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# The evolutionary characteristics and mechanisms of coal chemical structure in micro deformed domains under sub-high temperatures and high pressures

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ABSTRACT

To understand the physic-chemical evolutionary characteristics and mechanisms of coal chemical structure, sub-high temperature and high pressure coal deformation experiments were conducted by using the self-developed TRTP-2000 experimental system. The micro deformed features and the macromolecular structural characteristics of experimental samples were detected by various in-situ methods. With the decrease of strain rate, the ductile deformation features in samples gradually become distinct. Brittle deformation lead to the breakage of oxygen functional groups and side chains through the coupling of mechanochemistry and frictional thermal energy. Ductile deformation with a higher strain rate resulted in a total increase in aromatic carbon, a relative decrease in the disorder degree of the molecular structure, and a reduction in secondary structure defects respectively. While the excessive strain energy accumulation under ductile deformation at a lower strain rate can lead to the dislocation and slip of the aromatic layer in coal molecular structure and an increase in secondary structure defects. Besides, the alteration of coal molecular structure may increase the ultra micropore volume within coal that is critical for the retention of CBM.

## 1. Introduction

Organic matter is the main composition of highly heterogeneous coal [1] that contains some inorganic matter [2–4]. During the course of coal deformation induced by tectonic stress, not only does the physical structure of pores and fractures of the coal body transform [5–7], but the chemical structure of the organic matter is also regularly altered [8–14]. Pan et al. [15,17] proved that the diversity of coal chemical structure caused by tectonic stress can directly affect or change the nano-sized physical structure of the coal (e.g., nano-pores), which varies the permeability and other physical characteristics of the coal reservoir. The changes in the coal reservoir affect the occurrence of coalbed bed methane (CBM). Alexeev et al. [16] proposed that a level of excessive gas higher than the maximum adsorption of the coal originating from the coal gas outburst might exist in a solid solution state. The solid solution state gas is high and possibly adsorbed between the aromatic layers of coal molecular structure [15]. Therefore, it is of great practical significance to study the transformations and mechanisms of coal chemical structure under tectonic stress, which can be applied to coalbed methane exploitation and coal mine safety. Besides,

Early research carried out by Teichmüller et al. [18] and Bustin et al. [19,20] showed that chemical coalification of coal occurred under tectonic deformation, which led to a higher coal ranking and advanced evolution. Cao et al. [8,9] inferred that the higher chloroform yields of tectonically deformed coals (TDCs) compared to the yield of raw coal were caused by tectonic deformation of the coal chemical structure. The higher chloroform yields of TDCs promote hydrocarbon-generation in coal. With continuous development of quantum chemicals and the widespread application of precision detective technologies, research on the evolution mechanisms of coal macromolecular structure has become more thorough. Li et al. [11,12] discovered that regularity changes occurred on the length of the side chains, the amount of oxygen functional groups and the total aromatic carbon in coal macromolecules under brittle and ductile deformation according to detection results of Raman, Fourier transform infrared (FT IR) and X-ray diffraction (XRD). Pan et al. [14] proclaimed that there is a difference between strong and weak TDCs of the secondary structure defects and coalification degree through analysis of TDC Raman parameters. Cao et al. [21] suggested that tectonic stress (especially shear stress) accelerated the advanced evolution of coal and that stress polycondensation and stress degeneration could be applied to explain the chemical structural evolution of TDCs for the first time using XRD and FT IR technologies. Lin et al. [13]

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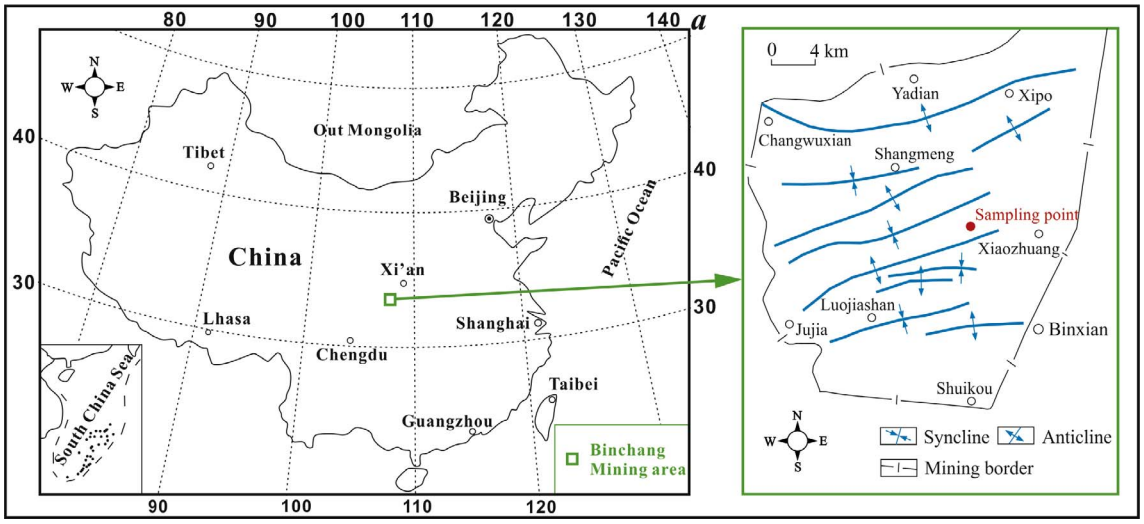


**Fig. 1.** Sketch map of sampling point.

claimed that strong and weak ductile deformation affected the development of secondary structure defects and the aromatization of coal to various degrees, which led to diverse evolutionary characteristics of coal macromolecular structure. Xu et al. [22] declared that sub-high temperature and pressure experimental research on anthracite proved the existence of stress polycondensation in coal macromolecules and that the strain energy supplied by the experimental stress is higher than the energy barrier of the side chain break up based on quantum chemistry calculation. Han et al. [23,24] deemed that the Stone-Wales secondary structural defects (SW) originated from the rotation of chemical bonds without the alteration of the number of atoms in the coal macromolecule on account of macromolecular simulation.

Previous pretreatment of coal samples (maceral purification) before coal macromolecular structure tests could not avoid damage to the coal macromolecular structure [25] and ignored the influence of the brittle and ductile deformation micro domains. Therefore, in situ detective methods were adopted to feature the characteristics of the macromolecular structure of the micro deformed domains within experimental samples in this study.

Coal as an organic rock is more sensitive to pressure and temperature compared to the surrounding rocks. The ductile deformation of coal with low strength develops more easily under a relatively low temperature and pressure compared to other rocks [26,27]. Bustin [28] found the megascopic “wild fold” structure in ductile deformed coal. Li [27] noted the similarity between ductile deformation features of coal and typical ductile deformation features developed in other rocks, and enumerated the diversified ductile deformation features of micro coal macerals in shear zones, including S-C fabric, superimposed folds and σ-structure at a small scale. Liu et al. [29] considered that the ductile deformation behavior of coal samples under high temperature and pressure experiments lead to an inertinite ductile flow at a low strain rate. Coal under higher strain rates is dominated by brittle deformation features, micro fractures and fracture zones for instance [29,30]. Brittle and ductile deformation of coal corresponds to particular deformation features, that is the mechanism of coal deformation is identical to the characteristics of the coal microstructure and micro deformation features, and micro deformation features could indicate the mechanism of coal deformation. Accordingly, representative coal deformation features are the basis in selecting test sites for in situ coal chemical structural detections, which is propitious to prevent samples from being contaminated and understanding the characteristics of coal chemical structure in micro deformed domains.

High temperature and pressure experiments are an effective technique to study the formation mechanism of TDCs, but previous experiments have tended to concentrate on experiments with a temperature above 200 °C, which is higher than the pyrolysis temperature of the coal samples. Higher temperatures than the pyrolysis temperature would affect the coal macromolecular structure [31–34]. In recent years, sub-high temperature and high pressure experiments have been designed to study coal chemical structure characteristics, and some favorable results were acquired [22,23]. This study follows the later experimental design. The temperatures in the experiments of this study were set below 200 °C, which aimed to eliminate the aforementioned influence. All experimental samples were first conducted on a self-developed high temperature and high pressure experimental system (TRTP2000) and then analyzed using micro-FT IR and micro-Raman. The results were resolved exhaustively to study the evolutionary characteristics of coal chemical structure and discuss the transformation conditions between brittle and ductile deformation, as well as the deformation mechanisms of stress-strain on the coal chemical structure.

## 2. Samples and experiments

### 2.1. Sample selection and preparation

According to national standard GB482-1995, primary structural coal samples (without any deformation compared to the TDCs) in the Triassic Yan’an formation, were collected from the Binchang mining area in Bin county Shanxi province (Figs. 1 and 2). The sampling point in the shared wing of a syncline and an anticline is of less tectonic deformation. The primary structural coal samples ($R_{o,\ max}$ = 0.67%, medium low-rank; [35]) consist of homogeneous components and clear bands, and endogenic cracks are sparsely developed. In addition, the sample is cut by two sets of vertical joints. It can be seen that calcite and pyrite minerals largely filled in the endogenic fractures. The content of vitrain and clarain is higher than other macerals. Five coal column samples (numbers 1–5) adjacent to each other were drilled parallel to the bedding plane using the industrial drilling machine Z4116, and the sample size is φ = 25 mm, H = 45 mm (Fig. 3). The effects of the sedimentary micro-environment and macerals on the coal chemical structure of the five samples can be ignored.

### 2.2. Experimental system and methods

The sub-high temperature and high pressure coal deformation experiments were completed using the self-developed coal high temperature and pressure deformation experimental system TRTP-2000. This experimental system includes experimental deformation, pressure,