit formula (apfu), based on 11 cations, for turquoise-group minerals from Zhushan country.

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**Notes:** a: Calculated by difference; b: sum of particular components without water contents.
Table 2.
Summary of microthermometric data of fluid inclusions from the quartz-barite-turquoise vein in Zhushan country.

<table>
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<tr>
<th>Host minerals&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Inclusion type</th>
<th>T&lt;sub&gt;m&lt;/sub&gt;(°C)</th>
<th>T&lt;sub&gt;m,ice&lt;/sub&gt;(°C)</th>
<th>T&lt;sub&gt;b&lt;/sub&gt;(°C)</th>
<th>Pressure-corrected T&lt;sub&gt;b&lt;/sub&gt;(°C)</th>
<th>Salinity (wt. % NaCl eq.)&lt;sup&gt;2&lt;/sup&gt;</th>
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<td>Quartz (Qtz)&lt;sup&gt;2&lt;/sup&gt;</td>
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<td>357-455</td>
<td>/</td>
<td>4.4-11.9</td>
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<tr>
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<td>Type I&lt;sub&gt;b&lt;/sub&gt;</td>
<td>/</td>
<td>-5.5--1.4 (-3.2 ± 1.0)</td>
<td>217-340 (276 ± 37)</td>
<td>347-470 (406 ± 37)</td>
<td>2.5-9.9 (5.8 ± 1.8)</td>
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<tr>
<td>Quartz (Qtz)&lt;sup&gt;2&lt;/sup&gt;</td>
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<td>/</td>
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<tr>
<td>Barite (Brt)&lt;sup&gt;1&lt;/sup&gt;</td>
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<td>-24.2</td>
<td>-2.3--0.7 (-1.3 ± 0.6)</td>
<td>195-355 (292 ± 43)</td>
<td>325-485 (422 ± 43)</td>
<td>1.2-4.1 (2.2 ± 1.0)</td>
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<tr>
<td>Barite (Brt)&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Type II</td>
<td>/</td>
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<td>Quartz (Qtz)&lt;sup&gt;3&lt;/sup&gt;</td>
<td>Type III</td>
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<td>-5.2--0.9 (-2.8 ± 0.8)</td>
<td>136-315 (239 ± 40)</td>
<td>186-365 (289 ± 40)</td>
<td>1.6-9.3 (5.0 ± 1.0)</td>
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<td>Quartz (Qtz)&lt;sup&gt;3&lt;/sup&gt;</td>
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<td>-2.7--1.1 (-1.9 ± 0.6)</td>
<td>222-341 (238 ± 11)</td>
<td>272-391 (288 ± 11)</td>
<td>1.8-6.6 (4.1 ± 1.6)</td>
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Abbreviations: T<sub>m</sub> = First ice melting temperature; T<sub>m,ice</sub> = Final ice-melting temperature; T<sub>b</sub> = analyzed temperature of final homogenization; Pressure-corrected T<sub>b</sub> = temperature of final homogenization after the pressure correction; Type I<sub>a</sub> = vapor-rich aqueous-carbonic fluid inclusion; Type I<sub>b</sub> = liquid-rich aqueous-carbonic fluid inclusion; type II = carbonic fluid inclusion; Type III = aqueous-salt fluid inclusion.

<sup>1</sup> Mineral abbreviation is same as Fig. 4
<sup>2</sup> Salinities of type I and III inclusions calculated from the equation of Davis et al. (1990)
<sup>3</sup> In parentheses, bold number denotes the average value with standard deviations
Table 3

Raman spectra and band assignment of the individual fluid inclusion.

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<th>Wavenumber/cm$^{-1}$</th>
<th>Assignment</th>
<th>Raman shift of peak/cm$^{-1}$</th>
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Table 4
Hydrogen, oxygen and carbon isotope analyses of the turquoise deposit in Zhushan Country.

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<th>Min¹</th>
<th>Average pressure-corrected T₀(°C)</th>
<th>δ¹⁸O_{Qtz}(‰)</th>
<th>δ¹⁸O_{fluid}(‰)²</th>
<th>δD (‰)</th>
<th>δ¹³C_{CO₂}(‰)</th>
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Abbreviations: Sample no. = sample number; Min = minerals;
¹ For mineral abbreviation see Fig. 4
² δ¹⁸O values of fluids in equilibrium with quartz were calculated using the equation of Clayton et al. (1972)