

## Carboniferous-Permian Carbon Isotope Stratigraphy of Succession from Xainza (Tibet), China

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Carbon isotopic composition recorded several major events in the development and evaluation of the earth. Possibly, Carbon isotopic composition is the cause or the result of such big events. Carboniferous-Permian, as the most important turning point of earth development history, developed the biggest Phanerozoic glacier whose drift beds are widely distributed among the various ancient Gondwanaland continental blocks. We can carry out comparative study with each continental block. Good outcrop of Chinese carboniferous sequence and continuously developed stratum are fit for building chronostratigraphic framework and proceeding global comparative studies. The paper researches on carbon and oxygen isotope of the samples from Carboniferous-Permian stratigraphic boundary which are collected from the east Yongzhu bridge of Xainza County in Tibet Autonomous Region, China. Moreover, we compare it with carbon isotope curve of the same period coming from the Kongshan section in Jiangsu Province, the Zhongdi section and Naqing section in Guizhou Province of the south China. It is the first time to propose the concrete beds location of Carboniferous-Permian stratigraphic boundary of Xainza district which is one set of yellow limestone below the Laga Formation. In previous studies, index fossils were not found in Laga Fm. It was roughly defined as a diachronous lithostratigraphic unit simply by 26 genera of brachiopods and 8 genera of rugose corals. In this paper, based on a comparative study with carbon isotope curves, the Laga Fm. is identified as a time-transgressive formation.

[**Keywords:** Tibet, carbon isotope, Carboniferous, Permian, boundary, glacial period]

### Introduction

Carboniferous-Permian is the most important turning point of the earth development history. During the period, while the sea level lowered to the bottom line of Phanerozoic eons, the developing glacial period, as the biggest Phanerozoic glacial period, has great significance in geological history which was the mark that the world has entered carboniferous period from Devonian “the Warm earth”. The carboniferous period-the early Permian “ice earth” has continued for approximately 100m.y<sup>1</sup>. and has arrived last glacial maximum in a time between late carboniferous and early Permian period<sup>2,3,4</sup>. The collision between Gondwanaland plate and Russian plate creating global circulation and climate changes may be possible causes for the event<sup>5,6,7,8,9,10</sup>. The ice formation of Gondwanaland during late Paleozoic not only impacts

the climate and sedimentary characteristics of high latitude area in south hemisphere but also changes the whole atmosphere composition and sea atmosphere<sup>11</sup>. It also has great influence on the evolution of communities and biological group on the land and under the sea. The study of Carboniferous-Permian sedimentary recordings is beneficial for us to understand Carboniferous-Permian ancient climate, ancient sea, and ancient ecological characteristics as well as the function of carbon cycle on climate and environment changes during geological history<sup>11</sup>.

The formation and evolution of the Qinghai-Tibet Plateau were related with the collisions between Eurasian and blocks or continents from Gondwanaland since the early Paleozoic<sup>12,13</sup>. It is generally considered that the Lhasa block had cracked

in Gondwanaland before collision of Qiangtang block in Mesozoic<sup>12,13,14,15,16</sup> (Fig.1). Xainza Region belonged to Lhasa Block and originated from a

uniform landmass at the norther margin of Gondwanaland.

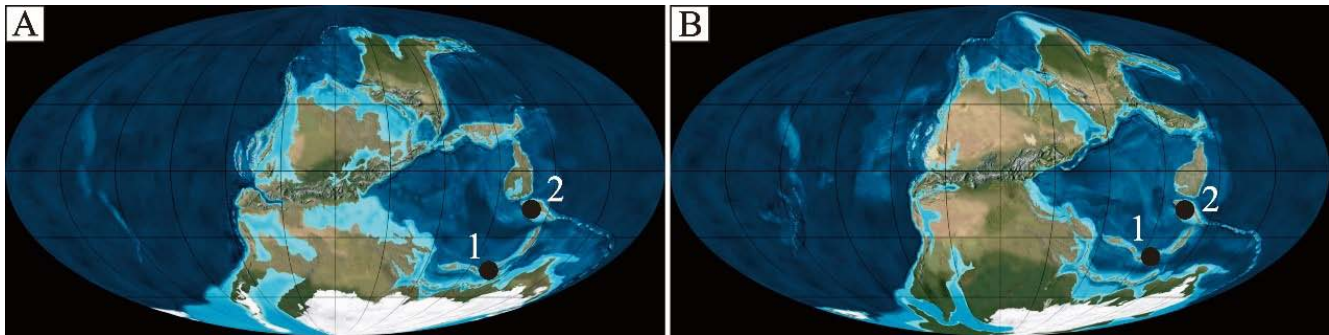


Fig. 1—Palaeogeography and position of study areas:  
A-300Ma Pennsylvanian, 1- Tibet, 2- Yangtze, (<http://jan.ucc.nau.edu/~rcb7/300moll.jpg>),  
B- 280Ma Early Permian, 1- Tibet, 2- Yangtze, (<http://jan.ucc.nau.edu/~rcb7/280moll.jpg>)

In stratigraphy study, initially, carbon isotope variation was used as a complimentary marker for stratigraphic boundary delineation and comparisons. With the discovery of abnormal negative carbon isotope which is corresponded to the abnormal black shale sedimentary positive carbon isotope and organism extinction, geologists connect causes of carbon isotope fluctuation with changes in ancient sea and ancient climate. In this way, carbon isotope alteration explanation deepens into linkage coupling process between sedimentary, hydrosphere, atmosphere and biosphere in geological history.

Carbon is the basis for the survival of life and also the most important element in biosphere. Quantum mechanical effects led to different physicochemical properties of element isotope and eventually formed a cycle of elements. There were two carbon cycles on the earth: biological cycle and chemical cycle of carbon. The cycle was 20 years, millions of years or even a longer scale. Carbon cycles included negative and positive feedback. The former made carbon dioxide in the earth's atmosphere and the global temperature increasingly lower, while the latter was just opposite. The reduction of atmospheric carbon dioxide was a result of the increased amount of atmospheric carbon dioxide dissolved by seawater. The reason was that the increase of the organic production rate of surface seawater led to a drop of inorganic carbon content in surface seawater and thus more atmospheric carbon dioxide was dissolved<sup>23</sup>. The increase of organic production rate and burial

enhanced  $\delta^{13}\text{C}$  value in carbonatite. The measurement of  $\delta^{13}\text{C}$  value in carbonatite and organic substances and synchronous change in  $\delta^{13}\text{C}$  value in long-distance space were widely used to discuss changes in global carbon reserves<sup>23,24</sup>. But still some people hold different opinions. The traditional measurement of carbon isotope ratio in Paleozoic carbonatite was done on brachiopod, whose shell was low-magnesium calcite, for brachiopod shell was more capable of withstanding diagenetic alteration<sup>25</sup>. Bulk-rock carbonatite also applied to the analysis of carbon isotope. It wasn't not altered under diagenesis<sup>24,26</sup>.

### Materials and Methods

The data which is used in this paper consists of two parts. The first part of data has been collected from the reference 23, the carbon and oxygen isotopes of the three sections in the South China were 845 and 854 values<sup>26</sup> (Fig.2A, 2B). The carbon and oxygen isotopes of the Kongshan section were both 76 values, and were both 123 values in Zhongdi section. Values of carbon and oxygen from Naqing section were respectively 646 and 655. The second part of data has been tested, the samples of data are from Luogong area, east of Yongzhu bridge in Xainza county (Fig.2A, 2B, 2C). The stratum of late Carboniferous-early Permian is divided into 4 formations, namely, Yongzhu, Laga, Angjie and Xiala (Fig.2D). We have collected 136 pieces of sample among which we pick 112 pieces of sample to conduct carbon and oxygen

isotope tests after thin slice analysis to the limestone samples. In this study, 52 samples of micrite and bioclastic limestone were tested for inorganic carbon and oxygen isotopes, and 60 samples of clay shale and mudstone were tested for organic carbon isotope.

In this study, inorganic carbon and oxygen isotope tests were carried out in the analysis and test research center of China nuclear industry Beijing Geological Research Institute. First of all, the whole rock of the

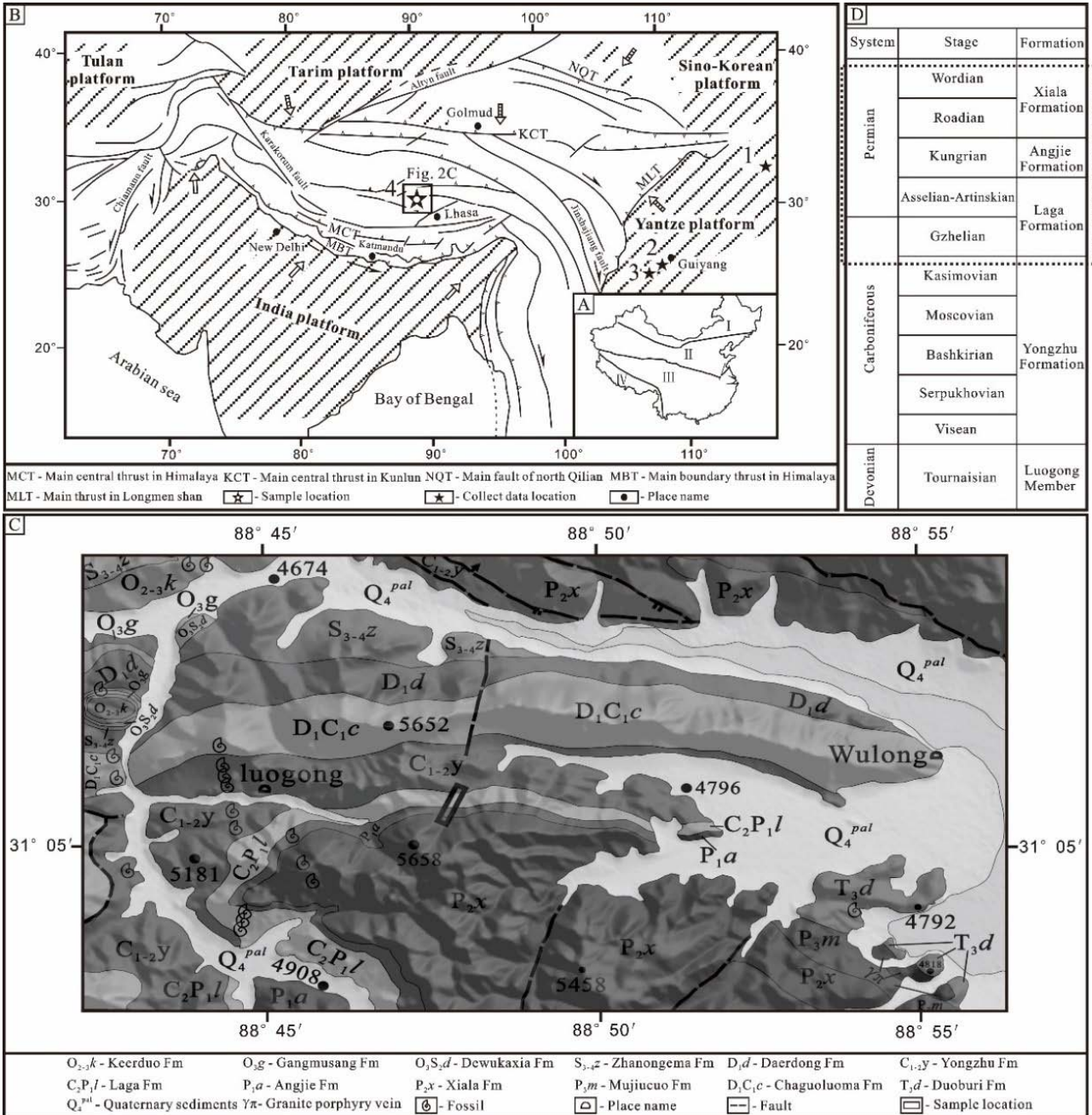


Fig.2—Maps of the study area

A-Tectonic map of the Qinghai-Tibet Plateau (Wang and Jin, 2003 a, b), B-Geological map of the Sample location (Tingdong Li, 1995), 1-Kongshan, 2-Zhongdi, 3- Naqing, 4-Xainza, C-The studied Formation, D- The studied stratum, ( the stratum with a dotted box are the sampled formation ).

fine-grained carbonate rock without alteration was selected. Peel them off from the surrounding rock and then selecting the fresh part of the sample without late alteration or rock veins with no contamination and grinded them into 200-mesh powder. CO<sub>2</sub> was prepared through orthophosphoric acid method, and it was tested in MAT-253 gas isotope mass spectrometer. The detection method and basis is DZ/T0184.17-1997 *pyrophosphate determination of carbon and oxygen isotopic composition in carbonate minerals or rocks*. The error ranges of carbon and oxygen isotopes are respectively ±0.05‰ and ±0.10‰.

Organic carbon and oxygen isotope tests were carried out in Sichuan Coalfield Geology Bureau. First of all, some fresh samples were selected and dried in low temperature and grinded into 100-mesh. Respectively add an excess of 10% hydrochloric acid into PC centrifuge tube and glass beaker to remove carbonate rock. Secondly, carbon dioxide gas preparation and mass spectrometry analysis were carried out by using two analysis methods, EA-IRMS online technology and off-line preparation technology. Standard samples are all using V-PDB standard. Repeated analysis error of standard samples is less than 0.2‰.

During Carboniferous and Permian, three well-documented island arcs belts and ophiolite suites separated China into four tectonic domains which

formed 4 stratigraphic regions and developed independent sedimentary sequence and fauna. From north to south, these stratigraphic regions were Junggar-Hinggan (I), North China-Tarim (II), South China-Qiangtang (III) and Himalaya (IV)<sup>5,6</sup>.

The study area was located in Lhasa Block of East Tethys Domain, the stratigraphic region was located in XainzaSubregion of Gangdise-Tengchong, Himalaya Stratigraphic Super Region. It extended to Yongzhu ophiolite suites in the north and reaches the YarlungZangbo suture zone in the south. Lhasa Block, which was located at a low latitude in Late Paleozoic<sup>27,28</sup>, lay in Paleo-Tethys Ocean in the form of isolated micro landmasses (Fig.1). The structure was stable. Carboniferous Xainza Region lay in a neritic shelf facies sedimentary environment. The lithology was mainly clastic rock. Permian Xainza Region lay in a neritic carbonate platform facies sedimentary environment. The lithology was mainly bioclast limestone and dolomite. In formations in Xainza Region, abundant conodont, coral, brachiopoda, ammonoid and other fossils were developed. It was confirmed that the formations outcropped continuously from lower Carboniferous Tournaisian Stage to upper Permian Wuchiapingian Stage<sup>7,8,9,10,21,22,29,30</sup>. It was appropriate for the study of Carboniferous-Permian stratigraphic boundary (Table 1).

Table 1—Table of stratigraphic history of Xainza, Tibet (According to Jianxin Yao modification, 2007)

Xia Daixiang		Lin Baoyu		Fan Yingnian		Lin Baoyu		Zheng Chunzi		Yao Jianxin				This Paper																	
Xiala Formation 552m	Xiala Formation	Xiala Formation		Xiala Formation Ri a Formation	Capitanian Wordian Roadian	Xiala Formation >643m	Permian	Late	Wordian	Xiala Formation		Permian	Wordian	Xiala Formation																	
									Roadian Kungrian				Roadian																		
Angjie Formation 118m	Angjie Formation 118m	P <sub>3</sub> Langmaria Formation 805m	C <sub>1</sub>	Angjie Formation	Kungrian	Angjie Formation 76m	Permian	Early	Artinskian	Angjie Formation		Permian	Kungrian	Angjie Formation																	
									No fossil data control				Asselian-Artinskian		Laga Formation	Laga Formation															
Yongzhu Group Upper 604m Lower 1245m	Yongzhu Group Upper 605m Lower 1247m	C <sub>2-3</sub> Angjie Formation 635m	C <sub>2-3</sub>	Laga Formation	Artinskian -Gzhelian	Laga Formation 391m	Carboniferous	Age controversial	Yongzhu Formation		Upper	Carboniferous	Yongzhu Formation																		
															C <sub>2</sub>	Yongzhu gongshe Formation	Kasimovian	Moscovian	Bashkirian	Serpukhovian	Yongzhu Formation 1568m	Carboniferous	Middle	Yongzhu Formation							
																									C <sub>2</sub>	Sisuo Formation 162m	Visean	Yongzhu Formation 1568m	Carboniferous	Lower	Yongzhu Formation
Chaguoluoma Formation	Luogong Member 34m	Barialangzhai Member 29m	Luogong Member	Chaguoluoma Formation	Early	Devonian	Luogong Member (Chaguoluoma Formation)	Tournaisian	Luogong Member																						

The stratumswith andotted box are the sampled formation.

The section in the present study was located near LuogongGaiga Section, Yongzhu District, Xainza Region. The positions of collected samples were in

Laga Fm., Angjie Fm., and Xiala Fm. The lower lithology of Laga Fm. was cinereus shale, accompanied by two layers of limestone occasionally.

The upper lithology was gray brown silty mudstone. The lithology of Angjie Fm. from bottom to top was amaranth bioclastic limestone, black bioclastic limestone and gray red bioclastic limestone. The top was gray white calcareous fine sandstone. The lithology of Xiala Fm. was cinereus limestone, gray red micrite and cinereus bioclastic limestone. In Gzhelian-Artinskian Stage, ice water shelf facies clastic rock outcropped in Xainza Section. While in Kungurian Stage, shallow water slope carbonatite outcropped on the top of Section.

Three successions were studied in the South China subprovince which palaeobiogeographically were part of the Palaeotethys<sup>25</sup>. The sedimentary environment of Nanqing Section was slope fan sedimentary facies typically in Yunnan-Guizhou-Guangxi Region.

**Results**

The  $\delta^{18}\text{O}$  values of 52 samples in three groups, i.e., Xiala Fm., Angjie Fm. and Laga Fm., in Late Carboniferous-Early Permian formation of Xainza Region in the present study was -17.1~-4‰. The average was -6.74‰, as shown in Fig. 3. The  $\delta^{18}\text{O}$  value of Zhongdi was -6~0‰. The average was -4.6‰. The  $\delta^{18}\text{O}$  value of Kongshan was -14~-3‰. The average was -7.6‰. The  $\delta^{18}\text{O}$  value of Late Carboniferous-Early Permian samples, as well as Kongshan, Zhongdi and Nanqing Section samples at low latitude in the same period in the study area was lower than that of bivalia fossils, suggesting that samples in this area suffered weak diagenetic alteration during diagenesis<sup>25</sup>. Therefore, the  $\delta^{18}\text{O}$  value was not appropriate for the study and comparison of boundary.

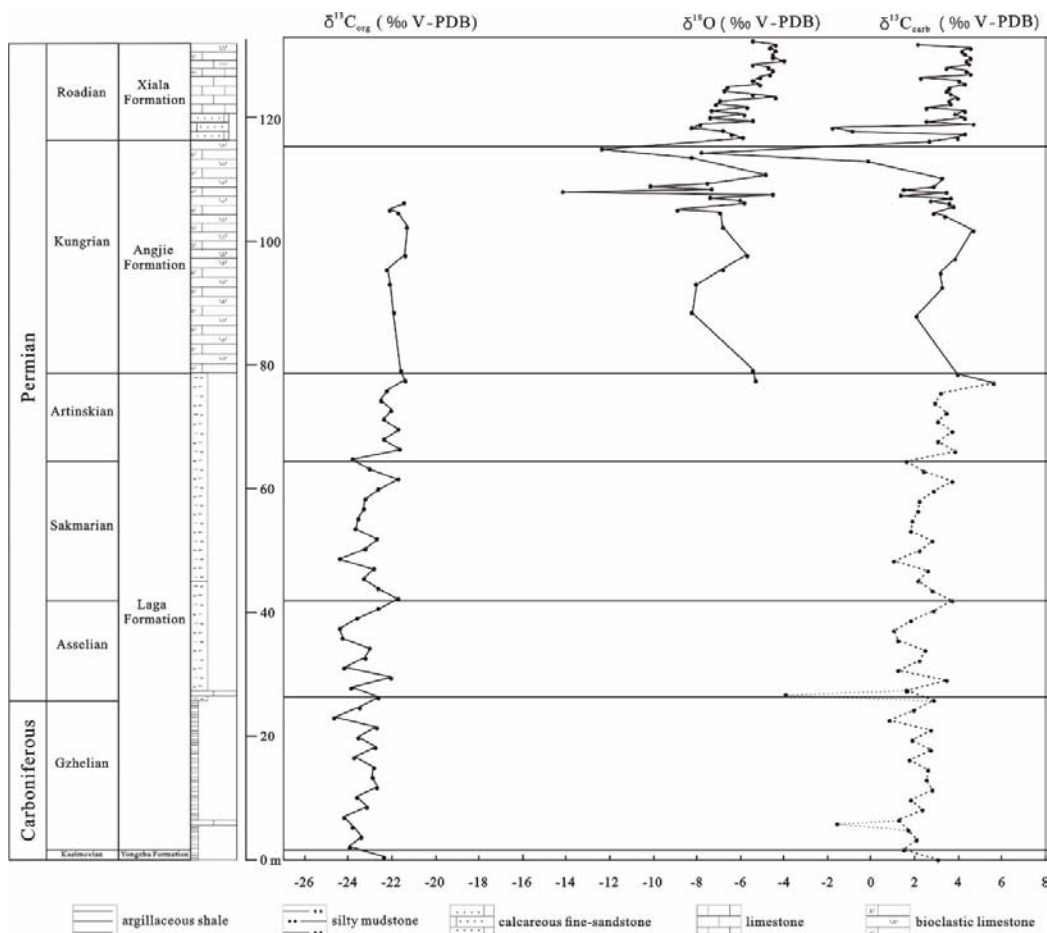


Fig.3—Carbon isotope and Oxygen isotope of whole-rock from Xainza succession, Tibet.

121 samples were selected from the samples collected from three groups, i.e., Xiala Fm., Angjie Fm. and Laga Fm. of Xainza Section in Tibet to test

$\delta^{13}\text{C}$ . In this paper, the  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  of 10 samples in the base of Angjie Fm. were determined as shown in Fig.4, curves of  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  were

basically consistent with the drift trends from Early Cambrian Fortunian Stage to Late Jurassic Oxfordian Stage, especially exactly consistent with drifts from Middle Mississippian Visean Stage to Early Triassic Olenekian Stage<sup>31</sup>. Therefore, the value of the dotted line in Fig.3 was  $\delta^{13}\text{C}_{\text{carb}} = 25.39\% + \delta^{13}\text{C}_{\text{org}}$ .

In Kasimovian Stage (Fig.3),  $\delta^{13}\text{C}_{\text{org}}$  gradually declined from -22.32‰ to -24.15‰ from bottom to top. Thereafter, at the top of Gzhelian Stage, it reached the minimum of -24.56‰ and reached the minimum of -24.33‰ near the top in Asselian Stage. During Sakmarian Stage, the average of  $\delta^{13}\text{C}_{\text{org}}$  rose

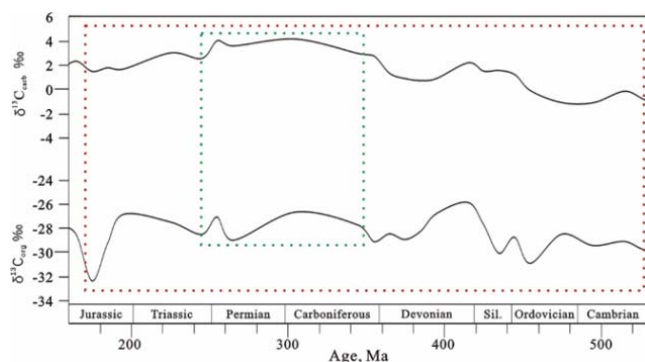


Fig.4—Carboniferous-Permian Carbon Isotope record.

and reached the maximum of -21.24‰ at the top of Kungurian Stage. At the bottom and top of Gzhelian Stage, 2 limestone interlayers developed. The  $\delta^{13}\text{C}_{\text{carb}}$  of yellowish gray limestone at the bottom was -1.6‰. The  $\delta^{13}\text{C}_{\text{carb}}$  of gray white limestone on the top was -3.9‰. The two values above were the first and second minimums in Xainza Section respectively. The  $\delta^{13}\text{C}_{\text{carb}}$  at the bottom of Kungurian Stage gradually reduced from the maximum of 5.6‰ to the minimum of -7.8‰ at the top of Kungurian Stage. The value of  $\delta^{13}\text{C}_{\text{carb}}$  in Roadian Stage rose rapidly from -7.8‰ and -1.8‰ next to it and fluctuated around the average of 3.76‰.

In this paper, a total of 918 carbon and oxygen isotopic data of three sections in Carboniferous-Permian in Yangtze Region were collected (Fig. 5).

The  $\delta^{13}\text{C}_{\text{carb}}$  at the top of Serpukhovian Stage of Kongshan Section was 2.8‰. Thereafter, it tended to decline to -3.39‰ in the middle of Bashkirian-Kasimovian Stage. From the middle of Kasimovian Stage to Late Gzhelian Stage, it tended to drift negatively as a whole. At Carboniferous-Permian boundary at the top of Gzhelian Stage, it reached the minimum of -4.94‰. On the top, during Asselian-Kungurian Stage,  $\delta^{13}\text{C}_{\text{carb}}$  fluctuated around the

average of 2.63‰. There were three relative peaks, 2.28‰ in Early Asselian Stage, 1.25‰ in Early Sakmarian Stage and 0.75‰ in Late Sakmarian Stage.

In Zhongdi Section from Serpukhovian Stage to Gzhelian Stage, the  $\delta^{13}\text{C}_{\text{carb}}$  gradually reduced as a whole and dropped to the minimum -3.9‰ in the late stage. During Late Gzhelian Stage,  $\delta^{13}\text{C}_{\text{carb}}$  rose sharply at the boundary with Asselian Stage. After that, the average in Asselian Stage was -1.48‰ and always in a negative drift. In Sakmanan- Artinskian Stage, it was in a positive drift as a whole, except a negative drift of -0.71‰ in the late stage in central area.

Nanqing Section generally presented a positive drift as a whole and the maximum of 5.79‰ occurred at the boundary between Gzhelian Stage and Asselian Stage. During Carboniferous, the  $\delta^{13}\text{C}_{\text{carb}}$  in this section tended to gradually rise from Early to Late as a whole, just like the trend in Permian Epoch.

## Discussion

The key to explaining carbon and oxygen isotopes is the degree of preservation of raw values. A general evidence of good preservation of isotope information was absence of cathode luminescence, low manganese, iron, magnesium and high strontium. But cathode luminescence microscopy and microelement analysis and evaluation for potential diagenetic alteration were subject to defects<sup>25</sup>. The average of isotopes in Laga Fm. and Xiala Fm. was -6.4‰. Only two values in Laga Fm. were lower than -10‰. The overall value of  $\delta^{18}\text{O} < -11\%$  indicated that it experienced weak diagenetic alterations<sup>31</sup>.

All the H/C values of kerogen isotope analysis of samples collected in this paper were greater than 0.2, suggesting that  $\delta^{13}\text{C}_{\text{org}}$  in Luogong Gaiga Section was approximate to isotopic composition of the original organic carbon<sup>32,33</sup>. In addition, among the ten samples in the base of Angjie Fm.,  $\Delta = 25.39\%$ . This value was very close to 25‰<sup>34</sup>, suggesting that  $\delta^{13}\text{C}$  of this batch of samples preserved raw values to a large extent. From the research data on biomarkers, such as n-alkanes, phytane, gonane and terpane, etc. in Xiala Fm., Angjie Fm., Laga Fm. in Xainza Region, hydrocarbon-generating parent materials in three groups of organic carbon source rocks above were principally low-grade marine algae. The sedimentary environment was featured with high salinity and strong reduction characteristics<sup>35</sup>. Therefore, the tested  $\delta^{13}\text{C}$  of collected samples

represent the original sea water composition. They can be compared with that of three sections in Yangtze Region. The value of  $\delta^{13}\text{C}$  at Carboniferous-Permian boundary in Xainza Region, Tibet dropped rapidly from 2.85‰ to the sub-minimum of -3.90‰ and then rose sharply to 1.61‰. A variation of 6.75‰ was the largest negative drift in this section. Similar

rapid negative drift was also present in Zhongdi Section and Kongshan Section in Yangtze Region, China. The  $\delta^{13}\text{C}$  value at Carboniferous-Permian boundary in Zhongdi Section dropped rapidly from 1.51‰ to the minimum of -3.56‰ and then rose sharply to 0.61‰. A variation of 5.07‰ was the largest negative drift in this section.

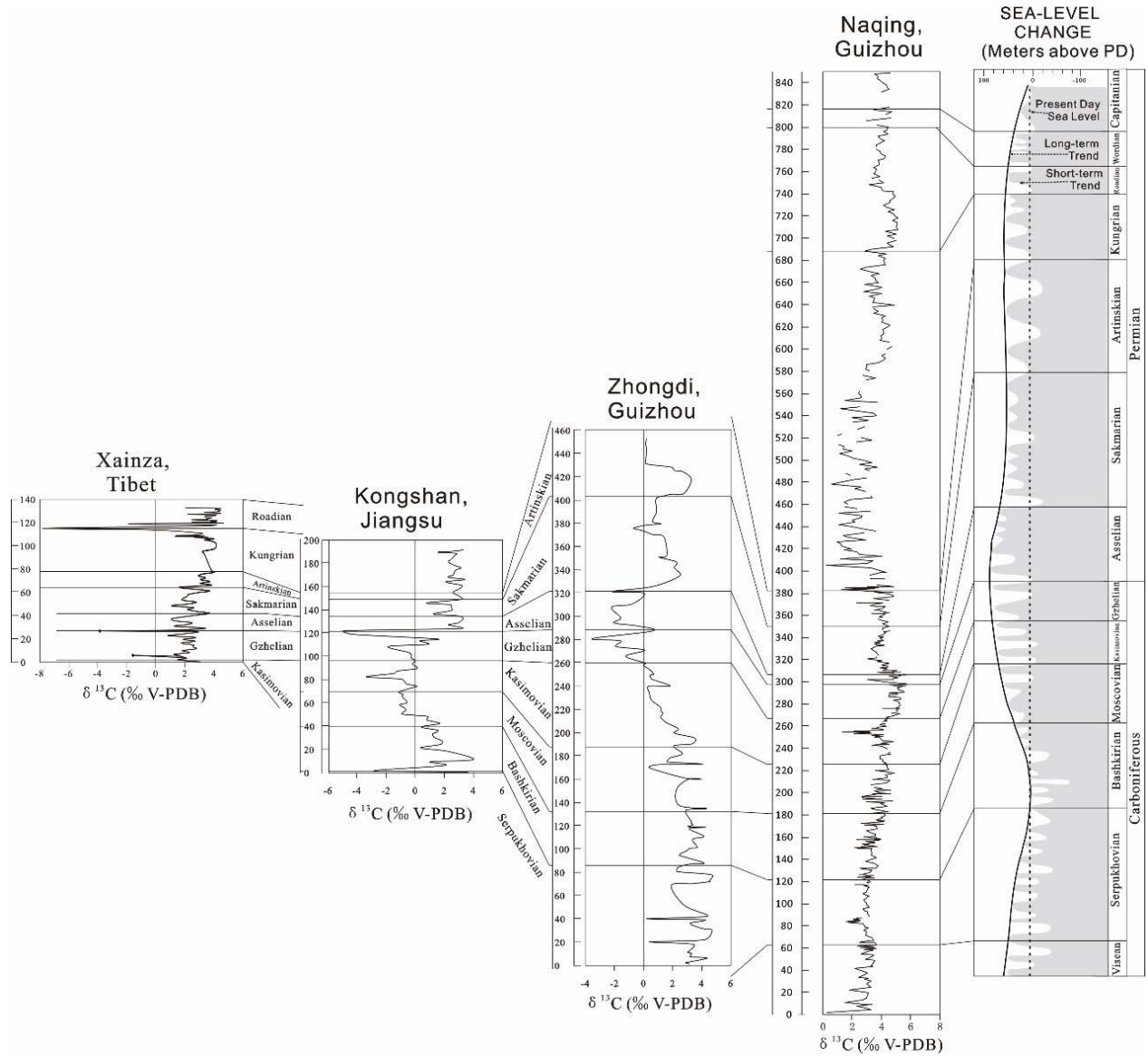


Fig.5—Carbon isotopes of the Xainza, Kongshan, Zhongdi and Naqing succession. Sea-level (according to Snedden *et al.* 2010).

The value of  $\delta^{13}\text{C}$  at Carboniferous-Permian boundary in Kongshann Section dropped rapidly from 0.07‰ to the minimum of -4.94‰ and then rose sharply to 3.2‰. A variation of 8.16‰ was the largest negative

drift in this section. All the negative drift values of  $\delta^{13}\text{C}$  at Carboniferous-Permian boundary in the above three sections were greater than 5‰. This shift was

one of the major carbon isotope events in the earth’s history. These  $\delta^{13}\text{C}$  values were very low because the sea level in the biggest extension period of Carboniferous-Permian ice cover was at the lowest level. The formation was exposed for a long term. Also, under atmospheric diagenesis, the value of original carbon isotope was reset<sup>25</sup>. The exposure evidence was that a large amount of ancient soil

existed in Kasimovian-Asselian Stage in Zhongdi Section<sup>36</sup>. In the absence of sedimentary evidence of atmospheric exposure in Nanqing Section, the carbon isotope values of sea water were well preserved. The  $\delta^{13}\text{C}$  at Carboniferous-Permian boundary in the glacial period was the largest positive shift. Outing standing examples are the Hirnantian<sup>37</sup>, Late Silurian event<sup>38,39,40</sup> and possibly Tournaisian event<sup>25,41,42,43,44,45,46,47</sup>. The reasons why the sea level reduces is not only because of the cooled down atmosphere and the increased continental ice sheet volume<sup>47</sup> but also because dramatic increase of organic carbon storage costing large amount of water which results in the reduction of sea level approximately by 10 meters<sup>48</sup>.

The waxing and waning of continental ice caps often coincides with positive and negative  $\delta^{13}\text{C}$  shifts, respectively<sup>41,43,49,50,51,52</sup>. During Asselian-Artinskian Stage,  $\delta^{13}\text{C}$  peaks of four sections, i.e., Xainza Section, Kongshan Section, Zhongdi Section and Nanqing Section were reduced as a whole, suggesting that Carboniferous- Permian ice cover was shrinking. There was a large negative shift in Zhongdi Section Asselian Stage, for the earth's surface was exposed to atmospheric diagenetic alteration.

Due to a lack of complete Kungurian data in Kongshan Section and Zhongdi Section, which had experienced short-term earth's surface exposure with Xainza Section, Tibet, Nanqing Section didn't experience the earth's surface exposure. It had huge Kungurian thickness. Therefore, the  $\delta^{13}\text{C}$  value of Xainza Section, Tibet cannot be compared and studied with the above three sections. But the lower lithology of Kungurian formation in Xainza Region, Tibet was bioclastic limestone, while the upper lithology was cinereous clastic rock. This characteristic had a distinct interface with overlying limestone of Xiala Fm. and underlying silty mudstone of Laga Fm. In addition, after identification, the conodonts, *Neostrep tognathodus* sp. A, *N. sp B* produced in bioclastic limestone in this formation were index fossils in Early Permian Kungurian Stage<sup>8</sup>.

## Conclusion

In the paper, the studied Carboniferous-Permian stratigraphic boundary in Xainza district of Tibet located in yellow-grey limestone under Laga group has settled the problem which has haunted people for a half century. The cause for the biggest Phanerozoic ice age is the low concentration of  $\text{CO}_2$  caused by carbon cycle and the high galactic cosmic radiation flux resulting in thick clouds covering low altitude district which lead to the earth receiving low amount

of solar radiation.

The change scope of Asselian-Artinskian Stage  $\delta^{13}\text{C}$  peak value is small, and the specific numerical displays slightly decreasing trend, which shows that the ice sheet is shrinking, the sea level is rising, but the range is limited.

The finding that Laga Fm. belonged to time-transgressive formations is consistent with many predecessors' paleontological studies<sup>19,21</sup>, confirming that the isotope curve drifts in the present study well reflect information about the original sea water.

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