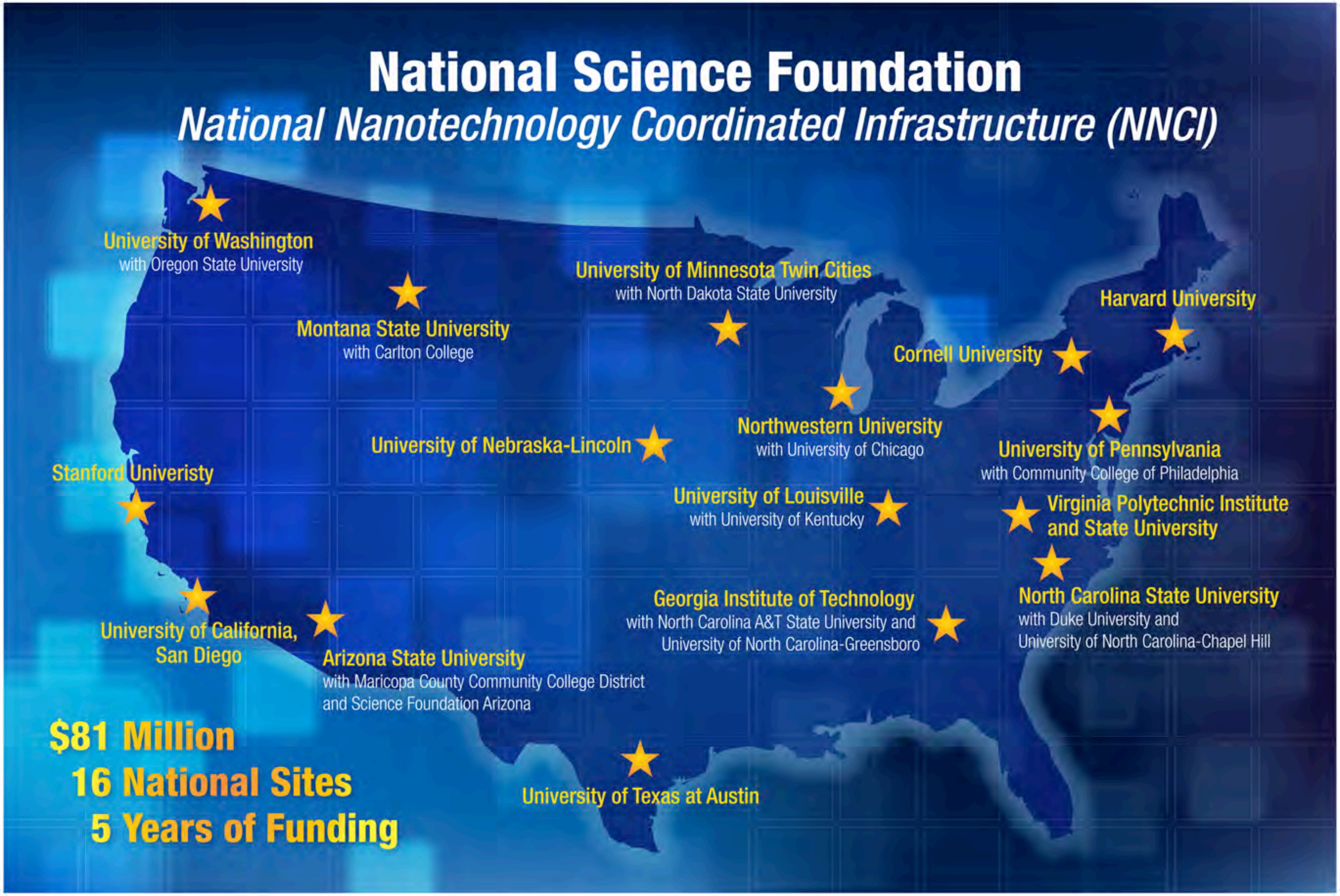


National Nanotechnology
Coordinated Infrastructure

NanoEarth

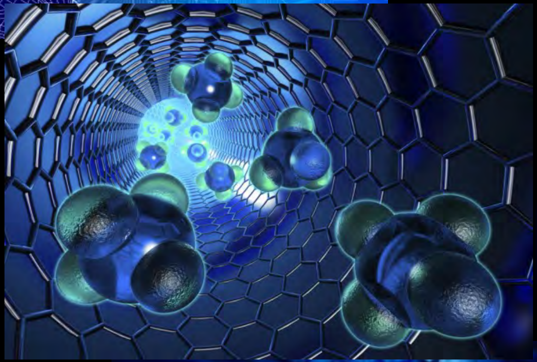

EARTH SYSTEM SCIENCE


Earth's nanomaterials

Major Technological Revolutions in Human History (cont.)

Molecular Biology Revolution

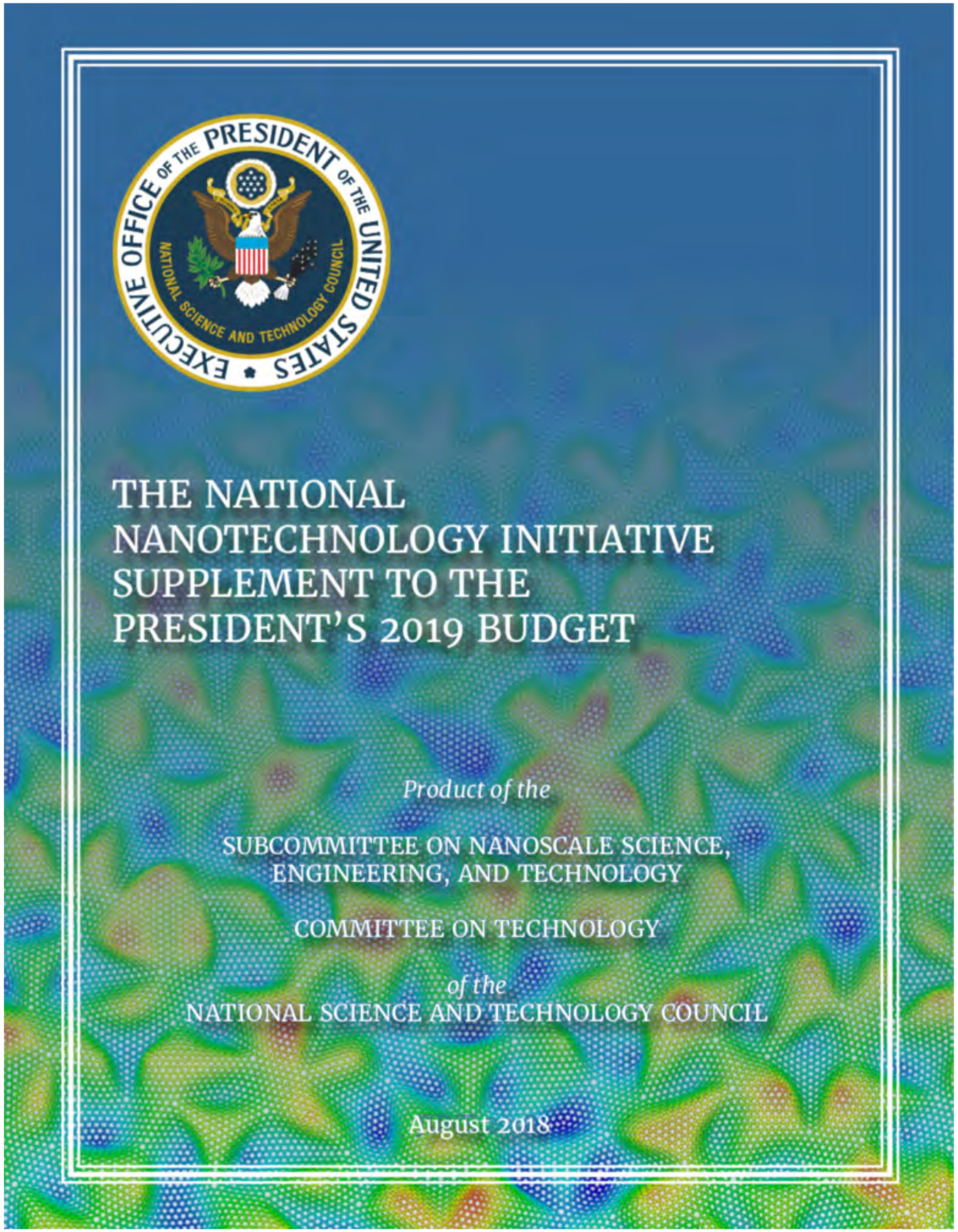
Cognition Revolution, “Decades” of the Brain



Nanotechnology Revolution

Digital / Information Revolution

1930 1940 1950 1960 1970 1980 1990 2000 2010



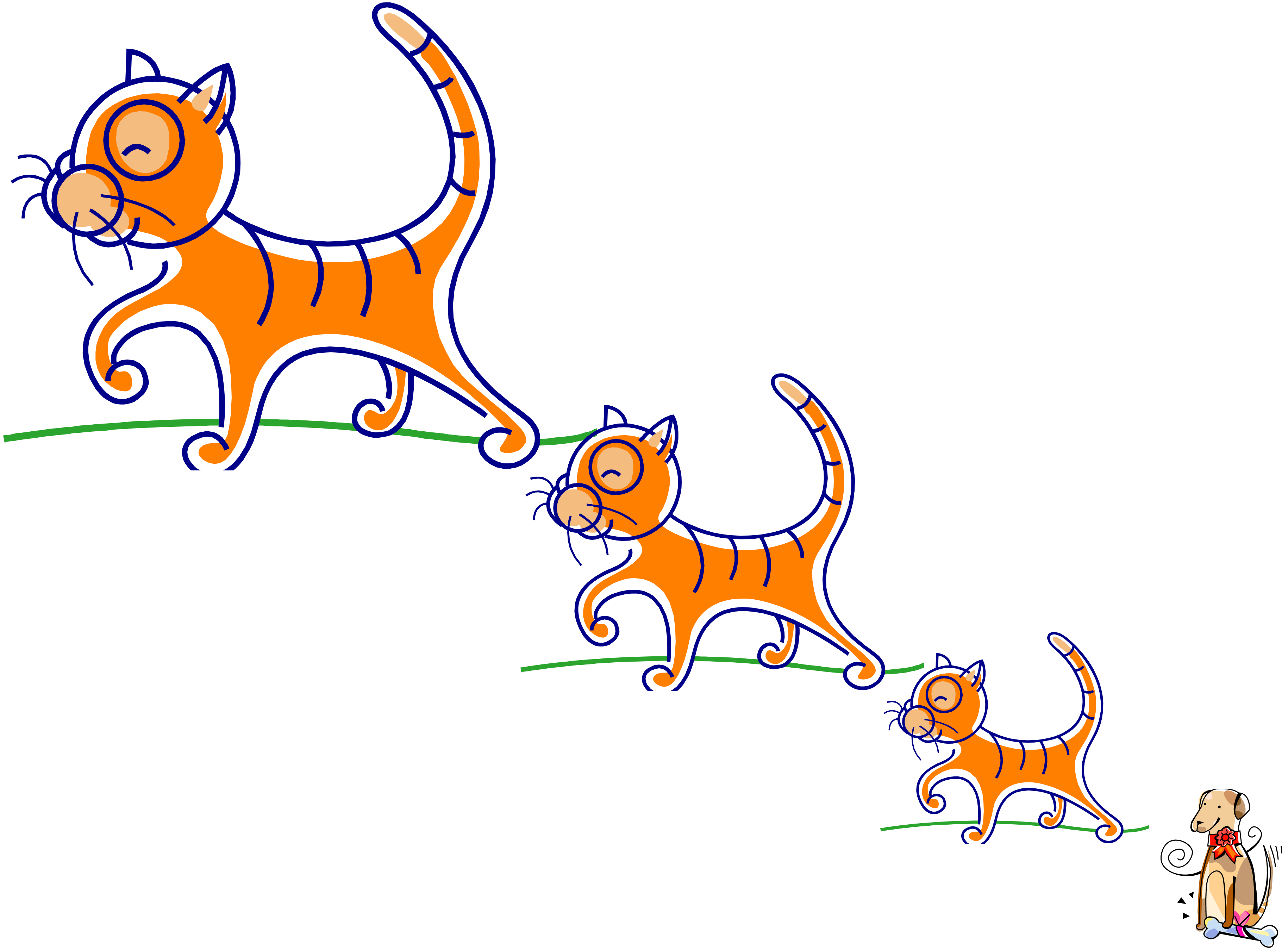
The President's 2019 Budget supports nanoscale science, engineering, and technology R&D at 12 agencies (approx. $1.5B). The five Federal organizations with the largest investments (representing 95% of the total) are:

HHS/NIH (nanotechnology-based biomedical research at the intersection of life and physical sciences).

NSF (fundamental research and education across all disciplines of science and engineering).

DOE (fundamental and applied research providing a basis for new and improved energy technologies).

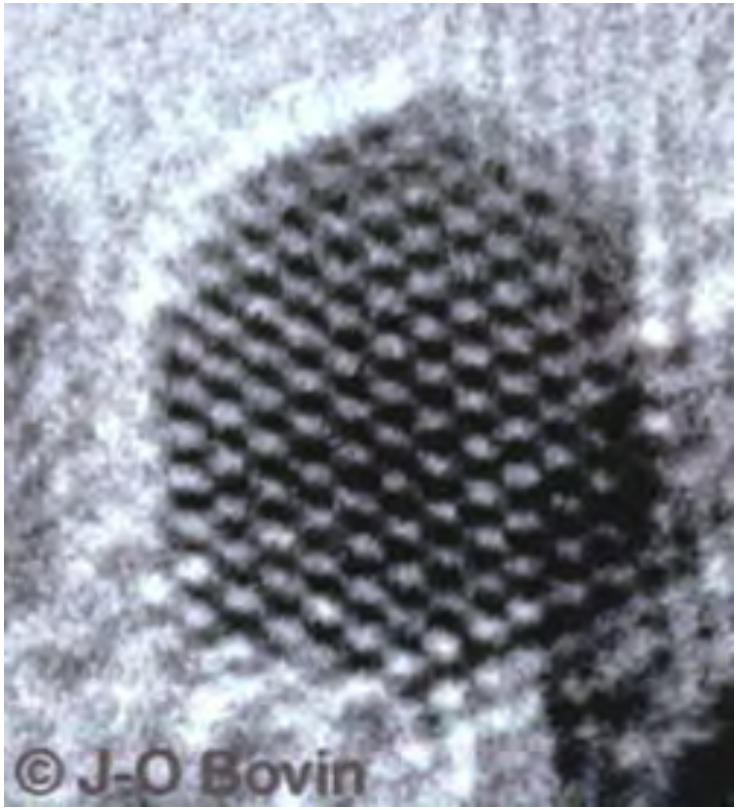
DOD (science and engineering research advancing defense and dual-use capabilities).



Melting temperature
= 1,064°C

GOLD

Melting temperature
= 427°C



Color = gold

GOLD

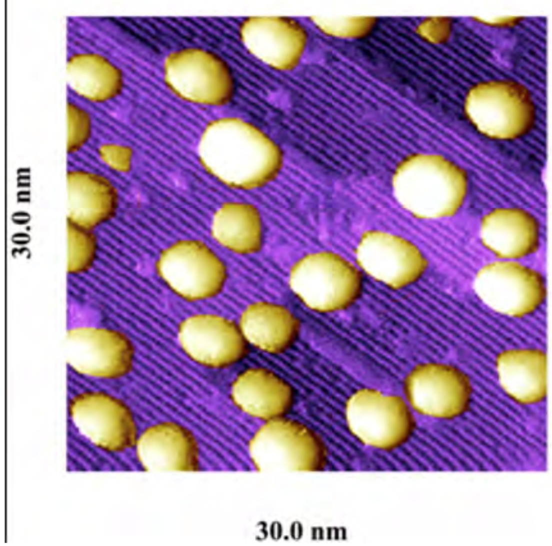
Nano gold

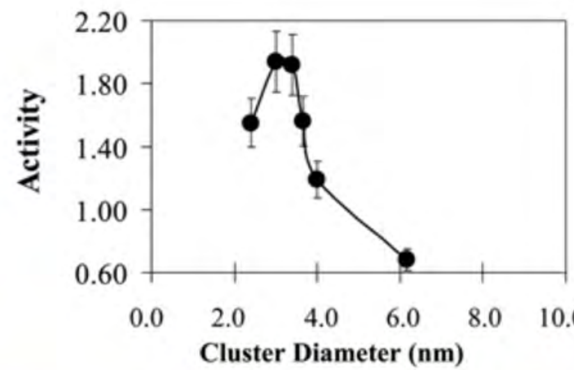
Color = pink, orange, red, purple, violet

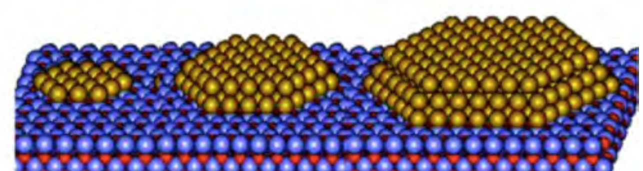
Inert gold in 1,000 year old shipwreck.

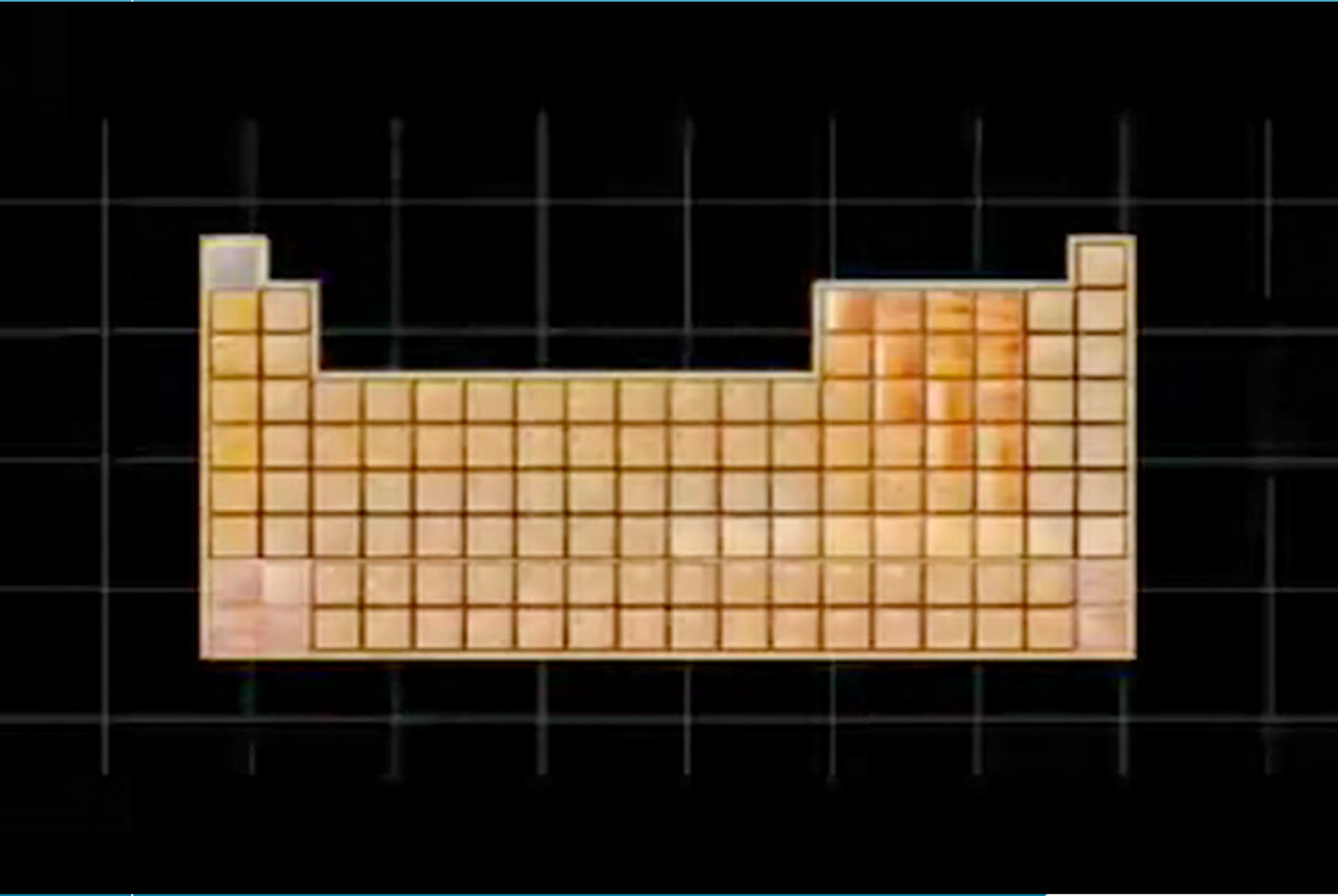
$CO + ½ O_2 \rightarrow CO_2$

Catalytic gold in gas reaction research



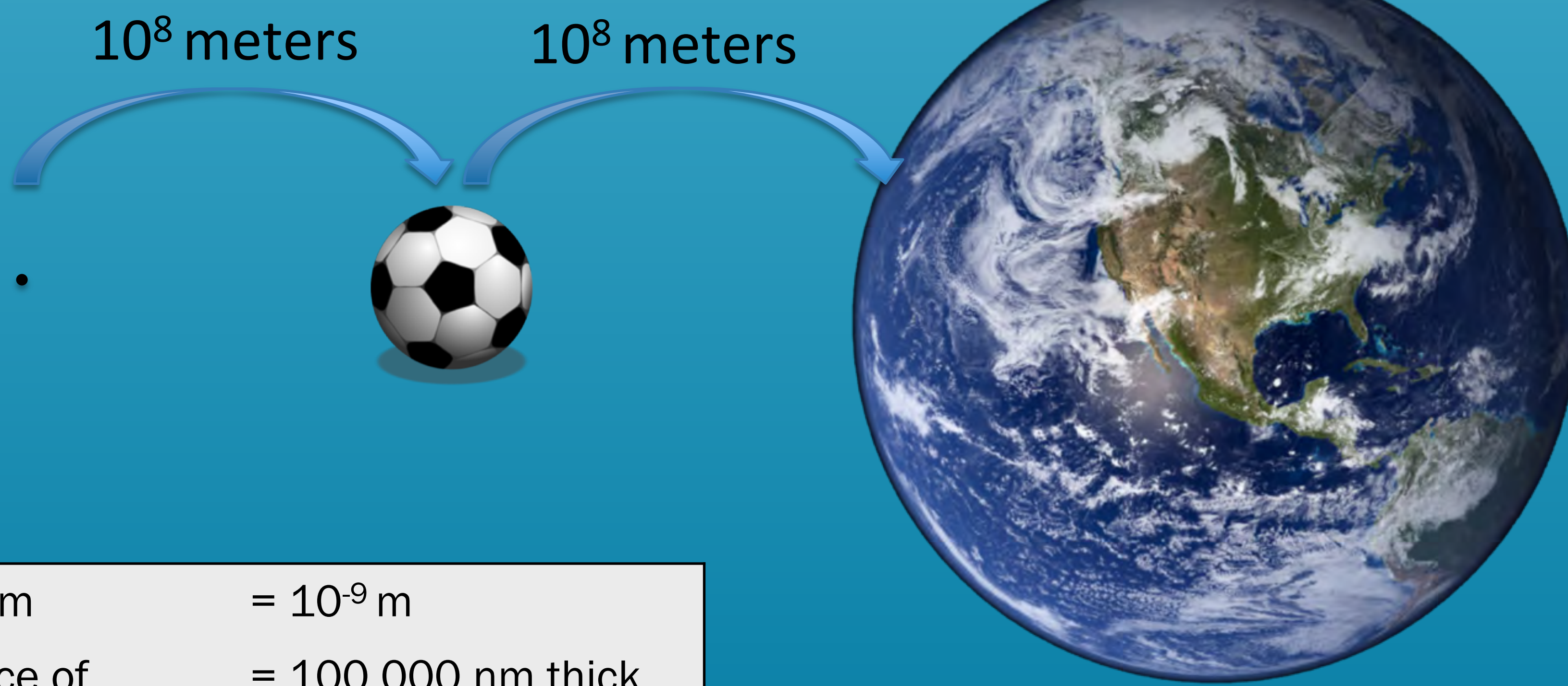






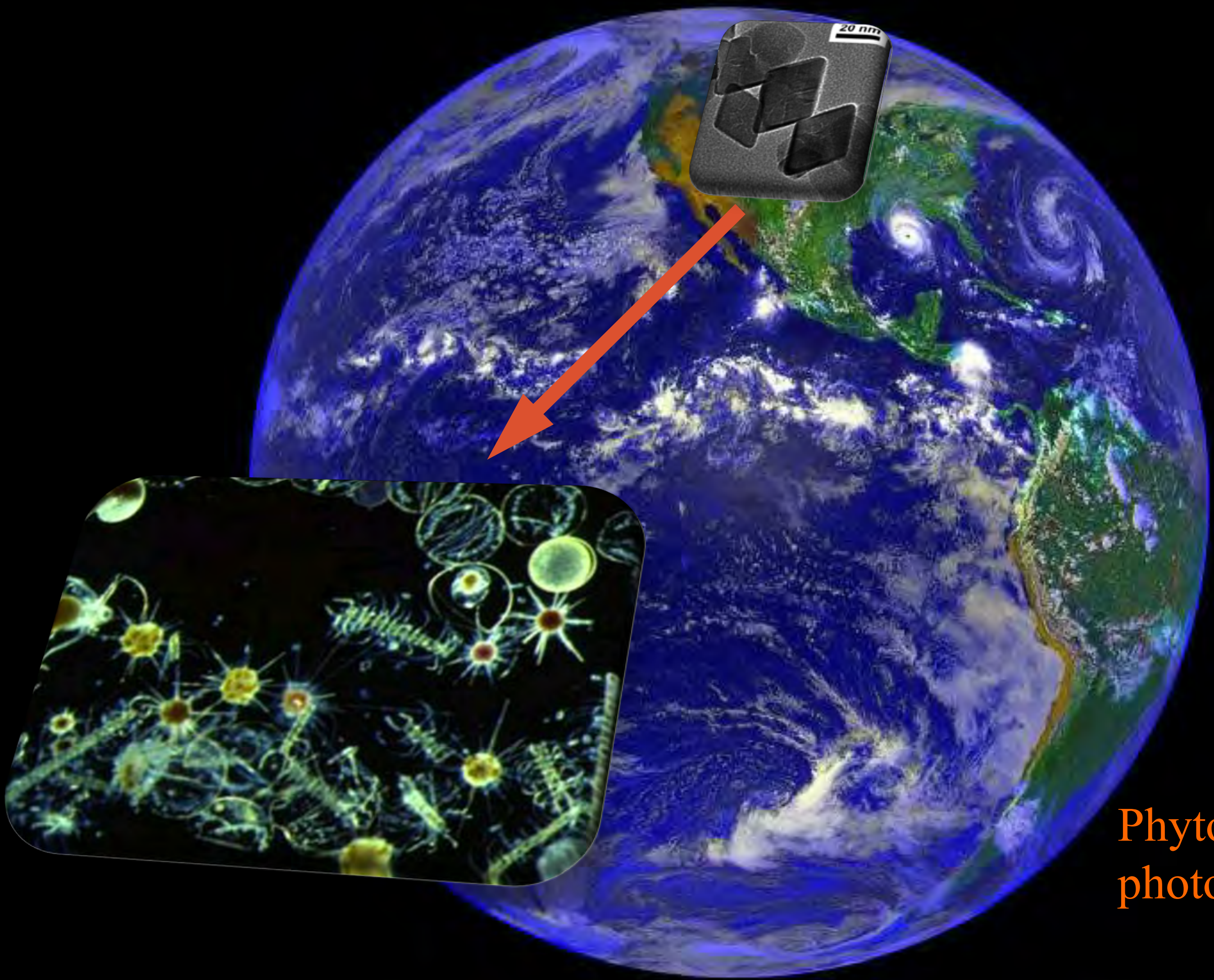
KQED San Francisco

How small is "nano"?



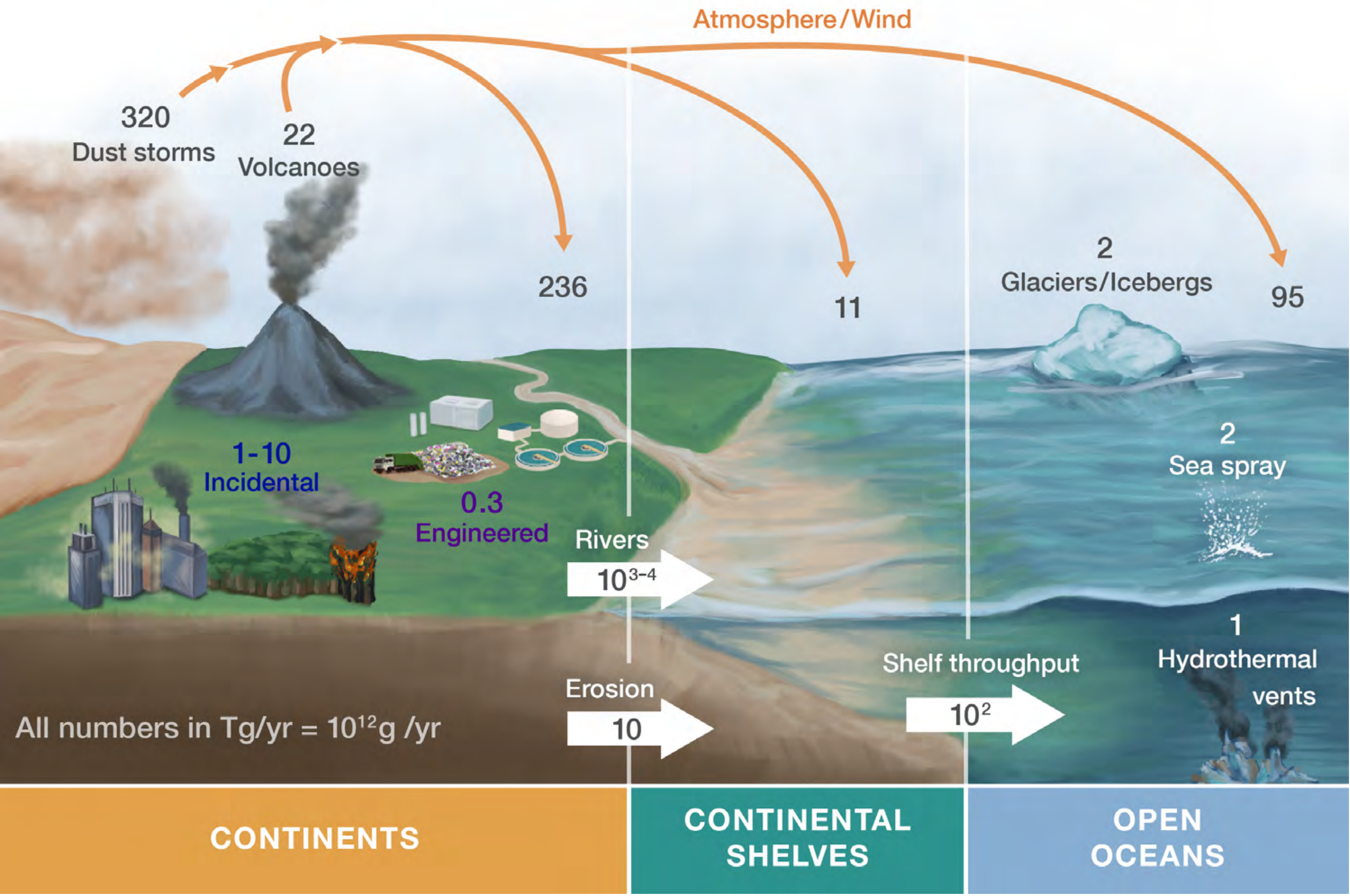
1 nm	= 10^{-9} m
Piece of paper	= 100,000 nm thick
Human hair	= 80,000 nm thick
DNA	= 2.5 nm diameter
Gold atom	= 0.3 nm diameter

So what's the big deal for the Earth sciences!? OK, an example . . .

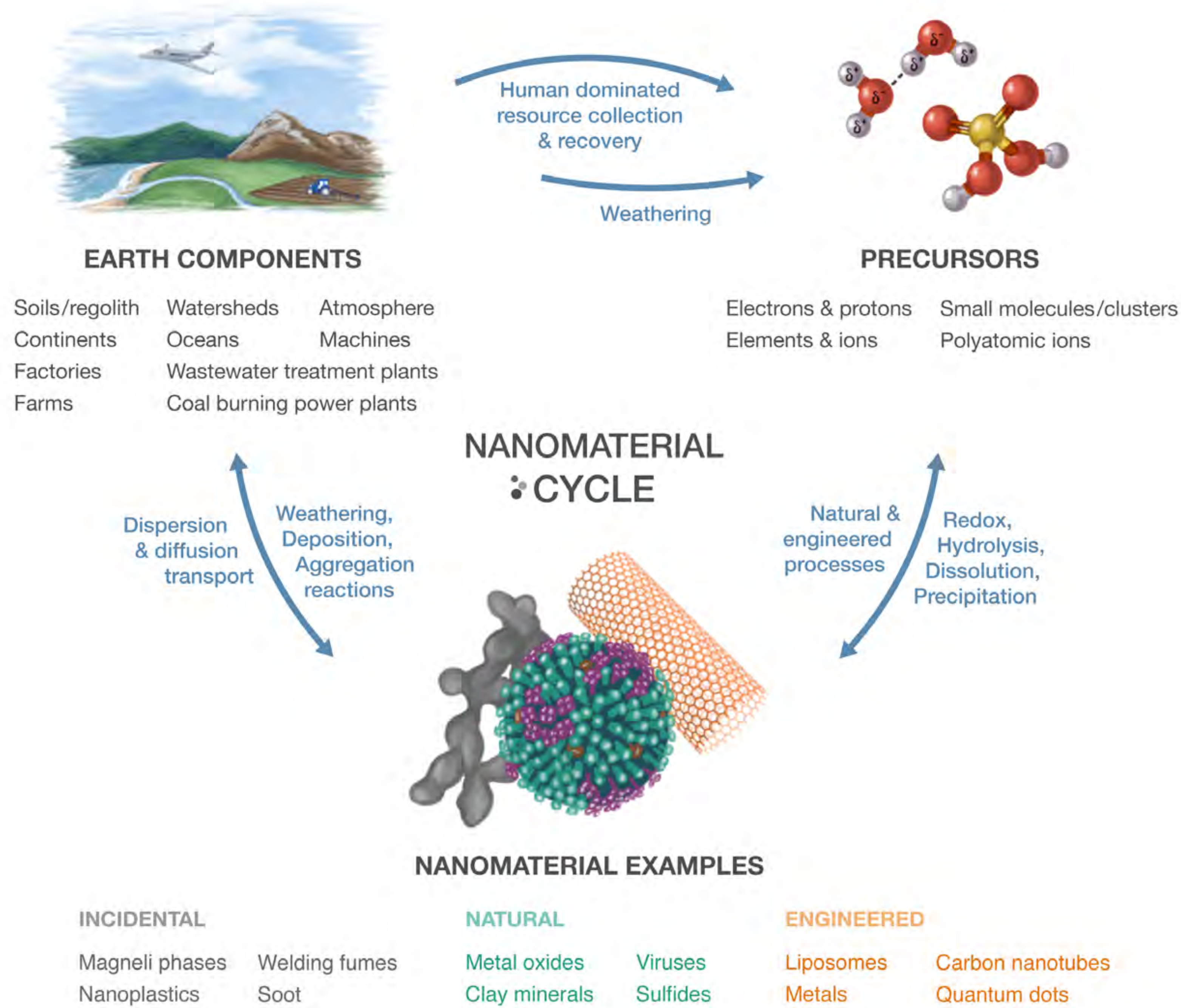


Phytoplankton: half of all photosynthesis on Earth!

Hochella et al. (2008) Science, v. 319, p. 1631-1635.



Atmosphere/Wind
320
Dust storms
22
Volcanoes
236
11
2
Glaciers/Icebergs
95
1-10
Incidental
0.3
Engineered
2
Sea spray
Rivers
10^{3-4}
1
Hydrothermal
vents
Shelf throughput
Erosion
10^2
All numbers in Tg/yr = 10^{12}g /yr
10
CONTINENTS
CONTINENTAL
SHELVES
OPEN
OCEANS


Human dominated
resource collection
& recovery
Weathering
EARTH COMPONENTS
Soils/regolith
Watersheds
Atmosphere
Continents
Oceans
Machines
Factories
Wastewater treatment plants
Farms
Coal burning power plants
PRECURSORS
Electrons & protons
Small molecules/clusters
Elements & ions
Polyatomic ions
NANOMATERIAL CYCLE
Dispersion
& diffusion
transport
Weathering,
Deposition,
Aggregation
reactions
Natural &
engineered
processes
Redox,
Hydrolysis,
Dissolution,
Precipitation
NANOMATERIAL EXAMPLES
INCIDENTAL
Magneli phases
Welding fumes
Nanoplastics
Soot
NATURAL
Metal oxides
Viruses
Clay minerals
Sulfides
ENGINEERED
Liposomes
Carbon nanotubes
Metals
Quantum dots

REVIEW SUMMARY

EARTH SYSTEM

Natural, incidental, and engineered nanomaterials and their impacts on the Earth system

Michael F. Hochella Jr.*, David W. Mogk, James Ranville, Irving C. Allen, George W. Luther, Linsey C. Marr, B. Peter McGrail, Mitsu Murayama, Nikolla P. Qafoku, Kevin M. Rosso, Nita Sahai, Paul A. Schroeder, Peter Vikesland, Paul Westerhoff, Yi Yang

BACKGROUND: Natural nanomaterials have always been abundant during Earth's formation and throughout its evolution over the past 4.54 billion years. Incidental nanomaterials, which arise as a by-product from human activity, have become unintentionally abundant since the beginning of the Industrial Revolution. Nanomaterials can also be engineered to have unusual, tunable properties that can be used to improve products in applications from human health to electronics, and in energy, water, and food production. Engineered nanomaterials are very much a recent phenomenon, not yet a century old, and are just a small mass fraction of the natural and incidental varieties. As with natural and incidental nanomaterials, engineered nanomaterials can have both positive and negative consequences in our environment.

Despite the ubiquity of nanomaterials on Earth, only in the past 20 years or so have their impacts on the Earth system been studied intensively. This is mostly due to a much better understanding of the distinct behavior of materials at the nanoscale and to multiple advances in analytic techniques. This progress continues to expand rapidly as it becomes clear that nanomaterials are relevant from molecular to planetary dimensions and that they operate from the shortest to the longest time scales over the entire Earth system.

ADVANCES: Nanomaterials can be defined as any organic, inorganic, or organometallic material that present chemical, physical, and/or electrical properties that change as a function of the size and shape of the material. This behavior is most often observed in the size range between 1 nm up to a few to several tens of nanometers in at least one dimension. These materials have very high proportions of surface atoms relative to interior ones. Also, they are often subject to property variation as a function of size owing to quantum confinement effects. Nanomaterial growth, dissolution or evaporation, surface reactivity, and aggregation states play key roles in their lifetime, behaviors, and local interactions in both natural and engineered environments, often with global consequences.

It is now possible to recognize and identify critical roles played by nanomaterials in vital Earth system components, including direct human impact. For example, nanomaterial surfaces may have been responsible for promoting the self-assembly of protocells in the origin of life and in the early evolution of bacterial cell walls. Also, weathering reactions on the continents produce various bioavailable iron (oxy)hydroxide natural and incidental nanomaterials, which are transported to the oceans via riverine and atmospheric pathways and which influence ocean surface primary productivity and thus the global carbon cycle. A third example involves nanomaterials in the atmosphere that travel locally, regionally, and globally. When inhaled, the smallest nanoparticles can pass through the alveolar membranes of the lungs and directly enter the bloodstream. From there, they enter vital organs, including the brain, with possible deleterious consequences.

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Read the full article at http://dx.doi.org/10.1126/science.aau8299

OUTLOOK: Earth system nanoscience requires a convergent approach that combines physical, biological, and social sciences, as well as engineering and economic disciplines. This convergence will drive developments for all types of intelligent and anticipatory conceptual models assisted by new analytical techniques and computational simulations.

Ultimately, scientists must learn how to recognize key roles of natural, incidental, and engineered nanomaterials in the complex Earth system, so that this understanding can be included in models of Earth processes and Earth history, as well as in ethical considerations regarding their positive and negative effects on present and predicted future environmental and human health issues. ■

Modern Earth, from a nanoperspective. Earth has thousands of terragrams of natural nanomaterials moving around the planet annually. This is now accompanied by 1 to 10 Tg of incidental nanomaterials formed in or delivered to the atmosphere from, for example, factory and transportation emissions, mining, forest fires, and urban processes, as well as less than a terragram annually from engineered nanomaterials that make their way into the environment mostly through wastewater treatment plants, holding ponds, and landfills. All of these, together, affect the entire Earth system.

CREDIT: ROSE PERRY/PACIFIC NORTHWEST NATIONAL LABORATORY'S CREATIVE SERVICES DEPARTMENT

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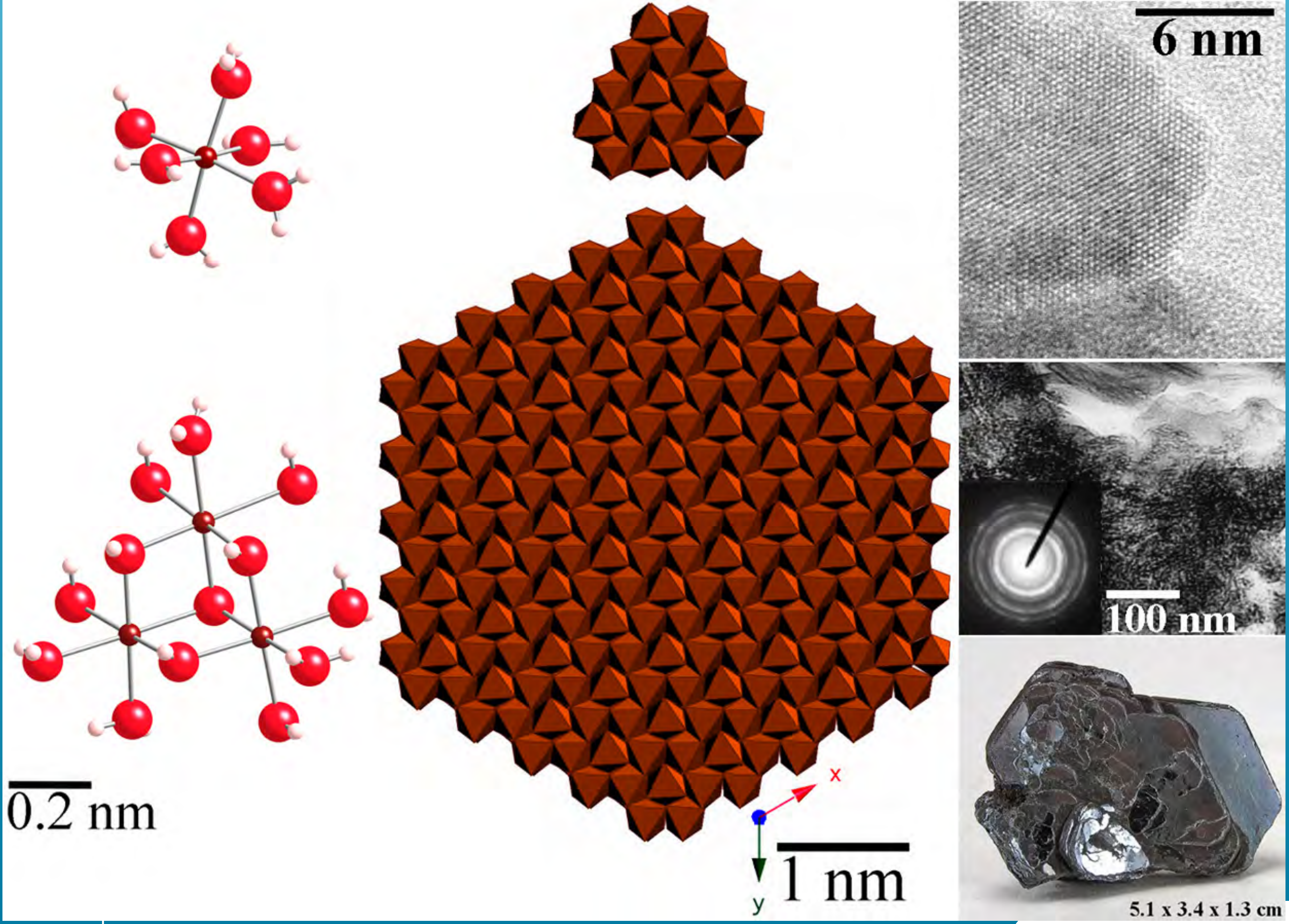
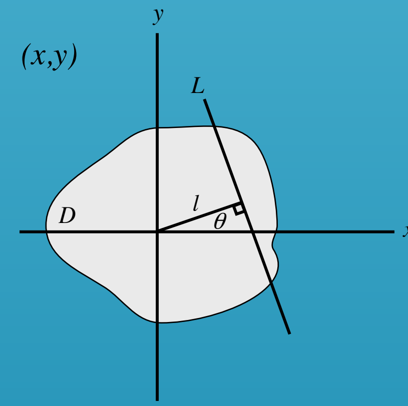


Hochella et al. (2008) Science, v. 319, p. 1631-1635.

Nano-hematite, HAADF-STEM tomography, aggregate, 30 nm

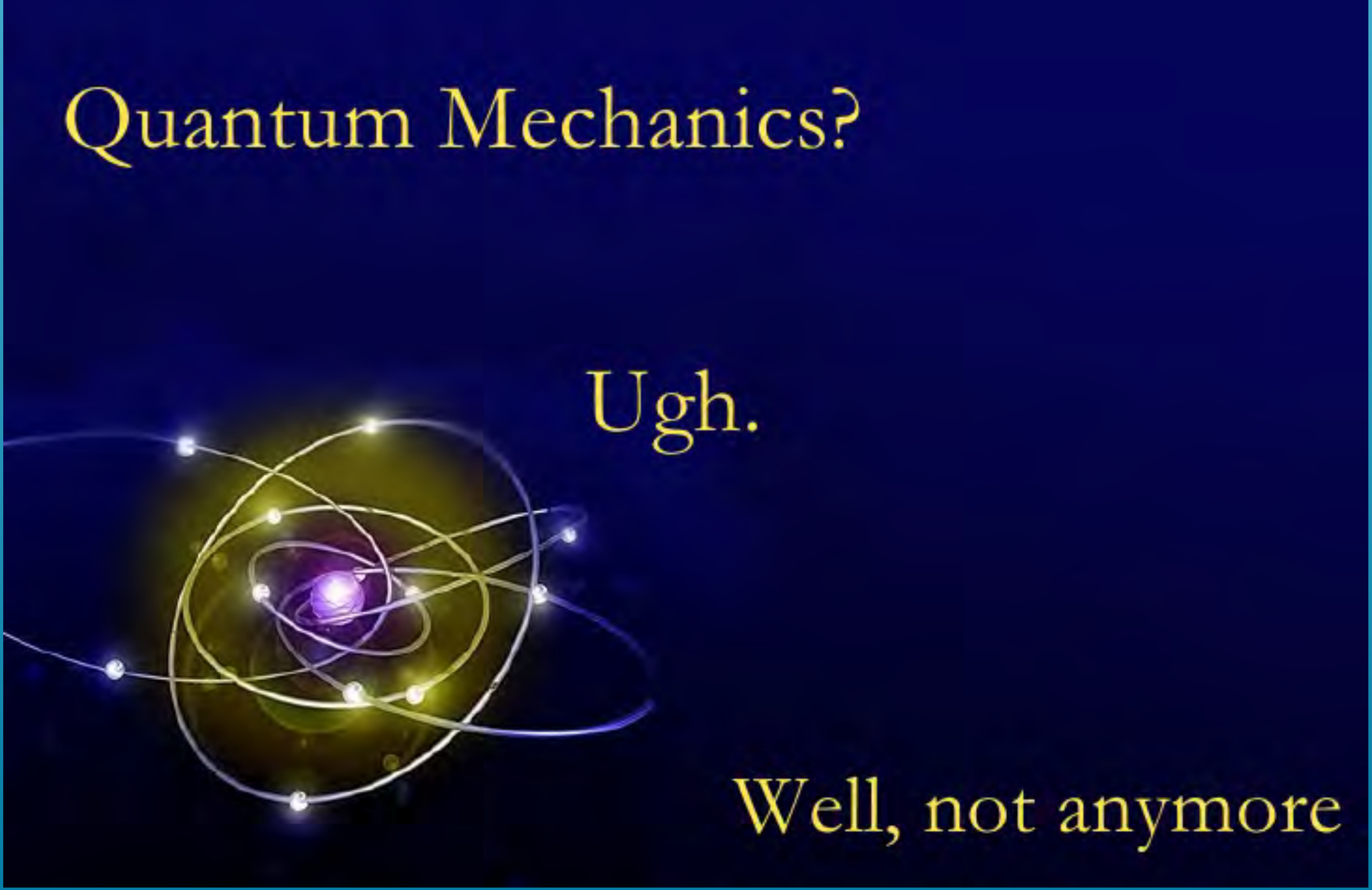


$$Rf = \int_L f(x,y)\,\mathrm{d}s.$$

Radon J. (1917)
Leipzig Math.-Phys.

Echigo et al. (2013) *Am. Min.*

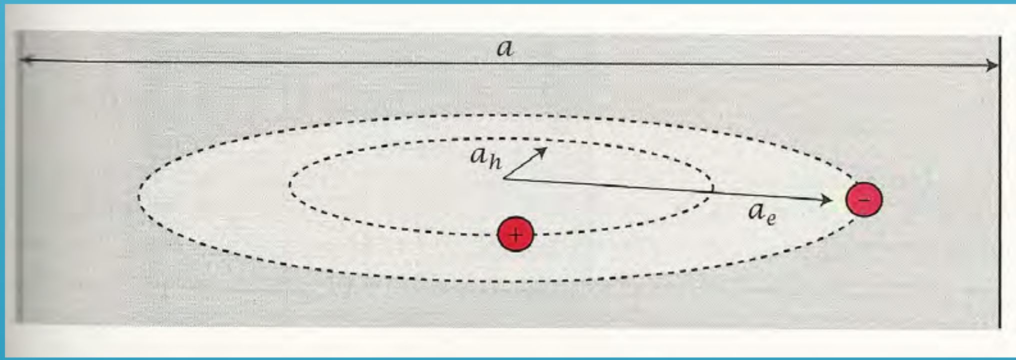
Purely quantum mechanical considerations




ψ!

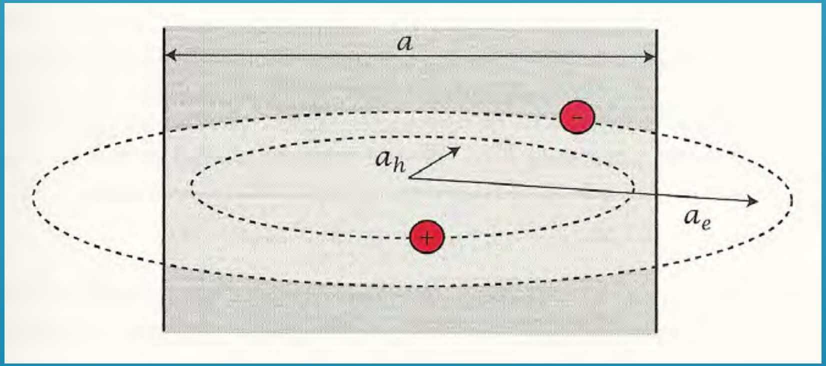
Weak quantum confinement regime:

$$a_e, a_h < a$$



Intermediate quantum confinement regime:

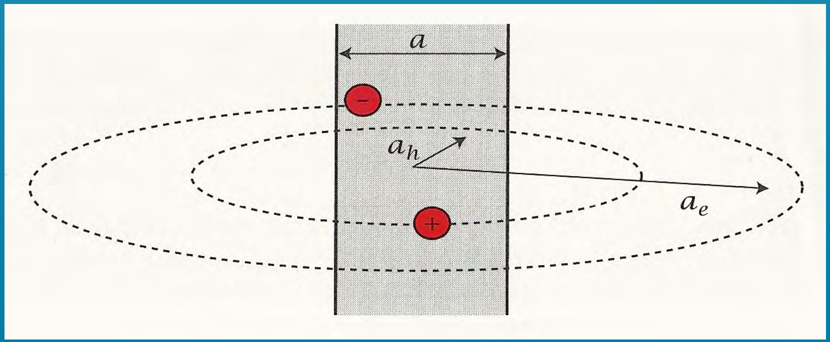
$$a_e < a < a_h$$



For hematite: 7.0 nm 3.8 nm

Strong quantum confinement regime:

$$a < a_e, a_h$$



a_B written in terms of a_0:

$$a_B = \frac{\varepsilon m_0}{\mu} a_0$$

Quantum Confinement in Hematite

$$a_B = \frac{(32)(9.11\times10^{-31})}{(1.43\times10^{-31})}(5.28\times10^{-11}) = 10.8\times10^{-9}m = 10.8nm$$

For PbS galena: $a_B = 18nm$