Abiotic and biotic-controlled nanomaterial formation pathways within the Earth's nanomaterial cycle

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ABSTRACT

Nanomaterials have unique properties and play critical roles in the budget, cycling, and chemical processing of elements on Earth. An understanding of the cycling of nanomaterials can be greatly improved if the pathways of their formation are clearly recognized and understood. Here, we show that nanomaterial formation pathways mediated by aqueous fluids can be grouped into four major categories, abiotic and biotic processes coupled and decoupled from weathering processes. These can be subdivided in 18 subcategories relevant to the critical zone, and environments such as ocean hydrothermal vents and the upper mantle. Similarly, pathways in the gas phase such as volcanic fumaroles, wildfires and particle formation in the stratosphere and troposphere can be grouped into two major groups and five subcategories. In the most fundamental sense, both aqueous-fluid and gaseous pathways provide an understanding of the formation of all minerals which are inherently based on nanoscale precursors and reactions.

The Earth system is unimaginably complex due to the abundance and diversity of life (from micro- to macro-organisms) intertwined with literally millions of organic and inorganic molecules and materials composed from atoms across the periodic table. To parse the system into less entangled portions, scientists have used what has become known as Earth cycles for more than a century. As such, one can more easily follow important chemical aspects of the planet, such as individual elements (e.g. carbon, nitrogen, or phosphorus), individual Earth components (e.g. rocks, water, or nutrients), or multiple related elements/components in living/non-living subsystems (e.g., one of the many useful biogeochemical cycles). Driven by the expansion of available methods and tools for examining the Earth system, more Earth cycles are realized and components studied, as for example Earth's nanomaterial (NM) cycle more recently recognized and introduced [1]. Like all cycles, the NM cycle encompasses (at least in

principle) where NM are, and how they form, are distributed, and then lost or consumed as a next generation of nano-components appear throughout the Earth system.

The reason that a NM cycle is useful for Earth science, and in fact necessary in the complete study of our planet, is because these materials behave differently than entities generally smaller (e.g., most molecules), and bigger (e.g., most minerals, and biological components such as cells, while at the same time realizing that viruses are complex organic nanoparticles, and large molecules like proteins can also be considered nanoparticles). In the mineral world, by far making up the bulk of this planet and a major part of the critical zone of the Earth, nanominerals and mineral nanoparticles are not only abundant and widespread, but it has been suggested that they have been one of the principal catalytic components of Earth throughout its history[1]. They may contain any element in the periodic table, may be atomically ordered (crystalline), disordered, or amorphous, and range in size from less than a nanometer (<0.001 microns) up to several tens of nanometers (often in the range of 0.03 to 0.05 microns). Their properties depend, like bulk materials, on their chemical composition and atomic structure. Changing either of these, even slightly, can result in very different chemical and/or physical properties. However, for NMs, their properties also depend on their size, shape, and surface topographic features. The reason that this is important is that NMs often have dramatically different chemical and physical properties relative to their macro-mineral equivalent in the bulk state (if one even exists with the same atomic structure), that is in sizes larger than a few to several tens of nanometers in one, two, or all three dimensions. It is these property changes that not only significantly impact the Earth system in many important ways, including their distribution around the planet [1, 2], but for NMs in general, have also produced the nanoscience and nanotechnology revolution in the last few decades in the medical, electronic, catalytic, and chemical fields valued at trillions of US dollars worldwide each year [3].

Formation, properties, cycling and budgets of NM's in Earth compartments (lithosphere, atmosphere and hydrosphere) have been reviewed numerous times [4,5] with these papers also focusing on specific types of NMs [6,7] and their role in a vast array of Earth and environmental processes [8]. However, this field is still in its infancy with new and often unexpected discoveries constantly reported. In addition, research challenges are great due to chemical and physical complexities of nano-processes, and the exceptionally small scales that must be navigated.

This review concerning the group recognition and current understanding of abiotic- and biotic-controlled formation pathways is to the best of our knowledge the first of its type. Pathways of NM formation can occur in highly diverse environments, for example in the presence of aqueous fluids in soils, sediments, and the biological environment therein, all the way to within the gases or magmas in volcanic systems. We will focus primarily on formation pathways of NM mediated by aqueous fluids as those occur in the Earth's critical zone (CZ). Within this zone, humans interact directly or indirectly with NMs as they impact the form and function of living and non-living things. [9] However, we will also show that pathways of NM formation similar to those observed in the CZ also occur in hydrothermal systems, as well as in gas-dominated systems such as volcanic fumaroles, wildfires, and particle formation in the stratosphere and lower troposphere. Addressing pathways of NM formation outside the CZ is important as they also play fundamental roles, for example, in the cycling of elements, the formation of ore deposits, and the radiation budget of the atmosphere.

Overall, we find that despite the complexity and wide-variations of abiotic and biotic-controlled formation pathways mediated by aqueous fluids, they can be reasonably categorized into just four general types, each embodying a few to several sub-categories. For gaseous formation pathways, we have also identified two major types representing several additional sub-categories. Finally, it should be stated that determining these nano-formation pathways in natural environments is challenging, especially in that it requires very sophisticated transmission

electron microscopes with the latest analytical chemistry attachments, as well as state-of-the-art sample preparation tools.

Pathways of nanomaterial formation

All the formation pathways described below are categorized in Tables 1-2. The great majority of inorganic NM formation in the CZ consists of clay minerals due to silicate rock weathering processes [1]. Clays are considered mineral nanoparticles, as they have nanoscale thicknesses. This is one of the key nano-related factors that give them their unique properties. However, in the weathering process, other less abundant but still critically important inorganic NMs form [1]. Pathways of NM formation that are mediated by aqueous fluids also occur in the deeper portions of Earth's crust at higher temperatures. These can be driven by alteration processes or direct precipitation from meteoric water mixed with water from hydrothermal and/or magmatic sources.

Abiotic and biotic-controlled formation pathways of NMs in aqueous fluids can be coupled or decoupled from a weathering/alteration process (categories I versus II and III versus IV; Fig. 1 and Table 1). Coupled pathways are commonly based on dissolution-precipitation processes, in which the dissolution of the parent and the precipitation of the daughter(s) are closely coupled in space and time (also called interface-coupled dissolution-precipitation reactions [10]). The key components of such a pathway are the interfacial fluid phase and the porosity in the altered part of the parent phase which facilitate the mass exchange between the interface (i.e. where the dissolution-precipitation occurs) and the bulk fluid. Supersaturations and chemical compositions of the interfacial fluid as well as surface energies and stability of potential phases control the type of daughter phases that precipitate along the interface [10,11]. Here, we consider coupling of NM-formation and dissolution process when the formation occurs in a porous alteration layer or mineral surface coating. This definition assumes that the formation of the NM can be shifted in space and time and become less relevant to the

dissolution process. This approach also allows us to define whether biotic-controlled formations of NMs are coupled or decoupled from associated weathering/alteration processes that may have provided the bio-community with key nutrients and energy. The biotic-controlled NM-formation is considered coupled when occurring in proximity to the "parent" dissolution sites, especially within a confined space; alternatively, the formation is considered decoupled when occurring far from the parent dissolution sites, independent of the mass transfer between the dissolving mineral surface and the bulk solution.

First generation NMs may become unstable with changes in environmental conditions, composition of the pore fluid, or degree of agglomeration as it undergoes weathering/alteration. As a consequence, a second generation of NMs may form, and their formation may again be coupled or decoupled from the dissolution of the first NM-generation (Fig. 1). An alternative pathway of the first or any consecutive NM-generation is (a) their agglomeration (or flocculation) and subsequent Ostwald ripening towards larger micrometer-size grains (note that Ostwald ripening can be also considered a dissolution-precipitation process) or (b) their attachment on the surface of a growing crystals. The latter mechanism is termed crystallization through particle attachment (CPA) [12], where the attachment of the *NM* can occur in a random or orientated fashion. For random attachment, structural re-organization is required for incorporation of the *NM* into the bulk crystal, whereas orientated attachment requires the rotation of the *NM* upon attachment [13].

A classification of abiotic-controlled pathways of nanomaterial formation in aqueous fluids (I and II)

Pathways to the NM-formation coupled with weathering/alteration processes, can be further distinguished based on whether the NM is part of a first (Ia) or second or consecutive NM-generation (Ib; Table 1). The formation of a first NM-generation coupled with a weathering/alteration process can be then further subdivided into I. those where the parent

material is also a NM (*Ia1*); II. the composition of the NM is controlled by the release of a minor (*Ia2*) or major element (*Ia3*) of the parent phase; and III. multiple types of NMs form simultaneously (I*a4*). Examples of pathways are listed in Table 1.

An example for *Ia1* is the illitization of smectite to interstratified illite-smectite mixtures (I-S). Following the Ostwald step rule, the pathway from smectite to I-S and to illite involves a sequence of metastable phases that form via dissolution precipitation reactions [14,15]. This pathway is favoured by temperature and has been used as an empirical geothermometer. An environmental relevant pathway in this category would be the sulfurization of engineered or incidental Ag nanoparticles into Ag_2S NMs [16,17] as the formation of the lower soluble Ag_2S decreases the bioavailability of Ag in aquatic systems [18].

In *Ia2*, the minor element in a dissolving phase will be the major constituent of the NM whereas the major elements form a bulk material hosting the NM. The bulk material may also be composed of nano-domains [19] that have undergone partial Ostwald ripening, but for simplification purposes, are not considered NM. Pathways in this category include the alteration of Cr-rich pyroxene and Au-bearing pyrite or a-rsenopyrite and the subsequent formation of clinochlore and hematite/ pyrite/arsenopyrite (bulk phases) and chromite- and gold-nanoparticles, respectively (Fig. 2a-b) [19-21]. The subsequent weathering of clinochlore results in the release of chromite nanoparticles, which appear in contrast to Cr^{3+} aqueous species less susceptible to oxidation by Mn-oxide phases towards hexavalent Cr [22]. The formation of gold nanoparticles along the pyrite-hematite interface (Fig. 2a, b) can lead to their agglomeration and formation of supergene gold deposits [20].

Environmental relevant pathways in *Ia3* include the formation of amorphous silica and ferrihydrite on the surfaces of altered feldspars/plagioclase and pyrite [23, 24]. The formation of an amorphous silica-gel coating provides nucleation sites for the subsequent formation of clay minerals (see below), and the gel's reorganization (as observed for borosilicate glass) can lead to the passivation of the underlying mineral [25]. The formation of such an armouring silica-rich

mineral surface coating on Ca-silicate minerals could affect the release of Ca into the ocean and thus the sequestration of CO_2 [26-30]. Similarly, the formation of ferrihydrite on pyrite and its potential transformation into the more stable Fe-oxide phases goethite and hematite decreases the dissolution rate of pyrite and thus the generation of acidity in mine tailings [31]. *Ia3* also includes the common pathway where a more soluble mineral is replaced by NMs of a less soluble mineral. An example would be the replacement of Ag_2S (acanthite) by NMs composed of HgS (cinnabar) (Table 1; Figure 2c-d) [32]. An example for Ia4 would be the simultaneous formation of a silica-rich amorphous NM and ferrihydrite during the weathering of volcanic basalt glass (Fig. 2e and f, [33]).

The formation of consecutive NM-generations (*Ib*) requires the formation of a first generation of NMs and is thus a subcategory of *Ia*. However, we treat *Ib* as its own as it allows for deciphering additional pathways of NM-formation. Formation of NMs of the second or consecutive generation can be further subdivided into those which form from an amorphous precursor (*Ib1*), through the addition or removal of a minor constituent from the alteration layer (*Ib2*) or to the addition or removal of a major constituent to the alteration layer (*Ib3*). As the NM-formation in these categories often requires the addition of chemical constituents from the bulk fluid, their formation is thus not entirely coupled to the weathering/alteration process of the underlying mineral.

An example for *Ib1* would be the pathways from an amorphous silica-rich precursor to consecutive generations of clay minerals on the surface of an altered feldspar [34] or the formation of different Fe-bearing NMs from an amorphous Fe-silica-rich precursor on the surface of an altered Fe-rich pyroxene (Fig. 2g and h)[35].

Pathway of *Ib2* occurs, for example, during the alteration of micas. Here the pathway is initiated with the hydration (addition of H_2O and OH groups) and oxidation of muscovite and biotite followed by the formation of multiple generations of clay minerals on their surfaces (removal of alkaline cations) [34,36,37]. Pathways of *Ib3* include for example the formation of

multiple generations of Fe-hydroxides, including a first generation of nano-crystalline ferrihydrite on the surface of pyrite (i.e. removal of sulfur; [24,38]) and the conversion of uraninite into a highly disordered silica-rich uraninite (addition of silica) followed by the formation of coffinite, $USiO_4$ (this process is also called coffinization of uraninite [39,40]). The latter process is common in uranium ore deposits and may also be relevant during the interaction of nuclear fuel waste (the natural analogue to uraninite) with silica-rich fluids.

Formation processes decoupled from weathering processes (II) involve the transport of released constituents from the dissolving mineral surface and alteration layer to areas of either higher reactivity or different environmental conditions.

Areas of higher reactivity can be reactive surface sites on minerals or organic material that chemically transform (oxidize or reduce) elements adsorbed to their surface (*IIa*). Reactive surface sites can be also highly underbonded surface terminations along surfaces, terraces, edges, or kink sites of organic matter, plants and minerals at which the initial adsorption of aqueous species results in the heterogeneous nucleation of NMs (*IIb*). The transport of constituents to areas of different environmental conditions such as pH, Eh, P, T often promote the homogeneous nucleation of NMs (*IIc*).

Examples for *IIa* include the diffusion of $Cu^{1+/2+}$ and Ag^{+}-bearing species into organic matter and their reduction by organic functional groups and the subsequent formation of Cu and Ag nanoparticles [41,42, 17,43]. A similar pathway occurs when $Cu^{1+/2+}$-bearing species enter the interlayer of Fe^{2+}-bearing phyllosilicates and become reduced by Fe^{2+} terminations along the octahedra layers of the sheet silicates [44-48]. Both processes are relevant to the sequestration of Cu in smelter- and mining-impacted soils.

The heterogeneous NM-nucleation in pores or on surfaces of organic matter, minerals, bacteria, fungi and plants is often induced through the provision of a nucleation site but can be also controlled by the pore size and pore shape. For example, a decrease in pore diameter enhances the formation of inner-sphere complexes on the surfaces of the nanopores (via a

decrease in the surface acidity constants of the surface functional groups) and thus leads to the accumulation of NM-constituents in the pore [49]. However, a decreasing pore size also increases the solubility of the material due to limiting its size (expressed in the Pore Controlled Solubility (PCS) model [50]). Hence, the formation of NMs in pore spaces can be based on a combination of different pathways (i.e. heterogeneous nucleation versus supersaturation) but is in this study assigned to only one category. Examples for the formation of NMs in porous materials include the formation of amorphous silica, Cu-(hydr)oxides and minerals of the spinel group (magnetite, Fe_3O_4 and franklinite, $ZnFe_2O_4$) in porous organic matter in Cu-contaminated soils [51]. The heterogeneous nucleation of NMs was observed on reactive surfaces of fungi, plants, bacteria and granite and include for example Ca-oxalate, gold, clays and schwertmannite, respectively (Table 1) [52-55]. Under hydrothermal conditions, Au and sulfide-NMs often nucleate on the surfaces of pyrite or As-rich pyrite and occur within growth zones of these minerals [19].

Many pathways exist for the homogeneous NM-nucleation due to changes in environmental conditions [34,56,57] (IIc). One important pathway affecting the transport of the nutrient Fe to the ocean is the formation of ferrihydrite in riverine or riparian zones due to changes in pH and Eh, respectively [58,59].

An important ore forming process is the pathway from dissolved metals in hydrothermal fluids to sulfate, sulfide and native element NMs around black smokers [60,61] and in hydrothermal veins [62].The pathway of their formation is initiated by the boiling of the hydrothermal fluids due to a decrease in pressure, the mixing of the fluids, and the loss of reducing gases such as H_2S and H_2 which subsequently result in the oxidation of redox-sensitive ions, an increase in the respective saturation indices, and homogeneous NM-nucleation.

A classification of biotic-controlled pathways of NM formation in aqueous fluids

The presence of naturally occurring NMs may play important, if not essential, roles in enabling and sustaining microbial metabolisms. Living organisms may be involved in the NM

formation through three ways: (1) directly utilizing a substrate (as an energy or nutrient source) and transform it into NMs (categories IIIa and IVa, Table 1); (2) actively control NM formation using their biomolecular toolbox (IIIb and IVb, Table1); and (3) passively cause NM formation through discharging metabolites into their immediate surroundings and through the presence of their cell surfaces and extracellular polymeric substances (EPS) (IIIc, IIId, and IVc, Table 1).

Most biotic NM-formations are considered decoupled (IVa, b, and c, Table 1) unless the substrate fueling the biological growth and subsequent NM formation is trackable or physically restricted within the biological communities responsible for the NM formation (IIIa, b, c, and d, Table 1). The coupled scenarios include bio-utilization of solid-phase substrate (IIIa and b, Fig 3) and NM formation within a confined space mediated by biological metabolisms, e.g., biofilms in the proximity to where the substrate is mobilized (IIIc, Fig 3). It is noted that the biotic NMs in IIIa versus IIIb (Fig. 3), despite their mineralogical similarities, may reflect distinctive formation processes based on their morphologies and size distributions. The former (IIIa) was likely a result of microbial reduction of pre-existing Fe(III) phases [63] whereas the latter likely involved actively controlled intracellular biomineralization [64].

The biotic NMs formed through active biomineralization more likely behave as functional and flexible “nano tools” that may assist the biological cells or community with electron transfer, chemotaxis, and substrate storage [65]. In these cases (IIIb and IVb, Table 1), the cells precisely control of the NM’s size, crystal structure, and stability through involving proteins, nucleic acids, and other biomolecules. For example, magnetite/greigite inclusions in magnetotactic bacteria as nano-compasses [66], elemental sulphur inclusions in sulfur-oxidizing microbes as nano-stockpiles [67] (although the sulfur NM formation is also a result of direct energy metabolism), and nano-carbonate inclusions in cyanobacteria that likely regulate the cells buoyancy [68] (Fig. 3h-i), all belong to the active biotic NM-formation category. Except for the cases where organisms use pre-existing phases restricted in their mass transfer within a confined space (e.g., Fig. 3b-c), most functional biogenic NMs are considered decoupled (IVb).

In comparison to active biotic NM-formation, it is more common to find their passive counterparts in nature. Passive biotic NM formation occurs simply due to the adsorption, reduction, and concentrating effects of the cell surfaces and EPS matrices, or due to metabolite (i.e., carbonate, sulfide, and ferric iron species etc.) accumulation in the biological microenvironments. In these cases, purposely biomolecular control of the NM-formation has not been identified (IIIc, IVc, and IIId). The passive formations that involve nucleation/condensation from dissolved species are considered decoupled processes in terms of NM-evolution, and those in which the mobility of precursor phases is restricted (e.g., in biofilms, Fig. 3d-e) [69,70] are considered coupled processes. If the NM-formation involves toxic heavy metals, these processes may help to detoxify the living organisms' immediate surrounding environment (Fig. 3j). Biological EPS matrices may facilitate new exopolymer NM formation out of the pre-existing polymeric components (IIId, Table 1) [71]. They may also concentrate mobile metal species through chelation and biosorption [72,73], which occasionally lead to NM formation [74,75]. We note that the category IVc in Table 1 is inclusive of decoupled, EPS-mediated NM formation processes as naturally occurring microbial communities, by default, exist as biofilms with EPS matrices. Although EPS of biological flocculates have been previously reported as effective traps and stabilizers for pre-existing, mostly engineered nanoparticles in the environment, the focus of this paper is on the formation pathways of naturally occurring NMs, and thus we will not elaborate on this aspect.

A classification of abiotic-controlled pathways of nanomaterial formation in gases (V)

The majority of particles formed in gases occur in the atmosphere. Their sizes ranges from 1 nm to 100 μm with coarser particles originating from sea spray and volcanic activities and finer particles from combustion and particle formation via gas-to-particle conversions [76]. All these processes result in the formation of NMs, which often occur in a higher number than their micrometer-size counterparts.

Similar to pathways mediated by aqueous fluids, the formation of NM in gases can include alteration of a first generation of NM or bulk materials as well as the heterogeneous and homogeneous nucleation [77,78]. Because the role of surfaces for the formation of NM from gases is less explored in the geoscience literature relative to those in soils, sediments and aqueous fluids, we group the pathways of NM formation in gases on the basis of their ambient temperature (Va and Vb Table 2).

High-T pathways of NM formation in gases occur during incidental combustion of plants (wildfires) [79] and coal (coal combustion) [80] (Va1, Table 2), and also during volcanic eruptions and within and in the vicinity of volcanic fumaroles (Va2). The pathways of NM formation during wildfires and coal combustion are complex and generally not well understood. They are strongly temperature dependent and occur via the thermal decomposition and volatilization of the C-based material, the release of metals and volatile elements such as H, N, O, S, Cl and Se, and the alteration of soil/sediment constituents. For example, NM composed of soot, nanotubes, fullerenes and tar form during (or shortly after) the combustion process, S-, N-, Cl- and Se-bearing phases during sublimation and solidification of hot gasses and liquids, and oxides during thermal alteration of hydroxides, clay minerals and carbonates (Table 2) [81-83].

Pathways of NM in gases during volcanic activities (Va2) include processes during eruptions and fumarolic activities. During eruptions, silica can be reduced by carbon monoxide to SiO and subsequently oxidized resulting in the nucleation of cristobalite NM [84]. Volcanic fumaroles are known to deposit minerals on surfaces of rocks and sediments such as native sulfur. Among these phases, nanoparticles of gold were identified at numerous locations [85,86].

Low-T NM pathways in gases (Vb) occur in stratosphere, troposphere and critical zone environments. In the troposphere and stratosphere, the freezing of water-containing HNO_3 and H_2SO_4 leads to the formation of ice and crystalline acid hydrates such as $H_2SO_4 \cdot 4H_2O$ and $HNO_3 \cdot 3H_2O$, an important process during annual polar ozone depletion [75]. In the troposphere, emitted volatile gases from the biosphere, volcanic activities and anthroposphere such as SO_2,

NH_3, or volatile organic compounds are oxidized to low volatile trace vapors through atmospheric oxidation, a process commonly referred to as new particle formation [87]. This process leads first to the formation of molecular clusters and subsequently to the nucleation and growth of larger aerosols [88], which are defined as liquid or solid particles suspended in a gas phase. Aerosol particles influence global climate change [89] and impact human health [90]. In the upper CZ and lower troposphere, the formation of salt NM from sea spray occurs through heterogeneous and homogeneous nucleation from a fluid-gas mixture and results predominantly in the formation of halite (NaCl), gypsum ($CaSO_4(H_2O)_2$) and other sulfates (Table 2) [77].

The formation of NMs in the gas phase often has an impact on human health. For example, the TiO_2 phases rutile, anatase and brookite transform into toxic O-deficient Ti_xO_{2x-1} Magnéli phases during coal combustion. The phases occur as NMs (tens to hundreds of nm in diameter) and are significant air pollutants in regions where coal fire plants contribute to PM [91,92]. Furthermore, the formation of NMs during the recent high frequencies and sizes of wildfires (e.g. 3.8 million hectares burned in the western USA in 2020) resulted in airborne NMs (as a part of fine particulate matter, diameter ≤2.5 μm; $PM_{2.5}$) which (a) have the ability to penetrate deep into lungs [93], (b) can contain harmful metals from anthropogenic sources (construction and automotive) [94] and (c) can mix with other atmospheric pollutants and NM formed during low T pathways [77]. Health studies have shown that wildfire $PM_{2.5}$ is more harmful than $PM_{2.5}$ emitted from many urban environments [95].

A classification of abiotic-controlled pathways of nanomaterial formation in magmas (VI)

Pathways of NM formation during magmatic processes are commonly controlled through changes in temperature, O_2-fugacity, silica- or sulfide-activity. An economically important process is the formation of platinum group element (PGE) NMs in mafic or ultramafic sulfide- or silicate-melts [78] (Table 2). The pathway of their formation resembles those of category Ib, where minor elements in a mineral form NMs upon weathering/alteration of their original host. Field

observations and experimental studies suggest that the highly siderophile and chalcophile PGEs segregate from mafic or ultramafic magmas initially into metal-rich immiscible melts (containing O, S, As, Te and Bi), followed by the formation of clusters and PGE-bearing NMs. The PGE-bearing NMs are commonly associated with ultra-mafic minerals such as chromite, pentlandite, chalcopyrite and pyrrhotite [96-98].

Overall assessment of Earth NM formation pathways

This assessment shows that the formation of nanomaterials mediated by aqueous fluids within the critical zone, as well as in many other Earth environments, follow four principal pathways which can be further subdivided into 10 abiotic and 6 biotic pathways (Table 1). Among these pathways, the most common are very likely those occurring in soils and regoliths (keeping in mind that nanomaterial formation in the oceans has not been thoroughly explored). From an economic viewpoint however, the role of NMs in the formation of ore deposits is especially intriguing as these nanoparticles provide an explanation for the transport of elements of low solubility such as Au in hydrothermal solutions [99]. In this regard, Au NM can form via five different pathways, ranging from abiotic and biotic pathways in an aqueous fluid to depositions during volcanic fumarole activity (Tables 1 and 2). This high number of pathways is most likely due to Au's low solubility and low compatibility with the structure of pyrite (i.e. which depends on T and the amount of As in the mineral).

Also, of great interest is the fact that the classification of inorganic- and organic-based pathways for NM formation based on factors such as multiple generations, amorphous precursors, energy resources, and heterogeneous and homogeneous nucleation now allow for comparisons of NM formations pathways that occur in very different chemical and physical environments. These include comparisons between NM formations during the weathering of silicates versus sulfides or between those in soils versus hydrothermal solutions. Hence, this formation pathway compilation allows for future studies by other researchers to identify

formation pathways of NM similar to those observed in this study, even though the formation environment is not necessarily in geologic environments discussed in this paper. An example of this is the recent observation that the alteration of Cd-bearing sphalerite (ZnS) leads to the formation of greenockite (CdS) NMs [100]. This example follows the same pathway as the formation of gold NMs during the alteration of Au-bearing pyrite [19,20], chromite NMs during the alteration of Cr-rich pyroxenes [21], rutile NMs formed during the alteration of Ti-bearing quartz, and platinum group element (PGE) NMs formed during the alteration of PGE-bearing chromite [78].

Finally, as mentioned above, the discovery and delineation of all of the chemical/physical/biological-based pathways of NM formation in both aqueous and gaseous mediated systems will result in a better understanding of the NM cycle of the Earth as a fully connected and evolving system[1]. There is also the possibility (likelihood) that completely new and/or novel NM formation pathways will be discovered. Such conceptual frameworks have been shown repeatedly to have great value, e.g. the rock cycle, the water cycle, and the many chemical cycles of the Earth. Ultimately, the nano-reactants that appear through this cycle, including those NMs that only exist for very short times, consequently impact the entire Earth system (atmosphere, hydrosphere, and terrestrial Earth) in highly consequential ways as has been recently reviewed[1].

Methods

Features of nanomaterials published in previous studies are shown in this review. These TEM images and STEM-EDS chemical distribution maps were processed with the TEM Imaging & Analysis (a trademark of FEI) and Esprit 1 (a trademark of Bruker Nano) software.

Data availability

Data sharing is not applicable to this article as no datasets were generated or analysed during the current study.

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Author contributions

All authors jointly wrote the paper. MS had the idea for the review, conducted data analysis for the abiotic pathways and wrote the abiotic section. JX compiled the data for the biotic pathways and wrote the biotic section. MH wrote the introduction, and the last section entitled "Overall assessment of Earth NM formation pathways".

Competing interests

The authors declare no competing interests.

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Fig. 1. Schematic overview of various pathways of nanomaterial formation in aqueous fluids within the critical zone (the sketch of the critical zone is adapted from [101]). Note that the upper half of the schematic is for biotic-controlled pathways, and the lower half for abiotic-controlled pathways.

766

Fig. 2 Abiotic pathways of nanomaterial formation. (a)-(b) Example for pathway *Ia2*: Scanning-TEM (STEM) images of the formation of gold nanoparticles (Au NP's) along the interface of pyrite and Fe-oxides (Fe-Ox); (c)-(d) Example for pathway I*a3* (and for *Ia1* if the Ag_2S grains are considered to be nano in size): (c) STEM image and (d) STEM-EDS chemical distribution map for Ag (red) and Hg (green) indicating the replacement of a Ag_2S grain (on the right) by HgS (green rim) [32] , (e)-(f) Example for pathway *Ia4*: TEM images of the simultaneous formation of ferrihydrite and amorphous silica NM during the weathering of volcanic glass [33]; (e) overview image depicting areas with high ("Fe-rich area") and low ("glass") degree of weathering; (f) higher magnification image of individual ferrihydrite particles (in the lower nanometer-size range) embedded in an amorphous silica matrix; (g)-(h) Example for pathway Ib1: SEM-BSE image of a part of a mineral surface coating on a Fe-rich pyroxene and TEM image depicting numerous Fe-(hydr)oxide formed in the matrix of an amorphous Fe-silica phase [35] , the area depicted in (h) is indicated with a white square in (g); (a), (b) (g) and (h) are unpublished images from features previously shown in 20,35; (c)-(f) are published with permission.

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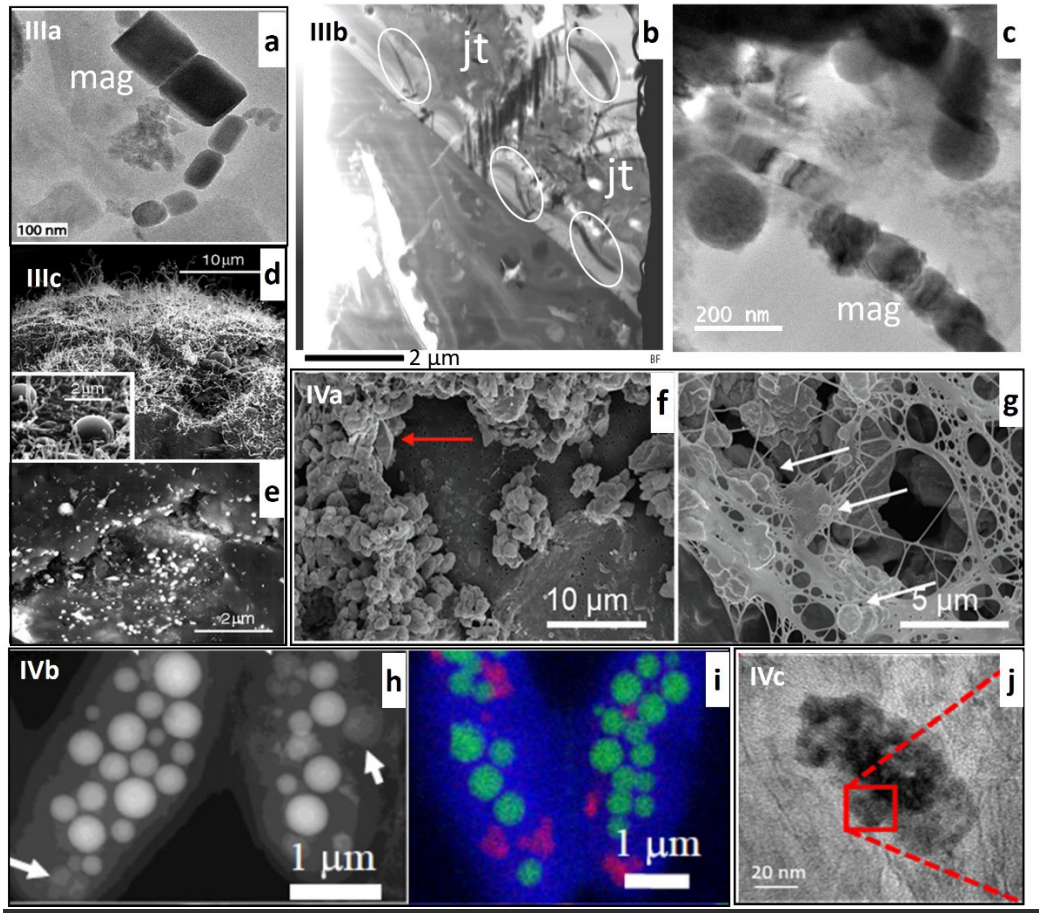

Fig 3 Biotic pathways of nanomaterial formation. (a) Example for pathway IIIa: transmission electron micrographs (TEM) of magnetite NMs (mag) formed via microbial alteration of hematite [63]; (b)-(c) example for IIIb: (b) scanning TEM image of a focused ion beam section extracted from a soil sample obtained near a smelting center in Ontario, Canada; occurrences of petrified spirilla with the same orientation on the surface of jarosite (jt) are encircled; (c) TEM image of biogenic magnetite NMs (mag) in close proximity to one of the spirilla encircled in (b) [35]; (d)-(e) example for IIIc: scanning electron micrographs (SEM) of gold NMs in biofilms through biological alteration of gold-containing ores [69]; (f)-(g) example for IVa: SEM of elemental sulfur formed in Sulfurovum-dominated streamer biofilms in the Frasassi Cave, Italy [102]; (h)-(i) example for IVb: TEM and STEM-EDS analysis of calcium carbonate nanoparticles (green) and polyP granules (red) formed inside cyanobacteria [68]; (j) example for IVc: TEM of metacinnabar nanoparticles formed in sulfidic niches of contaminated streambank soil [74]; Figures (a) and (d)-(j) are with permission and (b)-(c) are unpublished images from features shown in [35].

769 **Table 1. Formation mechanisms of natural and incidental NMs in fluids**

I. Abiotic formation coupled in space and time with weathering and alteration			
Location or environment of weathering/alteration	Parent	Daughter NM	Reference
a. Formation of a first-generation NMs			
1. Formation of NM replacing a first generation of NM			
Oceanic bentonite-sediments in subduction zone; altered rhyolitic hyaloclastite	Smectite	Interstratified illite-smectite mixtures with various illite-smectite ratios	14,103
Soils, sediments	Ferrihydrite	Nano-Goethite or hematite	33
Soils, sediments and wastewater	Engineered or incidental Ag nanoparticles	Ag_2S NM	16
2. Formation of only one type of NM which contains a minor element of the parent			
Alteration of ultra-basic rocks during greenschist metamorphisms	Cr-rich pyroxenes	Clinochlore (bulk) + chromite NMs	21
Low-T alteration	Au-bearing pyrite	Au NM + hematite (bulk)	20. Fig. 2a, b
Hydrothermal alteration	Au-bearing As-rich pyrite	Au NM +polycrystalline matrix of pyrite and arsenopyrite	19
3. Formation of only one type of NM which contains the major element of the parent			
Soil	K-Feldspar	“paracrystalline” phase or “gel”	23
Soil, sediment	Pyrite, Fe_2S	Ferrihydrite	24
Contaminated soils	Ag_2S	HgS	32, Fig. 2c, d
4. Syn-formation of more than one type of NM			
Pedogenic altered basaltic glass in	Volcanic glass	amorphous Si-Al-Fe-phase + ferrihydrite	33, Fig. 2e, f

volcanic ash (dry-cool conditions)			
Soil	Fe-rich chlorite	halloysite-kaolinite, goethite, hematite, interstratified chlorite-1:1 sheet silicate	104
b. Formation of a second or consecutive generation of NMs after the weathering/alteration of a first-generation nano-daughter phase			
1. Formation of NM via amorphous precursors			
Location or environment of weathering/alteration	Parent	Daughter NM	Reference
Soil	K-Feldspar	"protocrystalline layer" depleted in Ca, Na, K and Si, enriched in Fe → halloysite and kaolinite	34
Soil	Fe-rich pyroxene	1st Generation: amorphous Fe-Si-rich matrix → green rust 2nd generation: goethite, magnetite, jarosite, Ni-rich spinel; 3rd generation: P-rich ferrihydrite → illite+chlorite	35, Fig. 2g, f
2. Formation of chemically related NMs with the addition or removal of minor constituents from the alteration layer			
Soil, Weathering profiles	Biotite	oxybiotite → vermiculite → kaolinite + Fe/Al oxyhydroxides	36,37
Soil	Muscovite	Illite-smectite → smectite → kaolinite	34
3. Formation of chemically related NMs with the addition or removal of a major constituent from the alteration layer			
Mine tailings	Pyrite	Weak acidic to basic pH range: ferrihydrite → goethite	24,38
Groundwater	Uraninite	Si-rich uraninite → coffinite	39,40
II. Abiotic formation decoupled in space and time with weathering and alteration			

a. Heterogeneous nucleation of NMs on chemically reactive redox sites in pores or on surfaces			
Environment	Host	NM	Reference
Soils	Organic matter	Cu or Ag through reduction of $Cu^{+/2+}$ and Ag^{+} on functional groups	41-43, 17
Hydrothermal	Fe-bearing phyllosilicates	Cu in interlayer, reduction by Fe^{2+}	44-48
b. Heterogeneous nucleation of NMs on sites in pores or on surfaces			
Soils	Pores in organic matter	amorphous silica → Cu-Zn-bearing magnetite (Fe_3O_4), cuprite (Cu_2O) and spertiniite ($Cu(OH)_2$)	51
Soils	Pores in mineralized organic matter	franklinite	105
Soils	Fungi	Ca-oxalate	52
Soils	Interior surface of plant	Au	55
Soils and tailings	Bacteria	clays and silica	53
Tailings	Granite	Schwertmannite	54
Various types of hydrothermal ore deposits	Pyrite, As-rich pyrite Arsenopyrite	Au, other types of sulfides, sulfarsenides	19,106,107
c. Homogeneous nucleation of NMs due to changes in pH, P, T, O_2 fugacity and activity of species			
Environment	Variables/Processes	NM	Reference
1. Low T processes			
Riverine system	pH from acidic organic rich to neutral with less organics	Ferrihydrite	58
Riparian Zone	Changes in redox conditions	Ferrihydrite	59
2. High T processes			

Black smokers	P, T and mixing with seawater	Au, Bi, sulfides tellurides	61
Black smokers	P around ascending fluids	Au	60
Epithermal ore deposits	coagulation of Au NM due to cooling/ boiling/catalysis	Au	62
III. Biotic formation coupled in space and time with weathering and alteration			
a. Formation of NMs through energy metabolisms (redox reactions) of organisms			
Environment	Parent	Daughter NM	Reference
Mineral surface coatings in soils and Quaternary sediments	hematite/jarosite	Magnetite	63, Fig 3a
b. Formation of NMs that directly provide beneficial functions for the organism			
Environment	Parent	NM	Reference
Mineral surface coatings in soils	Jarosite	Magnetite	35, Fig. 3b-c
c. Formation of NMs involving organismal cellular components or through reactions with metabolites			
Mechanism	Parent	NM	Reference
biological mobilization and concentration of platinum-group elements within biofilms	ore grains	platinum-palladium	70
biological mobilization and concentration of gold within biofilms	gold-containing grains	Au	69, Fig. 3d-e
d. Formation of NMs within extracellular polymeric matrices			
Mechanism	Parent	NM	Reference
photochemistry-driven transformation	extracellular polymeric substances (freshwater lakes)	protein-like transparent particles	71

IV. Biotic formation decoupled in space and time with weathering and alteration			
a. Formation of NMs through energy metabolisms (redox reactions) of the organism			
Mechanism	Parent	NM	Reference
bacterial sulfur oxidation	hydrogen sulfide (from microbial sulfate reduction or hydrothermal venting)	elemental sulfur	67
Bacterial oxidation of sulfide for energy	Hydrogen sulfide	elemental sulfur	102, Fig. 3f-g
bacterial iron oxidation for energy	dissolved Fe(II)	2-line ferrihydrite, goethite, and amorphous phases	108
bacterial manganese oxidation for energy	dissolved Mn(II)	manganese (IV)/(III) oxide	109
fungal reduction of selenite	Dissolved Se	Selenium	110
b. Formation of NMs that directly provide beneficial functions for the organism			
Environment	Location	NM	Reference
A range of environments where cyanobacteria thrive	intracellular biomineralization (regulating bacterial buoyancy)	calcium carbonate	68, Fig. 3h-i
Marine and freshwater	intracellular biomineralization (storing iron source)	hydrated amorphous silica	111,112
c. Formation of NMs involving organismal cellular components or through reactions with metabolites			
Environment	Parent	NM	Reference
a range of anoxic/sulfide-rich environments	Microbial-reduced sulfate species	iron sulfide (greigite, mackinawite, pyrite, and pyrrhotite)	66
Lake sediments	sedimentary sulfate	Greigite	113
Messinian Black Sea sediments	Terrigenous input of sulfate	Greigite	114

Abandoned mine	microbial reduced sulfate	Sphalerite	115
contaminated streambank soils	biological- sulfidation	Metacinnabar	74, Fig. 3j
groundwater aquifers, uranium deposits/tailings	microbially mediated reduced species (usually through iron reduction or sulfate-reduction)	Uraninite	116,117
deep sea hydrothermal vents	biologically mediated reduction/adaptation of Hg species	Mercury	118

Table 2. Formation mechanisms of natural and incidental NMs in the gas phase and during magmatic processes

V. Abiotic pathways of NM formation in the gas phase: thermal decomposition, volatilization, oxidation, sublimation, solidification, freezing and thermal alteration during incidental combustions			
a. High-T processes			
Environment	Variables/Processes	NM	Reference
1. Wild- and coal fires			
Soil-plant interface	Wildfires set by lightning	amorphous carbon $CaCO_3$, $FeCl_2$, $FeSO_4$ $Fe(NO_3)_3$, $FeCl_3$, magnetite	79,94
Thermal alteration aureoles along coal-sediment interface	Coal fires set through spontaneous combustion or lightning	soot, nanotubes, fullerenes, tar at high T: oxides and silicates at < 630ºC: sulfates and sulfides	80
2. Volcanic activities			
Volcanic fumaroles	Changes in T	Au	85,86,119
Volcanic eruptions	Redox reactions between silica glass and carbon monoxide	Cristobalite	84
b. Low T processes			
Environment	Process/source	NM	Reference
1. Freezing			
Troposphere to Stratosphere	Freezing	ice, crystalline acid hydrates such as $H_2SO_4 \cdot 4H_2O$, $HNO_3 \cdot 3H_2O$	75
2. New particle formation			
Lower troposphere	New particle formation through oxidation of S- and N- species and organic components	mascagnite, $(NH_4)_2SO_4$, critical nuclei containing sulfates, nitrates, organic matter	75,76,120

	from natural (e.g. volcanic eruptions) and anthropogenic sources		
3. Sea spray			
CZ to Lower troposphere	Nucleation from sea spray, often associated with other atmospheric particles	halite, NaCl, gypsum, $CaSO_4 \cdot 2H_2O$, glauberite, $Na_2Ca(SO_4)_2$, loweite, $Na_{12}Mg_7(SO_4)_{13}$	77
VI. Pathways of NM formation during magmatic processes			
Host/environment	Processes	NM	References
pyrrhotite, millerite, pyrite, pentlandite and chalcopyrite in mafic-ultramafic Rocks	Changes in T, fO_2 and activity of sulfide and silica	PGE-alloys, -sulfides, -tellurides, -stannides	96,98,121-123

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