Characteristics of Nanoparticles in Late Pliocene Paleo-Mountain Fire Relics in Jinsuo Basin, Yunnan Province and Their Implications for Paleoclimate Evolution

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Abstract: Wildfires significantly affect climate and environmental changes, closely tied to extreme weather responses. Vegetation combustion emits greenhouse gases (CO2, CH4, CO), warming the climate. Climate shifts, in turn, impact vegetation growth, altering combustible material types and quantities, thus affecting wildfire intensity, duration, and frequency. Wildfires profoundly affect ecosystems, influenced by factors like atmospheric oxygen and climate. Their combustion gases impact climate and vegetation growth. Recent advancements in studying ancient wildfires include analyzing nanoparticles as key indicators. This study discovered six types of nanoparticles in ancient wildfire remains, with sizes ranging from 50 nm to 500 nm and diverse compositions including elements such as C, O, Mg, Al, Ti, Fe, S, Ca, and P. These findings indicate that wildfires generate a variety of nanoparticles, offering new insights into ancient fire events. Elemental analysis revealed low magnesium but high calcium and aluminum levels, suggesting a warm, humid paleoclimate during these fires. The presence of high Ti-O ratios and carbon-rich nanoparticles points to ground fires with incomplete combustion. This research underscores the significance of nanoparticles in understanding the history and characteristics of ancient wildfires.

Keywords: paleo-wildfire; nanoparticle; paleoclimate; transmission electron microscopy

1. Introduction

Historically, since the Devonian period, as vegetation on land massively expanded, wildfires became prevalent, evolving into a critical component of the Earth’s system [1]. Wildfires have a significant impact on climate and environmental changes, reflecting a close relationship between the two. Greenhouse gases (CO2, CH4, CO) emitted during vegetation combustion contribute to climate warming [1]. In turn, climate change affects vegetation growth, indirectly altering the types and quantities of combustible materials, thereby influencing the intensity, duration, and frequency of wildfires [2]. Wildfires play an indispensable role within Earth’s ecosystems, significantly impacting the planet’s circulation processes. The occurrence of wildfires is intricately linked to atmospheric oxygen levels, climate factors, environmental conditions, and the availability of combustible materials. Moreover, the gases produced by wildfires influence climate change, subsequently affecting vegetation growth. Thus, exploring the interplay between wildfires and climate offers vital insights into the paleoclimatic context of ancient wildfire occurrences, essential for understanding climate evolution during Earth’s history [3–5].

At present, with in-depth studies on paleo-wildfires, methods of studying paleo-wildfires are gradually being improved. As paleo-wildfires can change some parameters of
the corresponding strata, such as magnetic and geochemical parameters, the study of such parameters is important for reconstructing the history of paleo-wildfires [6]. In addition to producing various gases, combustion products of paleo-wildfires also include carbonized plant debris, carbon-containing particles of different sizes and degrees of carbonization, and organic molecules adsorbed by these particles [7]. Therefore, molecular markers such as microscopic charcoal (<180 µm), macroscopic charcoal and fine-grained charcoal (>180 µm) [8], polycyclic aromatic hydrocarbons (PAHs) [9–11], and magnetic parameters are important indicators of paleo-wildfires.

In recent years, with the application of transmission electron microscopy (TEM) in earth science, the research on nanoparticles has grown and is becoming more comprehensible [12–14]. A large number of previous studies have shown that the genesis and physicochemical characteristics of nanoparticles are closely related to their origin and formation process [12–15]. This information can be utilized to reconstruct the physical and chemical environment during the burning of ancient Gugu wildfires. Thus, the detection of nanoparticles offers a promising new method to identify ancient wildfires with high potential.

In this study, a large number of nanoparticles was found in the remains of paleo-wildfires in the Yunnan Province, in China. The form, structure, and elemental composition of these nanoparticles were analyzed. Thus, from a more micro level, the formation of ancient wildfire, the form of occurrence, and the type of its environment are indicated.

2. Study Area

The Jinsuo Basin, nestled in the low-lying hills of the eastern Yunnan Karst Plateau, is geographically positioned between the DongXiaojiang and XiXiaojiang faults, stretching from the south to the north (Figure 1). During the Himalayan Movement, the strata of this region experienced a gradual uplift, without encountering significant tectonic disturbances in the late Pliocene period, according to the Bureau of Geology and Mineral Resources (BGMR, 1990). The Ciying Formation from the late Pliocene era, extensively documented in the Jinsuo Basin [16–19], is notable for encompassing four lignite layers, numbered from one to four in descending order (as illustrated in Figure 1b). The stratigraphic sequence beneath the Ciying Formation displays an unconformity and predominantly consists of Middle Cambrian calcrete shales from the Douposhi Formation, dolostone from the Shuanglongtan Formation, Lower Ordovician shales from the Tangchi Formation, and sandstone from the Hongshiya Formation [16,20].

In the late Pliocene of Yunnan, at least two kinds of floristic regions existed: sclerophyllous evergreen broad-leaved forests in the northwest that represented a subalpine floristic region and subtropical evergreen broad-leaved forests in the southwest and eastern center that in each case represented a subtropical floristic region. The floristic importance of conifers such as Abies, Picea, Pinus, and Tsuga increased because some cool-temperate elements such as Abies and Picea formerly restricted to higher altitudes began to have broader occurrences in the studied area [17].

Various paleoclimate reconstructions indicate that Yunnan had higher precipitation in summer but less rainfall in winter during the late Pliocene [19,21,22]. The Pinaceae–Quercus–herbaceous pollen zone and the expansion of coniferous forest and herbaceous, along with the decrease in the thermophilic percentages (Quercus), imply a relatively cooling and drying climate trend from the early to the late Pliocene.
3. Sampling and Analysis Method

The samples were collected from the lignite seam in the Jinsuo Basin of Yunnan Province (Figure 1). The Ciying Formation of Jinsuo Basin is mainly composed of siltstone, mudstone, sandstone, conglomerate, and lignite bed [16,20]. There are four lignite layers (No. 1–4) from top to bottom, and the thickness of the No. 3 lignite layer studied is about 14~26 m. In this lignite seam, there are thick dark layers, thin pale layers, charcoal layers, and other sublayers. Charcoal particles isolated from the charcoal layers are also depicted in Figure 2 [23]. These samples are distinctly identifiable as charcoals originating from wildfire combustion. The palynology and plant residue studies of light and dark layers of lignite seam show that the light layer is dominated by herbal angiosperms with more gymnosperms, while the dark layer is dominated by woody angiosperms with a very low proportion of gymnosperms [24]. On site, each sample was wrapped in aluminum foil to minimize contamination and oxidation and stored in a plastic bag to seal immediately.
Figure 2. Examples of macroscopic charcoal particles in samples from the lignite seam. Samples from pale layers: (a,b); samples from dark layers: (c-d) (modified from [23]).

The collected samples were analyzed and tested using Hitachi SU8220 instruments at 5 kV and 10 kV (Guangzhou City, Guangdong Province, China). The instrument is equipped with an energy dispersion spectrometer (EDS) and a STEM (scanning transmission electron microscope)/HAADF (High-Angle Annular Dark-Field) detector with a TEM (transmission electron microscope) point resolution of 0.2 nm and a line resolution of 0.1 nm. Through high-resolution transmission electron microscopy, the energy spectrum map of coal nanoparticles, TEM and STEM micrographs, a STEM HAADF high-resolution map, and the SAED (Selected Area Electron Diffraction) diffractive pattern could be obtained. The elemental composition and content of the nanoparticles from the remains of paleo-wildfires could be determined using the energy spectrum analysis and EDS results. The morphology of the nanoparticles can be identified using the TEM and STEM microscopic images. The degree of crystallization and lattice spacing of the nanoparticles can be determined using high-resolution diffraction diagrams.
4. Characteristics of Nanoparticles in Ancient Wildfires and Their Indication to Paleo-Wildfire Types

According to the topography diagram (Figure 3), the nanoparticles found in the remains of paleo-wildfires occur in various forms, such as granular, layered, and columnar. Furthermore, these nanoparticles occur not only as single crystals but also as aggregates. At the same time, these nanoparticles have variable sizes, with smaller nanoparticles being only $50 \times 70$ nm, and larger ones, mostly aggregates, reaching $500$ nm. Moreover, the elemental composition of these nanoparticles also varies (Table 1), among which the representative nanoparticles have the characteristics shown below.

![Figure 3. Topography of nanoparticles in paleo-wildfire remains. Among them, (a–d) are different types of nanoparticles.](image)

The nanoparticle shown in Figure 4a is a granular aggregate, with a size of approximately $400 \times 400$ nm. The main components of the nanoparticle are Ti (66.7%) and O (33.3%) (Figure 5; Table 1). Distinct lattice fringes can be observed in the HRTEM (high-resolution transmission electron microscope) image (Figure 3c), indicating high crystallinity, and regular diffraction spots can be observed in the diffraction image (Figure 4b), indicating that the nanoparticle is a single crystal. The lattice spacing of the nanoparticles is 0.36 nm (Figure 4d). Similarly, the nanoparticle is speculated to possibly be Ti oxide.
The nanoparticle shown in Figure 6a is a flake aggregate, with a size of approximately 300 × 400 nm. The main components of the nanoparticle are Ti (54.3%) and O (40.3%), followed by Al (1.84%), P (0.80%), and Fe (2.80%) (Figure 7; Table 1). Distinct lattice fringes can be observed in the HRTEM image (Figure 6c), indicating high crystallinity, and regular diffraction spots can be observed in the diffraction image (Figure 6b), indicating that the
nanoparticle is a single crystal. The lattice spacing of the nanoparticle is 0.36 nm (Figure 6d). Similarly, the nanoparticle is speculated to possibly be Ti oxide.

Figure 6. Diagrams of morphology (a), diffraction (b), HRTEM (c), and lattice spacing (d) of nanoparticles in paleo-wildfire remains.

Figure 7. EDS diagram of nanoparticles in paleo-wildfire remains.

The nanoparticle shown in Figure 8a is granular, with a size of approximately 50 × 70 nm, and the main components are C (71.7%), followed by Ti (12.9%) and O (15.4%) (Figure 9;
Table 1). Distinct lattice fringes can be observed in the HRTEM image (Figure 8c), indicating high crystallinity, and regular diffraction spots can be observed in the diffraction image (Figure 8b), indicating that the nanoparticle is a single crystal. The lattice spacing of the nanoparticle is 0.48 nm (Figure 8d).

Figure 8. Diagrams of topography (a), diffraction (b), HRTEM (c), and lattice spacing (d) of nanoparticles in paleo-wildfire remains.

Figure 9. EDS diagram of nanoparticles in paleo-wildfire remains.
The nanoparticle shown in Figure 10a is in the shape of a long column, with a size of approximately 150 × 500 nm, and the main components of the nanoparticle are C (7.36%), O (59.9%), Al (15.8%), and Si (15.4%), followed by S (0.96%) and P (0.54%) (Figure 11; Table 1). No regular diffraction spots can be observed in the selected diffraction pattern (Figure 10b), indicating that the nanoparticle is amorphous.

![Figure 10](image1.png)

**Figure 10.** Topography (a) and selection diffraction (b) of nanoparticles in paleo-wildfire remains.

The nanoparticle shown in Figure 12a is granular, with a size of approximately 30 × 50 nm, and the main components are C (53.3%), O (30.0%), and Ti (15.4%), followed by Ca (0.55%) and Fe (0.73%) (Figure 13; Table 1). No regular diffraction spots can be observed in the selected diffraction pattern (Figure 12b), indicating that the nanoparticle is amorphous.

![Figure 11](image2.png)

**Figure 11.** EDS diagram of nanoparticles in paleo-wildfire remains.
The nanoparticle shown in Figure 14a is a flake aggregate, with a size of approximately 200 × 500 nm, and the main components are C (80.2%) and O (17.6%), followed by Ca (1.07%), Mg (0.16%), Al (0.41%), and S (0.52%) (Figure 15; Table 1). No regular diffraction spots can be observed in the selected diffraction pattern (Figure 14b), indicating that the nanoparticle is amorphous.


5. Discussion

5.1. New Indicators in the Study of Paleo-Wildfires

The study identified a significant presence of nanoparticles within samples of paleo-wildfire remnants. Predominant components of these nanoparticles include Ti (titanium), O (oxygen), Fe (iron), Ca (calcium), S (sulfur), C (carbon), and Al (aluminum). However, previous studies have primarily focused on charcoal [25], molecular markers [10], and magnetic parameters [26–28]. Notably, the Ti-O ratio in the elemental composition of the titanium oxide nanoparticles discovered in our investigation markedly differs from that of minerals such as rutile and anatase. Furthermore, an analysis of the lattice spacing of titanium nanoparticles in paleo-wildfire samples revealed dimensions larger than those of rutile, anatase, and other minerals. Previous research has indicated that rutile and anatase are the primary titanium-bearing minerals in coal seams, comprising mainly TiO₂ [29]. These findings suggest that the titanium oxide nanoparticles detected in paleo-wildfire samples differ from the typical deposition of titanium minerals in coal, instead likely representing combustion byproducts of paleo-wildfires.

Moreover, the characteristics including type, size, morphology, and elemental content of nano-mineral particles are closely linked to their physicochemical processes [13,15], underscoring the potential of nanoparticles to encapsulate significant physical and chemical information. Consequently, these nanoparticles can serve as pivotal indicators of paleo-wildfire occurrences. Specifically, the titanium oxide nanoparticles generated by these fires emerge as crucial markers for identifying past wildfire events. As research on paleo-wildfires progresses, nanoparticles are anticipated to become increasingly indispensable in discerning the occurrence and characteristics of such events.

5.2. Paleoclimate Indications from Paleo-Wildfires

The occurrence and combustion of paleo-wildfires are controlled by many factors, such as oxygen content, precipitation, temperature, and moisture [30]. The seasonality of precipitation, temperature, and humidity is an important factor for the occurrence of
regional wildfires [31–33]. Therefore, the study of paleo-wildfires has a certain indicative significance for the paleoclimate.

In this study, the examination of nanoparticles within paleo-wildfire remnants revealed a notably low Mg content, even lower than that of Ca (Table 1). Mg and Ca are highly active and prevalent rock-forming elements within the Earth’s crust [34]. Sediments containing Mg and Ca are typically transported via aqueous solutions during weathering and decomposition processes [35]. In warm and humid climates, both Ca and Mg undergo leaching migration [1]. However, in such environments, Ca depletion typically precedes Mg depletion due to the stronger reactivity of Ca. Consequently, a low Ca/Mg ratio often signifies a relatively warm and humid environment [36].

Simultaneously, the analysis of nanoparticles found within the paleo-wildfire remnants, particularly the examination of N4 nanoparticles, indicates that these nanoparticles are kaolinite nanoparticles (Figures 10 and 11). Kaolinite formation results from the intense leaching and hydrolysis of rock-forming minerals in hot and humid climates [37]. Therefore, the presence of kaolinite can also serve as an indicator of a warm and humid climate. Additionally, the Al/Mg ratio within kaolinite is frequently employed as an indicator of sedimentary paleoclimate change [38]. A higher ratio typically correlates with warmer and wetter climates and a weaker aquatic environment. The absence of Mg within the observed kaolinite nanoparticles further supports the notion that ancient wildfires occurred within a relatively warm and humid environment to some extent.

5.3. Categorization of Paleo-Wildfires

According to its spatial distribution characteristics, fuel can be divided into air fuel, surface fuel, and ground fuel, and the corresponding wildfires can be divided into canopy fire, surface fire, and ground fire [39]. Among them, canopy fire fuel includes the canopy of the understory, shrubs, lianas, and forest vegetation more than 1 m away from the surface soil [4]. Surface fire fuels include low shrub vegetation, herbs, or litter. Surface fuels mainly include soil humus layer, vegetation, decaying dead roots or peat, etc. [40]. In previous studies, the classification of paleo-wildfires was mainly based on the average inertinite reflectance. However, with research progress to the nanoscale, it is also possible to determine the type of paleo-wildfires from nanoparticles in the remains of paleo-wildfires.

During this study, we found a relatively high concentration of Ti-O-containing titanium nanoparticles in the paleo-wildfire remains. Specifically, the elemental concentration ratio of titanium to oxygen nanoparticles, as shown in Figure 3, reached 2:3. The Magnéli phase (\(Ti_xO_{2x-1},4 \leq x \leq 9\)), also one of the oxide forms of Ti, is a common combustion product in the coal combustion process [41]. Moreover, the process of Magnéli phase formation generally requires a relatively reducing environment [18], where the ratio of Ti to O is \(x: 2x – 1\) (4 \(\leq x \leq 9\)). The Ti-O ratio of the Magnéli phase is relatively lower than that of the nanoparticles found in paleo-wildfire remains, so the formation of the nanoparticles of Ti oxides we found requires a stronger reducing environment than the formation of the Magnéli phase. Since both of them are combustion products, the strong reducibility in the combustion process may be caused by the low oxygen content, so it can indicate that paleo-wildfires may have been in a low oxygen content environment during the combustion process. However, previous studies have shown that the oxygen content in the atmosphere during the deposition of lignite in the paleo-wildfire remains area is about 22.6% [23], which is a relatively high oxygen content level. Thus, canopy fires and surface fires are less likely to provide a reducing environment with less oxygen. However, surface wildfires on peatlands are usually in a wet reducing environment and may be seasonally covered with water [42], easily providing a reducing environment with less oxygen content, and thus indicating the type of paleo-wildfire as a ground fire.

6. Conclusions

In this study, through the analysis of samples from paleo-wildfire remains, a large number of nanoparticles were found. These nanoparticles have various shapes and sizes,
and their elemental composition is relatively complex, comprising C, O, Al, Si, Ti, Fe, Ca, Mg, and other elements. Through the analysis of the morphology, elemental composition, and lattice spacing, these nanoparticles were found to be mainly Ti oxides, kaolinite, and C nanoparticles. By analyzing the characteristics of these nanoparticles, the following conclusions can be drawn:

- Nanoparticles with high Ti-O ratios found in paleo-wildfire remains indicate a reducing environment with low oxygen content, indicating that the type of paleo-wildfire was a ground fire.
- Paleo-wildfires can indeed produce a large number of nanoparticles, which have been found in the paleo-wildfire remains, and these nanoparticles can preserve physico-chemical information about the occurrence of paleo-wildfires.
- The elemental composition revealed that the nanoparticles have very low Mg content but relatively high contents of Ca and Al, along with the presence of kaolinite, indicating that the paleoclimate was relatively warm and humid at the time of the occurrence of the paleo-wildfire.

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References
1. Xu, Y. Evidences of Widespread Wildfires in Coal Seams from the Middle Jurassic of the Northwest China and Its Impact on Paleoclimate; China University of Mining & Technology: Beijing, China, 2020. [CrossRef]
11. Sun, Y.; Zhao, C.; Püttmann, W.; Kalkreuth, W.; Qin, S. Evidence of widespread wildfires in a coal seam from the middle Permian of the North China Basin. Lithosphere 2017, 9, 595–608. [CrossRef]
*Geology* **2015**, *43*, 415–418. [CrossRef]


20. Liu, B.; Zhao, C.; Ma, J.; Sun, Y.; Püttmann, W. The origin of pale and dark layers in Pliocene lignite deposits from Yunnan Province, Southwest China, based on coal petrological and organic geochemical analyses. *Coal Geol.* **2018**, *195*, 172–188. [CrossRef]


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