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Nanometallogeny: The role of the nano-effect in the enrichment, migration and mineralization of rare element, rare earth element and precious metal deposits.

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## Abstract

Nanometallogeny is the application of the latest research on nanomaterials to modern earth sciences to better understand what is perhaps the most economically important field in geology: the enrichment, migration and deposition of mineral ore deposits. Ore-bearing fluids and ore particles behave differently at the nano-scale compared to the more familiar macro-scale. Nanometallogenical processes have been used to explain the mechanism in which rare elements with extremely low abundance in the earth's crust, such as Se, Te, Ga, Ge, In, Os, Re and Rh, are enriched into mineral deposits. It is suggested that similar nanometallogenical processes affect other deposit types including hydrothermal gold deposits in ways that are still not well studied. Research on nanomaterials and the understanding of the nano-effect has advanced considerably since the lead author first proposed that the nano-effect plays a role in the enrichment of rare element deposits in 1994. Research on the nano-effect in the formation of mineral deposits has expanded since then and the authors formally propose the term nanometallogeny for this field of research.

The nano effect influences the formation of mineral deposits in a number of ways. The physical properties of rocks and minerals alter at nano-scale. For example, the strength of rocks increases as volume decreases during the process of pressure deformation. The physical

and chemical properties of ore-bearing fluids changes within nanopores and micro-fractures with open spaces less than 100 nanometers. For example, ore-bearing fluids can migrate and diffuse vertically under enhanced surface tension conditions. The dielectric constant and hence the solubility of ore-bearing ionic compounds in water is reduced in nanopores compared to macroscopic conditions so that ore metals precipitate and aggregate to form nano-ore deposits. Clay is a common nanoporous rock forming mineral and so rocks rich in clays, such as primary mudstones and shales, and hydrothermally clay-altered rocks form nano-traps that can preferentially host some fine ore deposits. Similarly, zones with abundant micro-fractures are good trap sites for ore deposits. In contrast the same fluids in macro-scale open-space structures remain in solution and are more likely to act as unmineralized conduits, transporting ore to precipitation sites including nearby nano-porous material. The nano-effect can also be seen in the formation of supergene mineral enrichment. The weathering and oxidation of rocks to saprolite and soil involves the alteration of many primary rock forming minerals to nano-porous clay, providing an ideal environment for the enhanced migration and precipitation of ore metals.

By drawing on the latest research on nanomaterials and other related technologies across disciplines the nascent field of Nanometallogeny is allowing us to re-examine the role of fluids in the formation of mineral deposits and challenge some of the fundamental concepts of mineral geology.

**Keywords:** Nanometallogeny; nano effect; nanopore; nanofluid; nano-mineralization; nanoparticle nucleation and aggregation; enrichment and migration mechanism; rare elements; gold; metallogenic models

## 1. Introduction

It is commonly stated in the field of mineral deposit geology that the formation of any mineral deposit, especially metal mineral deposits, requires the right conditions for the interaction of several processes, the so-called mineralization conditions: a source of ore-forming elements, the dynamic mineralization mechanism, and the enrichment and deposition mechanism of ore-forming minerals.

Without the source of ore-forming elements, it is impossible for a mineral deposit to form. However, even with a source to supply the ore-forming elements, if there are no geological forces to activate and migrate these ore-forming elements then a mineral deposit will not form. Even if the first two conditions are met, if the ore-forming elements in the original dispersed state cannot be concentrated together then they will not form the economically extractable mineral resources that are essential for humans to change their living environment.

Since the inception of modern geology, especially mineral deposit geology, generations of scientists have devoted themselves to trying to understand these three processes. At present there is a relative consensus on the answers to the first two questions, albeit there are still disputes on the specific details. Regarding the elemental sources of various mineral deposits, the current consensus is that they are either crustal or mantle sources. Some mineral deposits may also be of mixed sources rather than a single source, for example a mixture of crustal and upper mantle material jointly providing the source of ore-forming materials.

The dynamic mechanisms that cause the ore-forming elements to concentrate into economic deposits are generally agreed upon. For endogenous deposits magmatic activity including volcanic activity, orogeny, metamorphism including migmatization are most common. In very rare cases a cosmic dynamic mechanism is proposed, namely impact from a meteorite, asteroid or comet. Currently, there are very few of the latter deposits that are

generally recognized. The Sudbury copper-nickel deposit in Ontario, Canada, is the only widely accepted example of the rare meteorite impact deposit type (Cowan & Schwerdtner, 1999; Bailey *et al.*, 2004, Boast *et al.*, 2006; Dreuse *et al.*, 2010; Morris *et al.*, 2023)<sup>1-5</sup>. Apart from this, there are almost no other recognized deposits of this type on the Earth. It is said that there may be deposits of similar origin in Siberia, Russia, but they have not been generally recognized and demonstrated. For exogenous deposits including liquid brine deposits, various placers and different sedimentary minerals the mineralization dynamics are mainly provided by solar energy, wind energy, and flowing water and ice (glaciers) that cause weathering and erosion, as well as external forces such as volcanic eruptions and sedimentary diagenesis.

Various enrichment and migration mechanisms have been proposed for ore deposits. Whilst there is consensus for many of the more common minerals, the enrichment and migration mechanism of rare elements, rare earth elements and precious metals is not well understood. These elements have extremely low abundance in the earth's crust and traditional mineral geology and geochemical theory cannot explain how these elements can concentrate to form ore deposits. For example, tellurium, a rare element that plays an important role in many fields of modern industry and national defense, has abundance in the earth's crust of only  $1.34 \times 10^{-9}$  or 1.34 ppb to  $5.0 \times 10^{-9}$  or 5.0 ppb worldwide (Li, 1976; Li & Ni, 1990; Wedepohl, 1995; Li *et al.*, 1999). Therefore, it has long been considered by traditional mineral geology and geochemistry that it cannot form independent deposits and can only appear as an associated component in other bulk deposits. However, in the early 1990s, a tellurium-only deposit was discovered and mined on the southeastern edge of the Qinghai-Tibet Plateau, namely the Dashuigou tellurium-only deposit located in the southwest of Sichuan Province, China (Yin, 1996; Yin *et al.*, 2024d). Likewise, selenium which is one of the emerging strategic/critical minerals has important applications in many fields such as

electronics, chemicals, medicine, semiconductors, photovoltaics and space exploration (Stiftner *et al.*, 2023; Liu *et al.*, 2024). Their enrichment mechanism of other rare metals such as lithium, cobalt, gallium, indium, germanium, thallium, rhenium, beryllium, titanium, vanadium, germanium, cesium, lanthanum, tungsten, radium and rhodium, rare earth elements and even precious metals such as gold, platinum and palladium, which are currently sought after by the world is also a mystery. In terms of the proportion of metals in the earth's crust and their importance to human society, rhodium, gold, platinum and tellurium are the rarest elements. The German world calls certain natural resources Gewürzmetall, which translates as 'spice metals'. This means that although these metals account for a very small fraction of some electronic devices, like spices in some food recipes, they are considered a vital and indispensable ingredient. Researchers have tried to find substitutes for many of these rare and precious metals but found that there was no substitute that could cover all the uses of these metals. If we were to switch to so-called substitutes, computers would slow down, engines would be less efficient and structures and tools weaker.

The results of research on nanomaterials that have emerged widely around the world in recent decades, especially the peculiar nano-effect phenomenon produced by nano-scale materials, attracted the attention of the lead author of this article. Nano-effect theories can be applied to model the enrichment and mineralization mechanisms of disseminated rare element mineralization. In 1994, the lead author published an article proposing that the nano-effect played a key role in the enrichment and mineralization of the rare element tellurium (Yin, 1994) and built on that with a postdoctoral research report on the mineralization mechanism and mineralization model of the world's first tellurium-only deposit (Yin, 1995). A theoretical hypothesis of the enrichment and mineralization of tellurium, a dispersed element with extremely low abundance in the earth's crust, through the nano-effect was subsequently discussed and published by Yin (1996) and Yin and Shi (2019b). The work was

124 featured in *the China Geology and Mineral Resources News* (now *the China Natural*  
125 *Resources News*) and *the China Mining News*. Chinese institutions have continued to advance  
126 the study of nano-effects in geology. The Guiyang Institute of Geochemistry, Chinese  
127 Academy of Sciences, set-up a laboratory to carry out research on the subject, and the  
128 Langfang Institute of Geophysical and Geochemical Exploration, Chinese Academy of  
129 Geological Sciences have published research on what they term nanogeochemistry (Wang *et*  
130 *al.*, 2020; Luo *et al.*, 2025).

131 This article is a review of the latest research results on nanomaterials and the latest  
132 research on the nano-effect in relation to geology and mineral enrichment, especially the  
133 mechanism of enrichment and migration of ore-forming elements. The terms nano-  
134 metallogenesis and the discipline of nanometallogeny are proposed for this new and rapidly  
135 developing field of research.

## 136 **2. Brief description of nanoparticles characteristics**

137 In this article nano (nm) refers to a unit of length, a nanometre which is one-billionth or  
138  $1 \times 10^{-9}$  of a metre, about one order of magnitude longer than a chemical bond. Nanomaterials  
139 refer to materials that have at least one dimension in three-dimensional space at the  
140 nanometer scale (1-100 nm) or are composed of them as basic units. There is a new  
141 generation of materials composed of nanoparticles with sizes filling the gap between atoms  
142 and molecules, and macroscopic systems, roughly equivalent to the scale of 10 to 1000 atoms  
143 closely packed together (Chinese Academy of Sciences, 2003; Xihua University, 2022).

144 Nanotechnology is a science and technology that studies the motion, interactions and  
145 possible technical problems in practical applications of systems composed of materials with  
146 sizes between 0.1 and 100 nanometers. So far, nanotechnology has spawned branch  
147 disciplines such as nanoelectronics, nanomechanics, nanobiology and nanomaterials

processing. Due to the small size of the constituent units of nanomaterials and the composition of the interface, systems composed of nanoparticles have many special properties that differ from the more familiar macroscopic material systems.

When the size of particles is reduced to the nanometer level, their acoustic, optical, electrical, magnetic and thermal properties have new characteristics. Nanoparticles often have a large specific surface area, with the specific surface area per gram of this solid reaching hundreds or even thousands of square meters. This makes them useful as highly active adsorbents and catalysts. In simple terms, nanomaterials have been summarized in three words: "lighter, higher, stronger" (Chinese Academy of Sciences, 2003). "Lighter" refers to components with nanomaterial technology being smaller in volume and lighter in weight than their macroscopic equivalents. "Higher" refers to nanomaterials having higher optical, electrical, magnetic and thermal properties. "Stronger" refers to nanomaterials improved mechanical properties such as strength and toughness.

In summary, compared to their bulk counterparts, nanoparticles possess many valuable properties that can be applied in various fields such as antimicrobials (Kumar and Pandita, 2015), catalysts (Liu *et al.*, 2013), cancer therapies (Yang *et al.*, 2018). The reason why nanoparticles have these unique applications is their special morphology with the huge surface area to volume ratio allowing them to excel in specific areas (Eastman *et al.*, 2001; Gupta & Gupta, 2005).

### **3. Evidence**

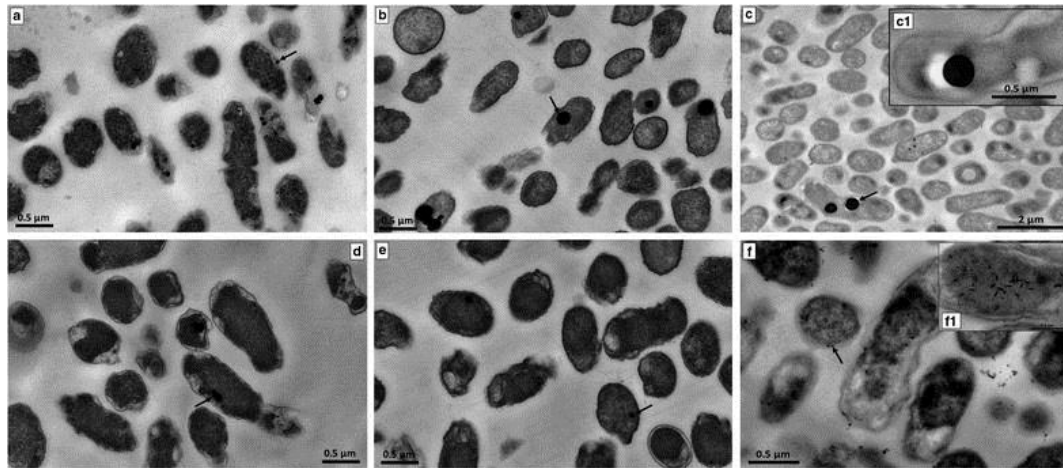
Scientists and researchers who specialize in nanomaterial research have confirmed from different experimental perspectives that the generation, development and growth of nanoparticles goes through several basic processes: nucleus formation, growth and aggregation. These are briefly described as follows.



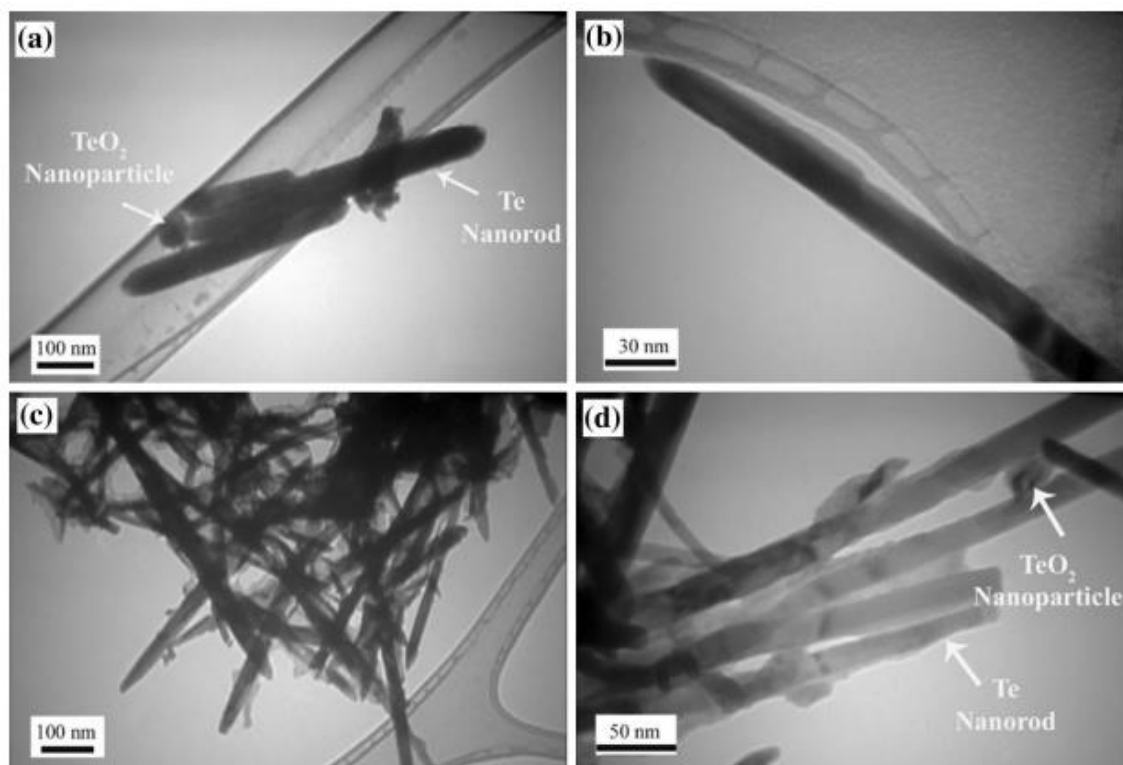
### 3.1. Nucleus formation

The formation of the initial nuclei is one of the most essential requirements for the growth and formation of a mineral deposit. The formation of nanoparticles falls into two categories: “top-down” and “bottom-up”, which can be differentiated by the nanoparticles being synthesized either from bulk materials or from ions (Qiu *et al.*, 2018). Synthesizing nanoparticles from aqueous ion solutions has been characterized as a typical “bottom-up” method to synthesize nanoparticles, which can be dated back to 1982 (Lee & Meisel, 1982). Since then, researchers have been using various approaches to reduce or oxidize ions to produce nanoparticles, and remarkable progress has been made on the biosynthesis of nanoparticles (Ovais *et al.*, 2018), making it possible to form elemental nanoparticles by microorganisms in nature (Bai *et al.*, 2009; Loshchinina *et al.*, 2018).

Experimental work has already demonstrated that two typical rare elements, selenium (Se) and tellurium (Te) nanoparticles can be produced in the laboratory by biogenesis or by chemical reduction from an alkaline solution. Both selenium and tellurium nanoparticles have been synthesized using *Ochrobactrum* sp. MPV1, an aerobic  $\alpha$ -proteobacterium isolated from a dump of roasted pyrite (Figure 1; Zonaro *et al.*, 2017). Se-nanoparticles and Te-nanoparticles were biosynthesized intracellularly using a two-phase process; Glutathione (GSH) and NADH-dependent reductase-mediated (Zonaro *et al.*, 2017). Tellurium nanoparticles have also been synthesized without biogenic input from solutions containing  $\text{TeCl}_4$  and  $\text{N}_2\text{H}_4\text{H}_2\text{O}$  in the presence of NaOH at 70°C. Such conditions are found in natural hydrothermal systems (Panahi-Kalamuei *et al.*, 2015). These laboratory experiments clearly show that selenium or tellurium nanoparticle nuclei should be able to form in nature. It is reasonable to postulate that mineral deposits could also form if conditions support further nanoparticle growth.



**Figure 1.** TEM micrographs of *Ochrobactrum* sp. MPV1 exposed to  $\text{SeO}_3^{2-}$  and  $\text{TeO}_3^{2-}$  cultures were grown in presence of 2 mM  $\text{SeO}_3^{2-}$  for 24 (a), 48 (b) and 72-h (c, c1) or 0.3 mM  $\text{TeO}_3^{2-}$  for 24 (d), 48 (e) and 72-h (f, f1) (Zonaro *et al.*, 2017).



**Figure 2:** TEM images of the products synthesized by a, b 5 mL and c, d 10 mL of NaOH solution (from Panahi-Kalamuei *et al.* 2015).

### 3.2. Nanoparticle growth

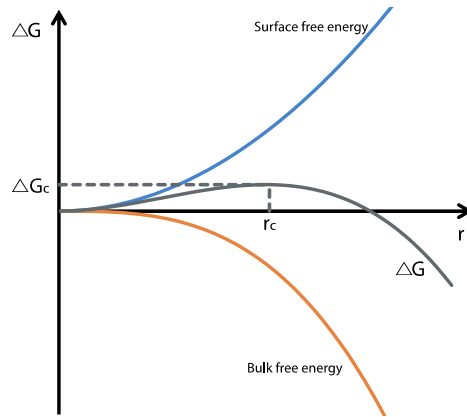
Once nanoparticles can be precipitated from solution by a process of nucleation from a supersaturated solution the newly formed nanoparticles usually contain a limited number of atoms, which means they are very small in size. However, these nanoparticles may further increase in size when continuously exposed to ion solution, growing either by simple coalescence or by ripening.

Growth by coalescence occurs when nanoparticles aggregate together. One of the driving forces is called van der Waals attraction, which commonly exists between neighboring molecules like nanoparticles in colloidal systems. Van der Waals attraction, as well as electrostatic repulsion forces emerge when the particle size is smaller than a few tens of nanometers and the distance between particles smaller than a few nanometers (Batista, Larson & Kotov, 2015). They are relatively weak short-distance interactions compared to other inter-molecular interactions like chemical bonds. Electrostatic-double layer repulsion counteracts the van der Waals attraction so to create agglomeration, the van der Waals attraction must be greater than the electrostatic repulsion (He & Alexandridis, 2015). The most common form of growth by ripening is termed Ostwald ripening whereby more soluble small particles are absorbed onto the less soluble and more stable larger particles (Mariscal *et al.*, 2012; Thanh *et al.*, 2014; Polte, 2015).

Another driving force to produce nanoparticle growth is to lower the system energy. From a thermodynamic perspective, the huge surface to volume ratio of nanoparticles provides them with high surface energy, so the nanoparticles tend to aggregate together to increase radius and minimize the total Gibbs free energy as previously shown in Figure 2. The Gibbs free energy ( $\Delta G$ ) of a cluster equals the sum of the surface free energy and the bulk free energy (Equation 1 below; Figure 2). The surface free energy is always positive while the bulk free energy (crystal free energy) is always negative. The cluster has the maximum free energy or critical energy ( $\Delta G_c$ ) when it is at the critical radius ( $r_c$ ). To lower the critical

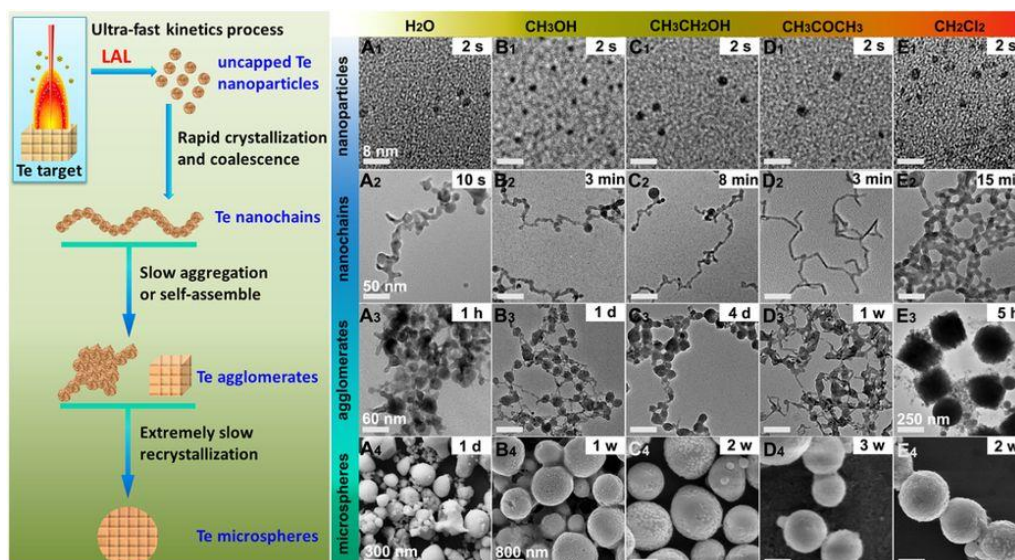
energy and make the cluster more stable when the radius is less than critical radius the cluster will tend to dissolve to a smaller radius. Conversely, it will tend to grow to a larger radius when its radius is greater than the critical radius because when a cluster possesses free energy greater than the critical energy barrier ( $\Delta G_c$ ), it will gain in particle size to increase stability (Mariscal *et al.*, 2012; Thanh *et al.*, 2014; Polte, 2015).

$$\Delta G = 4\pi r^2 \gamma - \frac{4}{3}\pi r^3 |\Delta G_v|$$



**Figure 2.** Diagram of the total free energy, surface free energy, and bulk free energy versus cluster radius (Grzelczak & Liz-Marzán, 2014)

As shown in Figure 3, in the absence of capping/stabilizing agents the uncapped colloidal Te-nanoparticles spontaneously and gradually form nanochains, agglomerations, and then microparticles at ambient temperature and pressure. The growth of nanoparticles is due to the surface-effects of nanoparticles (He & Alexandridis, 2015).



**Figure 3.** TEM images of uncapped Te Nanoparticles (A<sub>1</sub>–E<sub>1</sub>), nanochains (A<sub>2</sub>–E<sub>2</sub>), and agglomerates (A<sub>3</sub>–E<sub>3</sub>). SEM images of microspheres (A<sub>4</sub>–E<sub>4</sub>) in five kinds of solvents, namely, H<sub>2</sub>O, CH<sub>3</sub>OH, CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>3</sub>COCH<sub>3</sub>, and CH<sub>2</sub>Cl<sub>2</sub>. Scale bar: 8 nm for A<sub>1</sub>–E<sub>1</sub>, 50 nm for A<sub>2</sub>–E<sub>2</sub>, 60 nm for A<sub>3</sub>–D<sub>3</sub>, 250 nm for E<sub>3</sub>, 300 nm for A<sub>4</sub>, and 800 nm for B<sub>4</sub>–E<sub>4</sub>. Time of taking sample to perform TEM characterization: 2 s for A<sub>1</sub>–E<sub>1</sub>; 10 s for A<sub>2</sub>, 3 min for B<sub>2</sub> and D<sub>2</sub>, 8 min for C<sub>2</sub>, 15 min for E<sub>2</sub>; 1 h for A<sub>3</sub>, 1 day for B<sub>3</sub>, 4 days for C<sub>3</sub>, 1 week for D<sub>3</sub>, 5 h for E<sub>3</sub>; 1 day for A<sub>4</sub>, 1 week for B<sub>4</sub>, 2 weeks for C<sub>4</sub> and E<sub>4</sub>, and 3 weeks for D<sub>4</sub> (Liu *et al.*, 2016).

Surface-effects refer to the phenomenon that nanoparticles spontaneously aggregate in order to lower the system energy and stabilize (Mchale *et al.*, 1997). However, the effects of surfactants, especially biosurfactants, on nanoparticle growth also has to be considered. As part of the mechanism of nanoparticle synthesis mediated by microorganisms (bacteria, yeasts, fungi, etc.), most studies mention the involvement of some biomolecules (proteins, polysaccharides, etc.) as biosurfactants. When nanoparticles are synthesized by microorganisms, bioactive agents form cell caps on the nanoparticles to form micelle structures which increase the stability and biocompatibility of the capped nanoparticles (Mittal, Chisti & Banerjee, 2013). However, these biosurfactants prevent nanoparticles from growing, which is good for producing stable nanoparticles but slows down the formation.

The laboratory processes of nanoparticle formation and growth from ion solutions are termed homogeneous nucleation (nucleation and growth) and heterogeneous nucleation

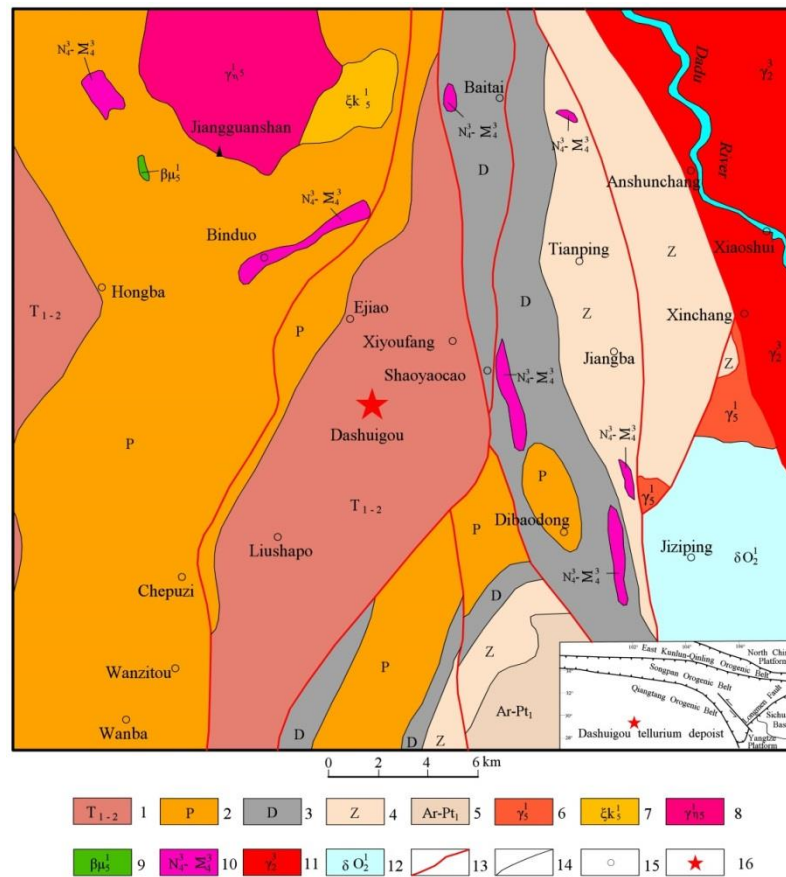
(seeded-growth; Figure 1, Grzelczak & Liz-Marzán, 2014). A study on Ag-nanoparticle synthesis reported that the particle size kept increasing as the reaction proceeded (Bao & Lan, 2018). Such a mechanism of elemental nanoparticle growth may contribute to mineral deposit formation.

#### **4. Nano-effect and mineral enrichment & migration**

In 1993, Yin, one of the authors of this article, began to study the mineralization mechanism of the Dashuigou tellurium-only deposit located on the southeastern edge of the Qinghai-Tibet Plateau, the world's only tellurium-only deposit. The article considers how Tellurium which has such low abundance in the earth's crust could be enriched and formed into an independent deposit. The article draws on research on nanomaterials and linked the nano-effect with the enrichment and mineralization of the disseminated tellurium deposit. The following year, the Author published a research article on nano-ore deposits in Earth Science Frontiers (Yin, 1994), This was the first in the Chinese world to announce that the nano-effect plays an important role in the enrichment and mineralization of rare elements such as tellurium, which have extremely low abundance in the earth's crust.

This work was amplified in a Chinese postdoctoral research report titled "The Mineralization Mechanism and Mineralization Model of the World's First Tellurium-only Deposit" (Yin 1995). This study describes the regional and deposit-scale geological setting of the Dashuigou tellurium-only deposit including the geology, mineralogy and isotope geochemistry of the deposit (Figure 4). The article proposes the important role of the nano-effect in the enrichment and mineralization process of the tellurium-only deposit (Yin, 1996). This was the first public geological research report to apply the understanding of nanotechnology of the 1990s to explain the formation mechanism of the deposit.



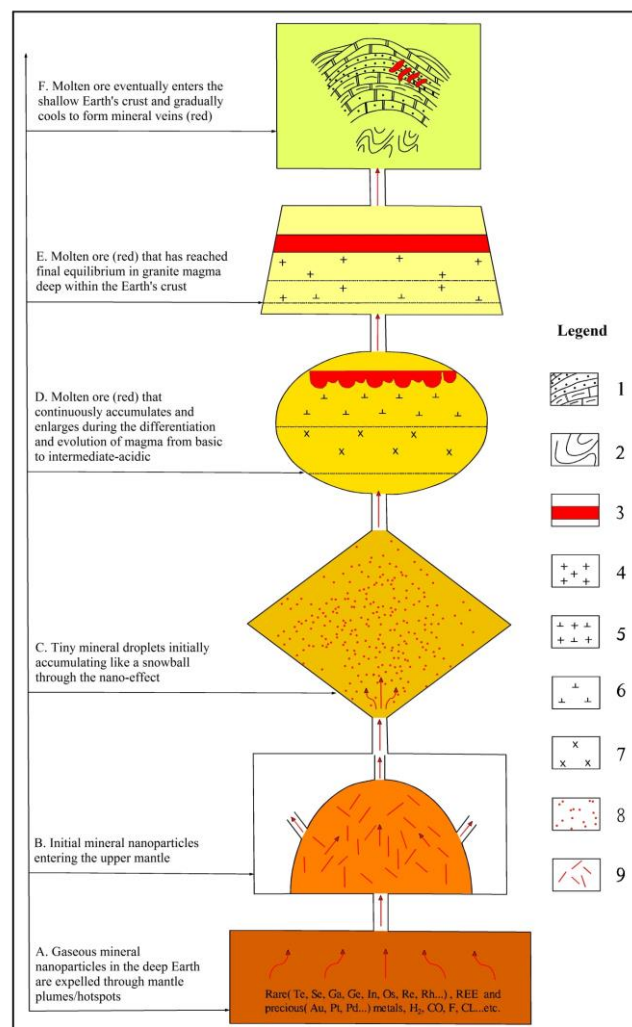


**Figure 4.** Location and regional geology of the Dashuigou tellurium deposit (after Yin, 1996; Yin *et al.*, 2022d)

1. The lower and middle Triassic metamorphic rocks; 2. The Permian metamorphic rocks; 3. The Devonian metamorphic rocks; 4. Metamorphic rocks of the Sinian system; 5. Metamorphic base complex of the Archean Kangding group; 6. Plutonic granite of the Indosinian orogeny; 7. Plutonic alkaline syenite of the Indosinian orogeny; 8. Plutonic monzonitic granite of the Indosinian orogeny; 9. Hypabyssal sillite of the Indosinian orogeny; 10. The late Hercynian basic-ultrabasic rocks; 11. The late Proterozoic plutonic granite; 12. The early Proterozoic-Archean plutonic quartz diorite; 13. The deep and large fault; 14. The geological boundary; 15. Village and/or town; 16. The Dashuigou tellurium-only deposit.

Yin used the theory of dissipative structures, synergetics and branching theory to explain why the tellurium-only deposit formed at the given location rather than in other tectonic spaces. Applying the latest research on geological processes such as deep degassing, mantle plumes and/or mantle hot spots, he proposed a three-level tellurium ore slurry evolution and mineralization model for the formation of this deposit (Figure 5). The model proposed that stage (I) cloud-like original nano-effect tellurium ore slurries developed into the stage (II)

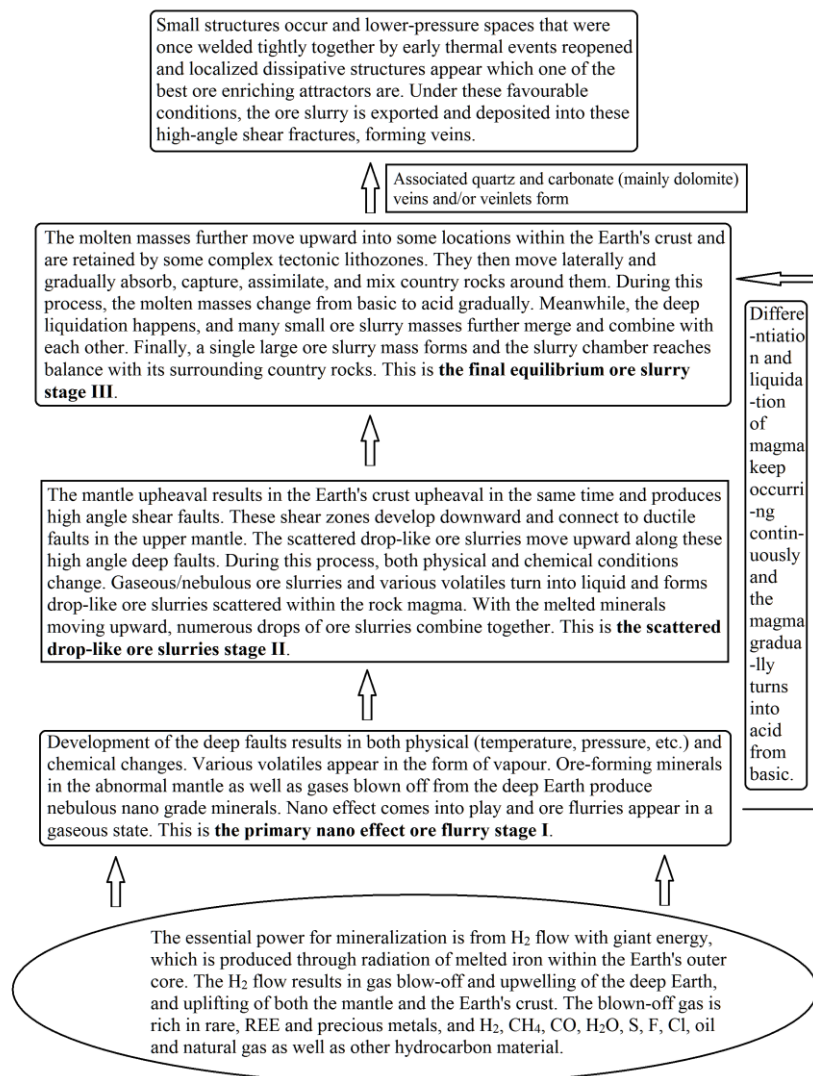
droplet-shaped dispersed tellurium ore slurry, until final equilibrium was reached as a stage (III) tellurium ore slurry. Finally, due to the difference in some weak external field, the tellurium slurries penetrated the localized dissipative structure, which is the best host for mineralization. Yin further pointed out that such deposits are generally formed in the transition zone between the platform periphery and the geosyncline, especially in areas with mantle uplift and geophysical anomalies, where mantle materials can rise to the crust (Yin, 1996). The specific mineralization process, or brief history of mineralization evolution, is shown in Figure 6.



**Figure 5.** Nanometallogenic model of endogenous metal deposits (modified from Yin, 1996 and Yin and Shi, 2022d)



310        Legend: 1. Mesozoic slate, marble and schist; 2. Folded basement rock; 3. Molten ore and ore body; 4. Granite magma; 5.  
 311        Granodiorite magma; 6. Diorite magma; 7. Basic rock (gabbro) magma; 8. Tiny mineral droplets initially accumulating like  
 312        a snowball through the nano-effect; 9. Initial mineral nanoparticles entering the upper mantle



313

314        **Figure 6. Nanometallogenic evolution diagram of endogenous metal deposits**

315        In 2019, Yin and Shi published an article entitled "Nano effect mineralization of rare  
 316        elements - taking the Dashuigou tellurium deposit, Tibet Plateau, Southwest China as the  
 317        example" (Yin and Shi, 2019b), which further discussed that the nano effect not only played  
 318        an important role in the enrichment and mineralization of tellurium, but also played a role in  
 319        the enrichment and mineralization of all rare dispersed elements.

## 5. Discussion

In recent years, more scholars in mainland China have noticed the important role of nano-effect in the migration and enrichment of mineral deposits. To this end, the Guiyang Institute of Geochemistry, Chinese Academy of Sciences, has established a laboratory to conduct special research on this field.

### Nanotechnology in mineral exploration

Since the late 1990s deep-penetrating geochemistry has emerged in the field of exploration geochemistry and has achieved theoretical and technological breakthroughs and contributed to the discovery of significant mineral bodies. In the past five years, the literature on ultrafine- and nano-geochemical technologies accounted for 14% and 9% respectively of major international exploration geochemistry papers published (Wang *et al.*, 2020). Among them, the breakthroughs made by nano-geochemistry in mineral deposit mechanism research are the most significant. The biggest theoretical progress in geochemistry in mainland China in recent years is the discovery of nano-metal crystals such as copper and gold that have been proven to come from deep concealed ore bodies (Wang and Ye, 2011; Wang *et al.*, 2016 and 2017; Zhang and Wang, 2018). Mainland China has achieved significant results in micro-grained (nano) geochemical measurements and has achieved success using these techniques prospecting for deep mineral deposits hidden beneath cover.

### Nano-effect in mineral deposition

Wang *et al.* (2020) found in their establishment of a three-dimensional geochemical exploration model for gold that the diffusion and migration of ore-forming metals in the surrounding rock must meet two basic conditions. First, the surrounding rock must have micro cracks or nanopores; and second, the ore-forming metals must exist in the carrier fluid in the form of compounds or fine particles (nanoparticles or colloidal particles). Through

344 their research on the replacement type gold deposit in Jiaodong of east China, they found that  
345 there are a large number of micro cracks or nanopores smaller than 1  $\mu\text{m}$  in the surrounding  
346 rock and they identified nano-gold and pyrite mineralization in the micro cracks using ion  
347 beam scanning electron microscopy. The formation of nano-gold in micro cracks suggests  
348 that the fluid carrying the gold diffuses vertically through the micro cracks and nanopores. As  
349 the fluid cools down, the pressure decreases, and/or the redox conditions and the fluid  
350 composition change so the gold solubility is reduced and the gold becomes saturated and  
351 precipitates, or the gold is dissolved after precipitation of pyrite to form nano-gold. After that,  
352 the rock weathered and released the nano-gold into the surface soil. Due to the presence of  
353 fine-grained soil geochemical barriers (clay, colloids, oxides, and organic matter, etc.), the  
354 nano-gold was captured, thus forming gold anomalies in the surface fine-grained soil. These  
355 anomalies were then used to discover deep gold deposits through drilling (Yu *et al.*, 2019).

356 The fact that nano-gold was found in the ore body and in the fault gouge and micro-cracks of  
357 the surrounding rock, and in the soil above indicates that nano-gold was precipitated due to  
358 changes in physical and chemical conditions such as cooling, a drop in fluid pressure or a  
359 change in chemistry due to mixing with groundwater or chemical reaction with the wallrock  
360 when the ore-bearing fluid migrated from deep to shallow during the mineralization process.

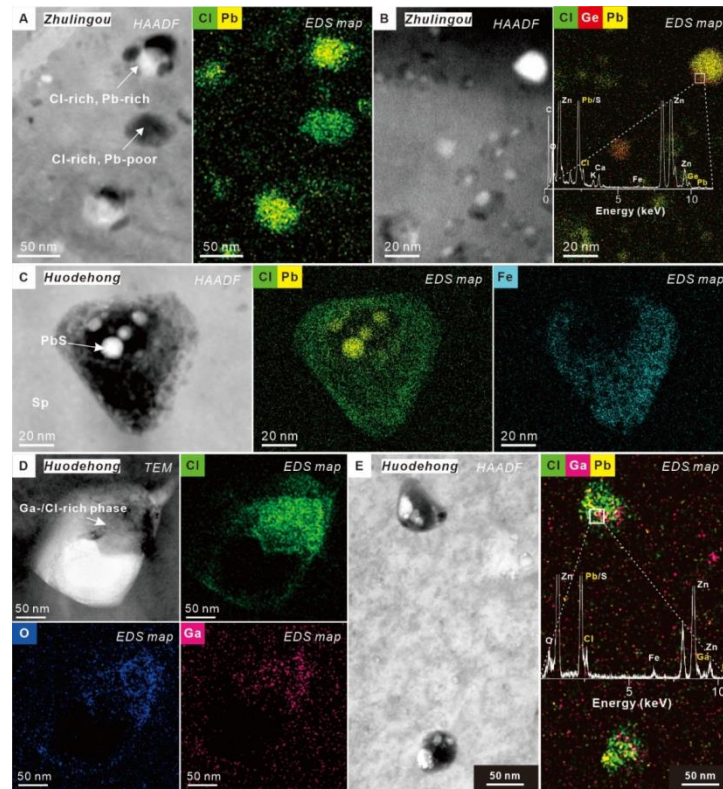
361 The nano-gold in the rock entered the surface soil through mechanical or chemical  
362 weathering, thus constituting a complete vertical migration process from the ore body to the  
363 surface overburden. The recognition of the nano-effect in gold has implications in  
364 understanding the dispersal of fine disseminated gold in systems with no apparent major  
365 feeder structure as well as the lower-grade, but often important fine disseminated gold halos  
366 found around many macro-scale fault or fracture-controlled gold veins. Nano-effect gold  
367 transport and mineralization may also be applied to a better understanding of the processes  
368 that form important concentrations of oxide gold in gossans and laterite deposits above more

structurally confined gold veins and that can provide some of the most profitable ore in modern mines.

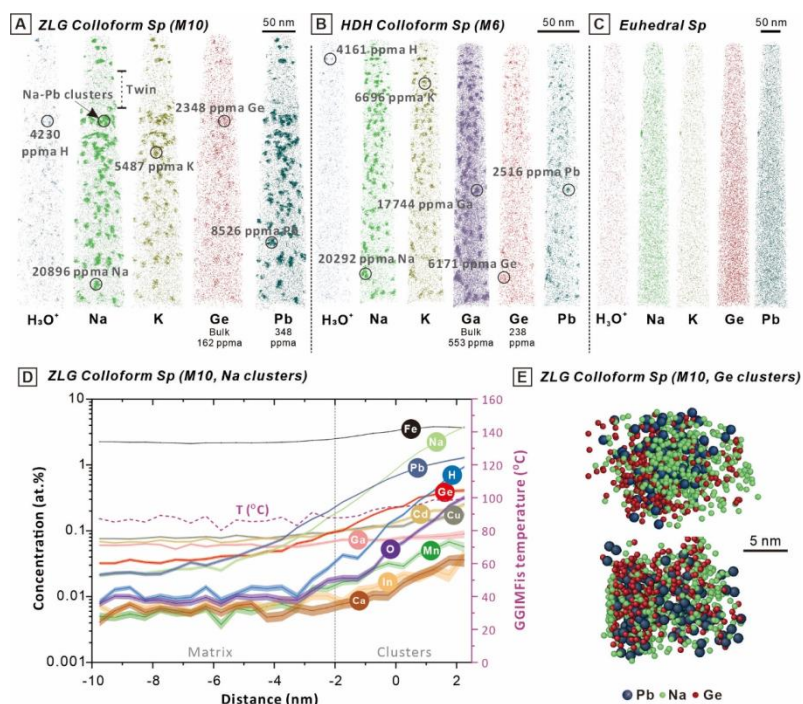
The theoretical basis of traditional primary halo measurement is that ore-forming elements and associated elements migrate along the axial direction of the ore-controlling structure and produce elemental zoning. The new discovery shows that ore-forming elements and associated elements not only migrate axially along the structure, but also migrate vertically along the micro-cracks, micro-faults or nanopores of the surrounding rock. Studies have confirmed that the vertical consistency of gold anomalies and the more volatile ‘gas-like’ element mercury reflects the vertical migration of fluids along micro cracks and nanopores (Wang and Ye, 2011; Wang *et al.*, 2016 and 2017; Zhang and Wang, 2018; Wang *et al.*, 2020).

As many as eight rare metal prospects and deposits including germanium, gallium, indium, thallium and selenium have been discovered in southwest China. Luo *et al.* (2025) selected rare metal-bearing colloidal and euhedral sphalerite commonly found in hydrothermal deposits to conduct micron-to-nanoscale mineral structure and composition characterization studies using  $\mu$ -LIBS, LA-ICP-MS, ToF-SIMS, APT, TEM, etc. The study aimed to reveal the enrichment mechanism of the rare metals and found that 10-20 nm nanofluid inclusions are commonly developed in colloidal sphalerite, and their complex composition includes solid phases such as galena and pyrite, and liquid phases that are significantly rich in alkali metals sodium (Na) and potassium (K), halogens such as chlorine (Cl), and other metal elements such as manganese (Mn), gallium (Ga) and germanium (Ge) (Figure 7). Nanofluid inclusions are significantly different from the ore-forming fluids (micrometer-sized fluid inclusions) of typical Mississippi Valley Type deposits due to their low salinity, low H<sub>2</sub>O and high metal content. On the other hand, the Ga and Ge contents in the nano-inclusions are abnormally enriched, reaching 16,307 ppm Ga and 5,671 ppm Ge, which are 1-2 orders of

magnitude higher than the corresponding element contents in the sphalerite lattice (Figure 8). The results show that the nano-fluid inclusions contribute 5%-78% of the total Ga and Ge in sphalerite and are important carriers of Ga and Ge.



**Figure 7.** HAADF images and STEM-EDS analysis results of colloidal sphalerite from the Zhulingou (A-B) and Huodehong (C-E) deposits in South China (after Luo *et al.*, 2025)



**Figure 8.** Atom probe tomography (APT) analysis results of colloidal sphalerite and euhedral sphalerite from the Zhulingou and Huodehong lead-zinc deposits in South China (after Luo *et al.*, 2025)

Luo *et al.* (2025) proposed a three-stage mechanism for the formation of the rare element-rich nanofluid inclusions: (1) Generation of dense liquid droplets: When the ore-forming fluid reaches a supersaturated state and colloidal sphalerite crystallizes rapidly. Since the ionic radius of elements such as  $\text{Ge}^{2+}$  and  $\text{Pb}^{2+}$  is significantly different from that of  $\text{Zn}^{2+}$ , it is difficult for them to enter the sphalerite lattice, resulting in their local enrichment in the fluid, and finally forming dense liquid droplets rich in metals such as Ge and Pb. (2) Capture and encapsulation of nanodroplets: During the continuous growth of sphalerite, these dense droplets rich in metals such as Ge and Pb are quickly encapsulated to form nanoscale fluid inclusions. (3) Differentiation and solid phase precipitation within nanodroplets: As the physical and chemical conditions of the ore-forming system changes differentiation occurs inside the droplets, and solid phase minerals such as galena and pyrite are locally precipitated while the residual liquid phase retains  $\text{H}_2\text{O}$ , alkali metals and halogens (Cl, Na, K, etc.) and trace metals such as Ga and Ge, etc.

This research result confirms that rare elements such as Ga and Ge are significantly enriched in nanofluid inclusions, rather than being mainly present in the sphalerite lattice in the form of isomorphous substitution as expected in traditional mineralization theory. In other words, this research confirms the important role played by the nano-effect in the mineral enrichment process. Similar trace element enrichment mechanisms may be widely present in other colloidal minerals such as pyrite and quartz, which provides a new perspective for understanding the behavior of mineralizing elements under non-equilibrium conditions.

The three-stage mechanism of nanofluid inclusion formation proposed by Luo *et al.* (2025) is similar to the enrichment and mineralization mechanism of disseminated rare elements like tellurium proposed by the author of this article, Yin, in 1996 and 2019.

#### Nano-effect on rock properties

Kumamoto *et al.* (2017) conducted spherical indentation experiments on single crystal and polycrystalline olivine using the MTS Nanoindenter XP system and found that the yield hardness decreases with the increase of contact radius, and the low-temperature plastic strength of olivine increases with the decrease of grain size, with the critical size being about 300  $\mu\text{m}$ . This discovery overturns the traditional understanding that "the smaller the grain, the weaker the strength" under high-temperature conditions. This is of great significance in understanding the formation of ultramylonite: low-temperature deformation may occur preferentially through brittle fracture rather than plastic flow. The micron-scale asperity on the fault surface undergoes indentation-like deformation during sliding, and its strength increases with decreasing size. This study revealed the size effect of low-temperature plasticity of olivine through nanoindentation technology, successfully reconciling the contradiction between experimental and geophysical data over the past 40 years. The study confirms that the actual strength of the lithospheric mantle is lower than previously estimated, and fine-grained olivine may exhibit anomalous strengthening behavior at low temperatures.

These findings highlight the core position of micro- and nanoscale mechanics in multidisciplinary intersections. Future research should further explore the universality of size effects in other geological materials and combine multi-scale simulation with experimental verification to promote innovation in earth science theory and technological breakthroughs.

It is well known that the interaction between fluids, mainly water, and various rocks affects some geological processes in the complex Earth lithosphere system, including mineralization. Traditional theory holds that when fluids flow in rocks, they are not significantly affected by the unique properties of materials at the nanoscale. However, the research of Chogani *et al.* (2025) shows that the "nanoscale" Earth system is far beyond our previous understanding. Chogani *et al.* used electron microscopy and neutron scattering data to demonstrate that the dielectric constant of water in nanopores is completely different from that under macroscopic conditions. The dielectric constant of water is significantly reduced at the nanoscale, that is, water is a less effective solvent for ionic compounds in nanopores. Water containing a high content of metals in ionic compounds will precipitate those minerals if forced into a nanoscale pore of fracture. Undoubtedly, this discovery also strongly challenges the existing theory of mineral deposits. Traditional theory has always believed that the properties of water or fluids are the same or extremely similar at all scales. Through molecular dynamics simulation, researchers tried to reveal the variation of the dielectric constant of water in nanopores under different temperature and pressure conditions. The results showed that even under extreme conditions such as 700°C and 5 GPa, water or fluids in nanopores still exhibit properties different from those of macroscopic water (Chogani *et al.*, 2025).

For this reason, some geologists have called for all future geological models of the Earth to consider fluid behavior at the nanoscale to more accurately predict geological processes. Obviously, even with the extremely advanced science and technology today, the Earth we



live on still hides many unsolved mysteries. And the "nanoscale" exploration of the Earth that is currently being conducted is expected to gradually reveal some of these secrets.

From the "denaturation" of water in nanopores to the "nano-reaction" between rocks, these new discoveries will allow us to further understand mineralization and other Earth processes. With the application of more nanotechnology scientific understanding of the mysteries of the Earth's internal functions will improve, thereby providing more scientific basis for the sustainable development of human society.

At the very least the study of nanometallogeny will help people understand the mineralization mechanism and mineral enrichment mechanism of the few independent rare element deposits in the world, such as the Dashuigou tellurium deposit located on the Tibetan Plateau and the Yutangba selenium deposit located in Enshi, western Hubei Province, China (Yin, 1994 & 1996; Yin and Shi, 2019b; Yin *et al.*, 2024d; Yin, 2025).

The above research makes suggests that the nano-effect plays an important role in the formation process of all metal and non-metal deposits in some way. In other words, whether it is an endogenous or exogenous deposits, under certain physical and chemical conditions at a certain stage in the mineralization process, the nano-effect is involved in mineral enrichment and plays a role in the migration of ore-forming minerals and the final formation of ore deposits. Furthermore, the role of the nano-effect in the enrichment and mineralization of rare elements, rare earths and precious metals with extremely low abundance in the earth's crust may well be the most important, or even indispensable factor.

Therefore, the authors feel that it is time to formally propose the discipline of nanometallogeny to encourage more discussion and research to better understand the enrichment and migration mechanism of ore-forming minerals.

## **6. Conclusions**

490 The contribution of the nano-effect in the formation of mineral deposits includes the  
491 following:

492 (1) Experimental results show that the strength of rocks and minerals increases with a  
493 decrease in size during the process of compression deformation. This helps us to re-examine  
494 the formation process of ore-controlling structures and their true influence on different ore-  
495 forming processes.

496 (2) Nanopores with pore sizes less than 100 nanometers are ubiquitous in many types of rock.  
497 These nano-structures have significant impacts on the properties of fluids. For example, the  
498 dielectric constant of water in nanopores is completely different from that under macroscopic  
499 conditions so that the solubility of water in nanopores is lower. This discovery has  
500 implications for the migration and precipitation of minerals in nanopores compared with  
501 associated macroscopic structures such as faults. Therefore, we have to re-examine the role of  
502 fluids in the formation of ore deposits and rethink the traditional ore deposit models.

503 (3) Nanofluid inclusions enriched in the rare elements gallium and germanium have been  
504 observed in 10-20 nm inclusions within the crystal lattice of hydrothermal sphalerite. In this  
505 example nanofluids appear to have helped achieve the enrichment of two dispersed, rare  
506 elements with extremely low concentrations in the crust. Nanofluids may be invoked to  
507 explain how some rare elements, rare earth elements and precious metals can form  
508 independent ore deposits enriched in elements that occur in such low concentrations  
509 elsewhere on the Earth's crust, rather than just existing as associated elements in other bulk  
510 mineral products such as copper.

511 (4) Ore-forming elements in the form of compounds or nanoparticles in the fluid can be  
512 gradually enriched through the unique adsorption and growth of the nano-effect. Elemental  
513 nanoparticles can grow by aggregating with other nanoparticles. One of the concentrating

514 forces is called van der Waals attraction. Van der Waals interactions usually occur when the  
515 particle size is smaller than a few tens of nanometers and the distance between particles  
516 smaller than a few nanometers. The growth of nanoparticles also owes to the surface-effects  
517 of nanoparticles.

518 Because of the peculiar role of the nano-effect, some important ore-controlling factors in  
519 traditional mineral deposit theory, such as sulfur fugacity, may not be as important as  
520 originally thought. The nano-effect can be invoked to explain some key processes in the  
521 formation of some metal deposits.

522 Pores with a pore size of less than 100 nanometers, such as micro-cracks and nanopores,  
523 which are commonly found in rocks, greatly promote the migration of ore-forming materials,  
524 especially vertical migration over long distances and deep depths. Traditional ore deposit  
525 models have always emphasized the role of different levels of macro-scale fault and fracture  
526 spaces as the migration channels for ore-forming fluids. Anomalies of ore-forming elements  
527 such as gold and their vertical relationship with the much lighter element mercury, as well as  
528 the discovery of mineralization such as nano-gold in micro cracks and nanopores,  
529 demonstrates the importance of vertical migration of ore-forming fluids under nano-  
530 conditions. Elemental geochemical zoning is not only controlled by major structures as  
531 described in traditional theories but is likely also controlled by the vertical or lateral  
532 migration of these elements along micro cracks such as nanopores in the surrounding rocks at  
533 nano-scale where the solubility of the fluids is reduced and the precipitation of minerals  
534 occurs earlier than expected in macro-conditions.

535 Using gold deposits as an example nanometallogeny hypothesises that the cycle of  
536 endogenous and exogenous mineralization under the action of the nano-effect includes  
537 vertical and horizontal migration and diffusion of gold-bearing fluids through micro cracks  
538 and nanopores. As the temperature and pressure drop, redox conditions and fluid composition

of the fluid environment changes, gold solubility is reduced and the fluid becomes saturated and gold is precipitated, or gold is dissolved with minerals such as quartz and pyrite to form nano-gold. After that, the gold-bearing rocks are weathered and eroded to dissociate nano-gold into surface sediments such as soil or enrich the saprolite or soil at the water table by nano-scale dissolution and re-precipitation of nano-gold. The presence of geochemical barriers such as clay, colloids, oxides and organic matter in fine-grained soils captures the nano-gold, and thus forms supergene gold anomalies at and near surface. Due to the nano-effect, even an element such as gold, which is classified as an inert substance by traditional theory, can complete a large-depth and long-distance migration from deep to shallow, from primary gold-bearing rocks to secondary saprolites, laterites and soils, sometimes followed by secondary or multiple migrations.

Nanometallurgical research is challenging many aspects of existing mineral deposit theory. The latest research results of nanomaterials and related technologies across disciplines is allowing us to re-examine the important role of fluids and the nano-effect on the formation of mineral deposits. It is proposed that the field of nanometallogeny can apply the findings of the rapidly advancing research of nanomaterials to improve or even revolutionize traditional mineral deposit models. The essence of nanometallogeny as a discipline is to try to better understand the enrichment and migration mechanism of ore-forming elements, one of the three fundamental problems in traditional mineral deposit geology, by studying the behaviour of ore-bearing fluids at the nano-scale.

#### **Data availability**

The data that support the findings of this study is available from the authors upon reasonable request; see author contributions for specific data sets.

#### **Contributions**

The first author Jianzhao Yin proposed the nanometallogeny theory and drafted the manuscript. Luc English edited and finalized the manuscript, Hongyun Shi reviewed the first draft and offered supplementary comments. All authors prepared, reviewed and approved the final version of the manuscript.

### **Competing interests**

The authors declare no competing interests.

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Nanometallogeny: The role of the nano-effect in the enrichment, migration and mineralization of rare element, rare earth element and precious metal deposits

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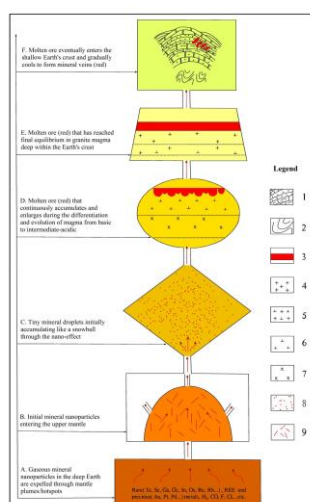
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To Whom It May Concern:

We are very glad to submit a manuscript entitled “Nanometallogeny: The role of the nano-effect in the enrichment, migration and mineralization of rare element, rare earth element and precious metal deposits” for your kind review. This is a non-peer-reviewed preprint submitted to EarthArXiv.

The graphic abstract of this article is as follows:



**Figure.** Nanometallogenic model of endogenous metal deposits

Legend: 1. Mesozoic slate, marble and schist; 2. Folded basement rock; 3. Molten ore and ore body; 4. Granite magma; 5. Granodiorite magma; 6. Diorite magma; 7. Basic rock (gabbro) magma; 8. Tiny mineral droplets initially accumulating like a snowball through the nano-effect; 9. Initial mineral nanoparticles entering the upper mantle

We testify that this article has neither been peer reviewed nor published for your consideration at this time. There is no conflict of interest concerning any governmental or private agencies and the publication has been approved by all the authors. We have read and have abided by the statement of ethical standards for manuscripts submitted EarthArXiv.

Thank you for your attention to our submission and we look forward to hearing your editorial decision shortly.

Best wishes,

Yours truly,

Jianzhao Yin, Luc English, and Hongyun Shi