

Nanogeosciences: Research History, Current Status, and Development Trends

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Nanogeosciences are the international frontier field for the recent cross-development of geosciences and nanotechnology, also are the combination of nanometer and earth. It is possible to research the morphology, structures, and components of the earth on a nanoscale and further reveal the nanoscale information recorded by the substances on the earth, relying on research means, experience, and achievements of fast-developing nanotechnology and in combination with geoscience. Based on the summarization of the existing academic achievements in ultra-microscopic research on geosciences, the concept of nanogeosciences is put forward. Nanogeosciences are a series of geosciences, taking the matters on different layers of the earth as a research target, to reveal the information of nanoparticles and nanopores and their relationship with geoscientific phenomena and especially genetic types during the geoscientific processes on the basis of nanoscience and geoscience, as well as nanotechnology and geoscientific tools. Nanotechnology has been introduced in various branches of geosciences, at first nanogeology since the 1980s. From the nanogeology to nanogeosciences, nanogeosciences have witnessed three major developmental stages: exploratory research, development of several research directions, and the preliminary formation of the subject based on comprehensive research. Among them, relevant nanophenomena found in the field of geoscience have been observed and relevant geoscientific issues have been explored. In the

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nanogeosciences, the various branches formed by the combination of nanotechnology and geosciences has analyzed systematically, including: nano-mineralogy, nano-petrology, nano-geochemistry, nano-structural geology, nano-energy geology, nano-ore deposit geology, nano-earthquake geology, nano-environmental geology, nano-atmospheric science, and nano-marine science. The significant and groundbreaking scientific issues, along with the developing trend of nanogeosciences also has discussed, mainly include basic geological study, nano-ore deposit and unconventional energy, nano-mineralogy and coal-based materials, nanoparticles and environmental pollution, and nanostructure and geological disaster. Nanogeosciences are still in its initial stages but with a revolutionary challenge and huge prospects for development in geosciences.

Keywords: Nanogeosciences, Nanoparticles, Nanopores, Nanotechnology, Science Cutting-Edge, Development Trend.

CONTENTS

1. Introduction	5931
2. Basic Concepts and Research Methods of Nanogeosciences	5937
3. Nanoparticles and Nanopores on The Earth	5939
4. Developing Stages of Nanogeosciences	5941
5. Research Progress of Nanogeosciences	5943
5.1. Nano-Mineralogy	5943
5.2. Nano-Petrology	5945
5.3. Nano-Geochemistry	5947
5.4. Nano-Structural Geology	5949
5.5. Nano-Energy Geology	5951
5.6. Nano-Ore Deposit Geology	5953
5.7. Nano-Earthquake Geology	5954
5.8. Nano-Environmental Geology	5955
5.9. Nano-Atmospheric Science	5956
5.10. Nano-Marine Science	5957
6. Cutting-Edge Scientific Issues and Development Trend of Nanogeosciences	5958
6.1. Basic Research on Nanogeosciences	5958
6.2. Nanogeosciences and National Strategic Needs	5959
7. Conclusions	5961
Acknowledgment	5962
References and Notes	5962

1. INTRODUCTION

A nanometer, or nano, is a unit of length ($1 \text{ nm} = 10^{-3} \mu\text{m}$). Nanoparticles have many physiochemical properties different from those of macroscopic objects: surface and interfacial effect, small size effect, macroscopic quantum tunneling effect, quantum size effect, and more.^{1,2} For materials with the same chemical composition and structure, size is the dominant factor affecting their properties.³

The research ideas of nanomaterials were first proposed by the physics community. American physicist R. P. Feynman, who won the Nobel Prize in Physics in 1965, proposed the idea of arranging atoms according to people's will to produce the desired products.⁴ In the 1970s, the Massachusetts Institute of Technology began molecular device research, naming it nanotechnology, and then set up a nanotechnology research group in Stanford University. In July 1990, the first International Nanoscience and Technology (Nano-ST) meeting was held in Baltimore, where nanotechnology was divided into six



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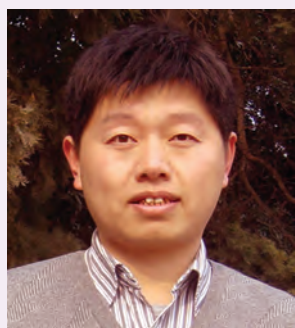
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Yan Sun was born in Shandong Province, China. He is a professor in School of Earth Sciences and Engineering, Nanjing University, and State Key Laboratory for Mineral Deposits Research. His research field covers structural geology, tectonophysics and tectonochemistry. He has attended and finished more than 30 scientific research projects, such as IGCP, National Natural Science Foundation of China and some basic explore programs. Moreover, he has published more than 200 research papers in magazines including *Science in China*, *Journal of Geophysical Research* and *Advanced Materials Research*, etc. He has written 4 monographs concerning faulted rock, regional structure and tectonochemistry. Since 1980s, he went to Japan, United States of American, France, United Kingdom and Australia for learning association, cooperation study and specimen determination. Recent years, he joins the science foundation project directed by Professor Yiwen Ju (University of Chinese Acadences), and he researches nano-scaled coating, weakening and delaminating in visco-elastic shearing zones with latent potentialities. Professor Sun pays attention to a preliminary identification of nano-sized textures in mineralization, hydrocarbon accumulation and seismic formation structure.



Quan Wan is a professor at the Institute of Geochemistry, Chinese Academy of Sciences (CAS). He was born in Sichuan, China in 1971. He received his B.S. in Chemistry in 1994 and M.S. in Polymer Science and Engineering in 1997 from Peking University, Beijing, China. In 2002, he received his Ph.D. degree in Materials Science and Engineering from the State University of New York at Stony Brook, USA. He worked in the Center for Bioengineering and Biomaterials in Temple University, Philadelphia, USA as a postdoctoral researcher and then an Associate Scientist from 2005 to 2010. In 2010, he joined the Institute of Geochemistry, CAS as a professor through the CAS "Hundred Talent Program." He has broad scientific interests in the fields of nanogeoscience and mineral materials science. Combining laboratory experimental simulation and field sample characterization, he and collaborators currently investigate the formation mechanisms, special properties and interfacial reactivity of nanoparticulate and nanoporous materials, as well as their relevance to the natural resources (such as the Carlin-type gold ore and shale gas reserve) and environment.



Xiancai Lu is a professor in mineralogy and computational geochemistry at Nanjing University (Nanjing, China), where he received B.Sc. (1993) and Ph.D. in geology (1999). Since 1998, he works as a lecturer, associate professor, and professor at the School of Earth Sciences and Engineering of Nanjing University. He is outstanding young researcher (the National Natural Science Foundation of China, NSFC). His research interests include surface chemistry of clay minerals, gas adsorption-desorption behaviors in micro-mesopores in geological materials (e.g., shale gas reservoirs), microbe-mineral interactions under redox-dynamic conditions. In the past ten years, his group developed an atomic-level knowledge of the surface chemistry and interface structure of clay minerals using strategies of computational chemistry. The microscopic structure of the interlayer space of swelling clays and surface acidity of edge surface have been well established. The surface adsorption of CO₂ and methane in coals and shales was quantitatively characterized. More recently he has a particular interest in the microbial oxidation/reduction of various minerals in mine waste and its environmental consequences. He is now devoting to multi-disciplinary studies, which have a common grounds of mineral surface and theoretical simulations.



Shuangfang Lu, was born in Hubei, China in 1962. He received his Ph.D. in petroleum geology from Research Institute of Petroleum Exploration and Development, China in 1993. Before September 2012, He engaged in research of petroleum geology and geochemistry in Northeast Petroleum University. He has focused on unconventional oil and gas research since 2011. From September 2012, He has been the professor and dean of research institute of unconventional oil and gas and renewable energy in China University of Petroleum (East China), and also is the director of the collaborative innovation center for tight (shale) oil and gas in Shandong province. His academic titles include mainly assistant director of education steering committee for geology of education ministry, deputy director of nanogeology Specialized Committee, deputy secretary general of specialized committee of unconventional oil and gas geology, geological society of China, and a council member

of Association of Asian-African petroleum geochemist. He has undertaken 26 state-level scientific research projects, 23 provincial projects, and more than 50 projects from oil company successively. He has published more than 300 papers with about 50 SCI-indexed and 5 books. He won the second prize of national natural science, China youth science and technology awards and the excellent talents of the ministry of education in new century.



Hongping He is a professor of mineralogy and the Deputy President of Guangzhou Institute of geochemistry, Chinese Academy of Sciences (GIGCAS). He received his B.Sc. in the Department of Geology, Nanjing University, China, in 1989, and Master degree and Ph.D. in GIGCAS in 1992 and 1999, respectively. He worked as a postdoctoral research associate in INSA-Lyon, France, in 2003–2004. In 2005, He moved to the School of Physical and Chemical Sciences, Queensland University of Technology as a visiting professor. He received Hou-Defeng Award from the Society of Mineralogy, Petrology and Geochemistry of China in 2003, and Golden Hammer Medal (Young Geologist Award) from China Geological Society in 2004, and Excellent Young Researcher from the Chinese Ceramic Society in 2007. Also, he was a laureate of Gilles Kahn Award (Fondation Franco-Chinoise pour la Science et ses Applications, FFCSA), and Outstanding Young

Researcher (the National Natural Science Foundation of China, NSFC) in 2007. His research fields include mineral structure and crystallography, clays and clay minerals, chemistry of mineral surface and natural nanomaterials. Dr. He is the authors of 18 patents and has published more than 180 SCI-indexed scientific papers. His H-index is 41. Now, he serves as an associate editor for *Clays and Clay Minerals* and *Solid Earth Science*, and an editorial board member for *Applied Clay Science*, *Acta Mineralogica Sinica* and *Bulletin of Mineralogy, Petrology and Geochemistry*.



Xueqiu Wang was born in Liaoning, China in 1963. He received his B.Sc., M.Sc. and Ph.D. in geochemistry from Jilin University in 1986, 1989 and 1998 respectively. Since 1989, he works as a geochemist, senior geochemist, chief geochemist, research fellow at the Institute of Geophysical and Geochemical Exploration (IGGE), Chinese Academy of Geological Sciences (CAGS). He was appointed as the director of the Key Laboratory of Geochemical Exploration of the Ministry of Land and Resources in 2012 and Executive director for UNESCO International Centre on Global-scale Geochemistry in 2014. He is an Emeritus Professor at China University of Geosciences, Chang'an University, Jilin University, and Chengdu University of Science and Technology. His research works focuses on exploration geochemistry, nano-geochemistry and global-scale geochemistry. He, as a professor at both universities and academy, have mentored 3 Post-doc, 16 Ph.D. and 7 Master students. He

has published more than 200 papers and 40 SCI-indexed papers. He was awarded for China State Government Outstanding Scientist Honor in 2008, China State Second-class Prize for Science and Technology Progress in 2012.

branches: nanophysics, nanochemistry, nanobiology, nano-electronics, nanofabrication technique, and nanometrology, marking the formal birth of nanotechnology. Meanwhile, two professional international publications, “Nanotechnology” and “Nanobiology” came into being. In March 1990, China held a symposium, organized by the Technical Institute of Physics and Chemistry of the Chinese Academy of Sciences, on nanosolids, demonstrating its foresight in cutting-edge disciplines.⁵ The International Conference on

Micro and Nanoengineering in 1994 and the World Technology Evaluation Center (WTEC) organized authoritative nano scientists to publish nano research works such as “Nano Structural Science and Technology: A Worldwide Study,” which pushed nanotechnology research into a new stage and extended it to various disciplines. Today’s society is in a rapid development of the “nano-era,” in which “nano” has evolved from a concept to technology and products, and is gradually becoming familiar to and



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Jianguang Wu, Professor of Engineering, Ph.D., Deputy General Manager of China United Coalbed Methane Corporation Ltd., Deputy Chief Engineer of National Major Science and Technology Projects of China "Large-scale Oil and Gas Field and CBM Development," A member of Coal geological Specialized Committee of China Coal Society, A member of the Coalbed Methane Specialized Committee of China Petroleum Society, Vice Chairman of the First CBM Technology Standardization Committee, The first group of experts in Coal Mining Industry Standardization, Expert of 863 Project of Ministry of Science and Technology and International Cooperation Projects. He has led more than 20 major scientific projects both nationally and provincially, with two awards of China Coal Industry Science and Technology and a First Prize of the National Energy. In particular, He started to participate in National Major Science and Technology Projects of China

(Large-scale Oil and Gas Field and CBM Development) from 2006, as the leader of the 39th Project and the 60th Pilot Project. Mr. Wu published over 30 papers in academic journals.



Hailing Liu was born in Guangdong, China in 1958. He received his B.Sc., M.Sc. and Ph.D. in exploration geology, marine geology, and geotectonics from East China Institute of Technology, South China Sea Institute of Oceanology, Chinese Academy of Sciences, and Nanjing University in 1984, 1989 and 1999 respectively. From 1984 to 1986, he worked as a teaching assistant at the East China Institute of Technology. Since 1989, he works as a research assistant, associate research fellow, and research fellow at South China Sea Institute of Oceanology, Chinese Academy of Sciences. He is a member of the nano-geology specialized committee of geological society of China. His research works focuses on the ancient Shuangfeng-Bijia collision orogenic belt in South China Sea, Qiongnan Paleo-Tethyan suture zone on north margin of the South China Sea, the Nansha lithospheric Layer-block structure, evolution model of Southeast Asian Tethyan tectonic domain, nano-

structural geology, and so on. He, as a Supervisor of Ph.D. at University of Chinese Academy of Sciences, have mentored 1 Post-doc, 2 Ph.D. and 8 Master students. He has published more than 170 papers, 17 SCI-indexed papers, and 4 monographs. He was awarded from governments of province and ministry for six times for his science and technology achievements.

applied by the majority of scientific and technical workers. The development of nanotechnology has provided fruitful new ideas and insights for humans to tackle the critical problems in the fields of environment, life, and energy.⁶⁻⁸

As early as the beginning of the 1980s, some geologists introduced nanotechnology into geology.⁹ And Chinese geologists initially formed the combination of nanotechnology and geology: they proposed the basic concept of nanogeology¹⁰⁻¹³ and obtained preliminary understanding of several branches, such as nano-mineralogy,¹ nano-ore deposit geology¹⁴ and nano-geochemistry.¹⁵ In addition, a significant number of early studies have

confirmed that nano-materials are widely found in the atmosphere, ocean, fresh water, rocks, soils, and even organisms and celestial bodies in a variety of states (aerosols, suspensions, solid deposition, etc.), forms (particles, coatings, pores, etc.), and with components (metals, oxides, sulfides, clay minerals).¹⁶⁻²¹ Geologists such as Hochella²² and Lower et al.²³ discussed the application of nanotechnology in the sphere of geoscience, and looked forward to the development of nanogeosciences.

In recent years, some geologists have conducted a series of research studies on the related fields of nanogeosciences. New research directions have been



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100 academic papers in peer-reviewed journals, and his current research interests include the coal geology and unconventional gas geology of Chinese coal basins as well as coal-related atmospheric chemistry in relation to air pollutions and human health.



Xiuling Wu was born in Hebei, China in 1956. She received her bachelor's degree in physics from Jilin University in 1982. She is a Professor in Faculty of Material Science and Chemistry, China University of Geosciences, Wuhan, China. She is a council member of Electron Microscopy Society of China and vice chairman of Electron Microscopy Society of Hubei province, China, a member of the Nanogeology specialized committee of Geological Society of China. She as a senior visiting fellow was invited respectively to The University of California, Berkeley, USA, 2011, and to The University of New South Wales, Australia, 2016. Her research interests include crystal structure and crystal chemistry of inorganic nonmetallic materials, nanometer materials and mineral and rock materials. She has mentored 17 Ph.D. students and 21 Master students. She has published more than 100 SCI-indexed scientific papers. She has (co)organized 5 international conferences.

She was awarded Second-class Prize for Natural Science of Ministry of Education, China in 2002 and First-class Prize for Teaching Achievements of Hubei Province, China in 2005.



Hongtai Chao was born in Shandong, China. He graduated from Department of Geology, Nanjing University and got his Bachelor's degree in 1986. He got his Master's degree and Ph.D. degree in 1986 and 1998 respectively from Institute of Geology, State Seismological Bureau, China. He currently is researcher and director general of Earthquake Administration of Shandong Province. He also is Chairperson of Shandong Seismological Society and President of Shandong Disaster Prevention Association. He has mainly engaged in seismological geology, active tectonics, seismic zoning and other related research work. He has investigated and studied geometry, kinematics and seismogenic structures of the Tanlu fault zone, and more than 50 papers have been published. In recent years, his research interest has focused on microstructure of active faults. He has obtained a lot of new information about clay mineral deformation in fault gouges at nano/micro-scale, which is of

great significance to help explain seismogenic mechanism of large earthquakes.



Qinfu Liu was born in Henan, China. He is a professor at China University of Mining and Technology, Beijing. He received his Master degree in Coalfield Geology in 1987 and Ph.D. degree in Coal, Oil and Gas Geology and Exploration in 1995, China University of Mining and Technology, Beijing. He got an outstanding young teacher award in 2000. From 2001 to 2002, Dr. Liu joined the Applied Clay Laboratory, Indiana University Bloomington, USA as a Visiting Scientist. In 2001, he became a Professor at China University of Mining and Technology, Beijing. He was appointed as the director of energy geology department of China University of Mining and Technology, Beijing, and vice-president of clay minerals specialized committee of China Non-metallic Mineral Association. He advocates the interdisciplinary research, seeks theoretical innovation and high-level application development. His scientific interests are layered mineral materials

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Guochang Wang was born in Qingzhou, China in 1983. Currently, he is an assistant professor of Petroleum and Natural Gas Engineering at Saint Francis University. Prior to that, he worked as a postdoctoral research fellow at University of Chinese Academy of Sciences from August 2012 to February 2015. He earned his doctorate (Ph.D.) in petroleum geology from West Virginia University in 2012 and B.S. in petroleum engineering from China University of Geosciences (Wuhan) in 2006. Dr. Wang has authored more than 50 scholarly publications in peer-review journals, conference proceedings and presentation. His research area including 3-D geological modeling, shale pore structure characterization, CO₂ sequestration and CO₂-EOR, and digital core modeling.



Yue Sun received his B.S. degrees in Environmental Engineering from China University of Mining and Technology, Xuzhou, China in 2006, and Ph.D. in Environmental Science from China University of Mining and Technology, Xuzhou, China in 2014. Currently he is a postdoctoral researcher in College of Earth Science, University of Chinese Academy Sciences, Beijing, China. He is a member of the nanogeology specialized committee of geological society of China. His main research interests include environmental hydro-geochemistry and water treatment technology. Sun participates in some great scientific research projects including National Science and Technology Major Project and the State Key Program of National Natural Science Foundation of China.

created, especially with regard to nano-petrology^{24–26} nano-structural geology,^{27–31} nano-energy geology,^{27, 32–36} nano-earthquake geology,^{37–39} nano-environmental geology^{20, 40–44} and new progress has also been made on the existing branches of nanogeosciences.^{18, 45–50} During this period, summaries of the research on geologic processing at the nanoscale^{51–53} made by European, American, and Japanese geologists also provided some theoretical basis for our further study of nanogeosciences and accumulation and mineralization.

After several hundred years of development, great progress has been made in geoscience in the macro and micro fields. Along with the great progress of science and technology, geoscience has developed toward two poles, i.e., more macroscopic and microscopic: celestial planetary science and nanogeosciences. As nanoparticles and nanopores have significant specific properties, it is of great scientific value to study the formation mechanism, evolution mechanism, and aggregation state of nanostructures during geological processes. Nanotechnology will bring a new leap to the development of geoscience in the 21st century, thus helping geoscience obtain breakthroughs at the mesoscopic scale. Nanotechnology has been introduced into various branches of geoscience. Among them, relevant phenomena found in the field of nanogeosciences have been predominantly observed, and relevant scientific issues have been explored. Since the concept of nanogeosciences has been put forward, to date a kind of comprehensive subject was formed.^{22, 23, 54, 55} However, no research on nanogeological effects and the mechanism of accumulation and mineralization has been systematically conducted. A nanogeosciences theory system has not been established, and the overall understanding of nano accumulation and mineralization is not perfect.

This paper, based on former research about nanogeosciences, aims to guide geoscience to a more microscopic level, to study nano-minerals and petrology (nanocrystals and surface effect as well as petrogenesis), nano-structural geology and geochemistry (nano-deformation and chemical behavior and its mechanism), nano-energy geology and ore deposits (nano accumulation and mineralization effects and dynamical mechanisms), and apply the nanogeoscientific theory to environmental protection and disaster

prediction, etc. At the same time, it further synthesizes and clarifies the important and key cutting-edge issues in the fields of nanogeosciences, and explores the essential contact between “Nano” and “Earth.” Thus enriching and developing nanogeosciences theories and methods, and providing an important scientific basis for the utilization of mineral and carbon based material, the exploration and development of energy and mineral resources, environmental protection, and disaster prediction.

2. BASIC CONCEPTS AND RESEARCH METHODS OF NANOGEOSCIENCES

Based on the foreseeability of the combination of nanotechnology and mineralogy, Hochella pointed out that with nanogeosciences, it is possible to understand a variety of geochemical processes and mechanisms from nanoscale, the law of element migration, the effect of nanoparticles and nanopore structure on geochemical processes and behaviors, as well as interpret geological evolution and Earth development information from the mesoscale.²² And on account of the summarization of the existing academic achievements in ultra-microscopic research on geosciences, Ju et al.⁵⁴ comprehensively put forward the initial concept of nanogeology. In this paper, nanogeosciences are further summarized as follows: nanogeosciences, relying on nanotechnology and geosciences, with the nanotechnology and geoscientific research method as the means and the matters of the earth as the object, are a series of sciences that explores and researches nanoparticles and pores known or to be known in different layers of the earth, for the purpose of revealing the relationship between nano-effect and geoscientific phenomena during the geological process as well as the law of the formation. Nanogeosciences are the highly integrated, cross-disciplinary fields, which require comprehensive study of several disciplines, and thus it is difficult to conduct traditionally single-disciplinary research.

The studies of nanogeosciences be related to the evolution processes and mechanism of the nanoparticles or nanopores in different layers of the earth, such as formation, migration, and accumulation. According to the current research direction and research progress, based on the frame of previous “nanogeology,”

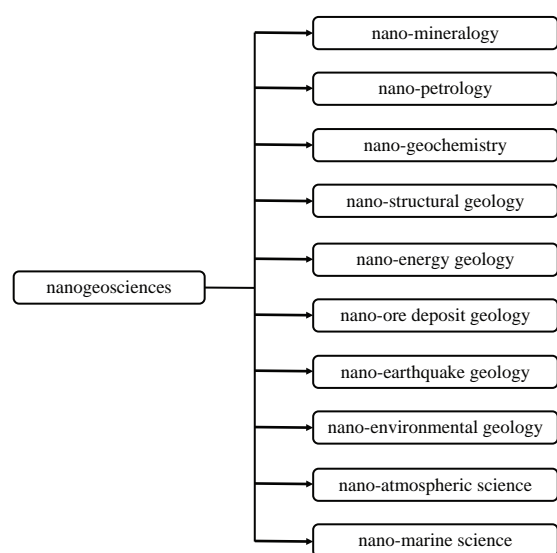


Figure 1. The main classification of nanogeosciences.

we divide nanogeosciences into ten branches: nano-mineralogy, nano-petrology, nano-geochemistry, nano-structural geology, nano-energy geology, nano-ore deposit geology, nano-earthquake geology, nano-environmental geology, nano-atmospheric science, and nano-marine science (Fig. 1). As a preliminary classification scheme, it needs to be complemented and perfected in the follow-up research work.

The different layers of the earth contains the largest amount of nanoparticles. In a sense, nanoparticles, which are different from both macroscopic matters and microcosmic matters, are an important constituent part of the layers. They are nanoscale materials assembled by atoms and molecules or crushed by the macro materials.^{55,56} Correspondingly, nanopores exist widely in porous geologic media, and because of their small size and large overall storage space, they may play an important role in the geological process. Research shows that the specific surface area of nanopores may occupy more than 90% of the total specific surface area of the medium.^{32,46,56}

Except regular ways, the technological means of nanogeosciences mainly rely on nanoscale material direct observation techniques which based on the scanning tunneling effect etc., nanostructure characterization of materials represented by various spectral methods, and characterization of nanopores such as low temperature and low pressure fluid adsorption, as well as numerical simulation methods represented by molecular dynamics simulation of seepage.

In detail, the direct observation techniques mentioned above include Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Scanning Tunneling Microscopy (STM), Atomic Force Microscopy (AFM), and CT scanning (CT), etc. These methods can be used for observation in the atmosphere and in solution and

can be developed into molecular and atomic control technology and nanoprocessing technology. They can fully be used in scientific research, processing and utilization in geological materials, geologic processing, and the mining industry at the nanometer level.^{7,13}

The characterization methods of nanostructure of materials includes X-ray diffraction, Fourier Transform Infrared Spectroscopy (FTIR), Laser Raman, ¹³C Nuclear Magnetic Resonance Spectroscopy (¹³C NMR), pulsed laser deposition for detecting the dynamic changes of nanostructure, etc.,^{26,57,58} which are applied in the study of macromolecular structure of organic matter.

The research of nanopores is inseparable from the technical means and analytical method, with the resolution up to nanoscale. The characterization and quantitative research of shale pores have shown important progress in the laboratory. TEM,^{59,60} AFM,^{52,61} Mercury Intrusion Capillary Pressure (MICP),⁶² Ultra-Low Pressure Liquid N₂/CO₂ Adsorption,^{32,63–65} NMR,^{26,66–68} etc. have been applied to the characterization of nanopores and have achieved good results. In recent years, for the study of the pore characteristics of tight reservoirs, especially organic-rich shale reservoirs, only the improvement of resolution has been unable to meet the demand, and thus observation and simulation of their three-dimensional pore characteristics are gradually developing.^{36,69–74} With Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) and Nano-Transmission Microscopy (Nano-TXM, also called Nano-CT) as the representative, these studies are based on a large amount of experimental data to make digital core models and explore the three-dimensional development characteristics of nanopores and their relationship with the surrounding material components.

In recent years, many scholars have combined the Monte Carlo method and the molecular dynamics method to study the law of material diffusion and adsorption behaviors under microcosmic conditions. The Monte Carlo method and the molecular dynamics simulation method provide an effective means for studying the characteristics of fluid occurrence in the nanopores of tight rock.^{75–78} The former, based on the theory of probability and statistics, uses corresponding mathematical methods to establish the probabilistic model and uses the computer to carry on the simulation experiment, to finally obtain the result that meets the requirements, while the latter, by setting the interaction (potential function) between the atoms (molecules) and the associated system (i.e., the action objects and conditions), determines the basic simulation categories. The lattice Boltzmann simulation method, developed based on molecular dynamics, is also a typical microcosmic method. It is not limited by the continuity hypothesis and can simulate the flow of oil and gas in micro-channels in porous media.^{79,80} At the same time, the lattice Boltzmann method has the advantages of high computational efficiency and easy realization of boundary conditions compared with other numerical methods. This method has been

applied to the study of fluid transport mechanism of shale reservoirs.^{53, 81}

3. NANOPARTICLES AND NANOPORES ON THE EARTH

With regard to scale, nanoparticles can be divided into: zero-dimensional nanoparticles, one-dimensional rod-like nanoparticles, and two-dimensional nanostructure.

Zero-dimensional nanoparticles (as shown in Fig. 2, observed by Hailing Liu), such as natural gold particles with a size of 7–10 nm in the Carlin-type gold mine, gold particles with a size of 5–20 nm in illite, colloidal particles in water, and more.^{41, 43, 82, 83} Li et al. found that nanoscale natural gold particles (Au₀) exist in coarse-grained pyrite by Scanning Electron Microscopy X-ray Energy Dispersive Microanalysis (SEM-EDX), Electron Probe Microanalysis, and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). At the end of the 1980s, 2–5 nm nanoscale ultrafine particles were found in late-Mesozoic granitic mylonite slippery blades when measurement of deep drilling core samples with SEM was taken in California, USA.²⁹ One-dimensional rod-like nanoparticles, (as shown in Fig. 2, observed by Chen and Liu) represented by nano-rod calcite, provides a new clue for reconstructing the paleoclimate and is of significance in the research of nanometer minerals in the environment, genesis of carbonate

in loess, and paleoclimate reconstruction.⁸⁴ Moreover, one-dimensional tubular nanoparticles, such as tubular nanometer halloysite,^{55, 84} have excellent adsorption performance in the removal of industrial wastewater containing chromium after being subject to chemical modification.⁸⁵ In addition, the one-dimensional nanoparticles include sepiolite, attapulgite, and more. The two-dimensional nanoparticles (as shown in Fig. 2, observed by Liu) include montmorillonite, hydrotalcite, etc. Porous nanoparticles include diatomite, perlite, etc. In addition, there is a series of research studies about organic rocks in nanoscale, especially macromolecular structure of coal, which help in understanding the physical properties of coal reservoirs and provide preventive measures for gas outburst.⁸⁶

Revealing the origin of nanoparticles in different layers of the earth is a prerequisite for deeper understanding. It is helpful to reveal the correlation between nanoparticles of minerals and macromolecule structures of organic matters in the earth system and also conducive to studying the extractive technology of the nanoparticles. Nanoparticles are produced under extreme conditions, which play an important role in the formation of macroscopic materials, the understanding of the formation of gemstones, the construction of the earth, and the exploitation and utilization of nanoparticles. Several major causes of natural nanomaterials have been discussed:^{47, 55} Some matter stays in the nanoscale stage during celestial evolution and geologic processing; on the fault zone formed by sliding, the

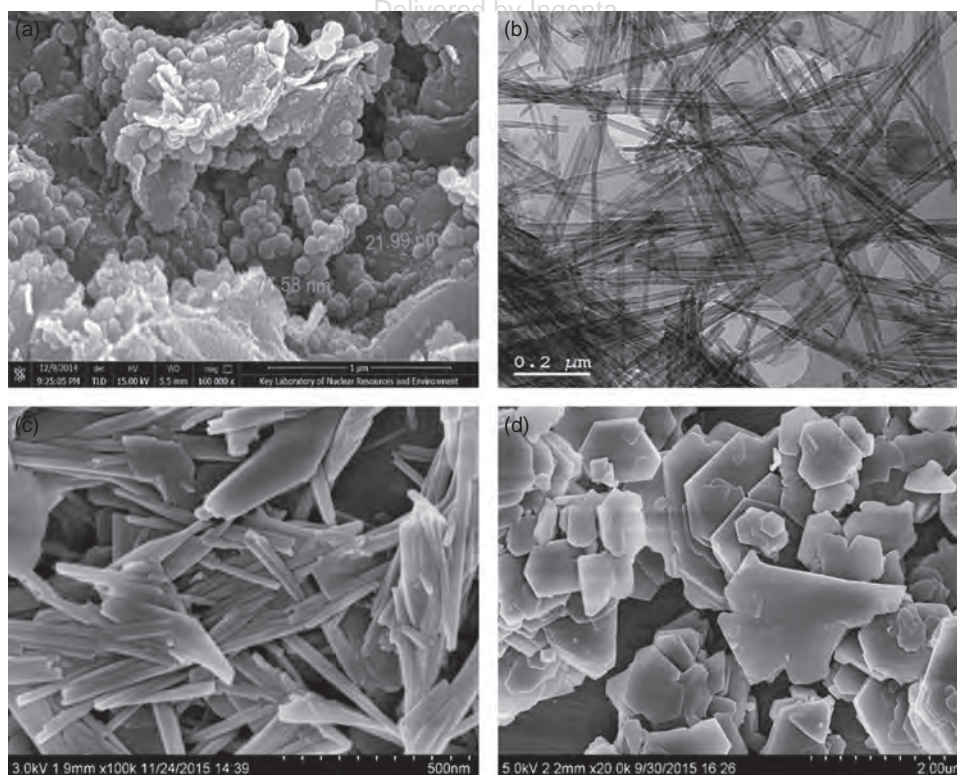


Figure 2. Several kinds of typical nanoparticles on the earth. (a) SEM image of loose accumulation of nanoparticles in granite, (b) TEM image of palygorskite in Anhui province, (c) SEM image of kaolinite nanoscroll exfoliated from plate kaolinite, (d) SEM image of original kaolinite plate.

rock can be ground into nanoparticles, round and spheric nanoparticles can be varied and formed into lamellar structures and various tectonic patterns. In the process of earthquake fission, the interaction between materials such as high-speed shearing force and collisional friction will generate nanomaterials by reason of thermal decomposition, abrasion, grinding, and powdering. Substances in the sea, lakes, groundwater, hydrothermal fluid, and magma will precipitate and grow up to form nanomaterials under certain conditions.

Natural nanoparticles are widespread in nature, and the complexity of the geological environment has resulted in the original diversity of natural nanoparticles. Deducing

the geological conditions at the time of the formation of nanoparticles through the study of the origin of nanoparticles, along with how they push the whole earth process in an unusual way, is of great research value and significance to reconstruct earth system science from the nanoscale.⁵⁵

The observation and analysis of the natural nanoparticles in nature can help us to understand the mechanism of the formation of macroscopic geological phenomena, while the study of nanoscale pores will help us to explore the enrichment law of energy from another aspect, develop the adsorption ability of the material, and explain the mechanism of gas outburst of coals, etc. At present, based on the worldwide exploration and development of oil and

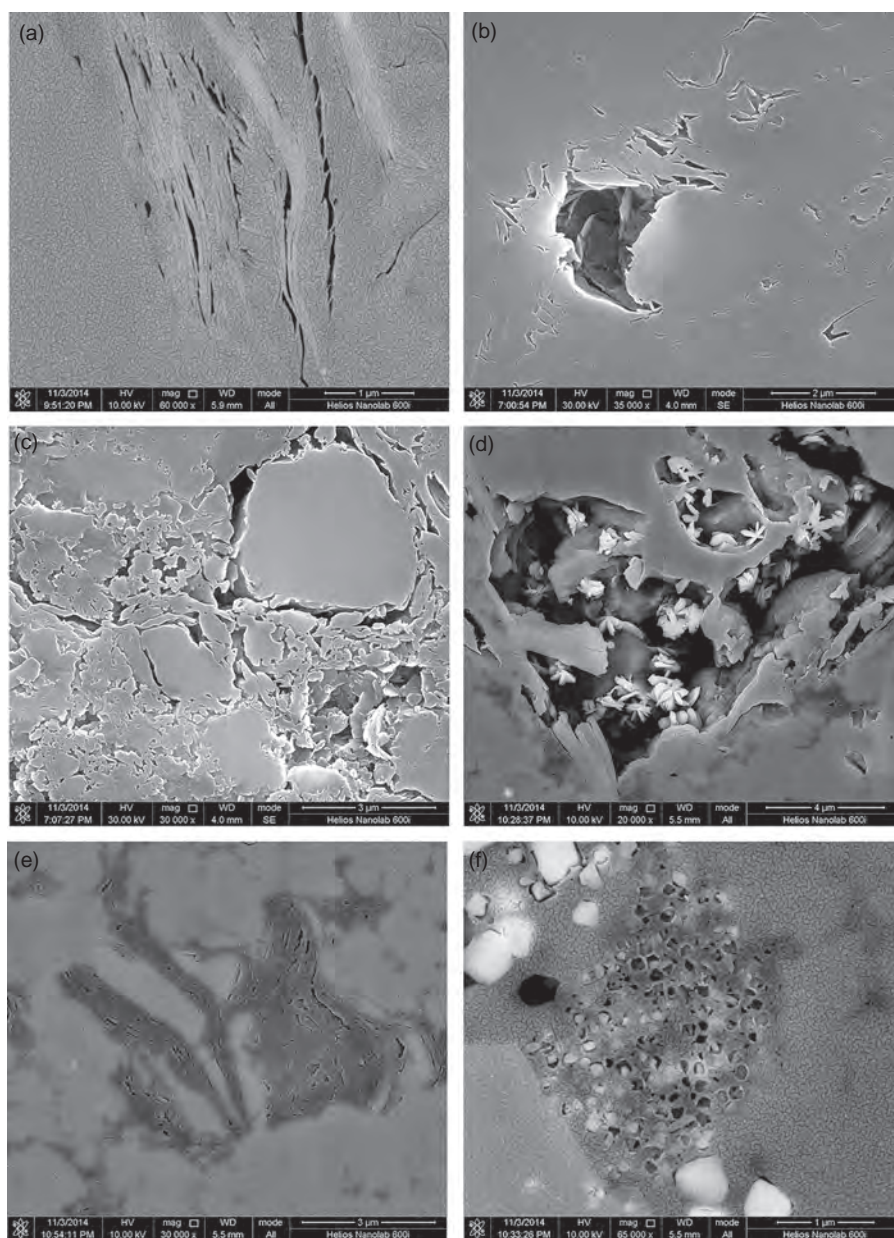


Figure 3. SEM images of nanopores of organic shales. (a–c) Samples from permian of Huaibei coalfield of China. (d–f) Samples from Longmaxi formation of Sichuan basin of China.

gas resources of tight rock strata, global oil and gas exploration targets have also changed from the conventional oil and gas trap fields of micrometer-millimeter pore throats to continuous oil-gas accumulation with source-reservoir integration or source-reservoir intergrowth of nanopore throats. Unconventional oil and gas (especially coalbed methane, shale oil and gas, tight sandstone oil and gas, etc.) has gradually become a kind of research hotspot of oil and gas exploration and development in the world.^{34, 87–91}

In recent years, more and more research has been done on the characteristics of porosity and permeability of tight reservoirs, and understanding has also improved. However, as the pores of unconventional reservoirs are extremely small (mostly nanoscale), and the forms are also complex, there are still many problems to be studied urgently.^{92, 93}

The new understanding of hydrocarbon storage capacity of the nanoscale pores of tight rock formations that originally act as source rock and cap rock not only subverts the traditional theory of oil and gas but also provides a new direction of oil and gas exploration. At present, many research papers have been published on the characteristics of nanoscale pores of tight reservoirs^{35, 36, 59, 64, 94–102} (Fig. 3, observed by Ju), covering the studies on classification of genetic types, heterogeneous distribution, and connectivity, as well as the relationship between material composition, geochemical characteristics, and the developmental condition of shale, the establishment of oil and gas storage and transportation models, and other aspects.

In geoscience, in addition to the tight unconventional oil and gas reservoirs, plenty of nanopores are also developed in minerals/matter such as natural zeolites and coal-based porous carbon.^{103, 104} Huge specific surface area and pore volume give them unparalleled adsorption capacity, and therefore, they can be used as adsorbents to remove harmful substances in gas or liquid for environmental pollution control. In natural minerals, clay minerals are most representative.^{105, 106} Also based on good adsorption property, liquefying and sequestering CO₂ into deep rock formations is a predictable ideal solution to the greenhouse effect. The nanoporous materials in nature are important storage media.^{107, 108}

4. DEVELOPING STAGES OF NANOGEOSCIENCES

Relying on the research means, experience, and achievements of fast-developing nanotechnology, and with the combination of geosciences, it is possible to research the morphology, structures, and components of the substances of the earth from nanoscale and further reveal the information of nanoscale recorded by different layers of the earth. Based on research progress in recent years (mainly since the 1980s), scholars in the fields of geoscience began to realize the importance of understanding the motion process of earth substances on a nanoscale, further resulting

in the emergence of nanogeosciences. From the nanogeology to nanogeosciences, nanogeosciences have witnessed three major development stages.

(1) Exploratory research on nanogeosciences (1980s to about year of 2000)

As early as the 1980s, some geologists introduced nanotechnology into geology, symbolizing a preliminary combination of nanotechnology and geoscience: They proposed the basic concept of nanogeology as well as preliminarily established several related branch subjects, carried on early-stage exploration.^{5, 9–14, 109–116} Chen¹ summarized the emerging nanotechnology, in which he introduced nanosolids as well as TEM, STM, AFM, and other research methods. He proposed that the development of nanotechnology initiated a new research area of geoscience, pushing the understanding and transformation of nature to a new level and enabling the development of geoscience to reach a higher level. Shi¹¹⁷ emphatically discussed the impacts of nano effect on geology, especially the theory of ore deposits, and concluded that nano effect was one of the major natural actions for the migration, enrichment, sedimentation, and mineralization of metallogenic materials. It had been already found that the geogas method was a new way to search for deep and concealed ore deposits,^{118, 119} they selected the sampling pieces with abnormal distribution of geogas in field geogas measurement and interior model test to observe with AFM, TEM and SEM, finally proving that geogas substances migrated in the form of nanoparticles. In the field of nanogeosciences, the preliminary exploration was focused on introducing its basic concept and predicting the application prospect of the combination of nanotechnology and geoscience.

(2) The introduction of nanogeosciences and researches on the development of several research directions (year of 2000 to year of 2010)

In the research on natural nanoparticles, nothing was better known than the discovery of sharp drop phenomenon of nanogold particles' fusing point.¹²⁰ However, its achievements were mainly about the material science or physicochemical properties of matter, but less related to geoscience. Until the early 21st century, Hochella,^{4, 22, 121} Lower et al.²³ and other geologists had discussed the prospect of applying nanotechnology into geoscience and predicted the development of nanogeosciences. They pointed out that natural nanoparticles widely existed in the natural world, and many of them had been known to us long ago. What made nanogeosciences really ascend to a scientific height was the research on materials and structures at the nanoscale in recent years, by which to measure, deduce, and even predict macro geological phenomena. From early research about nano-mineralogy to various of branches of nanogeosciences, remarkable achievements had been obtained.^{16, 17, 26, 32, 33, 38, 103, 122–129}

(3) Comprehensive researches on nanogeosciences and the initial formation of the subject (year of 2010 so far)

During the past few years, geologists all over the world have made a series of research studies in various fields related to nanogeosciences and made major improvements.^{90, 105, 106, 130–157} Nanogeosciences have gained more and more attention from the overall international geoscience field. Since 2009, the Annual Goldschmidt Geochemistry Conference has repeatedly listed geochemistry issues at the nanoscale as a special theme of equal importance to other major research fields.⁵⁶ By reason of demand for energy and mineral products, more concern about environmental problems, frequent geological disasters, and other matters, China has focused more attention on the study of the micro mechanism of the geological process, which has made nanogeosciences develop rapidly. The initial formation of nanogeosciences as academic subjects in China has been promoted by several landmark events below:

(1) The Xiangshan Science Conference in Beijing, China.

The Xiangshan Science Conference of China is a high-level, interdisciplinary, and small-scale standing academic meeting committed to exploring the cutting-edges of science and promoting knowledge innovation for the Chinese scientific community.

From November 5 to 7 of 2013, the Xiangshan Science Conference held the 476th Symposium with the theme “Cutting-edge Scientific Issues about Nanogeosciences and Nano Accumulation and Mineralization” (*Cutting-edge Scientific Issues about Nanogeosciences and Nano Accumulation and Mineralization*, 2016, the first author of this paper as the applicant and the organizer) in Beijing. This conference primarily covered the following central topics:

- ① Nano-mineralogy and petrology: nanolattice and surface effect and genesis of rock ore;
- ② Nano-structural geology and geochemistry: nano-deformation and chemical behavior and the mechanism;
- ③ Nano-energy geology and ore deposit: nano accumulation and mineralization effect and dynamic mechanism;
- ④ Nanogeosciences and environment and disaster problems: new prospect and challenges.

This conference deeply explored the future development trend of nanogeosciences and promoted development of the subject.

(2) Establishment of the Nanogeology Specialized Committee, Geological Society of China and holding of relevant academic conferences.

As no national research team has been established aiming at scientific exploration of advantages in research direction of the international cutting-edge in the nanogeosciences field, the Nanogeology Specialized Committee, Geological Society of China (GSC) was therefore founded in August 2014, and relevant research institutes and academic organizations were also formed. As the first international research organization in the area of nanogeology

and even nanogeosciences worldwide, this Committee helps in gathering dominant scientific forces, forging a high-level academic team, and solving major scientific problems arising in the field of nanogeosciences and study of the process of accumulation and mineralization.

The 2015 GSC Annual Meeting was held in Xi'an. At this meeting, the session of nanogeology and accumulation and mineralization was separately set, indicates strong indicator that nanogeosciences have attracted significant attention in China. In October of the same year, the Nanogeology Specialized Committee co-sponsored the Third Unconventional Petroleum Geology Symposium in Qingdao. In December, under the organization of the first author of this paper, the First Academic Symposium on Nanogeosciences of China and the Founding Conference of the Nanogeology Specialized Committee, Geological Society of China, under the theme of “Nanogeosciences: Revolutionary Challenge in Geoscience Fields,” was successfully held in Beijing. This meeting covered many research aspects of nanogeosciences, mainly including nano mineral and rock, nano structural geology and geochemistry, nano-energy geology and ore deposit, nano mineral and carbon-based new composite materials, nanogeology, disaster and environmental problems, application of nanotechnology into earth spheres and their interactions, research techniques and methods of nanogeosciences. To further display and exchange the latest domestic and foreign research achievements in nanogeosciences and summarize material and key scientific problems of the field, the Second Academic Symposium on Nanogeosciences of China and the 2016 International Academic Symposium on Nanogeosciences, which covers all aspects of nanogeosciences research, was held in November in Qingdao, China.

(3) Journals related to international nanogeosciences and financial support from national program-related funds.

In recent years, several journals related to international nanogeosciences have been published, including *Reviews in Mineralogy and Geochemistry* (2001, Volume 44), *Environmental Science and Technology* (2005, Volume 39), *Elements* (2008, Volume 4), *Ore Geology Reviews* (2011, Volume 42), *Bulletin of Mineralogy, Petrology and Geochemistry* (2016, Volume 35) of China, and other academic journals. In the special issue of nanogeosciences published in the first issue of *Bulletin of Mineralogy, Petrology and Geochemistry* of China in 2016, ten comprehensive representative papers of various directions were published, aiming to further strengthen basic and application research and improve self-innovation capability in the field of nanogeosciences with the help of nanotechnology and geology research means, experience, and achievements. The special issue on emerging nanogeosciences launched at this time by the *Journal of Nanoscience and Nanotechnology* further promoted international academic communication, gathered academic hot topics, and expanded the influence of nanogeosciences.

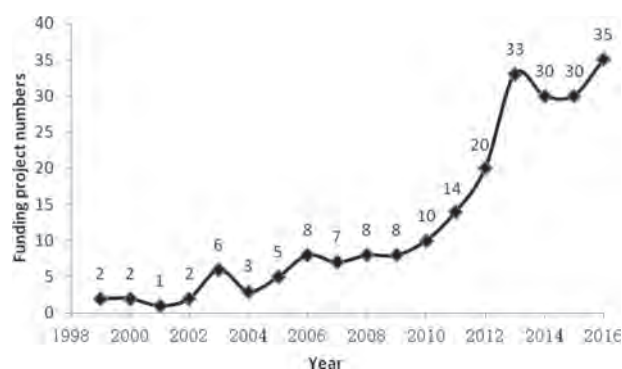


Figure 4. The funding for nanogeosciences of the national natural science foundation of China after 1999.

According to the statistics and surveys made by the author, just for China, strong support has been provided by the National Basic Research Program of China, the National Major Projects of China, the Natural Science Foundation of China, etc. Taking the Natural Science Foundation of China as an example, the first financial support was offered in 1999. Thereafter, the number of the funded programs has basically shown a year-by-year growing trend, and especially since 2010, has even soared (Fig. 4). In China, domestic research achievements with regard to nanogeosciences have increased sharply in recent years, signifying that a great upsurge of refreshing the understanding of geological phenomena and processes at the nanoscale has emerged, which would be impossible without the great funding at the national level.

5. RESEARCH PROGRESS OF NANOGEOSCIENCES

Nanogeosciences are a series of sciences intended to research the Earth with advanced nanotechnology and geoscience methods. In recent years, certain extent studies have been made in this field, achieving great progress. Now classified detailed exposition are being made on various branch subjects of nanogeosciences.

5.1. Nano-Mineralogy

A mineral has both a resource attribute and an environmental attribute, and is the information carrier and recorder of all geological processes. Mineralogy is a basic subject of geology, which uses Å as one of the basic measurements. As $1 \text{ nm} = 10 \text{ Å}$, the measurements used in nano science are closely related to those used in mineralogy. Research on crystal structure in the field of mineralogy involves many problems such as crystalline form, defect, order, and disorder, as well as color, optical property, paramagnetism, electric conductivity, piezoelectricity, and trace impure elements of minerals. In addition, critical zones of the earth are under the interactive effect of water-mineral-living beings and have extensively recorded nanoscale substances and geological processes, which are

also the emphases of nanotechnology research. The main means and methods used to research these problems are the same as those used in nanotechnology. Therefore, the main research content and methods of mineralogy and nanotechnology are basically the same.^{1,4,5}

Nano-mineralogy is the intersection and integration of nanotechnology and mineralogy. With HRTEM, STM, and AFM and other atomic-scale resolution technologies as the characterization methods, mineralogy reveals the mesoscopic structure, morphology, and interface relations and formation mechanism of minerals and is focused on the studies of mineral growth, dissolution, transformation and evolution, biomineralization, and interaction between living beings and minerals, so that mineralogy will have a broader development space and application prospect (Fig. 5, observed by Wu; Fig. 6, observed by He; Fig. 7, observed by Chen).^{17, 134, 143, 158–162} People's knowledge of mineralogy tends to be focused on the morphology and related characteristics of macro mineral monomer and polymer, without in-depth and intensive research on nano mineral particles, nano solid minerals, and structures of nano minerals. In traditional mineralogy research studies, minerals are regarded as ideal crystal lattice, but in nano-mineralogy research, emphasis is placed on nano mineral particles, nano mineral solids, and structural characteristics of nano mineral structure, as well as related petrology,

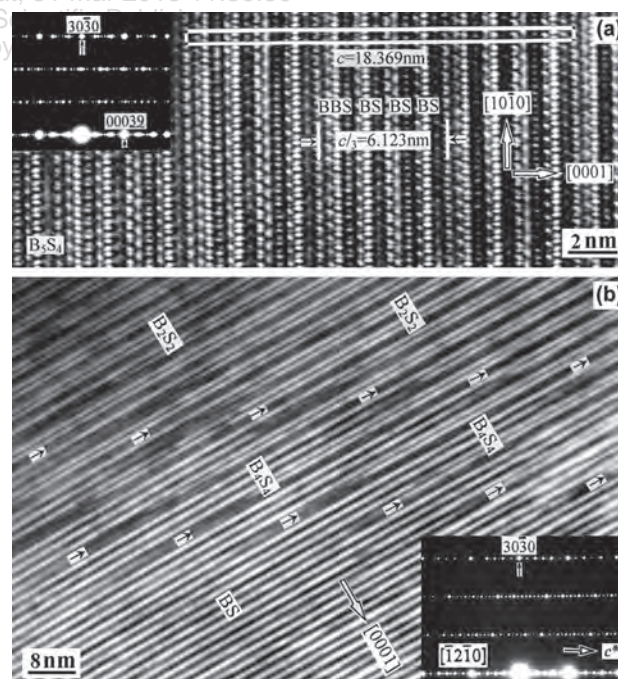


Figure 5. The new mixed-layer mineral phases (B_5S_4 , B_2S_2 and B_4S_4) were discovered by HRTEM in parisite $[BS(CaCe_2(CO_3)_3F_2)]$; B layer, $CeCO_3F$; S layer, $CeCO_3F \cdot CaCO_3$] of the calcium rare-earth fluorocarbonate mineral series in Sichuan province, Southwest China. (a) B_5S_4 , $Ca_4Ce_9(CO_3)_{13}F_9$; (b) the phase transformation and syntactic intergrowths among the BS, B_2S_2 ($Ca_2Ce_4(CO_3)_6F_4$) and B_4S_4 ($Ca_4Ce_8(CO_3)_{12}F_8$) formed by stacking faults in parisite.

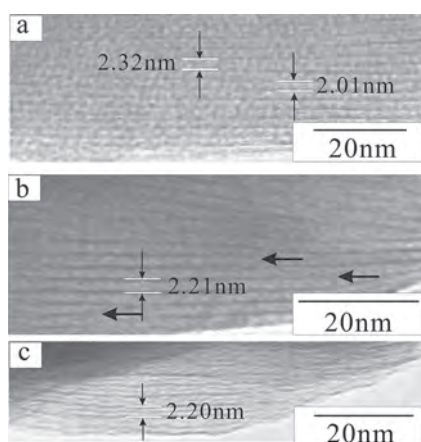


Figure 6. TEM images of nano-layer in organoclay.

ore deposits, structural geology, geochemistry, and other geological subjects.^{1,2} Nano-mineralogy, if combined with material science research, will provide a theoretical basis for the preparation, characterization, and structure interpretation of new nano materials.²⁵ If combined with microbiology, it will spur research on the growth of minerals inside and outside microbial cells at the nanoscale, providing theoretical and technical methods for biomineralization, interaction between living beings and minerals, biological chemical weathering, biological self-organizing material synthesis, the origin of life, etc. If combined with energy geology, it will enable research on the formation mechanism of nanoscale minerals existing in energy and mineral resources, further helping in inferring favorable energy storage environment and producing certain tracing significance.¹⁶³ If combined with geochemistry, it will facilitate research on geochemical behaviors of elements in the processes of mineral dissolution, crystallization, metasomatism, weathering, and transformation on a nanoscale, and exploration into element migration mechanism, geochemical cycle of elements, and more. Nowadays, nanoscale synthetic minerals are also acquired and observed under electron microscopes¹⁶⁴ (Fig. 8, observed by Wan and He).

Nano minerals themselves to nanoscale, or with nanostructure, appear together in the form of aggregate in most cases. They include mineral particles with a grain size as small as nanoscale, minerals of one-dimensional nanostructure (such as halloysite of nanotube structure), layered minerals of two-dimensional nanostructure (such as clay minerals). HRTEM, STM, and AFM studies of actual minerals have shown that nanoparticles and nanostructure objectively exist in minerals, and such nanophenomenon is more common in crystal surface and interface. Within several to dozens of nanometers' depth in the crystal surface, the composition is different from that inside the crystal, and such difference is represented by crystal surface composition segregation, surface adsorption of exotic atoms or molecules, and the interaction between the former two. The special nanostructure and composition of the crystal surface determine its surface properties, and therefore research on the surface properties of crystals plays an important role in discussing the physical and chemical environment for the formation of minerals as well as the formation reasons of minerals.¹⁶⁵ Between two mineral facies, not only nanoscale particles exist, but nanoparticle aggregates will also appear under particular physical and chemical conditions, such as clay mineral, zeolite, colloidal mineral, volcanic lava, volcanic glass, meteorite glass, fusion crust, and tectonite, and mainly includes four categories:

- (1) Clay minerals. Clay minerals are not only fine but also have complicated structures, and often show regular or irregular mixed layers within nanoscale. The surface reactivity of clay minerals is the key to determine their function and industrial value in geological and geochemical processes.
- (2) Quasi-crystal nanostructure. Numerous research studies indicate that ideal quasi-crystal structure can be deemed as the result of multiple-fractal-dimension arrangement of nanoparticles.¹⁶⁶
- (3) Nanostructure in colloids. Colloidal mineral is the aggregate of nanoparticles (1–100 nm) in minerals and included in the nano solid category; with particles

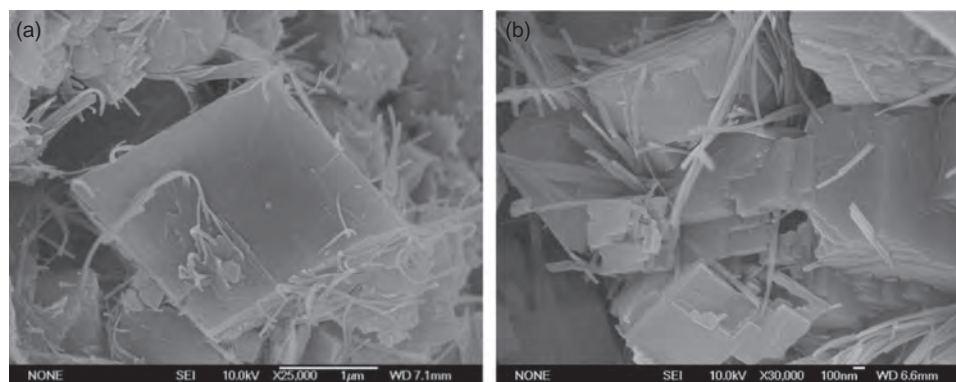


Figure 7. SEM images of genetic relationship between several kinds of minerals. (a) Genetic relationship between attapulgite-montmorillonite-dolomite, (b) genetic relationship between attapulgite and dolomite.

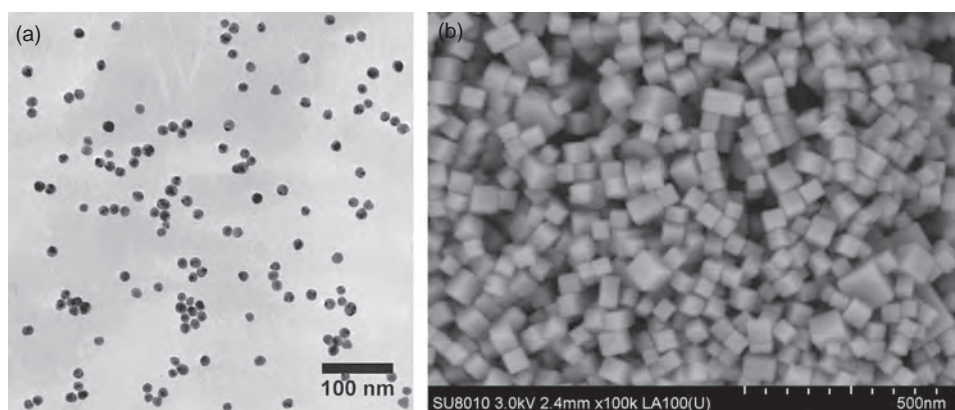


Figure 8. Nanoscale synthetic minerals. (a) Nanoparticles of synthetic gold. (b) Nanoparticles of synthetic pyrite.

arranged in an irregular and disorderly manner, colloidal mineral has an extremely large surface area.

(4) Nanostructure in crystalline rocks. Many kinds of nanoscale minerals have been discovered in volcanic rocks, meteorolites ever subject to strong impact metamorphism, and continental rocks ever subject to ultrahigh pressure metamorphism, which provide plenty of information and hard evidence for inferring the formation mechanism of rocks and deducing geological-tectonic environment.

Das et al. studied low-rank coal samples in Northeast India by means of SEM, HRTEM, X-ray diffraction, etc. and discovered carbon nanoparticles, free carbon nanotubes, and cluster carbon nanotubes of different sizes (with a diameter up to several or dozens of nanometers). He made a preliminary analysis on their favorable formation environment and explored their formation reasons as well as potential research and economic values.¹⁴⁸ As a typical representative of nano materials, carbon nanotube has been extensively used, but its preparation process is complicated, while the “extraction” of nanotube and other substances naturally formed in a natural environment undoubtedly provides a new research direction and thinking. By analysis of typical samples of Luochuan loess section with TEM and field emission scanning electron microscopy (FESEM), Chen, Xie and other scholars found there was nano-rod calcite in loess and observed their content and regular changes of micro structure. This kind of calcite has a diameter of 30 nm–50 nm and a length of several hundred nanometers to several micro meters. Nano-rod calcite crystals are round fibers with varying thicknesses. The crystals are bent along the direction of the crystal length. They sometimes display an interlaced arrangement and arborescent or frame forms. As estimated from nanoscale research results, the formation of such nano-rod calcite has something to do with the induced directional crystallization of biological derivatives.¹⁷ Nano-rod calcite is an important drought environment index mineral in the period of loess accumulation. The discovery of nano-rod calcite is of important value to research studies on nano minerals in the environment, formation reasons of carbonate in loess, and ancient

climate. Based on which, Xie et al.¹⁶⁷ discovered the distribution rule of attapulgite in loess-red sticky sequence clay, put forward a clay mineral response mechanism of ancient climate changes, and established genetic mineralogy theories for the strengthening of magnetic susceptibility of ancient soil.

Minerals with a grain size larger than 1 μm can provide information on the late growth stage of minerals; however, a grain size between 0.1 and 100 nm can provide information about the initial crystallization of minerals. Zhenhua Ding also believed the polymorph, polytype, multi-body, and micro-intergrowth of minerals at the nanoscale were the actual minimum keepers of geological information.¹⁶⁸ Therefore, these two kinds of information have to be integrated to more completely reflect the physical and chemical environment in which minerals were formed. Current research studies on minerals with larger grain size have been made rather thoroughly and have brought to light many important results, but the research studies on nanoscale particles are still in the starting stages. Consequently, nanoscale minerals are endowed with extensive development and application prospects. The size change of nano minerals and nanoscale particles will lead to big differences in mineral geochemical characteristics and biogeochemical characteristics, which might be caused by the change of atomic structure in or near the crystal surface.¹⁹ We should pursue active exploration into the techniques and methods for developing and utilizing nanoscale minerals and strive to make breakthroughs both in theory and in practice, so that mineralogists can ascend to a new level of understanding the natural world.

5.2. Nano-Petrology

Petrology is a subject aimed at the study of rocks' composition, structure, occurrence, distribution, formation reasons, and evolution history, and their relationship with mineralization, and is one of the important branches of geology. Rocks are classified into two categories: inorganic and organic rocks, and now relatively thorough research on inorganic rocks has been conducted.

Nano-petrology is a new subject formed by combining nanotechnology with petrology, and the discovery of nanoscale particles on the slip plane represents the typical progress of nano-petrology. By observing living examples of the penetrative foliation slip planes of metamorphic rock and dynamometamorphic rock with SEM, Sun et al. found that nanoparticle layered structure was widely distributed in its surface layer. And by proper simulation through tri-axial stress experimentation, they reproduced the actually observed phenomenon. According to detailed recognition, observation, formation stage division and other work performed on the individual and complex components of this nanolayer, they estimated that it was a friction—sticky zone with viscoelastic deformation in essence that had the effects of lubrication and drag reduction.^{30, 139} In addition, research studies on nanoscale rock characteristics of pressure-solution stylolites produced similar conclusions: Under the pressure-solution effect, clay minerals of low friction coefficient will be produced on the section (stylolite); their nanostructures are clearly characterized by obvious directional arrangement, and they have a certain effect of smearing and sealing.¹⁴⁶

The research on fluid geological process in the field of petrology has become one of the important cutting-edge research fields in the international geoscience domain. As research methods have been continuously renewed, the research work involving fluid inclusions and geological fluid has made a series of important achievements in both breadth and depth. So far, the research on fluid inclusions larger than 1 μm have been made mainly by way of optical microscopy, microscopic thermometer, electronic probe, laser Raman spectrometer, and other testing methods. For those less than 1 μm , especially for nanoscale fluid inclusions, fewer research studies have been made, which is mainly caused by the limitations of testing instruments and research methods. The emerging of TEM has created favorable conditions for research on the fine structure and chemical characteristics of fluid inclusions at the submicron order ($<1 \mu\text{m}$) or nanoscale ($<100 \text{ nm}$).

Jadeite quartzite has been researched in the ultrahigh-pressure metamorphic belts in the Dabie Mountain, Shuanghe, Anhui as well as mylonite and basic granulite in the middle part of the Himalayas, Tibet, and found the fluid inclusions in jadeite quartzite were distributed in the form of a network separately or in clusters. In mylonite and basic granulite, they found fluid inclusions were distributed along dislocation walls, subgrains, and healed nanofractures in host minerals and appeared in the state of single phase, multiphase, and melting phase. Meanwhile, the unexpected discovery of fluid residue in rocks and minerals pushed many aspects of fluid research to a core position of geoscience, which is greatly significant for understanding the formation reasons of rocks, fluid effects, etc.^{24, 169} (Fig. 9, observed by Wu). The structure and chemical characteristics of nanoscale fluid inclusions reflected the possible leakage routes of fluid in the

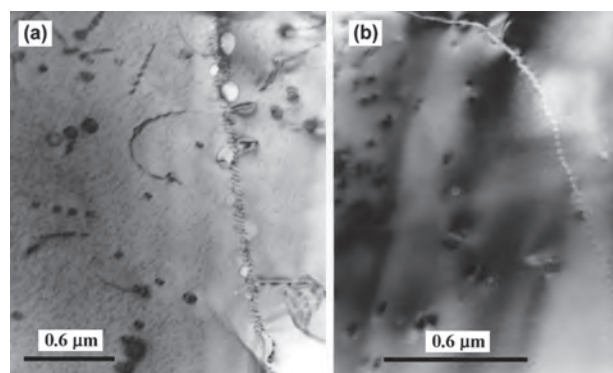


Figure 9. Fluid inclusions and cluster of water molecules on the nanoscale of quartz, and the clusters of water molecules show the feature of deformation in feldspar-quartz mylonite of the metamorphic core complex from Himalayan orogen belt. (a) Fluid inclusions spread along subgrain boundaries; (b) the right is the rice-shaped clusters of water molecules ($// \langle 001 \rangle$) that spread along healed nanocracks. These fluids and cluster of water molecules could accelerate the plastic deformation of the metamorphic core complexes.

circulation stage and changed the original components and density of fluid inclusions, which helps in understanding the relation between inclusions and structural defects and strain domains, interaction and boundary with original rocks, identification of development process, etc. They provided information about important interaction between fluid inclusions and host minerals from the nanoscale or submicron scale, showed important micro evidence for the formation process and exhumation mechanism of high-pressure and ultrahigh-pressure metamorphic rocks, and set a precedent for research on nanostructure, nanoparticles, and therefore, created a new research field for petrology, i.e., nano-petrology.¹²⁴ In metamorphic rocks, nanoparticle and nanostructure phenomena are rather common, especially on ab -axis fabric surfaces and narrow slip planes of the foliation of metamorphic rocks; under stress action, the internal friction, dynamic differentiation effect, etc. may lead to changes in the physicochemical field of rocks, further affecting the arrangement and distribution of nanoparticles in these kinds of narrow deformation concentration areas^{129, 170} and producing nano-modulated and nano-smear layering effects so-called in physics of metals through ductile slip-pelletization-plastic fluid changes.¹⁷¹

Organic rocks include various coals (lignite, bituminous coal, and anthracite coal), oil shale, dispersed organic shale, albanite, etc., and are an important energy resource. Many scholars also have conducted long-term research on them, and in recent years, have begun to pursue in-depth research from a more micro perspective. Ju et al. conducted careful analysis from the aspects of structure, stress, coal chemical structure, nanoscale deformation, etc., especially the impact of nanoscale pore and nanoscale deformation on the physical properties and gas storage capability of coal matrix, which plays a good guiding role in the development and utilization of

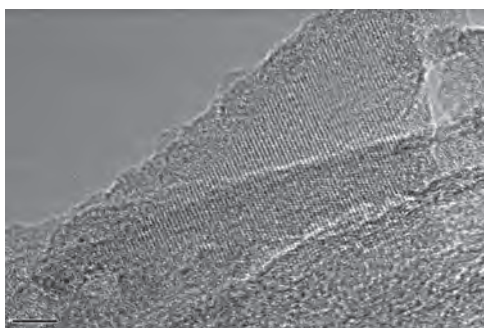


Figure 10. Nano-sized graphitic carbons are found in the HRTEM images of coals.

unconventional energies.^{125,172} How to realize refined and high value-added processing and utilization of organized rock resource is a major problem to be solved. Moreover, nano and micron carbon materials with unique structures and functions are a kind of new-type material currently attracting high domestic and foreign attention, and their controllable and cheap batch preparation is one of the cutting-edges and hot spots in the research field of the material chemical industry. At present, some nano-sized carbons and graphite in the coals have attracted much attention and achieved some progress^{25,173,174} (Fig. 10, observed by Ju; Fig. 11, observed by Qiu).

Nanoscale rock particles exist in all formational and developmental stages of rocks and have preserved plenty of important geological information that was unknown before due to the limitation of technical conditions, but the emergence of the high-resolution electron microscopy and other equipment has made direct observation of nanoscale particles possible. Although the research on nanoscale particles in the area of petrology has made certain achievements, it is still in the starting stage and more thorough research studies are needed.

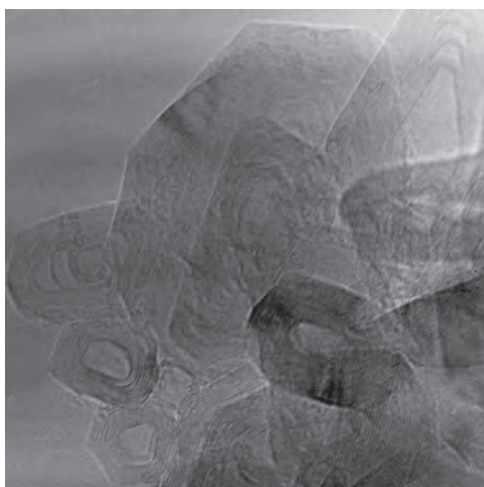


Figure 11. Coal-based nano carbons are observed in the HRTEM images.

5.3. Nano-Geochemistry

Nano-geochemistry is an interdisciplinary field evolving from a combination of nanotechnology and geochemistry. It studies formation and special properties of the ubiquitous, naturally-occurring nanoparticles as well as their impacts on geochemical processes.^{21,56} By using nanoporous carbonaceous materials to adsorb CCl_4 and NH_3 , Lee et al.¹⁰³ found that the surface area and nanopore volume of materials control the adsorption process at higher pressure, whereas the adsorption at lower pressure is dominated by surface chemical properties. This experiment proves both the strong adsorption capacity of nanoporous materials and the important effect of surface chemical properties on adsorption.

As a cutting-edge research field of geochemical detection, nanoscale geochemistry has made great achievements and geological discoveries in more and more areas.^{136,144} Geogas prospecting, developed in the early 1980s, is a new approach in the search for deep and concealed deposits, the mechanism of which is that the ascending air in the earth's crust carries mineralized materials to the earth's surface.^{111,115} After observation with AFM, TEM, and SEM, it is confirmed that the geogas substances migrate in the form of nanoparticles.^{119,175} According to research, the nanocrystal interface is of a gas-like structure in the solid state of higher disorder degree, different from either the crystalline state of long-range order or the amorphous state of short-range order. In addition, a nanoparticle is of shell structure on the surface layer and adsorption layer. The surface layer is close to the gaseous state and easy to absorb gas molecules due to good activity of surface atoms, so the nanoparticles of mineralized materials can absorb gas to become special gas-like structure and migrate together with the ascending air in the earth's crust. Therefore, with strong penetration capability, these nanoparticles can rise vertically from the deep to the surface to form a geogas anomaly, thus providing new information for prediction of mineral resources.^{119,176-178} It is able to obtain the morphology and composition information of these nanoparticles with the aid of TEM and other instruments of nanoscale resolution.^{50,149,179} Wang et al.¹⁸⁰ discovered the aggregates of copper, titanium, and other metal particles (Fig. 12, observed by Wang) in both gas ("geogas") and solid media in the upper soil of concealed copper-nickel deposits of 400 m depth. It has been verified through laboratory research that the two media are generally similar in terms of particle size, morphology feature, and composition, which indicates that there is certain genetic connection between them, and they are formed under endogenous conditions because the metal nanoparticles are of ordered crystal structure. The discovery not only provides direct microscopic evidence for deep penetrating geochemistry but also has great application value in the search for concealed deposits; that is, the separated particles can be used for direct detection of concealed

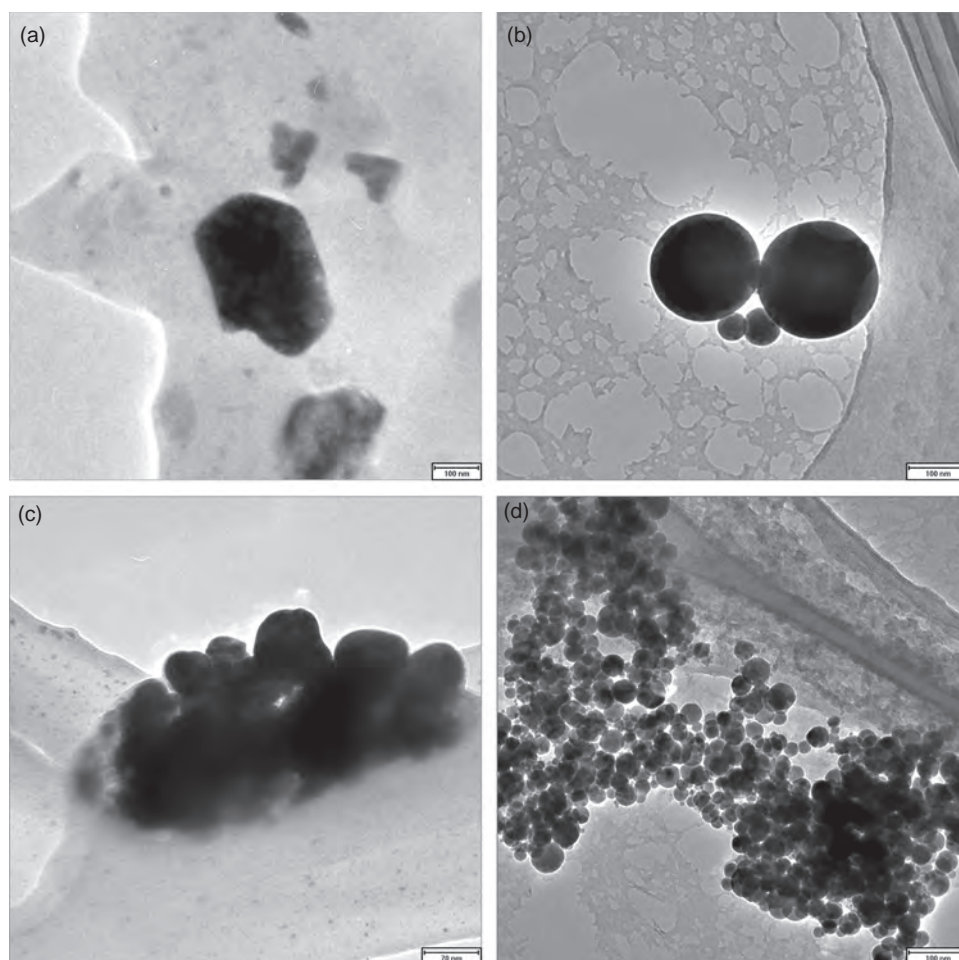


Figure 12. TEM images of some nanoscale metal particles. (a) The hexagonal nanoscale gold crystals. (b) Nanoscale cuprum particles. (c, d) Aggregate of nanoscale cuprum particles.

deposits with the soil as the sampling medium. The gold particles of the nano-micron scale are discovered in the plant root tissue above the ore body, which also provides direct microscopic evidence for the presence and migration mechanism of mineral nanoparticles.¹²⁸

The research content in the nano-geochemical field mainly includes: the structure and properties of water in nanopores; the chemical reaction and material migration in nanopores; the distribution of nanoparticles, nanophases, and nanostructure materials in the natural environment; the constraint of nano effect on growth of minerals and dissolution kinetics, as well as phase transition, phase stability, solubility, chemical reactivity, and element migration; the geochemical process of nanoparticle formation; the information records of geochemical processes of nanoscale and the geologic significance of nanoscale phenomena; knowledge of mineral-fluid interface processes and understanding the process and rule of distribution, retention, migration, and transformation of pollutants in the solid-liquid phases at the nanoscale; and knowledge of biological-mineral interaction and its

constraint on biological weathering and elemental geochemical cycle at the nanoscale, thus revealing the mechanism, composition, morphology, structural characteristics, and life indication of biomineralization, as well as its relationship with mineralization and enrichment of harmful elements.

The geological process is inseparable from the migration and enrichment of chemical elements, and especially the activity of some trace elements with a significant impact on the environment or geological activities. Therefore, it is a top priority to understand their migration mechanism. The discovery of nanoparticles proves that the elements can move in the form of nanoscale polymer. The particles will possess various special properties different from those of their macroscopic solids when their particle size reaches nanoscale, so the geochemical properties of nanoparticles will also be different. Therefore, the research on various physical and chemical properties of nanoparticles will help to explain various complicated geological phenomena from the microscopic and mesoscopic perspectives, which is of great theoretical significance and practical value.

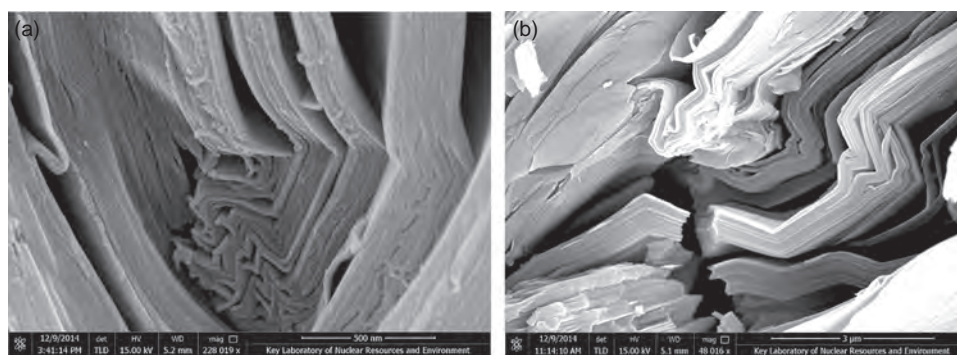


Figure 13. SEM images of quartz schist with strong deformation. (a) Layer structure with accumulated nanoparticles were formed at the first phase of activity. Nanoscale folds and interlayer sliding were formed at the second phase of activity which led to a loose accumulation between the layers. (b) Under the effect of extrusion stress, nanolayers developed ductile deformation (folds), then brittle deformation (fractures).

5.4. Nano-Structural Geology

In the middle of the 20th century, the research on structural geology mainly focused on the observation of elastic-plastic and brittle-ductile deformation, and then transferred to the investigation of rigid-viscous deformation. However, as the two research subjects of structural geology, the shear movements of folds and faults both demonstrate comprehensively elasticity, viscosity, and other mechanical behaviors according to rheological analysis.^{30, 133} Nanostructure can faithfully record the deformation process (Fig. 13, observed by Liu; Fig. 14, observed by Liu and Sun). The nanoparticles are ubiquitous on the slip layer of shear movement. The motion of its structural plane is dominated by rolling slip, and the nanoparticle layer plays the role of lubrication and drag reduction, which can accelerate fault activity and expand the scale. Moreover, grinding grain structure of nanoscale contains abundant geological information, especially of great significance in microcosmic dynamics (dynamic thermal metamorphism, fluid infiltration, particle self-spin and geological catalysis), and requires our further thorough research and exploration.^{129, 153, 181}

The research on nanostructures on a shear plane can reveal the microscopic kinematic mechanism of tectonic shearing movement, and then explore the tectonic dynamic

behavior in combination with macroscopic tectonics.³⁰ After the relevant observation and research on the lubrication effect of nanoparticles on the fault plane, it has been proved that the nanoparticles in the fault slip process give rise to the macroscopic mirror slip developed widely on the fault plane, which is of great significance for understanding the frictional slip mechanism.^{140, 141} The ductile shearing zone is a system of nano lineation, foliation, and fabric formed by nanoparticles, nanowires, and nanolayers, and the directional fabrics dominated by its slip are all parallel to and consistent with intuitive lineation and foliation.¹⁸² Nanoparticles have been discovered in mylonite of ductile shear zones in many areas such as the Tanlu fault.¹⁸³ Different from dynamic friction, ductile shear is a kind of approximately static but gradual slip. The research on ductile shearing mechanism at the nanoscale is helpful to promote the development of microscopic tectonodynamics and open up a new field of tectonics. In the light of research of granulation, fabrication, and lubrication at the nano-scale on shear slip planes,^{140, 153, 184} overall studies clearly indicate that fundamental nano actions in visco-elastic formation fault zones can be subdivided into three kinds, i.e., nano-coating caused by hardening strain, nano-weakening caused by softening strain, and nano-delaminating caused by degenerating strain, and

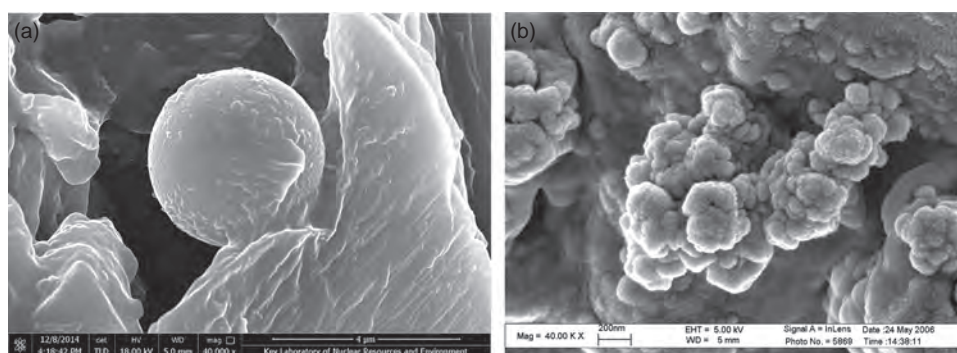


Figure 14. SEM images of nanoparticles. (a) Nanoparticle compound in the fractures of quartz schist with good roundness and sphericity. (b) Nanograin aggregates on the shear slip surface.

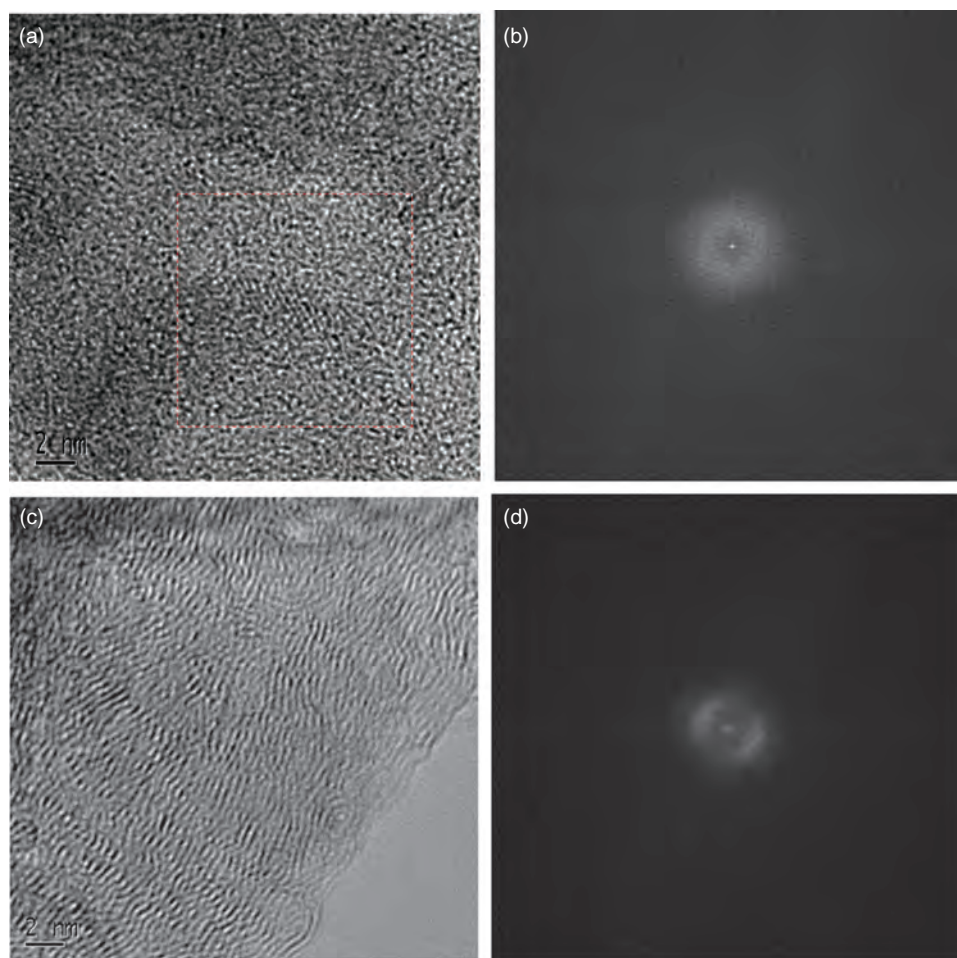


Figure 15. HRTEM images of tectonically deformed coals. Brittle deformation: (a, b) basic structure units are scattered and isolated with small diameter and no directionality; small brightness of diffraction ring (002). Ductile deformation: (c, d) basic structure units are stripy and variegated with large diameter and strong directionality; dispersed brightness of diffraction ring (002).

these fundamental actions are closely relative with mineralization, hydrocarbon accumulation, and seismic formation structure.

There are also abundant research achievements regarding organic rock deformation on nanoscale (Figs. 15, 16, observed by Ju). After a preliminary study by Ju et al.,^{26,86} the results showed that a large number of brittle fractures

and nanopores are found in brittle deformed shale samples, and the ductile crumples and nanopores can be seen in the ductile deformed shale samples. In the same vein, micro-deformation can occur to the structure of coal rocks in different metamorphic deformation environments, and can even be present at the nanoscale, giving rise to changes in molecular structure. The research results show that the

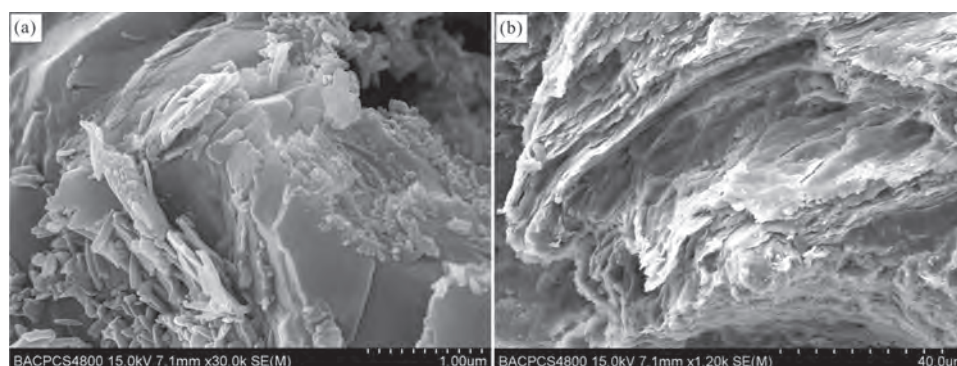


Figure 16. SEM images of tectonically deformed shales. (a) Brittle deformation. (b) Ductile deformation.

stacking degree L_c of the Basic Structure Unit (BSU) of the tectonic coal macromolecule structures grows rapidly from the metamorphic deformation environment of low coal rank to that of high coal rank, which mainly reflects the difference of tectonic coals in various metamorphic deformation environments and deformation mechanisms. The change in the stacking degree L_c and La/Lc parameter of coal BSU reflects the change in tectonic deformation strength, which can be used as an indicator of nanoscale deformation degree of tectonic coal structure. The physical and chemical degree of order of carbon networks within BSU and of arrangements among BSU is significantly strengthened mainly due to the role of directional stress, that is, the local directionality of molecules is strengthened.²⁸ Li et al. studied tectonic coals of different deformation mechanisms and degrees by means of spectral analysis and nitrogen isotherms, etc., found a significant impact of microcosmic tectonic deformation on macromolecular structure of coal rock.^{138, 185, 186} After research on the changeable property of macromolecular structure of high-rank coal rock under different rheological conditions, Yu et al.¹⁸⁷ concluded that different rheological effects (brittleness, brittle ductility, ductility, etc.) will appear under the conditions of various temperatures and pressures, thus affecting the change in macromolecular structure of coal rock.

Nano structural geology is the study of different tectonic phenomena, especially microcosmic structure, at the nanoscale, and then discussion of the mechanism of tectonic dynamics in combination with macroscopic regional structure. As for the deformable geologic body, the nano-coating structure is inseparable from the shear slip motion. Has the feedback relationship between the two revealed the mechanism and essence of shear motion of the geologic body? Is the nano-micron particle structure developed in the tectonic zone of fault caused by effects such as the extraction behavior of supercritical fluid? These problems are still to be solved.¹⁷⁰ However, some controversial or unclear tectonic phenomena can be reconsidered within the new research method of nanoscale, and it is believed that there will be new breakthroughs.

5.5. Nano-Energy Geology

Energy geology is mainly the study of fossil fuels and some other energy sources. The fossil fuels include conventional coal, oil, natural gas, and unconventional coalbed methane, shale gas, tight sandstone gas, and natural gas hydrates, and other energy sources that include solar energy, wind energy, geothermal energy, nuclear energy, biomass energy, hydraulic energy, and hydrogen energy, etc. The predecessors have conducted much research on the theory of the conventional oil and gas reservoir and established a relatively perfect theoretical system, but the research on nanotechnology application in energy geology brings a new bright spotlight to the field.

As the production and storage site of unconventional coalbed methane, coal rock is of great significance for research on such issues as formation mechanism, development and utilization, and gas outburst.^{87, 188} Coal rock is a complex solid composed of matrixes and pore fissures. The pore structure and porosity affect not only the migration behavior of gas in coal but also the storage and adsorption mechanism of gas in coal rock. Ju et al. considered that tectonic deformation not only changes the macromolecular structure and chemical composition of coal to different degrees but also affects the nanoscale pore structure (<100 nm), and the nanoscale pore is the main adsorption space of coalbed methane.^{86, 87} In the liquid N_2 adsorption method, Fan et al. conducted a thorough and systematic research on the nanopore structure properties of tectonic coals of different deformation series in various metamorphic deformation environments, and classified the nanopores of tectonic coal into four groups, i.e., transition pores (15–100 nm), micropores (5–15 nm), sub-micropores (2–5 nm), and ultra-micropores (<2 nm), in combination with the analysis of macromolecular structure and pore structure with HRTEM and X-ray diffraction. These nanopores are influenced significantly by the evolution of microstructure of tectonic coal, and have different effects on the adsorption of coalbed methane.¹⁸⁹ As for many aspects such as mining, beneficiation, coking, gasification, liquefaction, extraction of coalbed methane, and risk evaluation of gas outburst, the research on coal nanopores is of great significance.^{32, 66, 67, 87, 131, 137, 190}

Marta Krzesińska studied molecular and macromolecular structure of coal with the method of molecular acoustics, analyzed and contrasted raw coal samples with those extracted from solvent, the coal samples from normal mines with those from gas outburst mines, and concluded that mineral impurities affect the microstructure and outburst tendency of coal and play an indicative role in coal mine safety.¹⁹¹ Yao and Ouyang, et al. respectively applied AFM technology to research on coal nanopores, observed the microporous structure of coals of different ranks through the unique AFM high-resolution imaging advantages and many quantitative analysis functions, and made quantitative analysis of micropore size distribution and porosity, to attempt to provide a scientific basis for research on the adsorption mechanism of coalbed methane and the gas outburst prediction of mines.^{137, 192} With the Quasi-Elastic Neutron Scattering (QENS) and Small-Angle Neutron Scattering (SANS) techniques, Chathoth et al. analyzed what impact the injection of CO_2 and N_2 into nanoporous carbonaceous aerogels could have on the diffusion of CH_4 , so as to study the approach of raising extraction of coalbed methane.¹³⁵ In addition, the material composition of coal rock is more changeable. After the observation and analysis with HRTEM, ICP-MS, and other instruments, it has been found that coal rock, cap rock, and coal ash contain many nanoscale minerals of different forms such as anatase, anhydrite, and barite, generally

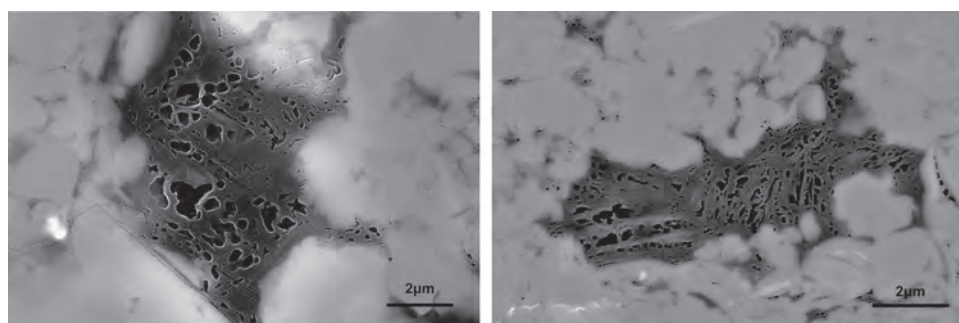


Figure 17. SEM images showing variations in nanopore morphology in organic matter of shale. (Samples are taken from 201 well of Weiyuan—the first bite of shale gas well in China).

accompanied by enrichment of trace elements such as V and Cr,¹⁹³ and direct combustion of coal will not only be harmful to the environment but also waste many of these minerals and trace elements.

The exploration and exploitation of natural oil and gas in organic-rich shale also promotes the development of nano-energy geology at the same time as mitigating a global energy crisis. The pore fissure system of micro-nano scale developed from this typical tight reservoir plays an important role in hydrocarbon enrichment and seepage. The relevant scholars have conducted much research on this “subtle” but “huge” system^{33, 35, 36, 52, 63, 64, 88, 132, 194} (Fig. 17, observed by Zou; Fig. 18, observed by Wang; Fig. 19, observed by Lu), especially the productive research in recent years. With the micro/nano media models as the shale reservoirs, Ma et al.¹⁹⁵ simulated non-ideal gas seepage patterns, and then deduced the gas flow coefficients in the pore network and the roles of several ideal flow models. By changing the experimental conditions of adsorption patterns such as low-pressure liquid N₂ adsorption and CO₂ adsorption and comparing the difference between various interpretation models and actual data measurements, Wang et al.¹⁹⁶ attempted to explore the best way to describe the pore characteristics of organic-rich shales based on fluid injection. By means

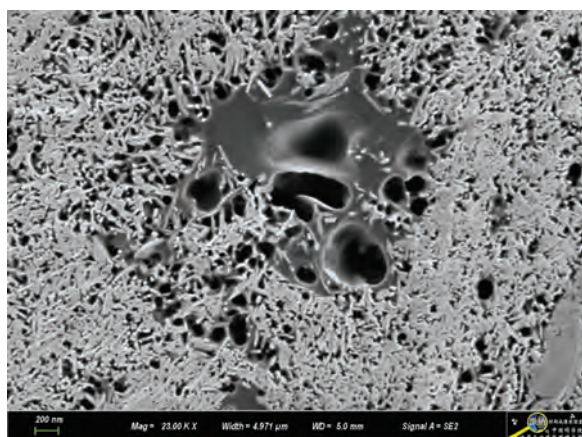


Figure 18. Oil/oil film were observed in nanopores of apatite in organic shale.

of high-pressure mercury intrusion, low-pressure liquid N₂ adsorption, FESEM, and other techniques, Zhang et al.¹⁹⁷ observed and analyzed the pore genesis type, shape, distribution, and other characteristics of Longmaxi Formation shale in southern China, and concluded that the openings of nanopores are preferable in the studied layers and beneficial to enrichment and seepage of shale gas. The research on shale pore system is drawing more and more attention to the geometric characteristics of shale, and the quantitative pore characteristics obtained by digital image technology are providing important support for more comprehensive and meticulous mapping of the pore system.^{102, 198}

The nanoscale viewpoint also provides more accurate interpretation of the research on tight reservoirs and the mechanism of sealing cap rocks.^{35, 90} Sun et al. found nanoscale ultra-microsphere structure in the granitic mylonite slices of slip in late Mesozoic, and called it the “grinding grain.” The slip layer existing in mud rock and containing grinding grains of nanoscale has a coating effect and plays a role of oil gas sealing, which has been verified in the oil and gas fields in northern Shaanxi.²⁹ In recent years, Zou et al.³⁴ have focused on the mud shale and tight sandstone reservoirs developed extensively in the marine continental basins of China, and have made multi-dimensional multiscale elaborate representation of microcosmic reservoir space through FESEM, nano-CT, FIB-SEM, synchrotron radiation, and other techniques, reconstructed three-dimensional pore-throat system model, and carried out quantitative evaluation of size and distribution of pore throat system in combination with image analysis, mercury intrusion test, and gas adsorption data, and all of the above is of great significance for exploration and exploitation of shale gas and tight sandstone. Wang et al. described meticulously the classification and micropore structure characteristics of nanopores in coal-bearing shales through ultra-low pressure N₂ physical absorption, fluid intrusion, and other experiments.^{64, 196} After studying the sedimentary facies and the sedimentary origin of rocks in deep-water areas of lake basins in China, Pang et al.¹⁹⁹ have found that the pores are developed in fine-grained sediments in deep-water areas, adjacent to hydrocarbon

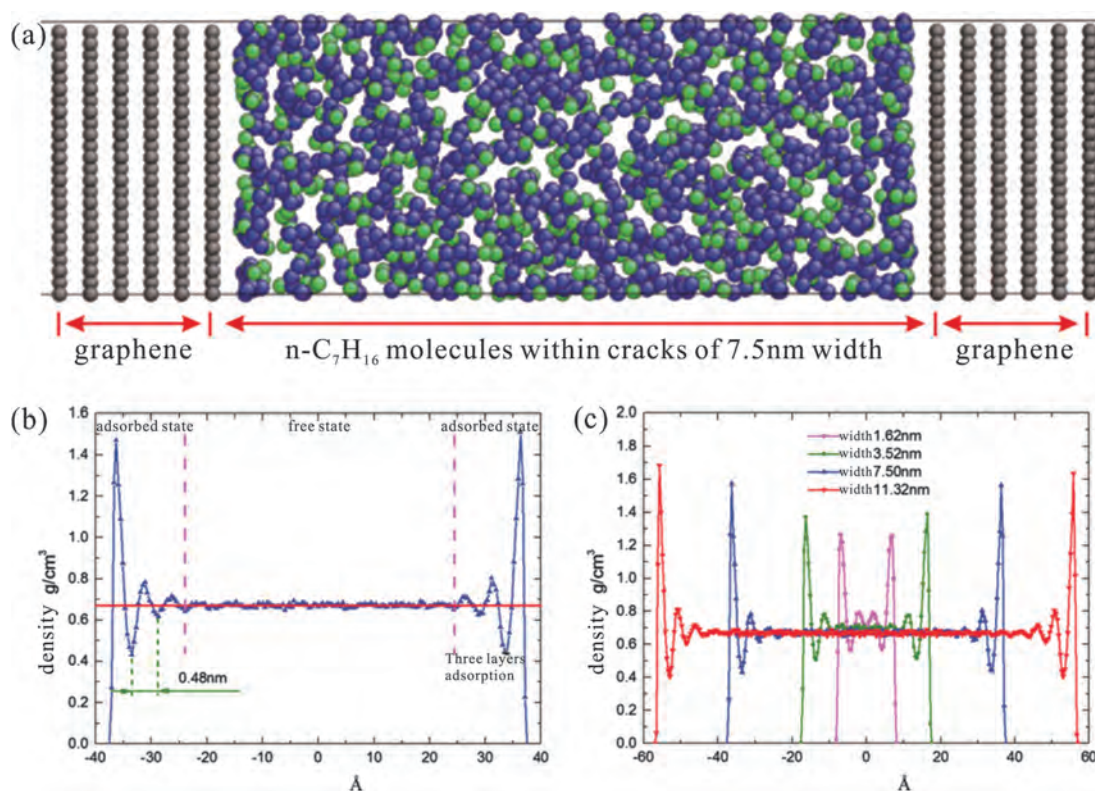


Figure 19. Under the condition of 80 °C and 30 MPa, (a) the microstructure, (b) density distribution of $n\text{-C}_7\text{H}_{16}$ molecules within graphene crack of 7.5 nm width and (c) density distribution of $n\text{-C}_7\text{H}_{16}$ molecules within graphene cracks of different widths after the adsorption equilibrium.

source rocks and prone to aggregation and accumulation, and have put forward nanotechnology as an important research method at present and in the future. Therefore, the application of nanotechnology in energy geology is giving rise to nano-energy geology.

5.6. Nano-Ore Deposit Geology

The study of ore deposit is multidisciplinary and comprehensive. It refers to comprehensive research on mineral, rock, tectonics, geochemistry, geophysics, physics, and chemistry. One of the research focuses is the mineralization process, including the origin, excitation, migration and sediment of mineralized materials, and the mineralization mechanism, and the essential issues it involves are the physical and chemical properties of mineralized materials. Nanoparticles of the same composition have different physical and chemical properties, which has led to geologists' new understanding of ore deposit formation theory.²⁰⁰ Zhenggen Zhang has re-explained the mineralization of ore deposits such as "micro-fine-disseminated gold deposit" with the evidence provided by nanotechnology, tried to establish a new mineralization model, and believed that the gold in these types of ore deposits is mainly composed of nanoparticles, and it is hard to make reasonable explanation with conventional typical models.^{2,5,14} The "micro-fine-disseminated gold deposit," i.e., Carlin-type gold deposit, is the most typical nano-ore

deposit. It is basically characterized by the fact that the gold in these deposits is invisible to the naked eye and mostly in the form of natural nanoscale gold particles and solid solution.^{14,82} The research on arsenic-bearing pyrites developed widely in Carlin-type gold deposits shows that there is a certain relationship between the existence of gold nanoparticles and the ratio of Au/As in the pyrite, and the melting point of gold nanoparticles falls rapidly with the decreased size of gold nanoparticles, which is of great significance for prediction of storage form and capacity of gold.^{126,127} With a series of high-resolution research techniques such as STM and STS, Mikhlin et al. studied the adsorption properties of nanoparticles of pure Au, Ag, and other metals and of their sulfides on pyrite surface, and found that the pure metals generally form globular nanoparticles and their sulfides tend to form flaky ones, which has a great impact on mineral aggregation and sorting.²⁰¹ They also observed the enrichment of nanoparticles of pure trace elements and of their sulfides on pyrite surface, and proved through research that the high content of trace elements on the pyrites observed with EMPA and TEM-EDX is mainly attributed to the nanoparticles.²⁰²

Due to special properties, the nanoparticles in geologic bodies are obviously different from macroscopic materials in geophysical and geochemical behaviors. A nano-material field is formed around the geologic bodies, especially around the deposits.^{45,203} The ascending air carries these nanoparticles vertically to the earth's surface.

The acquisition and analysis of these nanoparticles closely related to ore deposits can be used for mineral exploration, which leads to the emergence of a new kind of science—nano prospecting. In recent years, there have been abundant research results on occurrence, migration mechanism, and prospection significance of metal nanoparticles in the topsoil of China, and the methods of nano prospecting are being developed and perfected.^{204–206} This part was discussed in detail in Section 3.3.

Recent studies show that the black rock series of Sinian and Cambrian periods developed widely in southern China extend in over ten provinces and cities such as Yunnan, Guizhou, Sichuan, Hubei, Hunan, Chongqing, Jiangxi, Guangxi, and Zhejiang and present the symbiosis and enrichment of several useful metallic elements.^{207,208} The abnormal enrichment of organic matters in the black rock series is related to the complex interaction between metallic elements. The abnormal enrichment macroscopically controls the accumulation quantity and grade of metallic elements in the black rock series, and the special microstructure relationship between organic matters and metals may restrict the occurrence of metal minerals in the form of dispersed ultra-fine particles and their separable properties from ores. In addition, a number of large and super-large deposits with reserves of several million to ten million tons have been found in some mining areas in southern China, which contain highly purified non-metallic minerals of nano-micron scale and have great resource potentiality.

Nano-ore deposit geology is the study of the formation, migration, and occurrence mechanisms of minerals with nano techniques and methods and prospecting concealed deposits from a new perspective. As nanotechnology is developed and applied in the field of geology, ore deposit geology will certainly make milestone progress with its own unique advantages.

5.7. Nano-Earthquake Geology

Currently, no complete theoretical system has been formed to explain the earthquake mechanism, and the cause of earthquakes is not clear. In order to predict an earthquake accurately, we need to thoroughly understand its formation process and mechanism, and seismic geologists have been making unremitting efforts. The development of nanotechnology brings new hope to many seismologists, and it is considered that the study of friction theory at the nanoscale may be able to explain seismic mechanisms.^{209,210} Lower believed that the slide of objects along the nanoscale pulses of self-healing cracks of interface radiation can be used to explain the paradox of seismic heat generation in geophysics, but it still needs to be verified experimentally. Moreover, he considered that the plate movement of the earth lithosphere at kilometer scale can be studied at single nanoscale.²³

According to the criticality theory of physics, the macrostate and microstate are complementary to each

other, and the instability of the macrosystem is attributed to the release of energy from a very large number of microparticles. Seismic geologists have observed the Kobe earthquake in Japan, the Jiji earthquake in Taiwan, and the Quaternary fault near the Tanlu fault, and found that their seismic faults are slip zones with a width of only several millimeters to several centimeters. It is inferred from the study of the nanostructures on shear slip foliation that the narrow seismic faults are the frictional viscous zones of nanoparticle and microparticle layers, and their shear movement in the microcosmic mechanism has undergone the development stages of strain-hardening, strain-softening, and strain-degeneration.³⁰ Nanoscale clay plays a role of “lubricant” in the fault zone and drives the perturbation of ancient faults, which may be the main reason for the relative stability of seismic fault zones.

Through research on the main surface fault zone coseismic with the Wenchuan earthquake, that is, the Beichuan–Yingxiu fault zone. Yuan et al. have found that the particles and structures of micro-nano scale can be seen on multiple fault slip planes, and they are formed in the fault slip of the Wenchuan earthquake, despite a temporarily unclear formation mechanism, and reduce significantly the frictional strength of fault.¹⁴⁵ On this point, the relevant scholars have made many fault simulation experiments at different temperatures and slip rates in recent years. These experiments show that the initial high-strain frictional heat generation (small displacement) on the fault plane results in “grain boundary sliding” at the nanoscale, thus forming nanoparticles of lubrication, appearing in the form of a weak zone in the subsequent earthquake (about 1 m/s) and fault spread, reducing the fault intensity, and accelerating the large-scale development of the fault.^{142,147,211} Further experimental studies have shown that a rapid temperature rise is an important factor leading to the weakening of the fault, but mere formation of nanoparticles on the fault plane is difficult in effectively lubricating the initial movement of the fault.²¹² Other scholars have focused on the weakening mechanism of a fault zone to confirm that the nanostructures or nanoparticles on the fault zone are generated by aseismic slip, coseismic slip, or both, with the former based on the observed phenomena such as pressure dissolution and mineral corrosion and the latter explained by phenomena such as friction melting and migration of trace elements.^{213,214}

Based on the certainty that the nanoparticle structure layers are ubiquitous on the tectonic shear plane, Chao et al. observed and analyzed the active Tanlu fault zone in eastern China with much concern and research, and discussed preliminarily the microscopic kinematic mechanism of brittle viscous seismic fault and ductile creep seismogenic fault. According to the analysis, it is considered that the fault zone has undergone the earlier development of ductile shearing foliation plane and the later development of brittle fault friction plane.³⁸ Both the dynamic friction of brittle seismic fault and the static friction of ductile

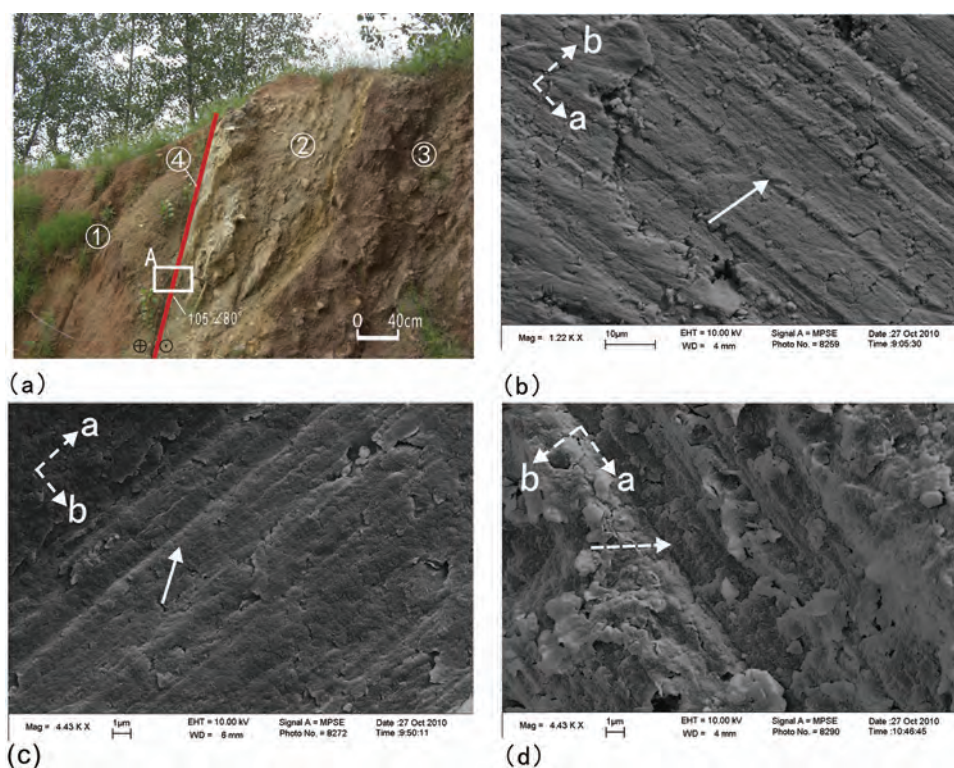


Figure 20. Photos showing nano/micro-scale structure of scratches on the principle sliding zone. (a) Geological profile of the Tanlu fault zone at Zuoshan, Junan county, Shandong province. Here was the seismogenic fault of the Tancheng 8½ earthquake in 1668. ① the late Quaternary iron and manganese nodule bearing brown sandy clay (Q_3). ② the fault cataclasite, its parent rock is the Cretaceous Qingshan group volcanoclastic rock (K_1q). ③ fault fracture zone, the parent rock is the Cretaceous Wangshi group sandstone (K_2w). ④ fault plane and the gouge belt. The area A indicates the location of the sampling site. (b–d) SEM images, showing slickenside and grinding lines. The solid arrow points to the grind ridge and the dashed arrow points to the grind valley.

seismogenic fault can form nanoparticles of better roundness and sphericity characterized by rigid shaping and an elongated rheological property, indicating the viscoelastic deformation behavior of shear movement. The seismic and seismogenic faults are consistent with the common brittle and ductile faults in terms of nano-kinetic mechanism despite the great difference in development degree, scale, and magnitude. However, much efficacy and information regarding nanoparticles in an earthquake still needs further study^{38,215} (Figs. 20, 21, observed by Chao).

It is the important research content of nano seismology to study the development mechanism of fault activity from the nanometer point of view and then to reveal the microcosmic process of earthquake formation, which lays a foundation for a breakthrough in seismic theory.

5.8. Nano-Environmental Geology

Nanotechnology has provided new opportunities and pushed further development of the study of environmental geology. It makes people aware of unconscious pollutions,

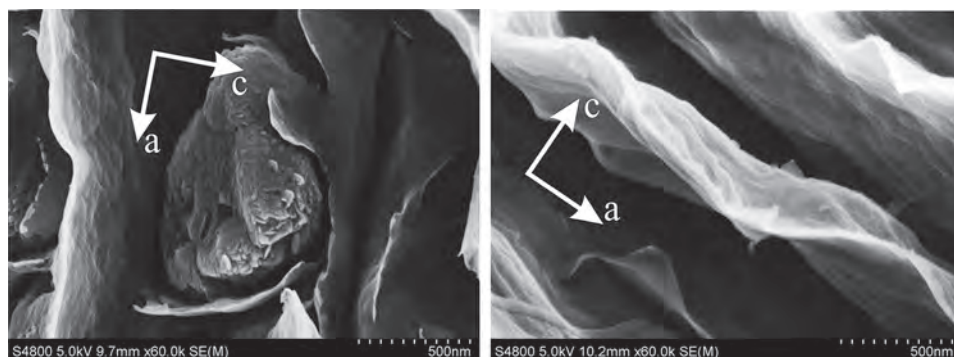


Figure 21. SEM images of nanolayer structure of ac-fabric in the fault zone, showing creep slipping at nano/micro-scale.

allows detection and identification of unobservable pollutants, and deals with problems of environmental pollution that could not be undertaken before. Current research progress includes the following aspects:

- (1) Study of the emission characteristics, rules, and risk assessment methods of nanoparticles in the process of production, application, and disposal;
- (2) Study of the environmental behaviors of nanoparticles in rock, soil, and water, and their compound behaviors with the coexisting pollutants in the environment;
- (3) Rapid determination and characterization of nanoscale matter in the geological environment.

Natural nanoparticles play an important but overlooked role in regulating the behavior of complex water pollutants. After entering a body of water in nature, the deposited particles at the micro-nano scale will become an important source of nutrients and even toxic and harmful substances, which will cause huge damage to the ecosystems of rivers and lakes—but which is rarely taken seriously. With the help of high-resolution technology like FE-SEM/EDS and HRTEM, recently some researchers have studied the body of water around a coal mining area where a large amount of coal ash had been poured down, and found that the water body is rich in substances that can destroy the environment, for example, TiO₂ nanoparticles.^{216, 217} Their study shows that the residual effects of coal combustion can lead to increased concentrations of toxic metal elements in surface water and underground water, which have a long-term negative effect on the environment and the human body. Though research studies on these long-term effects are still limited, some results have confirmed that diffusion and long-distance transport in water of these toxic elements in coal ash are key factors in controlling environmental risks.^{218–220} According to the study of iron-rich or silicon-rich nanoparticles and colloid polymers in weak acidic mine drainage, Johnson et al. argued that in order to comprehensively understand complex metal pollutant systems, it is more important to analyze the structure of the environment at the nanoscale, rather than depending only on conventional macro-systems.²²¹

Because of its large specific surface area and good adsorption properties, the nanopores of minerals can be used as adsorbent for the treatment of environment pollution, and the most representative one is the clay minerals.^{105, 106} In recent years, the groundwater remediation technology of nanometer zero-valent iron has developed rapidly. It can degrade various halogenated hydrocarbons and some organic pollutants without halogen elements. However, as a kind of efficient environmental remediation materials, the size effect of nanoscale zero-valent iron may lead to a potential toxicity risk in nature. Therefore, the importance of potential toxicity and environmental effects should be adequately assessed before the application of nanoparticles.^{222–224} The geological storage of CO₂, the major greenhouse gas, is also a worldwide hot

issue, and CO₂ liquefaction and sequestration in deep rock formations is an ideal solution to the greenhouse effect. The reason why nano porous materials are important storage media is that the surface atomic number and surface energy of micro-nano rocks are quite different from those of ions and crystals, and the velocity and efficiency of CO₂ fluid-rock interaction at the nanoscale are far greater than those of other scales.^{44, 107, 108}

With the fast development of the economy, the demand for energy, mineral resources, and water resources is growing day by day in every country around the world. In addition, due to increasing environmental pressure, the development of low-carbon energy has become the most important subject, which provides a good opportunity for the exploration and development of unconventional energy. However, in recent years, the formation of water has been created by different causes in the development of unconventional natural gas and a large amount of fracturing wastewater has been produced by commonly-used hydraulic fracturing methods in reservoir fracturing reform.²²⁵ Therefore, a treatment technology for fracturing flowback wastewater, which is efficient and economical based on the nanotechnology, is badly needed to deal with the potential pollution issues of fracturing wastewater. According to present situation of China and the experience of the developed countries in the development of unconventional natural gas, now the main focus is on comprehensive research in the following areas:

- (1) Efficient and environmentally friendly fracturing fluid;
- (2) Nano intelligent tracers, nano-sensors, and high-resolution three-dimensional imaging technology of oil/gas reservoir;
- (3) Efficient and economical fracturing wastewater treatment technology based on nanotechnology;
- (4) Study of nanomaterial and fracturing fluid used in the exploitation of unconventional natural gas, and the influence on the environment and human health caused by volatile organic pollutants and other pollutants that are produced during exploitation.

5.9. Nano-Atmospheric Science

The Earth's atmosphere consists of a variety of gases and liquid and solid particles suspended therein. Its total mass is about 5.136×10^{18} kg, only equivalent to one millionth of the Earth's mass. Nevertheless, it plays an important role in Earth's life, and the physical phenomena and physical processes in it are closely related to human activities. In addition to gas composition, there is also significant solid and liquid particulate matter in the Earth's atmosphere, namely aerosol. It is generally believed that the aerosol particles have diameters from a few nanometers to tens of micrometers, which can form condensation nuclei and ice nuclei, and play a role in many chemical processes in the atmosphere.^{20, 40, 152}

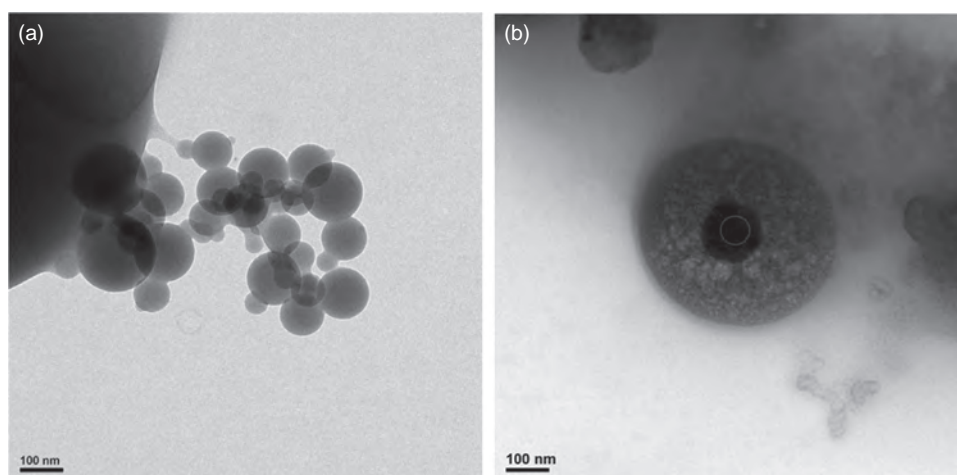


Figure 22. TEM images of different types of the individual aerosol particles in tibetan pleatau based on morphology and compositions. (a) Fly ash, mainly Al and Si, with miner Ca or Fe, regular rounded shape, main source: Coal combustion. (b) Metal particles, main source: industry activities metal particles.

As early as 2003, with the mutual verification of the TEM and X-ray diffraction experimental data, Chen and Xu⁴⁰ studied the phase composition of atmospheric dust and the morphology characteristics of various phases and confirmed the source of atmospheric aerosols in a semi-quantitative way, which provided a scientific basis for the plan of controlling the sources and impact of air pollutants in the city. China in recent years has gone through continuous air pollution periods,²²⁶ and terms like “Haze” and “PM 2.5” have been widely known. The nature of these pollutants consists of suspended and floating particles at the micro-nano scale, causing great harm to human health. The haze of the city is mainly related to artificial particulate matter (PM) and gas-to-particle transformation, and cause and composition of matter have been studied and reported by many scholars in succession.^{227, 228} With the help of TEM/EDX and X-ray Photoelectron Spectroscopy (XPS), scholars have observed these particles’ images, analyzed their element distribution, and discovered that organic matter is more concentrated in fine particles, while the main sources of pollutants, such as the S, N elements, are mainly distributed in larger particles of 0.56–1.8 μm .^{229, 230} The different sizes and morphology of the particles can be clearly distinguished via the TEM images, and combined with EDX, the elemental composition of these nanoparticles can be intuitively discerned. Learning its elemental composition is an important aspect of understanding the properties of PM. Therefore, many methods for detecting the composition of organic elements and macromolecular structures have been used to study the composition/structure changes of PM in different environments. They are as follows: applying Ion Chromatography (IC) and ICP-MS etc. to analyze the inorganic components, using Gas Chromatography-Mass Spectrometry (GC/MS) to analyze the organic components, and working with

the FTIR and NMR and more to detect the composition of the organic matter’s functional groups.^{231–234} To improve our knowledge regarding particles in the Tibetan Plateau, atmospheric aerosol particles were collected on the Tibetan Plateau. And eight different individual particle types were identified based on their morphology and chemical composition¹⁵² (Fig. 22, observed by Shao). The research helps us to understand the source of air pollutants.

Large-scale air pollution events have repeatedly occurred all over the world in recent years. All countries have devoted painstaking effort to environmental protection. With the aid of high-resolution equipment and technical means, analyzing the composition and structure characteristics of nanoscale particles of pollutants can provide not only accurate data and evidence for the formation of atmospheric aerosol particles, the sources of urban air pollutants, and pollution control measures, but also effective research methods and provenance discrimination marks for the determination of atmospheric particulate matter sources.

5.10. Nano-Marine Science

Deep-sea sedimentology is a key link in the geoscience system, but the study of the sedimentation and diagenesis of fine particles is a relatively weak link in the field of sedimentology. Deep-sea sediments are dominated by fine particles. Apart from traditional chemical analysis and clay minerals analysis, diversified analytical methods, especially nanoscale observation methods, urgently need to be extensively studied and applied.^{235–237} In the research of fine-particle sediments and oil-gas accumulation in deep water, most of the early studies focused on the potential analysis of oil generation of source rock. Based on the analysis of the development trend of fine sedimentology,

it has been pointed out that the cutting-edge of current research is to perfect the pertinent research method, reconstruct the ancient sedimentary environment, and establish the classification system and genesis modes of fine sedimentary rocks.²³⁸ In order to better understand the types and genesis of fine-grained deposits in deep water and guide unconventional oil-gas exploration, nanotechnology will be an important research method at present and in future.¹⁹⁹

For example, people find many manganese nodules when studying the substances of the ocean basin. These fist-sized clumps are rich in the element Mn, thus forming a huge manganese deposit. It is because, in the mid-ocean ridges, slow materials continuously erupt, and these substances quickly cool and form small colloids. These colloids settle at the bottom, finally form concretion, and slowly move to other places with the drift of the ocean floor plate. These manganese colloids are initially nanoparticles that aggregate under the action of seawater electrolytes.^{45, 239, 240}

The “black smoker” produced by the hydrothermal vents of the seafloor are enriched with a large number of natural nanoparticles, which has become a research hotspot in recent years. Recent research results have confirmed this point.^{241, 242} After contrasting the hydrothermal vents located at a slow spreading mid-ocean ridge, a fast spreading mid-ocean ridge, and a back-arc basin, Gartman and other scholars have found that pyrite nanoparticles are a widespread component of black smoker emissions, and these nanoparticles may be an important source of iron of the world’s oceans. It is also intended to show that pyrite and other nanoparticles are common components of black smoker emissions from different geological settings.^{243, 244} At the same time, the presence of elements Si and Cu detected in the EDX data indicates that pyrite is not the only mineral in the nanoparticle aggregates. Observational analysis at the nanoscale reveals important differences in the morphology of these nanoparticles, which can affect their aggregation in seawater and their stability to oxidation. A lot of silicate nanoparticles and metals such as Cu and Zn are also identified in the black smoker, indicating that the hydrothermal vents are the “factory” of nature, continuously providing nanoparticles to the seawater.²⁴⁴

The widespread identification of nanoparticles in a “black smoker” may provide new mechanisms for the global transport of elements from hydrothermal vent emissions, especially iron and the potential for interaction with local organisms. Studies have shown that hydrothermal iron nanoparticles migrate more than 2,000 km.²⁴⁵ Nanoparticles of the hydrothermal vents on the seafloor in other parts of the world are bound to be gradually discovered. With further research on these nanoparticles, the transportation law of entire marine elements will also be clearer.

6. CUTTING-EDGE SCIENTIFIC ISSUES AND DEVELOPMENT TREND OF NANOGEOSCIENCES

Nanotechnology is one of the research hotspots all over the world, propelling humans into a new stage in the transformation of nature and driving geological scientists to obtain a new ability for the recognition and transformation of nature from micron scale to nano scale. Although there are some achievements, nanogeosciences is still in its earliest stages, because it falls short of intensive and detailed comprehension of the mineral microscopic formation mechanism, microelement migration path, mesostructure in-depth understanding, and nanoparticle force to an earthquake, etc. Therefore, there are good prospects for development in nanogeosciences. Especially in recent years, from the dimension of nano effect, geologists in Europe, America, Japan, and Korea have devoted themselves to intensive study of various formation mechanisms and model paradigms of geological, mineral, and geochemical phenomena, such as dynamic weakening of nanoparticles,²⁴⁶ ordered stacking of nanoparticles,³⁹ secondary clay nano-coating,¹³⁰ and in particular, mineral nanoscale deformation and metamorphism due to tectonic change. This has brought the geoscience into the so-called carrier revolution in which the maximum density of information could be extracted from the smallest carrier and is also the inevitable trend for modern scientific and technological development.

6.1. Basic Research on Nanogeosciences

The new inspiration for geoscience from the perspective of nanotechnology: Many issues can be researched on the basis of nano theory, such as the relationship between the Big Bang and the formation of the earth; the effect and consequence caused to the earth by impacts from planets, meteorolites, and meteors and the formation of mineral resources; the formation of black-holes in the universe; “white smokers” and “black smokers” in the ocean; the catacausis of coal and pyrrhotite; explosion caused by dust; abnormal curve in thermodynamic calculation when the solute tends to zero; and the development of new mineral materials.⁵

Nanotechnology is extraordinary when applied in geoscience, and every subdiscipline can make a breakthrough under the guidance of nano theory. As one of the pillar theories of nanogeosciences, the development of nano-mineralogy and the development and utilization of nanoscale mineral grains are another breakthrough in the progress of the history of mineralogy; nano-petrology proposes the observation view in nanoscale for petrologists; and nano-geochemistry will step into the micromechanism of the element migration process. Along with the development and application of nanotechnology in geoscience, the research of nano-ore deposit will certainly make a landmark progress with its unique advantages.

Nano-structural geology provides the methods and basis for the research of ultramicro-scale structure; nanotechnology has a good developing prospect for energy, especially for unconventional energy. Nano-earthquake geology is expected to make a breakthrough in earthquake emergency mechanisms; nanotechnology provides a new research opportunity for the field of environmental geology. The development of nano-atmospheric science contributes to the explanation of the source and cause of contamination particles such as smog in order to thoroughly prevent and control air pollution. And nano-marine science helps us to recognize the sedimentation process of marine grains and the migration rule of marine elements from a new viewpoint.

Additionally, the development of clay mineral materials is anticipated because clay minerals possess stratified structure and nano clay mineral materials can be obtained by intercalating and delaminating technology. Compared with the traditional preparative technique for nanoparticles, this technology has the advantages of abundant raw materials, simple technology, and low cost, thus offering broad application prospects. Furthermore, the appearance of mesoporous materials provides a new growing point for the development of nanotechnology.²⁴⁷ The application of nanotechnology not only has significant scientific research value and economic benefits but is also closely related to human daily life.

6.2. Nanogeosciences and National Strategic Needs

6.2.1. Nano-Ore Deposit and Unconventional Energy

The study of ore deposits is disciplinary and comprehensive. In recent years, a series of achievements has been made in studying the occurrence and migration mechanism for nanoscale metal grains in China's topsoil, following the development and improvement of nanomineral exploration methods.^{50, 205} The recent research indicates that the extensively developed black rock series formed from Sinian to Cambrian, spread over ten and more provinces in southern China, display features of symbiosis and enrichment of valuable metallic elements.^{207, 208} Furthermore, several large–super large ore deposits with million–ten-million tons of reserves have been discovered. These deposits contain high-purity nano-micron grade non-metallic minerals, which have huge resource value. As the traditional ore deposit is combined with nanotechnology and concepts, revolutionary prospecting methods will certainly be developed to provide source assistance to resolve the mineral resource shortage problems of the world.

As conventional fossil energy shows a trend of gradual decrease in exploration, it is extremely urgent to develop and utilize new energy resources. Relying on new technology and methods, the development of nanogeosciences helps people to use new technology and new methods to develop and utilize new energy resources, such as coal bed gas, shale gas, tight sandstone gas, concealed deposits,

and more, which make up for the shortage of conventional energy resources and enhance the national strategic reserve capacity.

Some countries have obtained success in the exploration and development of coalbed methane. However, there is still no final conclusion regarding the occurrence condition, the mechanism of adsorption and desorption, the migration path, and the exploitation methods for gas in the coal bed, but the appearance of nano theory provides the means and basis to study the nanoscale pores and macromolecular structure of coal and establishes the theoretical foundation to obtain a high yield of coalbed methane. Unconventional gas, such as shale gas and tight sandstone gas, normally occurs in the nanoscale pores of the reservoir stratum, and hence it is inevitable to study the nanoscale structure of the reservoir stratum in order to exploit these types of gas. In brief, the development of nanogeosciences provides an important theoretical direction for the discovery, exploitation, and utilization of unconventional energy.

6.2.2. Nano-Mineralogy and Nano Coal-Based Materials

Carbon nanoparticles, free carbon nanotubes, and tufted carbon nanotubes with different sizes (several or dozens of nanometers in diameter) have been found in coal samples exploited in northeastern India. The positive formation environment, the cause of formation, and their potential economic value have also been analyzed and discussed.¹⁴⁸ As a typical example of nanoparticles, carbon nanotubes can be widely utilized but with a complicated manufacturing process, but the extraction of materials formed in the natural environment such as carbon nanotubes undoubtedly offers a new research direction and ideas.

Nano-mineralogy focuses on studying the componential and structural characteristics of nanoscale rock particles and nanoscale mineral particles. Combined with materials science, nano-mineralogy provides a theoretical basis for the preparation, representation, and structural explanation of new nanoparticles. Combined with microbiology and by studying mineral growth inside and outside of microbial cells from the nanoscale, it can provide the theory and techniques for biomineralization, interaction between organisms and minerals, biochemical weathering, materials synthesis of biological self-organization, and origin of life. Combined with energy geology, it can help in studying the formation mechanism of nanoscale minerals in an energy mineral resource, and then deduce the favorable environment of an energy reservoir with certain tracing significance.¹⁶³ Combined with geochemistry, it can aid in studying the elemental geochemical behaviors in the course of mineral dissolution, crystallization, metasomatism, weathering, and deformation from the nanoscale, and discuss the element migration mechanism, elemental geochemical cycle, etc.

Nanoscale rock particles exist in each stage of the formation of rocks, and they store much important geological information. They were unknown before, due to the limitation of technology, but now the nanoparticles can be observed directly with the appearance of high-resolution equipment. In the area of petrology, in-depth research on nanoscale particles shall be conducted because it is still at the fledgling stage with some initial achievements.

6.2.3. Nanoparticles and Environmental Pollution

Environmental problems are a major global issue facing today's world. Even with a number of ways to resolve them, there is no efficient measure to solve some worldwide pollution problems such as the greenhouse effect. However, the application of nanotechnology in geoscience provides new concepts and means to resolve environmental problems. Many environmental pollution problems are actually nanoparticle pollution problems.¹² Besides radioactive substances, solar radiation, and bacteria and viruses, nanoparticles are likely to invade and harm the human body. Because nanoparticles can exist in solid, liquid, and gas, and thus they can easily invade the human body, stay in cells, and cause lesions, disease, and even death. The suspended dust attaching a large number of pollutants in the air and heavy metal nanoparticle aggregation in the water are the essential reason for pollution. Analyzing the source, elements, structure, and migration rules of these nanoscale particles can fundamentally determine the cause of pollution, leading to the right solution. The application of nano theory in research in environmental sciences will have an important effect on environmental protection as well as disease prevention and treatment.

CO₂ is the primary cause for the greenhouse effect, so it is extremely urgent to cope with climate change and reduce emissions of greenhouse gases. Today it is widely accepted that geologic sequestration is an efficient approach to reduce CO₂ emissions. The fundamental principle of CO₂ geologic sequestration is to liquefy CO₂ and store it in the pores of deep underground rock strata. Along with the development and utilization of nanotechnology, the research from the nanoscale on interaction between CO₂ fluid and rocks may improve the capacity of rock geologic sequestration, providing economic, efficient, and safe materials and methods for CO₂ emission.⁴⁴ Always a hot topic of research on environmental engineering, environmental chemistry, interfacial chemistry, and mineral-petrological materials, the pollution of heavy metal ions in industrial effluents has threatened the survival and development of mankind as well as flora and fauna. As a nano mineral material, the utilization of attapulgite carves out a new way to resolve heavy mineral pollution. The attapulgite has developed inner ducts and a large specific surface area, thus having a perfect adsorptive property. It can be used as an adsorbent of environmental mineral materials to effectively solve environmental pollution problems.

6.2.4. Nanostructure and Geological Disaster

Geological disasters, especially coalbed gas outburst, earthquake, and debris flow, cause huge property damage and casualties to mankind, which seriously impedes social development and evolution. Coalbed gas outburst is a major geological disaster, and its generating mechanism still cannot be explained scientifically and reasonably. Nonetheless, it is well known that there is a close relationship between gas outburst and tectonic coal development. Tectonic coal generally has a crushed structure and contains lots of coal dust and particles, and thus it is bound to contain plenty of nanoparticles. The application of nano theory is likely to lead to a breakthrough in understanding of the relationship between tectonic coal and gas outburst as well as its generating mechanism from a new viewpoint. The research on the bursting mechanism of earthquake and debris flow has been the focus of scientists, and the existence of nanoparticles in bursting may provide a basis to understand the disaster generating mechanism. Thus, the production of nanogeosciences theory provides a powerful theoretical basis to prevent and treat geological disasters.

Similar to other disciplines, the development of nanogeosciences generally needs to experience four steps or phases, i.e., phenomenon determination, mechanism verification, efficacy development, and digital modeling.

(1) Phenomenon determination: The geological determination of the existence of nanophenomenon shall depend on recurrent and repetitive appearance with internal organic connection but not individual and sporadic observation. For instance, the dispersive nanoparticles in rocks generate nano-lines and nano-layers structure.

(2) Mechanism verification: The classical rule of macro natural phenomenon virtually is an approximation of micro rule. This micro generating mechanism needs to be verified in certain geomechanics, physical, and chemical conditions. Besides conventional macro experiments, unconventional micro experiments shall also be done, such as supercritical state, etc.²⁴⁸

(3) Efficacy development: From the viewpoint of nano scientists, the world of nanotechnology is full of magic,⁶ but it is necessary to continuously exploit and develop in depth. For example, for kinematic mineral shells or films that consist of nanoparticles on rock shearing surface,¹²⁹ also called coating in materials science,¹⁷¹ it is requisite to develop its function of petrogenation and mineralization, aseismogeny and seismogeny, covering and plugging of oil and gas.

(4) Digital modeling: Based on the above-mentioned three phases inclusive of determination, verification, and development, or in the case of abundant information accumulation, it is necessary to synthetically discuss and establish digital libraries, patterns, and forms, to the height of nano theory, breadth of areal geology, depth of

historical geology, accuracy of microbeam analysis, and intensity of practical application.

It is admittedly difficult to complete this phase, but also essential for the maturing of a discipline. Without doubt, there is a long way for the research of nanogeosciences.

As one of the forefront sciences with the most promising development prospects, nanotechnology combined with geoscience produces a number of unexpected results with brilliant scientific sparks, giving geologists many real surprises. Nowadays, nanogeosciences is still in the initial stage but with huge development prospects. It is believed that the nano era is coming and the leap of geology in the 21st century will depend on nanogeosciences.

7. CONCLUSIONS

Nanotechnology is a subject at the forefront of science, and a new research area that is cutting-edge and interdisciplinary. It has made remarkable achievements in the fields of chemistry, physics, biology, medical science, materials science, and microelectronics, while geologists also have recognized the potential of nano theory for the development of geology in recent years. Predecessors have used nanotechnology to make some fragmentary research on geoscientific issues, but these studies lack a systematic and complete theoretical direction. In this paper, based on the summarization of the existing academic achievements in ultra-microscopic studies, the concept of nanogeosciences is further put forward. We systematically analyzed new disciplines generated from nanotechnology combined with various subdisciplines of geosciences, including nano-mineralogy, nano-petrology, nano-geochemistry, nano-structural geology, nano-energy geology, nano-ore deposit geology, nano-earthquake geology, nano-environmental geology, nano-atmospheric sciences, nano-marine science, etc.

In the fields of mineralogy and geochemistry, the atom and its lattice arrangement have been studied and the effects of adsorption, infiltration, corrosion, and replacement on mineral surface have been discussed. The paragenesis of nano minerals and the syntagmatic relation between nano minerals and other larger minerals have also attracted much attention. Nanoscale fluid inclusion has been found, while the causes of rock formation and the effects of fluid have been discussed from the micro dimension in the field of petrology. The nanostructures of organic matters have been revealed; nanometer minerals and organic matter particles as well as their nanoscale pores have been analysed. With discovery of nano-deformation and nanolayers, the movement mechanism of nanoscale particles transferring and slipping has been added to the theory of the ductile shearing zone in the field of tectonic geology. In the field of energy geology, the carbon macromolecule structure and nanoscale pore change in coals have been analyzed and studied, through which

we have the result that the tectonic deformation would significantly affect the adsorption, storage, and resolution of coalbed gas, and also initially explain the structural characteristics of size, form, and connectedness of micro-nano throats in unconventional oil and gas reservoirs as well as the evolution rule and the occurrence mode of oil and gas. The formation of superfine disseminated gold ore has been analyzed from the nanoscale in the field of ore deposits, and the new geogas method is found to explore blind deposits. In the field of earthquake geology, it is known that a narrow seismogenic fault zone is the viscoelastic friction tape of nanoparticles, so the instability of a macro system might be caused by the energy release of micro particles, which provides nano structural methods to solve the gas outburst problem in colliery. The emission characteristics and rules as well as the risk assessment caused by the production, utilization, and discarding of nanomaterials have been discussed in the field of environmental geology. In the field of atmospheric science, regarding air pollution events occurring in a few regions throughout the world, the material composition and structural characteristics of nanoscale particles of pollutants have been analyzed, providing correct information and foundations for finding the source of air pollution and countermeasures for pollution control. In the field of marine science, starting from research on deepwater fine-grained deposits and nanoparticles in the marine "black smoker," a new viewpoint has been provided to establish the paleo-ocean environment and understand marine elements migration rules.

Nanogeosciences are facing a new strategic opportunity and a revolutionary challenge. In the future, we need to clarify the basic connotation and the main research direction of nanogeosciences with the help of nanoscience and earth science research methods, experience, and achievements, involving the following topics: nanostructure and surface effect of minerals and genesis of rock; evolution mechanism of nanoparticles and nanopores in a natural geological body; characteristics and formation mechanism of nano-deformation; nanogeochemical processes and their behavior; nanometer effects of hydrocarbon accumulation and their dynamic mechanisms; nano metallogenesis and their patterns; nanomineral, carbon radicals, and new composite material: resource potential and processing application; nanogeology and disaster/environmental problems: nanogeoscience in geological hazards and prevention, environmental evolution, and regulation, and environmental pollution and remediation; study of the application of nanometer technology in the earth's lithosphere, atmosphere, hydrosphere, and biosphere spheres and their interaction; research techniques and methods in nanogeosciences; a detailed interpretation of geological evolution and the information of the earth's development from nano-scale. At present, we should give full play to the advantages of multi-disciplinary study, extensively cooperate with global geoscientists, and promote the research

of nanogeosciences, that we may fully communicate the latest research achievements in nanogeosciences worldwide and identify key scientific issues in this field, enrich and develop the theory and methods of nanogeosciences so as to provide an important theoretical basis for the utilization of mineral and carbon-based material, exploration and development of energy resources and mineral resources, and disaster prevention and environmental protection, as well.

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References and Notes

- J. Z. Chen, *Geological Science and Technology Information (Chinese with English Abstract)* 13, 2 (1994).
- Q. Tang, Y. Zhang, and J. Wang, *Public Communication of Science and Technology (Chinese with English Abstract)* 11, 22 (2010).
- A. P. Alivisatos, *Science* 271, 5251 (1996).
- M. F. Hochella, Jr., *Ann. Ny. Acad. Sci.* 1093, 1 (2006).
- Z. G. Zhang, *Geotectonica Et. Metallogenia (Chinese with English Abstract)* 19, 1 (1995).
- R. Wirth, *Eur. J. Mineral* 16, 6 (2004).
- B. Bhushan, *Wear* 259, 7 (2005).
- A. L. Porter and J. Youtie, *J. Nanopart. Res.* 11, 5 (2009).
- G. Binnig, H. Rohrer, C. Gerber, and E. Weibel, *Phys. Rev. Lett.* 49, 1 (1982).
- X. W. Tang, Z. W. Hu, Y. L. Xu, and Q. M. Wang, *Nature Magazine (Chinese with English Abstract)* 14, 8 (1991).
- Z. C. Jiang, *Geology-Geochemistry (Chinese with English Abstract)* 2, 22 (1993).
- Z. G. Zhang, *Geology-Geochemistry (Chinese with English Abstract)* 04, 38 (1994).
- X. F. Liu, *Journal of Electronic Science and Technology (Chinese with English Abstract)* 1, 22 (1995).
- Z. G. Zhang and Z. C. Jiang, *Mineral Resources and Geology (Chinese with English Abstract)* 03, 161 (1993).
- X. J. Xie, *Earth Science Frontiers (Chinese with English Abstract)* 02, 2 (1998).
- J. F. Banfield and H. Z. Zhang, *Nanoparticles and the Environment Reviews in Mineralogy and Geochemistry* 44, 1 (2001).
- T. H. Chen, J. Chen, J. F. Ji, H. F. Xu, and X. F. Sheng, *Geological Review (Chinese with English Abstract)* 51, 6 (2005).
- S. L. Hwang, P. Shen, T. F. Yui, and H. T. Chu, *J. Metamorph. Geol.* 25, 4 (2007).
- M. F. Hochella, Jr., S. K. Lower, P. A. Maurice, R. L. Penn, N. Sahai, D. L. Sparks, and B. S. Twining, *Science* 319, 5870 (2008).
- P. R. Buseck and K. Adachi, *Elements* 4, 6 (2008).
- Y. F. Wang, *Chem. Geol.* 378, 1 (2014).
- M. F. Hochella, Jr., *Earth. Planet Sc. Lett.* 203, 2 (2002).
- S. K. Lower, M. F. Hochella, Jr., J. F. Banfield, and K. M. Rosso, *EOS* 83, 6 (2002).
- X. L. Wu, Y. J. Han, D. W. Meng, and D. X. Li, *Earth Planet Sc. Lett.* 197, 3 (2002).
- J. S. Qiu, Y. F. Li, Y. P. Wang, C. H. Liang, T. H. Wang, and D. H. Wang, *Carbon* 41, 4 (2003).
- Y. W. Ju, B. Jiang, Q. L. Hou, G. L. Wang, and S. Q. Ni, *Sci. China Ser. D* 48, 9 (2005).
- Y. W. Ju, G. L. Wang, and B. Jiang, *Science in China, Ser. D (Chinese with English Abstract)* 33, 7 (2003).
- Y. W. Ju, B. Jiang, Q. L. Hou, and G. L. Wang, *Chinese Science Bulletin (Chinese with English Abstract)* 17, 90 (2005).
- Y. Sun, X. C. Lu, D. L. Liu, L. S. Shu, W. B. Zhu, and J. C. Guo, *Geological Journal of China Universities (Chinese with English Abstract)* 11, 4 (2005).
- Y. Sun, X. C. Lu, X. H. Zhang, H. Liu, and A. M. Lin, *Science in China, Ser. D (Chinese with English Abstract)* 39, 8 (2009).
- C. Colletini, A. Niemeijer, C. Viti, and C. Marone, *Nature* 462, 7275 (2009).
- Y. W. Ju, B. Jiang, Q. L. Hou, and G. L. Wang, *Chinese Sci. Bull.* 50, 16 (2005).
- R. G. Loucks, R. M. Reed, S. C. Ruppel, and D. M. Jarvie, *J. Sediment Res.* 79, 12 (2009).
- C. N. Zou, S. Z. Tao, and L. H. Hou, Geological Publishing House, Beijing, China (2011).
- M. E. Curtis, C. H. Sondergeld, R. J. Ambrose, and C. S. Rai, *AAPG Bull.* 96, 4 (2012).
- M. E. Curtis, B. J. Cardott, C. H. Sondergeld, and C. S. Rai, *Int. J. Coal Geol.* 103, 26 (2012).
- B. Wilson, T. Dewers, Z. Reches, and J. Brune, *Nature* 434, 7034 (2005).
- H. T. Chao, Y. Sun, Z. C. Wang, Z. W. Cui, and T. L. Qu, *Progress in Natural Science (Chinese with English Abstract)* 19, 10 (2009).
- C. Viti and T. Hirose, *J. Struct. Geol.* 32, 10 (2010).
- T. H. Chen and H. F. Xu, *Acta Petrologica Et. Mineralogica (Chinese with English Abstract)* 04, 425 (2003).
- L. Y. Shao, J. J. Li, H. Y. Zhao, S. S. Yang, H. Li, W. J. Li, T. Jones, K. Sexton, and K. Bérubé, *Atmos Environ.* 41, 26 (2007).
- M. Hasselöv and F. von der Kammer, *Elements* 4, 6 (2008).
- B. K. G. Theng and G. Yuan, *Elements* 4, 6 (2008).
- Y. X. Wang, X. M. Mao, and D. DePaolo, *Earth Science (Journal of China University of Geosciences) (Chinese with English Abstract)* 36, 1 (2011).
- Y. Ye, Z. Y. Shen, D. H. Xiao, Y. H. Zhou, Z. Q. Liu, and X. Y. Zhu, *Progress in Geophysics (Chinese with English Abstract)* 04, 651 (2002).
- Y. F. Wang, C. Bryan, H. F. Xu, and H. Z. Gao, *Geology* 31, 5 (2003).
- G. A. Waychunas and H. Z. Zhang, *Elements* 4, 6 (2008).
- J. Liu, D. M. Aruguete, J. R. Jinschek, R. J. Donald, and M. F. Hochella, Jr., *Geochim. Cosmochim.* 72, 24 (2008).
- J. Liu, D. M. Aruguete, M. Murayama, and M. F. Hochella, Jr., *Environ. Sci. Technol.* 43, 21 (2009).
- X. Q. Wang, B. M. Zhang, X. Lin, S. F. Xu, W. S. Yao, and R. Ye, *Ore Geol. Rev.* 73, 417 (2016).
- M. F. Hochella, Jr., *Elements* 4, 6 (2008).
- F. Javadpour, *J. Can. Petrol Technol.* 48, 8 (2009).
- E. Fathi and I. Y. Akkutlu, *SPE J.* 18, 1 (2012).
- Y. W. Ju, Y. Sun, Q. Wan, S. F. Lu, H. P. He, J. G. Wu, W. J. Zhang, G. C. Wang, and C. Huang, *Bulletin of Mineralogy, Petrology and Geochemistry (Chinese with English Abstract)* 35, 1 (2016).
- Y. X. Wang and X. K. Tian, *Bulletin of Mineralogy, Petrology and Geochemistry (Chinese with English Abstract)* 35, 1 (2016).
- Q. Wan, Z. H. Qin, Y. W. Ju, S. S. Li, Y. H. Fu, and Y. T. Gu, *Bulletin of Mineralogy, Petrology and Geochemistry (Chinese with English Abstract)* 35, 1 (2016).
- X. S. Li, Y. W. Ju, Q. L. Hou, and J. J. Fan, *Acta Geol. Sin.-Engl.* 87, 1 (2013).
- Y. C. Ge, X. J. Ge, and H. P. He, *Chinese Phys. B* 23, 11 (2014).
- G. R. L. Chalmers, R. M. Bustin, and I. M. Power, *AAPG Bull.* 96, 6 (2012).

60. S. Bernard, B. Horsfield, H. M. Schulz, R. Wirth, A. Schreiber, and N. Sherwood, *Mar. Petrol. Geol.* 31, 1 (2012).
61. K. Jiao, S. P. Yao, H. Wu, M. C. Li, and Z. Y. Tang, *Geological Journal of China Universities (Chinese with English Abstract)* 01, 151 (2014).
62. Z. M. Sun, X. C. Lu, X. C. Jia, Y. S. Bai, and W. X. Hu, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
63. C. R. Clarkson, N. Solano, R. M. Bustin, A. M. M. Bustin, G. R. L. Chalmers, L. He, Y. B. Melnichenko, A. P. Radliński, and T. P. Blach, *Fuel* 103, 606 (2013).
64. G. C. Wang and Y. W. Ju, *J. Nat. Gas. Sci. Eng.* 27, 452 (2015).
65. M. M. Wei, L. Zhang, Y. Q. Xiong, J. H. Li, and P. A. Peng, *Micropor. Mesopor. Mat.* 227, 88 (2016).
66. Y. B. Yao, D. M. Liu, Y. Che, D. Z. Tang, S. H. Tang, and W. H. Huang, *Fuel* 89, 7 (2010).
67. Y. B. Yao and D. M. Liu, *Fuel* 95, 152 (2012).
68. E. Odusina and R. F. Sigal, *Petrophysics* 52, 1 (2011).
69. C. N. Zou, R. K. Zhu, B. Bai, Z. Yang, S. T. Wu, L. Su, D. Z. Dong, and X. J. Li, *Acta Petrologica Sinica (Chinese with English Abstract)* 27, 6 (2011).
70. Y. Ma, N. N. Zhong, D. H. Li, Z. J. Pan, L. J. Cheng, and K. Y. Liu, *Int. J. Coal Geol.* 137, 38 (2015).
71. L. Sun, X. Q. Wang, X. Jin, J. M. Li, and S. T. Wu, *Petrol. Explor. Dev.* 43, 3 (2016).
72. S. W. Zhou, G. Yan, H. Q. Xue, W. Guo, and X. B. Li, *Mar. Petrol. Geol.* 73, 174 (2016).
73. Y. Wang, J. Pu, L. H. Wang, J. Q. Wang, Z. Zhang, Y. F. Song, C. C. Wang, Y. F. Wang, and C. Jin, *Fuel* 170, 84 (2016).
74. J. H. Zeng, X. Feng, S. Feng, Y. C. Zhang, J. C. Qiao, and Z. F. Yang, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
75. K. Bartuś and A. Bródka, *Mol. Phys.* 109, 13 (2011).
76. K. Mosher, J. J. He, Y. Y. Liu, E. Rupp, and J. Wilcox, *Int. J. Coal Geol.* 109, 36 (2013).
77. J. F. Zhang, M. B. Clennell, D. N. Dewhurst, and K. Y. Liu, *Fuel* 122, 186 (2014).
78. S. Wang, Q. H. Feng, F. Javadpour, T. Xia, and Z. Li, *Int. J. Coal Geol.* 147, 9 (2015).
79. J. Yao, H. Sun, D. Y. Fan, Z. Q. Huang, Z. X. Sun, and G. H. Zhang, *Journal of China University of Petroleum (Edition of Natural Science) (Chinese with English Abstract)* 01, 91 (2013).
80. X. L. Zhang, L. Z. Xiao, X. W. Shan, and L. Guo, *Sci. Rep.-UK* 4, 4843 (2014).
81. S. F. Lu, Y. N. Zhang, J. Q. Li, and Y. W. Ju, *Bulletin of Mineralogy, Petrology and Geochemistry (Chinese with English Abstract)* 35, 1 (2016).
82. S. G. Hua, L. J. Wang, X. F. Jia, L. Chen, and J. W. Li, *Earth Science (Journal of China University of Geosciences) (Chinese with English Abstract)* 37, 5 (2012).
83. H. L. Liu, R. W. Zhu, B. Y. Shen, Z. R. Cai, C. D. Liu, X. F. Zhang, Y. Zhou, Y. Wang, and Y. H. Li, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
84. T. H. Chen and Q. Q. Xie, *Journal of Hefei University of Technology (Natural Science)* 28, 9 (2005).
85. X. K. Tian, W. W. Wang, Y. X. Wang, S. Komarneni, and C. Yang, *Micropor. Mesopor. Mat.* 207, 46 (2015).
86. Y. W. Ju, B. Jiang, G. L. Wang, and Q. L. Hou, China Mining University Press, Xuzhou, China (2005).
87. Y. W. Ju, B. Jiang, Q. L. Hou, G. L. Wang, and A. M. Fang, *Acta Geologica Sinica (Chinese with English Abstract)* 79, 2 (2005).
88. C. N. Zou, Z. Yang, S. Z. Tao, X. J. Yuan, R. K. Zhu, L. H. Hou, S. T. Wu, L. Sun, G. S. Zhang, B. Bai, L. Wang, X. H. Gao, and Z. L. Pang, *Earth-Sci. Rev.* 126, 358 (2013).
89. J. D. Hughes, *Nature* 494, 7437 (2013).
90. Y. W. Ju, S. F. Lu, Y. Sun, F. Q. Tan, G. C. Wang, K. Han, Y. Bao, and Q. G. Li, *Acta Geol. Sin.-Engl.* 89, s1 (2015).
91. S. Jiang, D. S. Xiao, X. L. Tang, F. C. Xing, C. F. Xiang, P. Pahnke, T. Anderson, and S. F. Lu, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
92. M. M. Labani, R. Rezaee, A. Saeedi, and A. A. Hinai, *J. Petrol. Sci. Eng.* 112, 7 (2013).
93. U. Kuila, D. K. McCarty, A. Derkowski, T. B. Fischer, T. Topór, and M. Prasad, *Fuel* 135, 359 (2014).
94. G. R. L. Chalmers and R. M. Bustin, *Int. J. Coal Geol.* 69, 4 (2007).
95. D. J. K. Ross and R. M. Bustin, *Mar. Petrol. Geol.* 26, 6 (2009).
96. X. C. Zhao, M. J. Blunt, and J. Yao, *J. Petrol. Sci. Eng.* 71, 3 (2010).
97. G. R. L. Chalmers, D. J. K. Ross, and R. M. Bustin, *Int. J. Coal Geol.* 103, 120 (2012).
98. R. Yang, S. He, J. Z. Yi, and Q. H. Hu, *Mar. Petrol. Geol.* 70, 27 (2016).
99. Q. Z. Guan, D. Z. Dong, S. F. Wang, J. L. Huang, Y. M. Wang, H. Lu, and C. C. Zhang, *J. Nat. Gas. Sci. Eng.* 31, 382 (2016).
100. C. L. Fang, M. Amro, G. S. Jiang, and H. Z. Lu, *J. Nat. Gas. Sci. Eng.* 33, 1181 (2016).
101. G. J. Sang, D. Elsworth, X. X. Miao, X. B. Mao, and J. H. Wang, *J. Nat. Gas. Sci. Eng.* 32, 423 (2016).
102. P. F. Wang, Z. X. Jiang, W. M. Wei, C. Zhang, Y. Yuan, L. Chen, and L. S. Yin, *Mar. Petrol. Geol.* 72, 122 (2016).
103. W. H. Lee, J. S. Park, J. H. Sok, and P. J. Reucroft, *Appl. Surf. Sci.* 246, 1 (2005).
104. A. P. Wang, F. Y. Kang, Z. H. Huang, and Z. C. Guo, *New Carbon Materials (Chinese with English Abstract)* 02, 141 (2007).
105. H. F. Cheng, E. D. Hu, and Y. A. Hu, *J. Contam. Hydrol.* 129, 80 (2012).
106. A. W. Miller and Y. F. Wang, *Environ. Sci. Technol.* 46, 4 (2012).
107. X. M. Mao, X. K. Tian, and C. Y. Yu, *Chinese Journal of Geochemistry* 30, 4 (2011).
108. G. Rother, E. G. Krukowski, D. Wallacher, N. Grimm, R. J. Bodnar, D. R. Cole, *J. Phys. Chem. C* 116, 1 (2012).
109. J. F. Banfield and W. W. Barker, *Geochim. Cosmochim. Ac.* 58, 5 (1994).
110. T. J. Katsube, M. A. Williamson, *Clay Miner.* 29, 4 (1994).
111. X. Q. Wang, X. J. Xie, and S. Y. Ye, *J. Geochem. Explor.* 55, 1 (1995).
112. X. Q. Zhu and Z. G. Zhang, *Mineral Resources and Geology (Chinese with English Abstract)* 02, 55 (1996).
113. T. L. Daulton, D. D. Eisenhour, T. J. Bernatowicz, R. S. Lewis, and P. R. Buseck, *Geochim. Cosmochim.* 60, 23 (1996).
114. A. A. Gribb and J. F. Banfield, *Am. Mineral.* 82, 7 (1997).
115. X. Q. Wang, Z. Z. Cheng, Y. X. Lu, L. Xu, and X. J. Xie, *J. Geochem. Explor.* 58, 1 (1997).
116. H. Z. Zhang, R. L. Penn, R. J. Hamers, and J. F. Banfield, *J. Phys. Chem. B* 103, 22 (1999).
117. H. Y. Shi, *Journal of Earth Sciences and Environment (Chinese with English Abstract)* S1, 90 (1998).
118. X. J. Xie and X. Q. Wang, *J. Geochem. Explor.* 40, 1 (1991).
119. C. H. Tong, J. C. Li, L. Q. Ge, and F. G. Yang, *Sci. China Ser. D* 41, 3 (1998).
120. P. Buffat and J. P. Borel, *Phys. Rev. A* 13, 6 (1976).
121. M. F. Hochella, Jr., *Geochim. Cosmochim. Ac.* 66, 5 (2002).
122. C. Ferraris, C. Chopin, and R. Wessicken, *Am. Mineral.* 85, 9 (2000).
123. S. Veprek, A. Niederhofer, K. Moto, T. Bolom, H. D. Männling, P. Nesladek, G. Dollinger, and A. Bergmaier, *Surf. Coat. Tech.* 133 (2000).
124. M. Herwegh and K. Kunze, *J. Struct. Geol.* 24, 9 (2002).
125. Y. W. Ju, B. Jiang, Q. L. Hou, and G. L. Wang, *Journal of China Coal Society (Chinese with English Abstract)* 29, 5 (2004).
126. M. Reich, S. E. Kesler, S. Utsunomiya, C. S. Palenik, S. L. Chrystoulis, and R. C. Ewing, *Geochim. Cosmochim.* 69, 11 (2005).
127. M. Reich, S. Utsunomiya, S. E. Kesler, L. M. Wang, R. C. Ewing, and U. Becker, *Geology* 34, 12 (2006).
128. R. R. Anand, M. Cornelius, and C. Phang, *Geochemistry: Exploration, Environment, Analysis* 7, 3 (2007).

129. Y. Sun, L. S. Shu, X. C. Lu, H. Liu, X. H. Zhang, K. Kosaka, and A. M. Lin, *Chinese Sci. Bull.* 53, 8 (2008).
130. A. M. Schleicher, *Geology* 38, 7 (2010).
131. Y. W. Ju, K. Luxbacher, X. S. Li, G. C. Wang, Z. F. Yan, M. M. Wei, and L. Y. Yu, *International Journal of Coal Science and Technology* 1, 3 (2014).
132. R. G. Loucks, R. M. Reed, S. C. Ruppel, and U. Hammes, *AAPG Bull.* 96, 6 (2012).
133. K. A. Langworthy, D. H. Krinsley, and R. I. Dorn, *Scanning* 33, 2 (2011).
134. S. Emmanuel and J. J. Ague, *Chem. Geol.* 282, 1 (2011).
135. S. M. Chathoth, L. He, E. Mamontov, and Y. B. Melnichenko, *Micropor. Mesopor. M* 148, 1 (2011).
136. G. A. Oleynikova and E. G. Panova, *Journal of Earth Science and Engineering* 1, 3 (2011).
137. S. P. Yao, K. Jiao, K. Zhang, W. X. Hu, H. Ding, M. C. Li, and W. M. Pei, *Chinese Sci. Bull.* 56, 25 (2011).
138. X. S. Li, Y. W. Ju, Q. L. Hou, and H. Lin, *Sci. China Earth Sci.* 55, 8 (2012).
139. Y. Sun, S. Y. Jiang, Z. Wei, and X. C. Lu, *Advanced Materials Research* 669, 108 (2013).
140. S. S. Tov, E. Aharonov, A. Sagy, and S. Emmanuel, *Geology* 41, 6 (2013).
141. N. De Paola, *Geology* 41, 6 (2013).
142. N. De Paola, R. E. Holdsworth, C. Viti, C. Collettini, and R. Bullock, *Earth Planet Sc. Lett.* 431, 48 (2015).
143. H. P. He, T. Li, Q. Tan, T. H. Chen, D. Zhang, J. X. Zhu, P. Yuan, and R. L. Zhu, *Am. Mineral* 99, 1 (2014).
144. X. Q. Wang, B. M. Zhang, W. S. Yao, and X. M. Liu, *Earth Science Frontiers (Chinese with English Abstract)* 21, 1 (2014).
145. R. M. Yuan, B. L. Zhang, X. W. Xu, C. Y. Lin, L. B. Shi, and X. Li, *Scientia Sinica (Terrae) (Chinese with English Abstract)* 44, 8 (2014).
146. C. Viti, C. Collettini, and T. Tesci, *Contrib. Mineral. Petr.* 167, 2 (2014).
147. B. A. Verberne, O. Plümpner, D. A. M. De Winter, and C. J. Spiers, *Science* 346, 6215 (2014).
148. T. Das, B. K. Saikia, and B. P. Baruah, *Gondwana. Res.* 31, 295 (2016).
149. X. Q. Wang, B. M. Zhang, and R. Ye, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
150. H. F. Chen, Y. Wang, M. Wang, and S. F. Lu, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
151. Y. Song, B. Jiang, M. Li, J. G. Liu, G. X. Cheng, and Z. Tang, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
152. L. Y. Shao, Y. Hu, J. S. Fan, J. Y. Wang, J. Wang, and J. Z. Ma, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
153. Y. Sun, Y. W. Ju, S. Y. Jiang, W. Zhou, H. T. Chao, and Z. C. Wang, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
154. Y. C. Ge and X. J. Ge, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
155. H. R. Wang, H. R. Ding, Y. Li, X. X. Yang, C. Q. Wang, and A. H. Lu, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
156. Z. D. Xi, S. H. Tang, S. H. Zhang, and J. Li, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
157. Z. H. Qin, Q. Wan, S. S. Li, Y. H. Fu, Y. T. Gu, S. Q. Yang, and J. G. Zhang, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
158. L. J. Wang, A. H. Lu, C. Q. Wang, X. S. Zheng, D. J. Zhao, and R. Liu, *J. Colloid Interf. Sci.* 295, 2 (2006).
159. X. D. Liu, X. C. Lu, R. C. Wang, H. Q. Zhou, and S. J. Xu, *Clay Clay Miner.* 55, 6 (2007).
160. L. M. Ji, J. L. Qiu, Y. Q. Xia, and T. W. Zhang, *Acta Petrolei Sinica (Chinese with English Abstract)* 33, 2 (2012).
161. M. S. Román, D. F. Remolar, R. Amils, A. S. Navas, T. Schmid, P. S. M. Uriz, N. Rodríguez, J. A. McKenzie, and C. Vasconcelos, *Sci. Rep.-UK* 4, 4767 (2014).
162. L. Meng, F. Huang, J. Liu, M. M. Xing, Q. Wan, J. Q. Ling, S. Gao, and W. Y. Gao, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
163. M. Zhang, X. M. Sun, L. Xu, H. F. Xu, H. Konishi, Y. Lu, H. F. Lu, and Z. W. Wu, *Chinese Science Bulletin (Chinese with English Abstract)* 56, 21 (2011).
164. J. J. Cao, X. Y. Hu, and D. Jiang, *e-Journal of Surface Science and Nanotechnology* 7, 813 (2009).
165. A. G. Jongmans, F. van Oort, L. Denaix, and A. M. Jaunet, *Catena* 35, 2 (1999).
166. Y. Chen, S. N. Gong, G. Z. Long, X. L. Sun, and J. Z. Chen, *Earth Science (Journal of China University of Geosciences) (Chinese with English Abstract)* 36, 3 (2011).
167. Q. Q. Xie, X. Zhang, and T. H. Chen, *Bulletin of Mineralogy, Petrology and Geochemistry (Chinese with English Abstract)* 35, 1 (2016).
168. Z. H. Ding, *Acta Mineralogica Sinica (Chinese with English Abstract)* 19, 3 (1999).
169. E. Y. Yan and X. L. Wu, *Journal of Jiaozuo University (Chinese with English Abstract)* 1, 61 (2004).
170. Y. Sun, Y. W. Ju, X. C. Lu, H. T. Chao, and Z. C. Wang, *Bulletin of Mineralogy, Petrology and Geochemistry (Chinese with English Abstract)* 35, 1 (2016).
171. J. Musil, *Surf. Coat. Tech.* 125, 1 (2000).
172. Y. W. Ju and X. S. Li, *Prog. Nat. Sci.* 19, 11 (2009).
173. D. Y. Cao, H. Zhang, Y. J. Dong, and C. W. Yang, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
174. M. M. Wei and Y. W. Ju, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
175. C. H. Tong and J. C. Li, *China Univ. Geosci.* 10, 4 (1999).
176. Q. Wu, A. Z. Xu, D. L. Dong, and B. L. Tian, *Coal Geology and Exploration (Chinese with English Abstract)* 31, 4 (2003).
177. J. J. Cao, R. Z. Hu, Z. R. Liang, and Z. L. Peng, *J. Geochem. Explor.* 101, 3 (2009).
178. J. J. Cao, *Geochem. J.* 45, 3 (2011).
179. X. J. Wei, J. J. Cao, R. F. Holub, P. K. Hopke, and S. J. Zhao, *J. Geochem. Explor.* 128, 124 (2013).
180. X. Q. Wang and R. Ye, *Acta Geoscientia Sinica (Chinese with English Abstract)* 32, 1 (2011).
181. Z. R. Cai, Q. T. Huang, J. F. Li, J. Y. Xiang, H. L. Liu, B. Xia, and W. L. Liu, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
182. H. Liu, Y. Sun, L. S. Shu, and X. C. Lu, *Acta Geologica Sinica (Chinese with English Abstract)* 83, 5 (2009).
183. D. L. Liu, Q. Yang, Y. Y. Li, Y. Sun, and C. X. Zhang, *Science Technology and Engineer (Chinese with English Abstract)* 4, 1 (2004).
184. C. Viti, *J. Struct. Geol.* 33, 12 (2011).
185. X. S. Li, Y. W. Ju, Q. L. Hou, and H. Lin, *Spectroscopy and Spectral Analysis (Chinese with English Abstract)* 31, 8 (2011).
186. X. S. Li, Y. W. Ju, Q. L. Hou, Z. Li, Q. G. Li, and G. C. Wang, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
187. L. Y. Yu, Y. W. Ju, and X. S. Li, *Spectroscopy and Spectral Analysis (Chinese with English Abstract)* 35, 4 (2015).
188. W. D. Lu, J. R. Wang, and Y. W. Ju, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
189. J. J. Fan, Y. W. Ju, S. B. Liu, and X. S. Li, *Journal of China Coal Society (Chinese with English Abstract)* 38, 3 (2013).
190. X. M. Li, D. Y. Cao, and D. M. Liu, *Mining Science and Technology (Chinese with English Abstract)* 20, 6 (2010).
191. M. Krzesińska, *Fuel Process Technol.* 77, 33 (2002).
192. J. F. Ouyang, L. J. Fan, H. G. Yang, and Y. M. Chang, *Acta Mineralogica Sinica (Chinese with English Abstract)* 27, 3A (2006).
193. B. K. Saikia, C. R. Ward, M. L. S. Oliveira, J. C. Hower, F. De Leao, M. N. Johnston, A. O'Bryan, A. Sharma, B. P. Baruah, and L. F. O. Silva, *Int. J. Coal Geol.* 137, 19 (2015).
194. S. F. Lu, F. W. Chen, and Y. W. Ju, *J. Nanosci. Nanotechnol.* 17, 1 (2017).
195. J. S. Ma, J. P. Sanchez, K. J. Wu, G. D. Couples, and Z. Y. Jiang, *Fuel* 116, 498 (2014).
196. G. C. Wang, Y. W. Ju, Z. F. Yan, and Q. G. Li, *Mar. Petrol. Geol.* 62, 1 (2015).

197. Q. Zhang, R. H. Liu, Z. L. Pang, W. Lin, W. H. Bai, and H. Y. Wang, *Mar. Petrol. Geol.* 71, 250 (2016).
198. H. Zhang, Y. M. Zhu, Y. Wang, W. Kang, and S. B. Chen, *J. Nat. Gas Sci. Eng.* 32, 356 (2016).
199. J. G. Pang, S. Li, Y. Y. Yang, L. J. Liu, J. Zhu, and D. Chen, *Petroleum Geology and Experiment (Chinese with English Abstract)* 36, 6 (2014).
200. J. Z. Yin, *Earth Science Frontiers (Chinese with English Abstract)* 03, 8 (1994).
201. Y. Mikhlin, A. Romanchenko, M. Likhatski, A. Karacharov, S. Erenburg, and S. Trubina, 42, 1 (2011).
202. A. P. Deditius, S. Utsunomiya, M. Reich, S. E. Kesler, R. C. Ewing, R. Hough, and J. Walshe, *Ore. Geol. Rev.* 42, 1 (2011).
203. J. R. Bargar, R. B. Latmani, D. E. Giammar, and B. M. Tebo, *Elements* 4, 6 (2008).
204. X. Q. Zhu and Z. G. Wang, *Progress in Natural Science (Chinese with English Abstract)* 15, 4 (2005).
205. R. Ye, B. M. Zhang, W. S. Yao, and Y. Wang, *Earth Science Frontiers (Chinese with English Abstract)* 19, 3 (2012).
206. X. Q. Wang, B. M. Zhang, and R. Ye, *Bulletin of Mineralogy, Petrology and Geochemistry (Chinese with English Abstract)* 35, 1 (2016).
207. X. L. Yang, M. Y. Zhu, Y. L. Zhao, J. M. Zhang, Q. J. Guo, and D. H. Pi, *Geological Review (Chinese with English Abstract)* 54, 1 (2008).
208. F. X. Zhang, L. S. Wang, and J. F. Hou, *Geology in China (Chinese with English Abstract)* 36, 3 (2009).
209. R. Han, T. Shimamoto, T. Hirose, J. H. Ree, and J. I. Ando, *Science* 316, 5826 (2007).
210. X. F. Chen, A. S. Madden, B. R. Bickmore, and Z. Reches, *Geology* 41, 7 (2013).
211. H. W. Green, II, F. Shi, K. Bozhilov, G. Xia, and Z. Reches, *Nat. Geosci.* 8, 6 (2015).
212. L. Yao, S. L. Ma, A. R. Niemeijer, T. Shimamoto, and J. D. Platt, *Geophys. Res. Lett.* 43, 13 (2016).
213. C. D. Rowe and W. A. Griffith, *J. Struct. Geol.* 78, 1 (2015).
214. C. Janssen, H. R. Wenk, R. Wirth, L. Morales, H. Kemnitz, J. Sulem, and G. Dresen, *J. Struct. Geol.* 86, 62 (2016).
215. H. T. Chao, Y. Sun, Z. C. Wang, Z. W. Cui, G. Xue, and L. Wang, *Bulletin of Mineralogy, Petrology and Geochemistry (Chinese with English Abstract)* 35, 1 (2016).
216. Y. Yang, B. P. Colman, E. S. Bernhardt, and M. F. Hochella, *Environ. Sci. Technol.* 49, 6 (2015).
217. M. S. Civeira, C. G. Ramos, M. L. S. Oliveira, R. M. Kautzmann, S. R. Taffarel, E. C. Teixeira, and L. F. O. Silva, *Chemosphere* 145, 142 (2016).
218. L. Ruhl, A. Vengosh, G. S. Dwyer, H. H. Kim, A. Deonarine, M. Bergin, and J. Kravchenko, *Environ. Sci. Technol.* 43, 16 (2009).
219. L. Ruhl, A. Vengosh, G. S. Dwyer, H. H. Kim, and A. Deonarine, *Environ. Sci. Technol.* 44, 24 (2010).
220. L. Ruhl, A. Vengosh, G. S. Dwyer, H. H. Kim, G. Schwartz, A. Romanski, and S. D. Smith, *Environ. Sci. Technol.* 46, 21 (2012).
221. C. A. Johnson, G. Freyer, M. Fabisch, M. A. Caraballo, K. Küsel, and M. F. Hochella, Jr., *Environ. Chem.* 11, 4 (2014).
222. J. J. Wang and J. W. Chen, *Geoscience (Chinese with English Abstract)* 5, 926 (2012).
223. Z. T. Han, X. L. Lv, W. Zhang, L. S. Ma, and P. Wang, *Hydrogeology and Engineering Geology (Chinese with English Abstract)* 40, 1 (2013).
224. C. Noubactep, S. Caré, and R. Crane, *Water Air Soil Poll.* 223, 3 (2012).
225. B. Z. Qian and W. G. Li, *Natural Gas and Oil (Chinese with English Abstract)* 31, 1 (2013).
226. J. Z. Ma, X. B. Xu, C. S. Zhao, and P. Yan, *Adv. Atmos. Sci.* 29, 1006 (2012).
227. D. S. Ji, L. Li, Y. S. Wang, J. K. Zhang, M. T. Cheng, Y. Sun, Z. R. Liu, L. L. Wang, G. Q. Tang, B. Hu, N. Chao, T. X. Wen, and H. Y. Miao, *Atmos. Environ.* 92, 546 (2014).
228. J. Lelieveld, J. S. Evans, M. Fnais, D. Giannadaki, and A. Pozzer, *Nature* 525, 7569 (2015).
229. P. Xu, J. X. Xu, M. He, L. X. Song, D. L. Chen, G. S. Guo, and H. X. Dai, *Sci. Total Environ.* 565, 827 (2016).
230. Q. H. Zhou, L. X. Wang, Z. Y. Cao, X. H. Zhou, F. Yang, P. Q. Fu, Z. H. Wang, J. T. Hu, L. Ding, and W. Jiang, 542, 36 (2016).
231. V. P. Aneja, B. Y. Wang, D. Q. Tong, H. Kimball, and J. Steger, *J. Air Waste Manage.* 56, 8 (2006).
232. L. Y. He, M. Hu, X. F. Huang, Y. H. Zhang, B. D. Yu, and D. Q. Liu, *Chemosphere* 62, 10 (2006).
233. R. M. B. O. Duarte, E. B. H. Santos, C. A. Pio, and A. C. Duarte, *Atmos. Environ.* 41, 37 (2007).
234. J. J. Gao, H. Z. Tian, K. Cheng, L. Lu, M. Zheng, S. X. Wang, J. M. Hao, K. Wang, S. B. Hua, C. Y. Zhu, and Y. Wang, *Atmos. Environ.* 107, 1 (2015).
235. P. D. Crevello, J. M. Rine, and D. E. Lanesky, *J. Sediment Res.* 51, 2 (1981).
236. S. A. Kuehl, C. A. Nittrouer, and D. J. DeMaster, *J. Sediment Res.* 58, 1 (1988).
237. P. X. Wang, *Marine Geology and Quaternary Geology (Chinese with English Abstract)* 04, 1 (2009).
238. X. J. Yuan, S. H. Lin, Q. Liu, J. L. Yao, L. Wang, H. Guo, X. Q. Deng, and D. W. Cheng, *Petroleum Exploration and Development (Chinese with English Abstract)* 01, 34 (2015).
239. D. A. Crerar and H. L. Barnes, *Geochim. Cosmochim. Ac.* 38, 2 (1974).
240. N. C. Shi, Z. S. Ma, W. Z. He, and J. M. Luo, *Science in China, Ser. B (Chinese with English Abstract)* 25, 7 (1995).
241. E. Kadar, A. Fisher, B. Stolpe, R. M. Harrison, F. Parello, and J. Lead, *Mar. Chem.* 140, 24 (2012).
242. C. M. Sands, D. P. Connelly, P. J. Statham, and C. R. German, *Earth Planet Sc. Lett.* 319, 15 (2012).
243. M. Yücel, A. Gartman, C. S. Chan, and G. W. Luther, III, *Nat. Geosci.* 4, 6 (2011).
244. A. Gartman, A. J. Findlay, and G. W. Luther, *Chem. Geol.* 366, 32 (2014).
245. J. Wu, M. L. Wells, and R. Rember, *Geochim. Cosmochim. Ac.* 75, 2 (2011).
246. R. Han, T. Hirose, T. Shimamoto, Y. Lee, and J. I. Ando, *Geology* 39, 6 (2011).
247. X. Z. Yang, *Acta Petrologica Et Mineralogica (Chinese with English Abstract)* 22, 2 (2003).
248. S. Colussi, N. Elvassore, and I. Kikic, *J. Supercrit. Fluid* 39, 1 (2006).

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