

NANOTECHNOLOGY APPLICATIONS IN GEOSCIENCE

e – Learning Material - Unit: 3 & 4

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NANODIAMONDS FROM AGB STARS: A NEW TYPE OF PRESOLAR GRAIN IN METEORITES

Presolar nanodiamonds found in meteorites (Lewis et al. 1987) and available for study in the laboratory are traditionally believed to have been formed in association with Type II supernovae (Clayton 1989) at some point before formation of the solar system (4.6 Gyr ago)

The major argument for this is the presence within the diamonds of xenon displaying an isotopic signature thought to arise from supernovae

However, as has long been known, since only 1 out of 10^6 nanodiamond grains contains an atom of xenon, only a fraction (10^6) of the total diamond population may actually arise from supernovae

Indeed, it has been demonstrated that some nanodiamonds probably formed in the solar nebula (Dai et al. 2002; Gilmour et al. 2005). Furthermore, the mechanism of the formation of diamonds, which is supposed to be mostly a chemical vapor deposition (CVD) process (Daulton et al. 1996).

Recently, nanodiamonds have been identified spectroscopically in a few stars (Kerckhoven et al. 2002) one of which (HR 4049) is at the post-AGB phase of evolution.

This means that nanodiamonds from AGB stars could also be present in meteorites

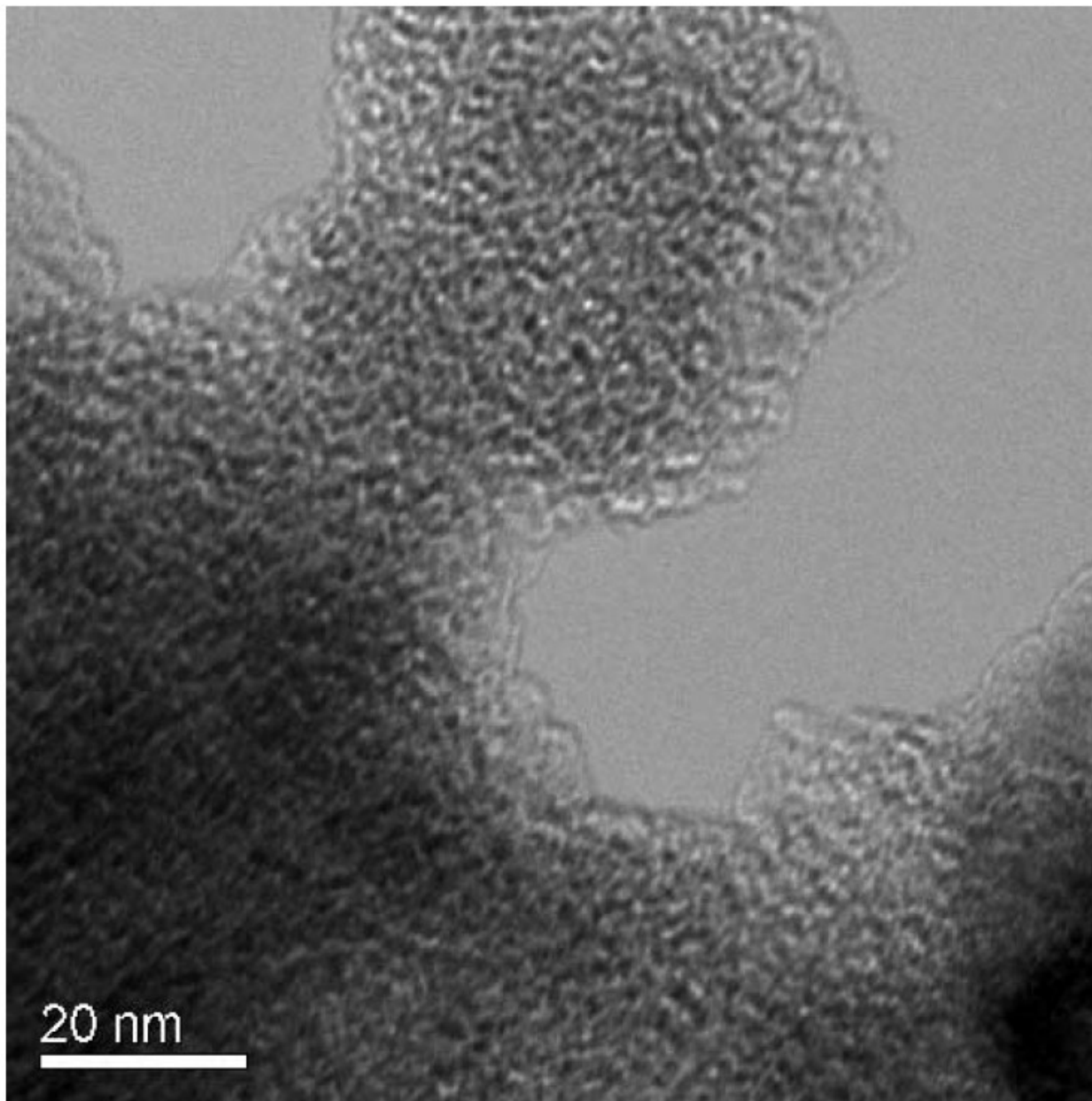


FIG. 10.—High-resolution TEM image of the nanoparticles clump of BD-9.

Deep Diamonds Shed Light on Ancient Continental Movements

Deep inside Earth, hellish heat and pressure have been cooking rocks and altering their chemical structure since the planet formed about 4.5 billion years ago.

But not everything gets roasted. Tiny part of mineral that became trapped in diamonds billions of years ago remain pristine, because diamonds are for the most part chemically inert. "In essence, diamonds are time capsules from Earth's mantle," says Steven Shirey, a geochemist at the Carnegie Institution for Science in Washington, D.C.



Analyses of inclusions in diamonds, such as the garnet (red) trapped inside this gem when it formed, suggest that modern-style plate tectonics began about 3 billion years ago.

EXPECTED STORAGES OF NANO-DIAMONDS AND/OR DIAMONDS IN THE LUNAR ROCKS.

Diamonds with large size formed at deeper mantle are main characteristics of the active water-planet Earth due to main sources of carbon from life-materials on the dynamic surface and circulated plate-tectonics and mantle convection, though there is still problem to explain to move down and up by light element carbon.

Main carbon storage on the Moon without ocean and air is mainly in the brecciated or metamorphosed rocks. The main purpose of the paper is to discuss source of diamonds with nano- and large sizes probably found in the lunar breccias.

Expected diamond crystal in the lunar rocks:

If carbon-bearing materials (such as carbon dioxides) are stored in deeper Moon during giant impact event with air-planets of primordial Earth, these carbon bearing materials are main sources of diamond carbon of the lunar mantle.

Evidences of such deeper carbon are found by increased carbon content of lunar brecciated rocks, and deeper sources of terrestrial diamonds which has big event of giant impact.

This suggests that smaller diamond crystal will be found at rim of impact craters, some boundary of the highland and lunar Mare, or deeper cliffs on the Moon in future explorations.

As nano-diamonds formed by shock-wave process with quenched reaction can be found at lunar surfaces of meteoritic impacts, and deeper interiors of moonquake explosions (i.e. underground explosions similar with surface quake).



Magnetic nanostructures in organic gases – Palaeotectonic Study

The studies were carried out to produce nanostructures in both permalloy (80:20 Ni:Fe) and in iron (later oxidised to magnetite Fe_3O_4) to test and verify the theoretical predictions used to reconstruct the motion of tectonic plates from the magnetisation of rocks containing natural magnetite particles.

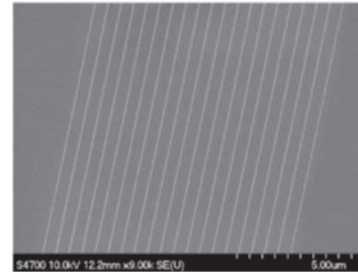


Figure 1: 50nm lines (pitch 500nm) transferred into a NiFe layer using $\text{CH}_4/\text{H}_2/\text{O}_2$.

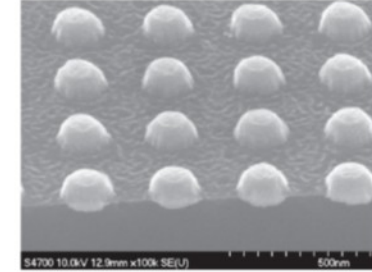


Figure 2: 180nm dots on 310nm pitch transferred into a Fe layer using CO/NH_3 .

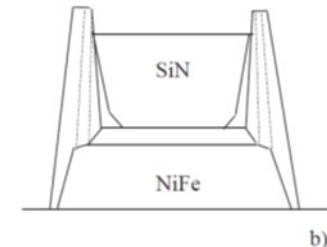
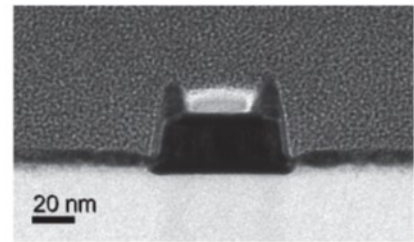
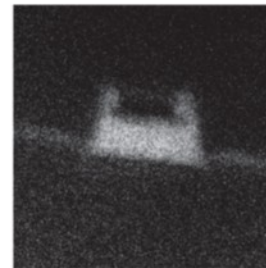
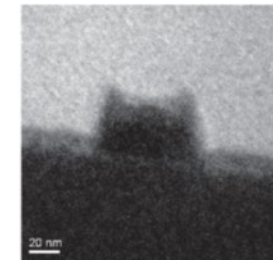


Figure 3 a) TEM cross-section of Ni:Fe after etching in $\text{CH}_4/\text{H}_2/\text{O}_2$. b) composition of the nanostructure - details of all regions will be given c) composition mapping of same sample.



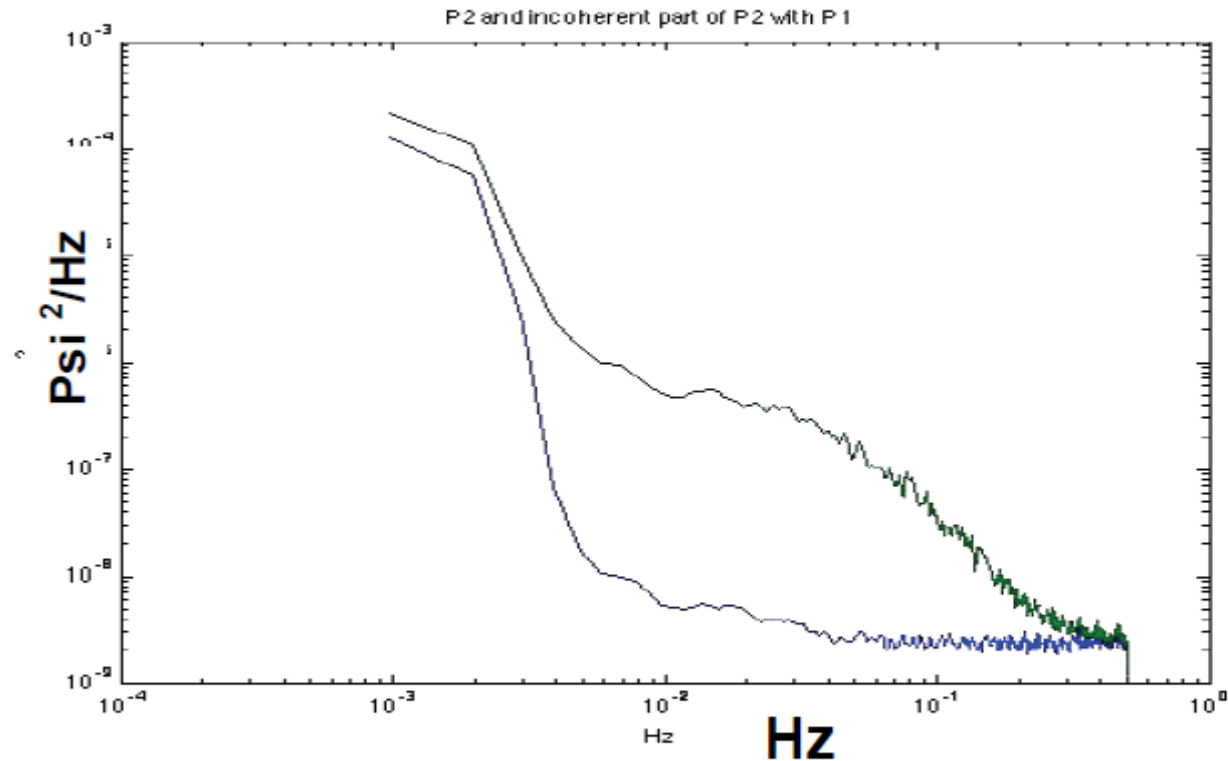
c) Ni map



O map

Nano-Resolution (parts-per-billion) Oceanic and Atmospheric Pressure Sensors

Digiquartz® Depth Sensor Noise Floor

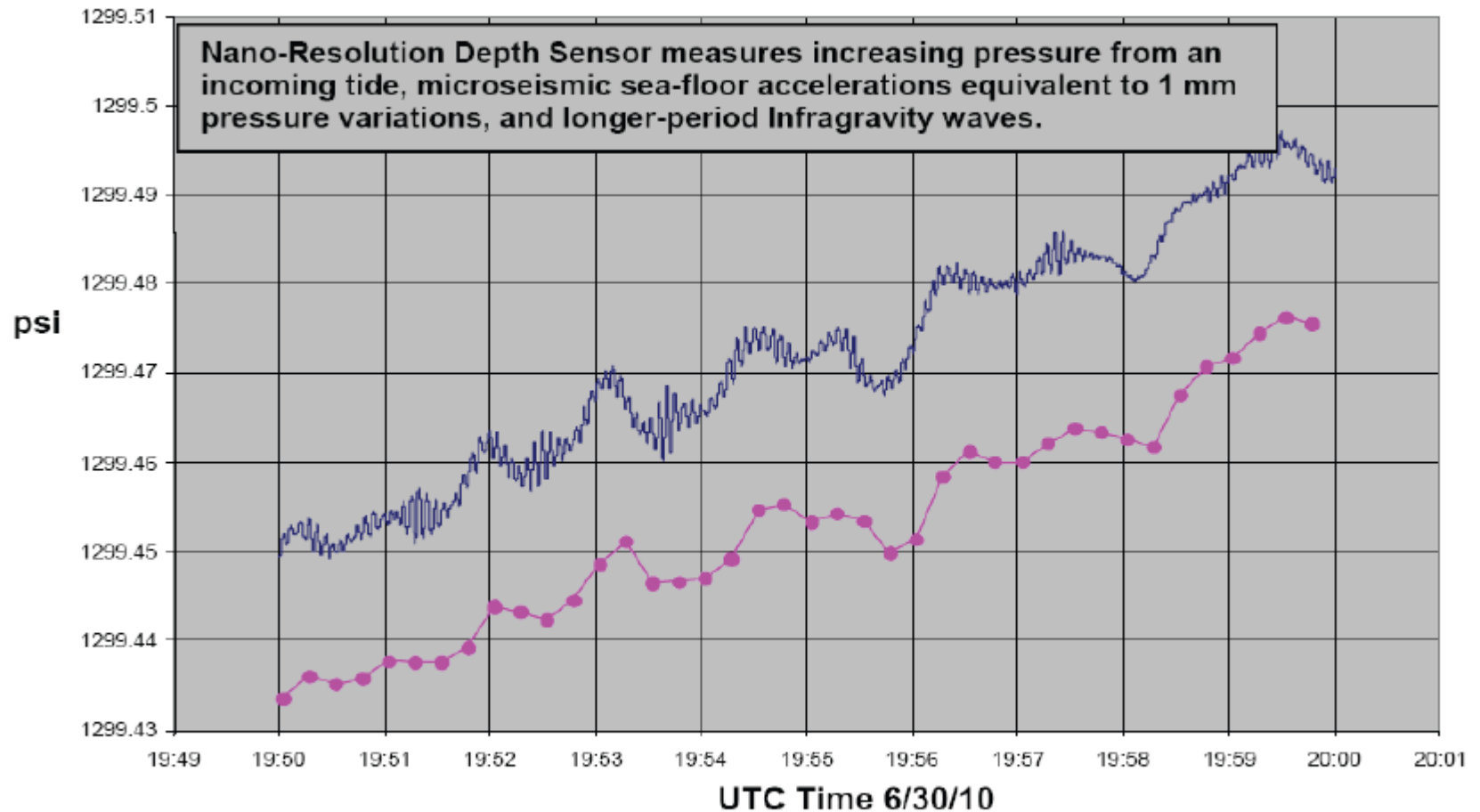


Infrasound ambient measured with a 7000 meter depth sensor

Instrument self-noise less than $0.14 \text{ Pa}^2/\text{Hz}$

Noise floor of a 2000 m depth sensor is $0.01 \text{ Pa}^2/\text{Hz}$

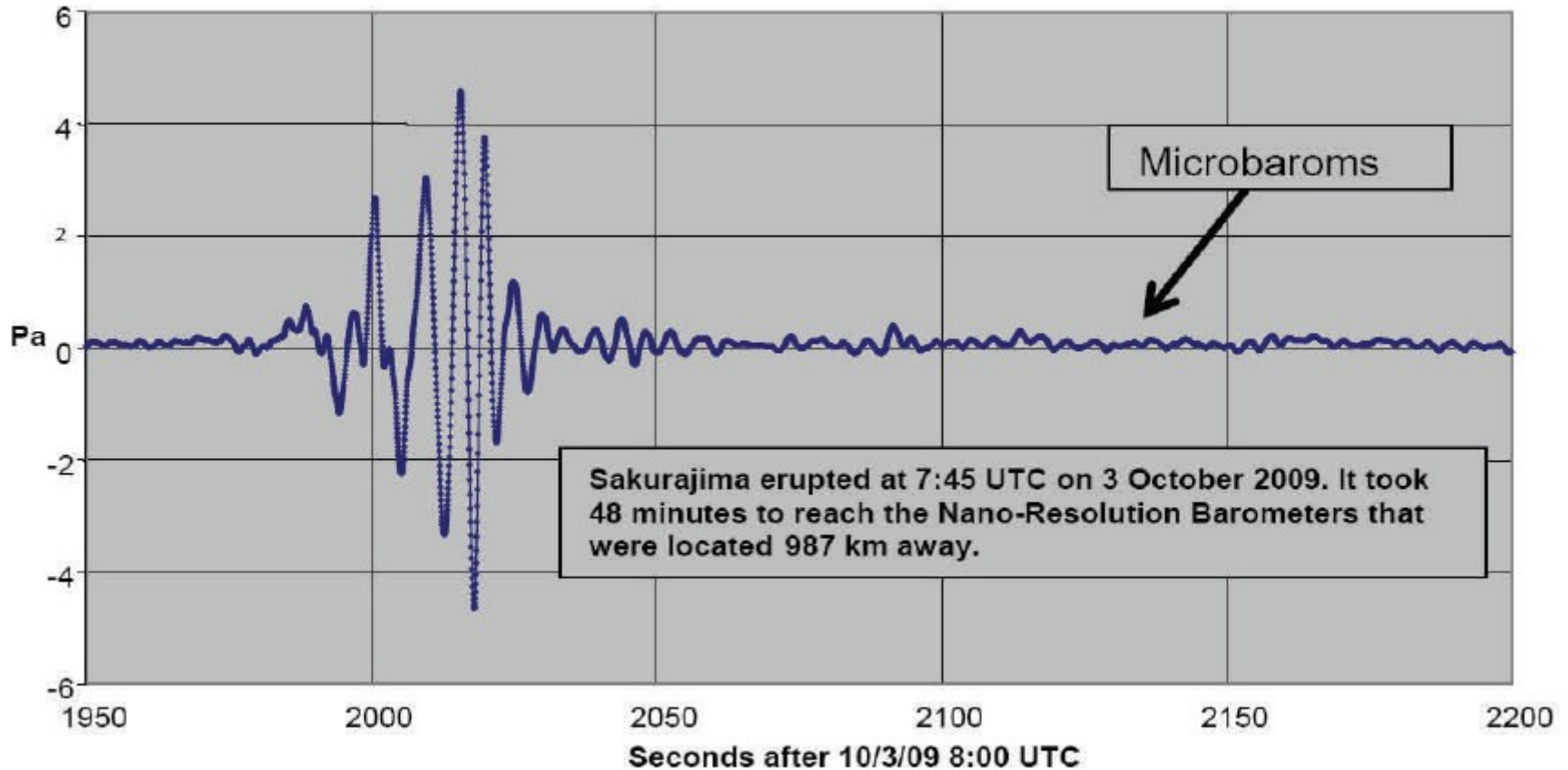
Comparison Nano-Resolution Depth Sensor / Standard BPR



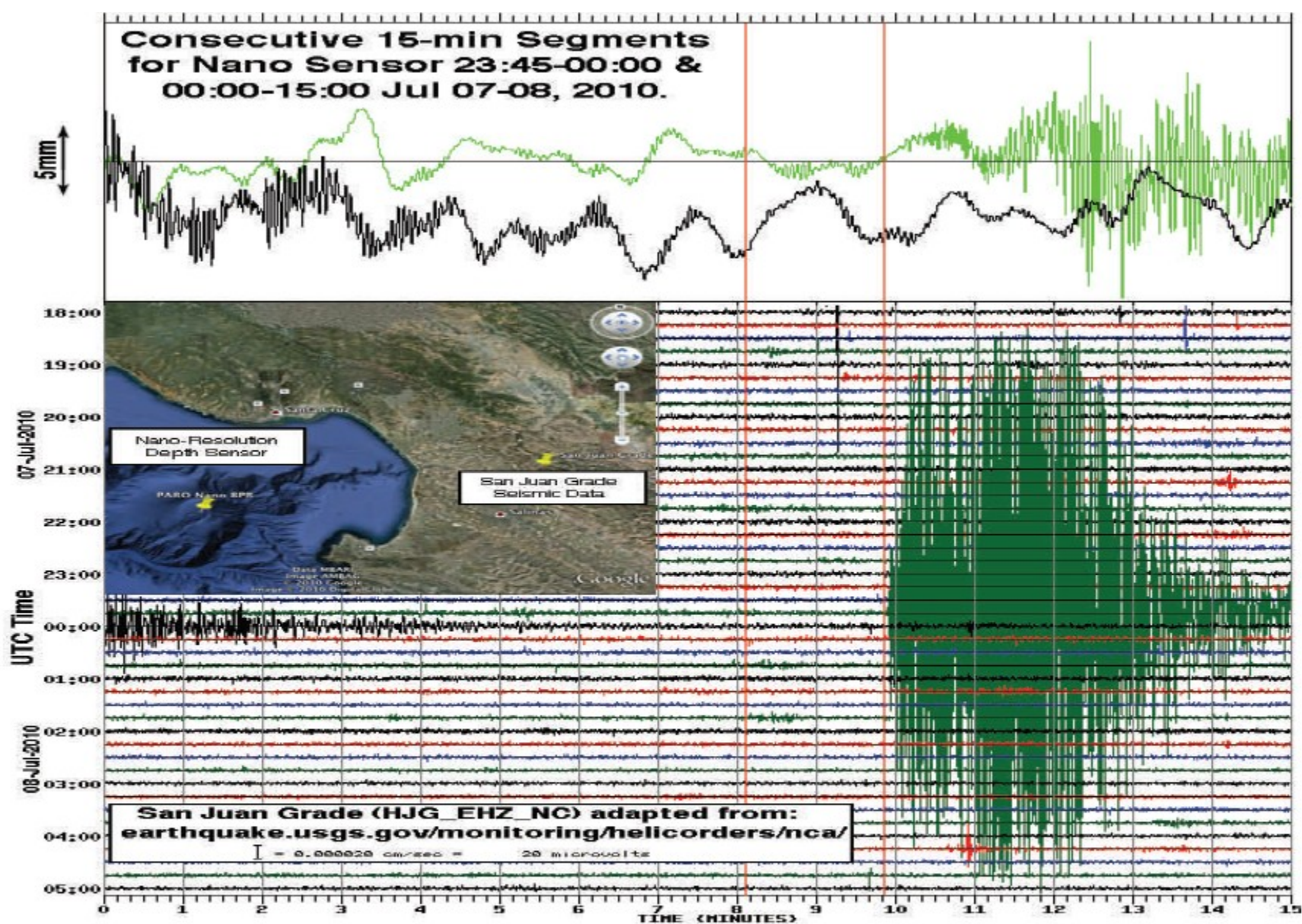
Nano-Resolution Depth Sensor Measurements

Sakurajima Eruption 10/3/09 7:45 UTC

Station IS30 S/N 111244 Bandwidth 0.05 - 1.4 Hz



Nano-Resolution Barometer Measurement of Volcanic Eruption



Nano-resolution Depth Sensor & Land-based Seismometer Comparison
Plot courtesy of NOAA-PMEL

FAULTS AND NANOCOATINGS

Geologists Discover Slippery Rocks Coat the San Andreas Fault

In an underground observatory located on the San Andreas Fault, geologists are studying samples of rock from deep inside the Earth's crust.

Most earthquakes are the result of tectonic plates unlocking from one another in a sudden release of energy. Researchers found that nano-coatings of clay on these rocks grease the faults, reducing friction between plates, which changes the dynamics of earthquakes. Understanding more about the fault allows geologists to more deeply comprehend earthquake cycles

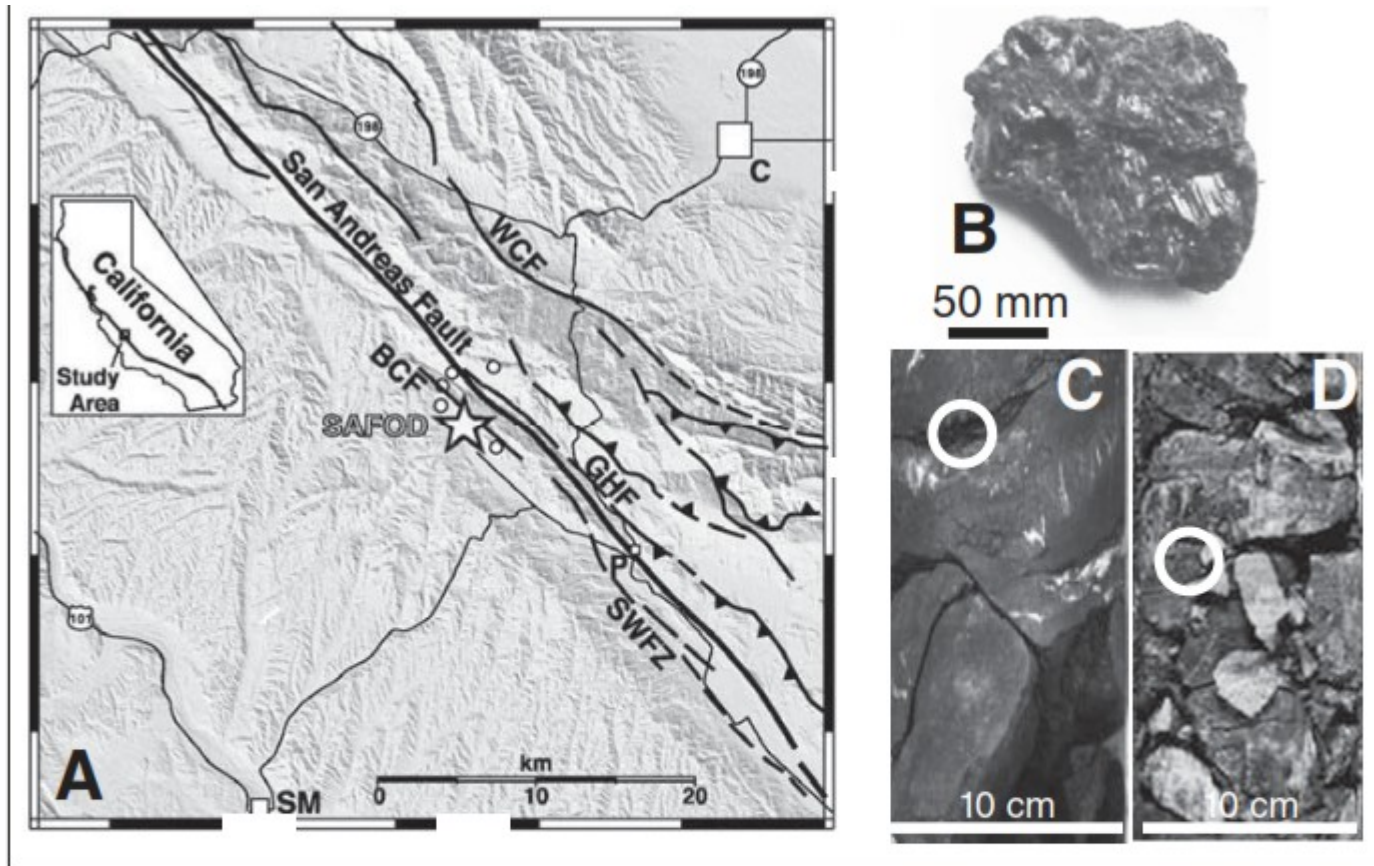


Figure 1. A: Fault map of San Andreas Fault Observatory at Depth (SAFOD) location (after Bradbury et al., 2007). BCF—Buzzard Canyon fault; WCF—Waltham Canyon fault; GHF—Gold Hill fault; SWFZ—Southwest fracture zone; P—Parkfield; SM—San Miguel; C—Coalinga. **B:** Typical rock chip with polished surfaces and slickensides. **C, D:** Fault rocks sampled from the 2005 and 2007 cores.

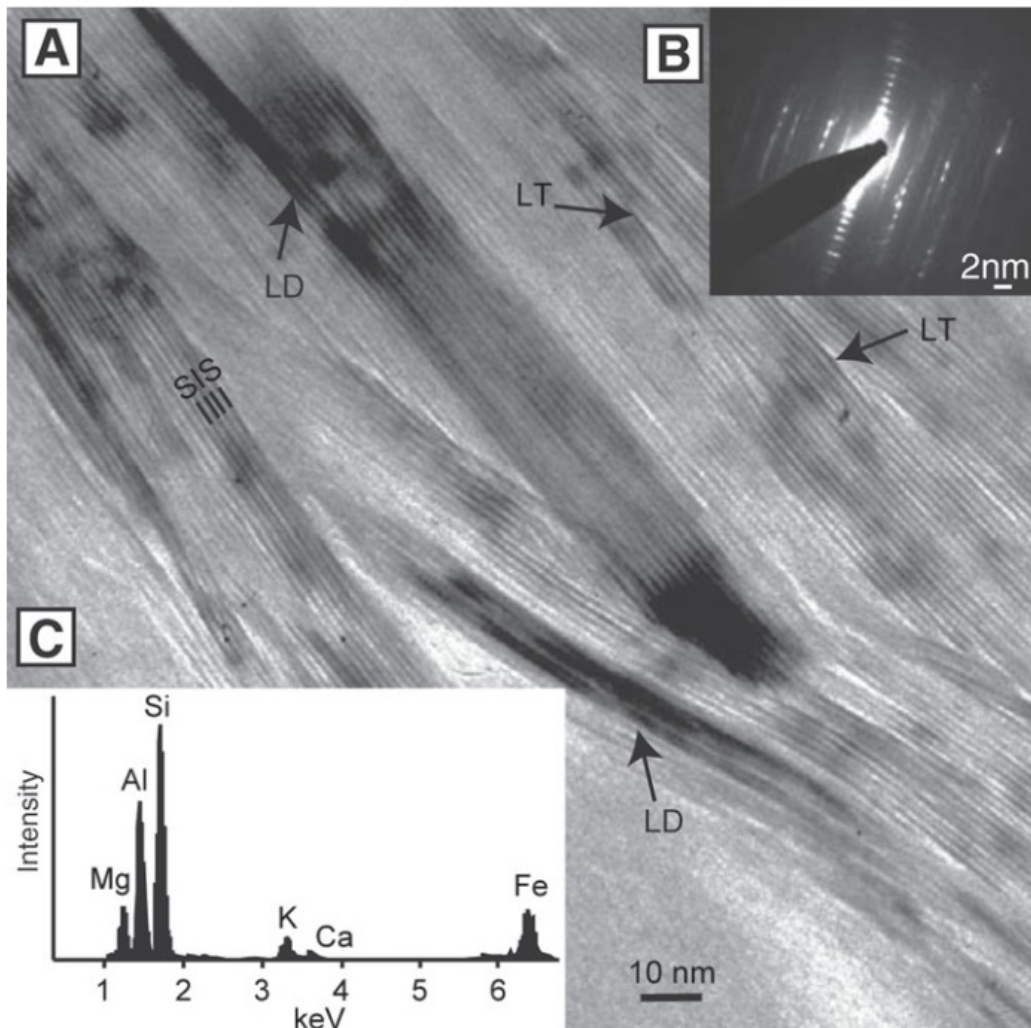


Figure 2. A: High-resolution transmission electron microscopy image of nanoclay coatings. Low-angle arrays of 5–20-nm-thick, ordered illite-smectite particles are arranged in <100-nm-thick mineralized sheets. I—illite; S—smectite layers; LD—lattice distortion; LT—lattice termination. B: Diffraction pattern of illite particles (1Md polytype) with streaking of nonbasal (hkl) planes. C: Chemical composition of authigenic I-S, with notable Mg and Ca in smectite interlayers.

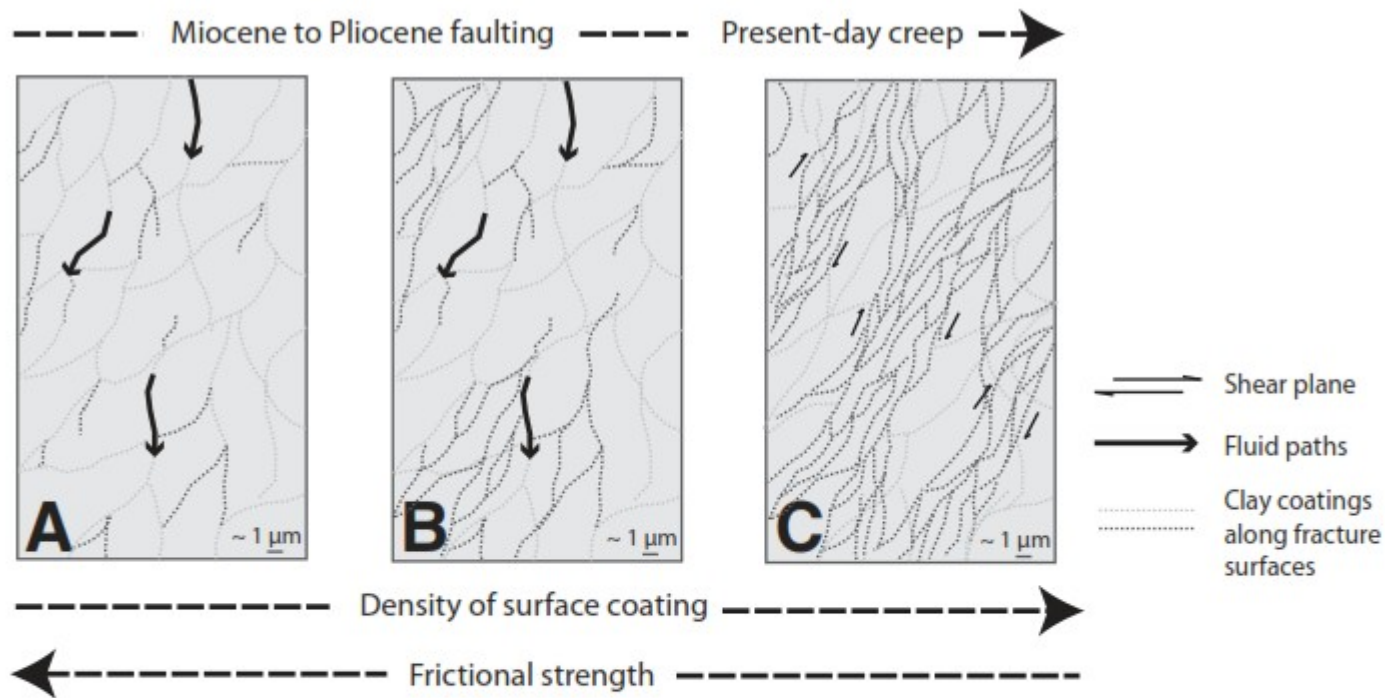


Figure 4. Schematic illustration of evolution of fault rocks and development and role of nanocoatings in mechanically weak San Andreas fault. A: Initial fracture generation during (microseismic) displacement is followed by fluid circulation and (B) nucleation, dissolution, and mineralization processes on fracture surfaces with deposition of hydrated clay phases. C: Creep is then located along the interconnected nano-coated fractures within mudrock fractured shale horizons.

Earthquakes are most common along fault lines. The most famous fault is the San Andreas Fault in California which marks the plate boundary between the Pacific oceanic plate and the North American continental plate. It is more than 650 miles long.

There are many different kinds of faults, but all of them involve different plates of rock pushing tightly together and creating friction as they move. The nanocoatings recently found by geologists are changing how they understand the behavior of faults. These slick nanocoatings, fractions of a millimeter thick, have been found at fault boundaries, where they can make it weaker and more susceptible to movement.

Layer-Block Tectonics, a New Concept of Plate Tectonics - An Example from Nansha Micro-Plate, Southern South China Sea

The Layer-block tectonics (LBT) is a new theory describing the layer-slip structure of lithosphere (Liu et al., 2002, 1999; Sun et al., 1991).

According to this theory, a lithosphere plate, continental lithosphere plate in particular, is considered a composite of sub-plates connecting with each other horizontally and overlapping with each other vertically.

The term “Layer” in the LBT emphasizes the rheological and stratifying characteristics of the lithosphere and the guiding and controlling role of mechanically “soft” layers with different deepness in the layer-slip movement of the lithosphere during the process of tectonic deformation.

The term “block”, on the other hand, emphasizes the discontinuity of various types of geological bodies segmentalized by dip-slip or strike-slip movement of lithosphere in horizontal direction.

The obvious difference of the LBT from the from the plate tectonics theory, is that the LBT emphasizes the geotectonic effect of multi-levels of gliding surfaces within lithosphere upper mantle including rheospheric top surface, Moho surface, mid-crust, top surface of sedimentary basement, and so on, rather than only emphasized singular Moho gliding surface in plate tectonics or the plate tectonics.

The lithosphere can be divided into different layers by the characteristics of material, energy, structure, rheological and chemical stratification at different depths (Su et al., 1996; Song et al., 1996; Wang et al., 1996; Wang, 1992; Rushentsev and Trifonov, 1985; Oxburgh, 1972).

These layers interrelate with each other and stack-and-piece together to form an integral lithospheric aggregate. As the manifestation of this nature of stratification, the LBT is the result of bedding layer-slip, dip-slip (both in positive and negative direction) and strike-slip (in slant direction, sinistral or dextral) of geologic bodies under tectonic forces (vertically or horizontally).

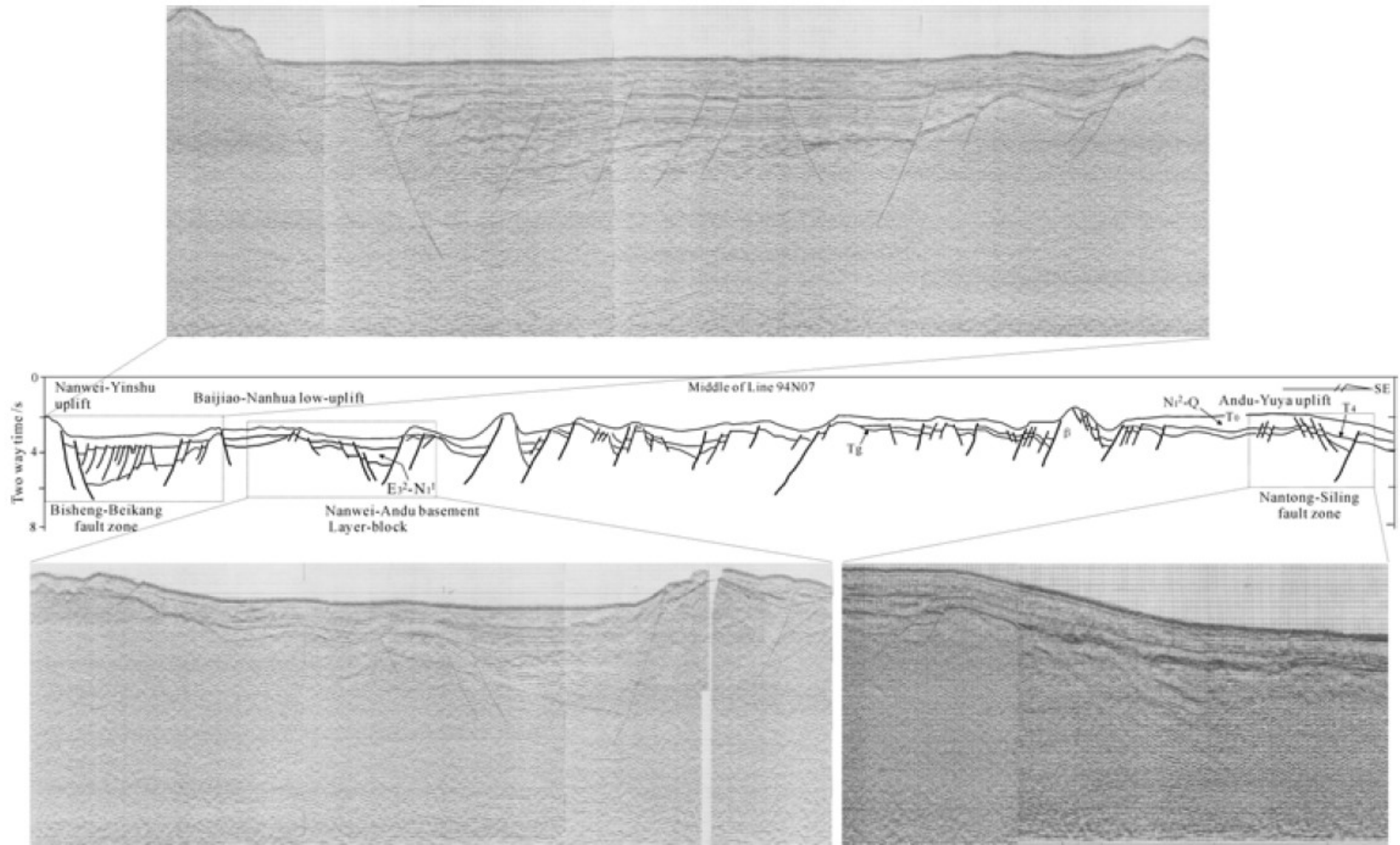


Fig. 7. Interpreted seismic profile 94N07 transecting Nanwei-Andu basemental layer-block. See Fig.1 for the location of the profile.

Forming mechanisms of LBT

The cause why the upper crust can easily slide on the middle crust surface is that there are nano-sized particle layers developed between the upper-crust and mid-crust.

The nanoparticles are characterized by higher density, higher strength, and lower rolling friction force (f_2 in Fig); and exist in almostly all faults and layer-slip surfaces in natural world. I

n the case with nano-particles, the friction is rolling friction. Under the same normal pressure force (P in Fig), the rolling friction force is far less than the sliding friction force (f_1/f_2 can be up to 18) (f_1 in Fig.11). So, the upper crust can easily move along the mid-crust layer.

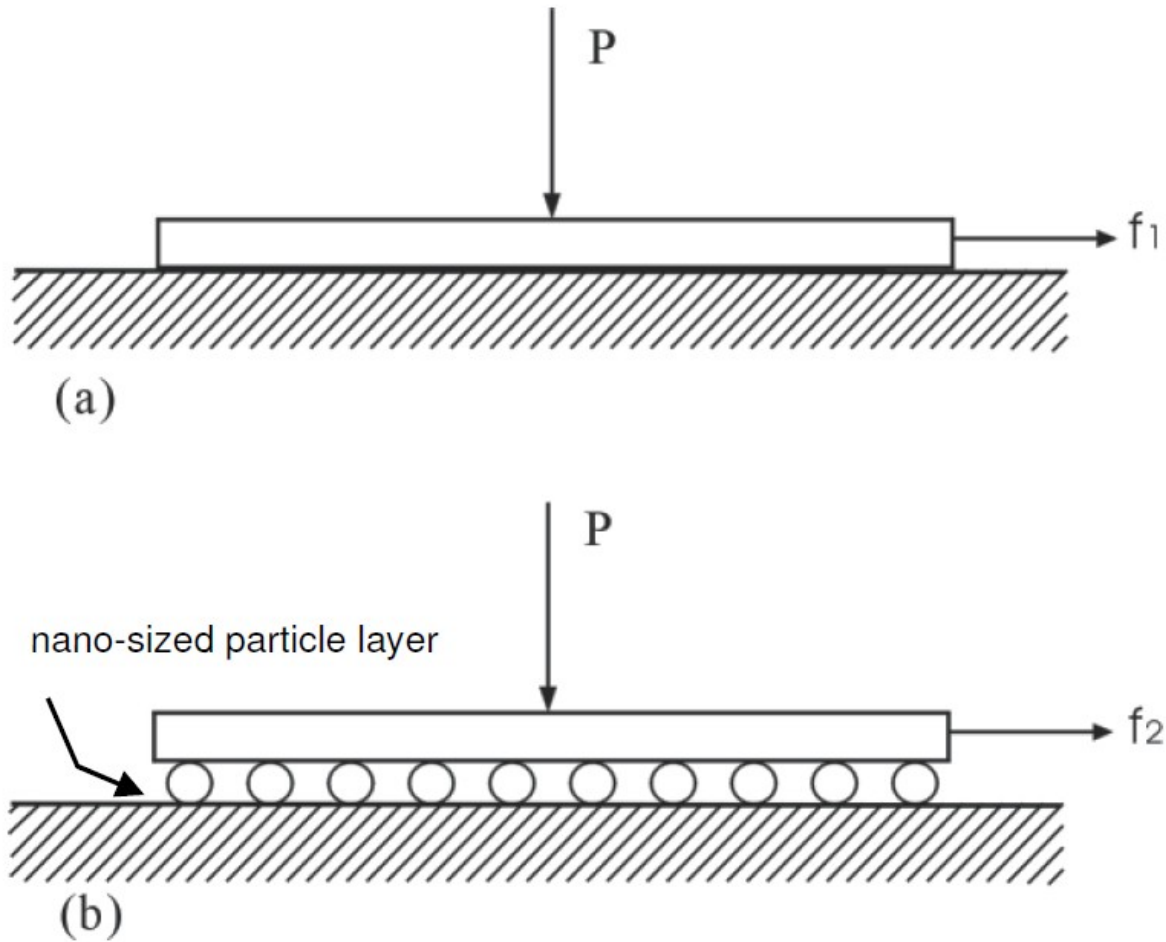


Fig. 11. Rolling friction comparing with sliding friction. (a) f_1 : sliding friction force in the case without nano-particles; (b) f_2 : rolling friction force in the case with nano-particles. Generally, the f_2 is far smaller than the f_1 .

Biomineral Nanostructures of Manganese Oxides in Oceanic Ferromanganese Nodules

Many Mn minerals, especially their finely dispersed oxides, are distinguished by a low degree of structural ordering and unstable structure

The study of structural transformations of finely dispersed minerals is a clue to understanding the processes of noncrystalline material transformation into the crystalline state and vice versa.

Manganese oxides, which are widespread and of great practical importance, are formed and transformed by an active role of microorganisms.

Finely dispersed Mn oxides are the most abundant in oceanic ferromanganese nodules (FMNs) and in products of weathering on land

The effect of biogenic factors on the formation and growth of FMNs has been discussed from the moment of their discovery by the Challenger expedition in 1873–1876.

In the land–sea transitional zone, ore material is absorbed by living organisms. This leads to the formation of organometallic complexes as abundant species of Fe, Cu, and Zn dissolved in seawater.

This leads to the formation of organometallic complexes as abundant species of Fe, Cu, and Zn dissolved in seawater. Bacteria play a certain role in the formation of major minerals in FMNs.

A part of soft organic matter reaches the ocean floor and the upper sedimentary layer, where it is oxidized. As a result, the redox potential decreases and the diagenetic redistribution of manganese leads to the formation of **todorokite**

Chukhrov et al. (1978), vernadite is formed only as a product of fast Mn^{2+} oxidation to Mn^{+4}

Finely dispersed Mn oxides (asbolane, todorokite, buzerite, birnessite, and vernadite) are characterized by phase transformations observed in nature and in experiments.

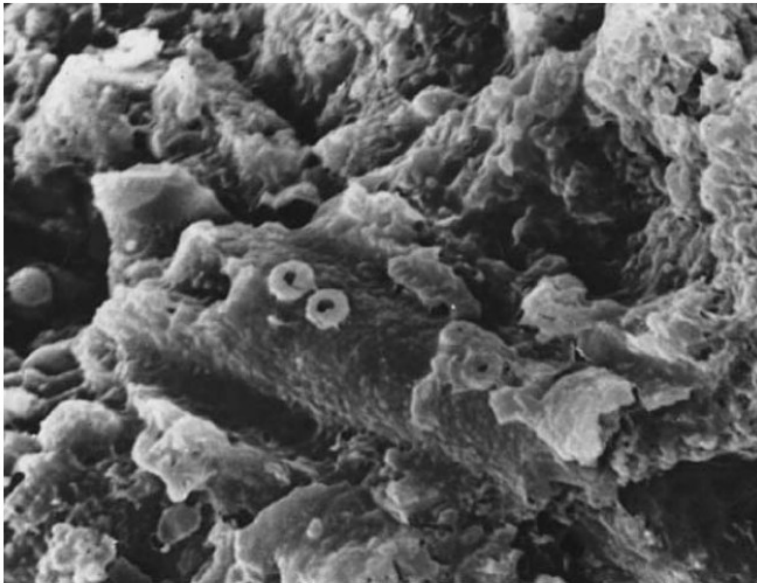


Fig. 1. Mineralized plankton in a nodule.

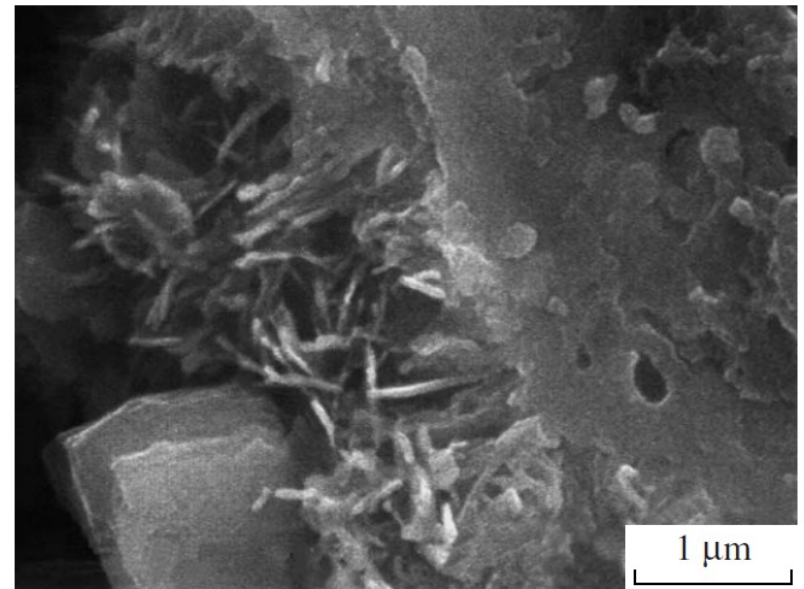


Fig. 2. Layer of fossilized cyanobacteria in the inner zone of a nodule.

Formation of Gold Spheroidal Nanoparticles

Nanosized spheroidal gold particles are most abundant in deposits of the volcanogenic type among the studied gold–silver deposits of the Far East.

Among volcanogenic deposits, spheroidal particles of electrum (Au and Ag) are the most abundant in the May deposit, Primor'e.

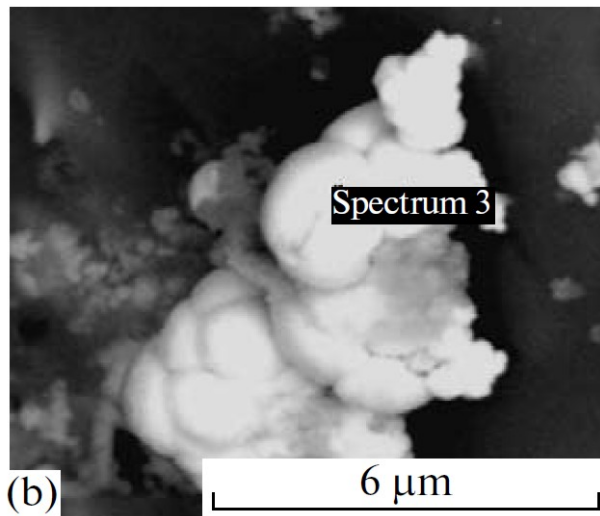
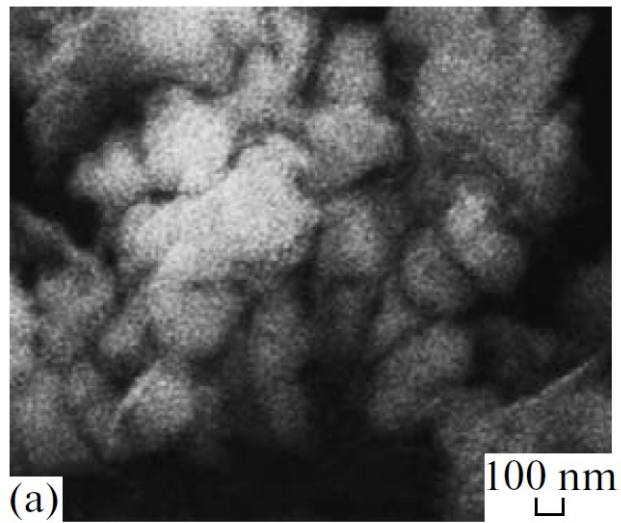
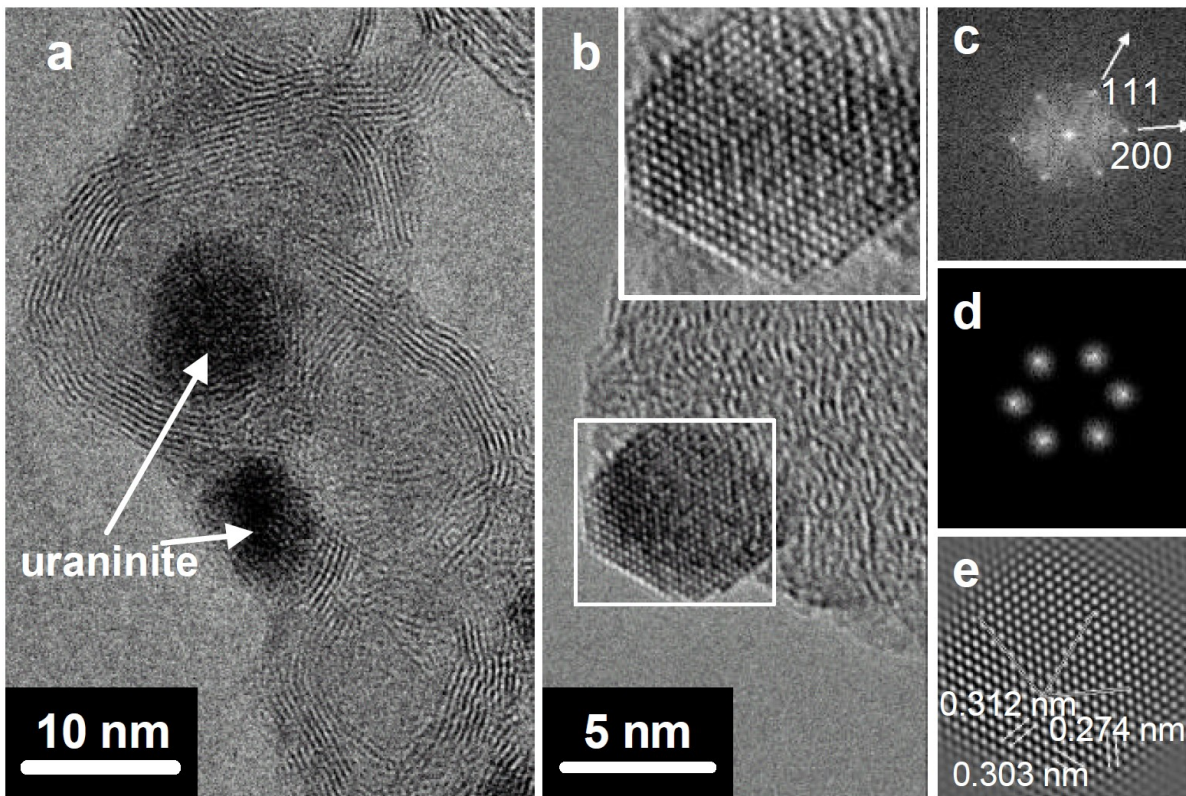


Fig. 3. Shape and composition of spheroidal particles on the first (a) and second (b) stages of the run. ((a) spectrum, wt %: Al 2.78, S 9.14, Cu 30.25, As 6.99, Ag 34.61, Au 11.84, Pb 4.39. (b) Spectrum 3, wt %: Au 35.17, Ag 43.84, Al 4.49, Cu 4.84, C 3.1, O 2.3, Zn 2.29, U 3.97.

Uraninite nanocrystals in carbonaceous particles in the atmosphere



There is increasing concern for the health effects of fine particles (less than a micron) inhaled from polluted air. Aerosols collected from Detroit contain very small amounts of uranium. Due to these extremely low concentrations (< 10 ppm), the form of the uranium has been unknown. We identified nanocrystals of uraninite, UO_{2+x} , encapsulated in carbonaceous matter (about 50 nm) with a structure similar to that of fullerene. (a) HRTEM image of U-bearing nanoparticles encapsulated in a "cage" of fulleroid. (b) HRTEM of the U-particle. The matrix carbon has lost its structure because of the focused electron. The inset is the Wiener-filtered image of the area outlined by the white square. In the Fast Fourier Transformed (FFT) image (c), the main diffraction maxima were selected (d) and a reverse FFT completed to produce a clear image (e). The lattice spacing in three directions can be determined and the diffraction spots (c) can be indexed as those of uraninite. The "carbon-caged" nanocrystals of uraninite are protected from the immediate oxidation that would lead to increased mobility of uranium in the environment. Still, the presence of uranium in the very fine fraction of atmospheric particulates provides another pathway for radiation exposure. (S. Utsunomiya and R. C. Ewing, submitted (2002) to Environmental Science & Technology)

Biologically Produced Iron Oxyhydroxide Nanoparticles

Recent investigations have explored nanoscale interactions between microbially produced polymers and iron oxyhydroxides. Banfield et al. (2000) and Nesterova et al. used transmission electron microscopy to study polymer biomineralization reactions in the environment

Nanoseismic monitoring

Microseismicity: Earthquakes below the level of human sensitivity, say ML 3.0, recorded locally (within 100 km) or at regional scale (up to 3000 km).

Nanoearthquake: Suggested phrase for earthquakes below ML 0.0; however, not yet commonly accepted by the seismological community (Butler, 2003).

Nanoseismic monitoring: Location and identification of low-SNR fracture processes, e.g., nanoearthquakes by jackknife analysis of tripartite array networks.

Passive seismics: Location of energy release from fracture processes by means of seismic exploration-like equipment and software tools, e.g., in the concept of instrumented oil fields.

Forensic seismology: Location and identification of nonseismic sources by seismic networks, e.g., airplane crashes, submarine explosions (Zucca, 1998).

Nanoseismic monitoring, acting like a moderate effort seismic microscope of previously unavailable sensitivity, offers many new chances to resolve ambient fracture processes.

Wust-Bloch and Joswig (2006) derive a process identification of pending sinkhole collapses at the Dead Sea, Häge and Joswig (2008) report on improved resolution of seismicity during an inter-swarm period at Vogtland, Czech Republic, and Walter and Joswig (2008), in a forthcoming issue of First Break, describe the first-time discovery of cracks in a creeping, clayey landslide during heavy rainfall in Vorarlberg, Austria.

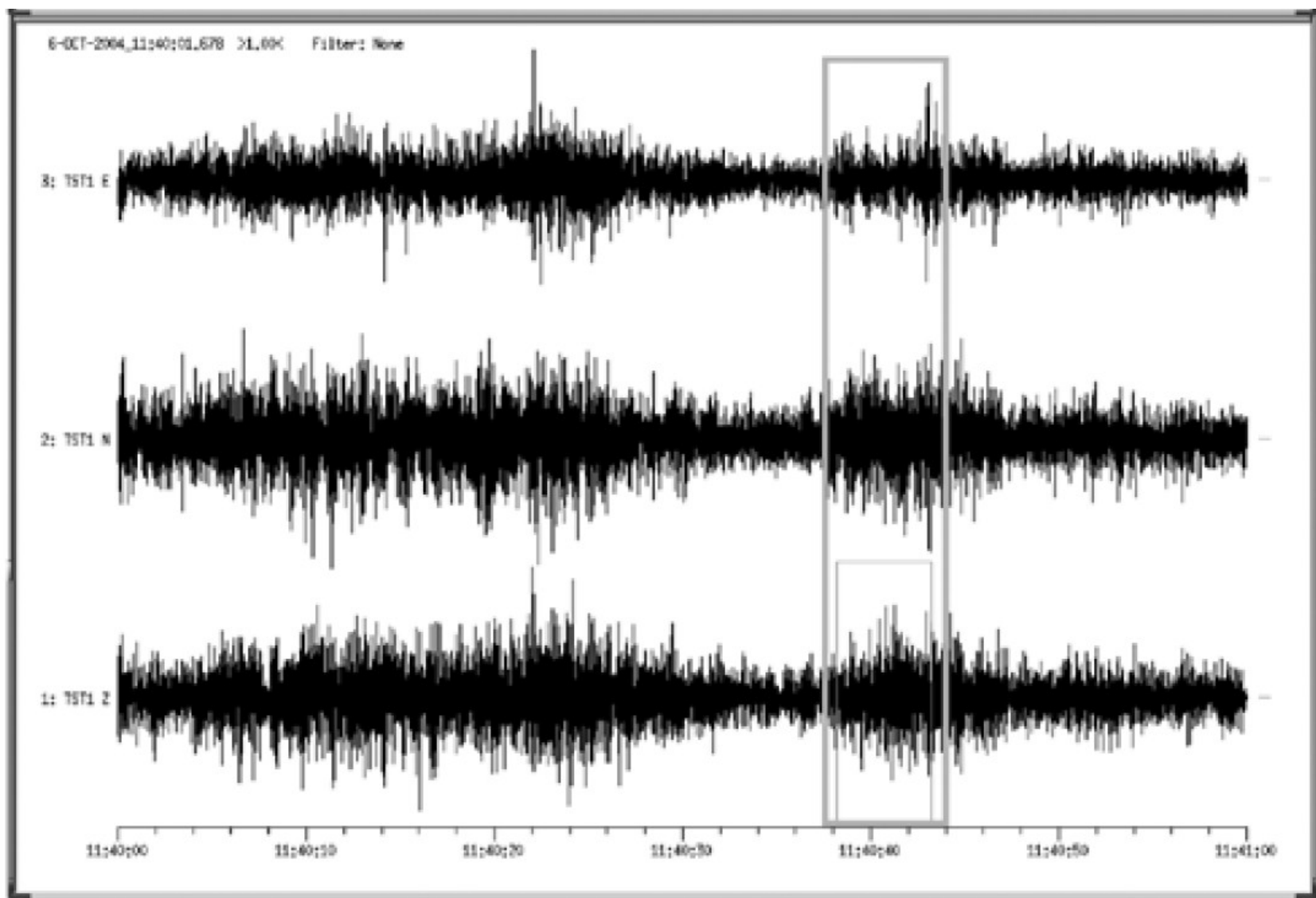
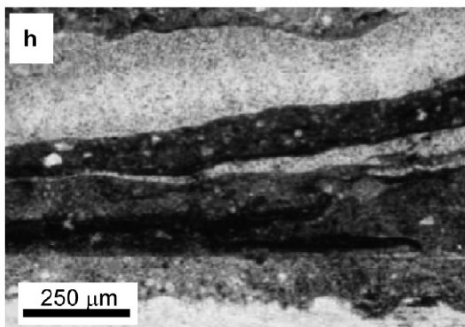
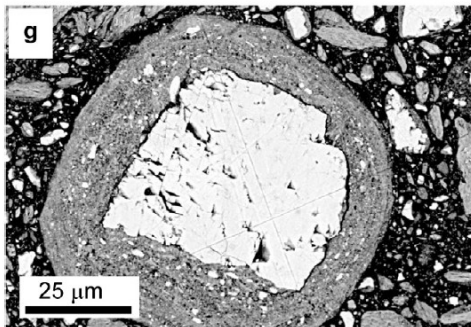
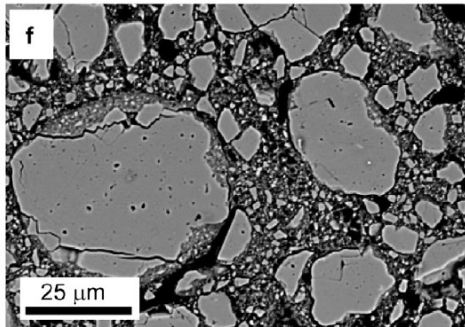
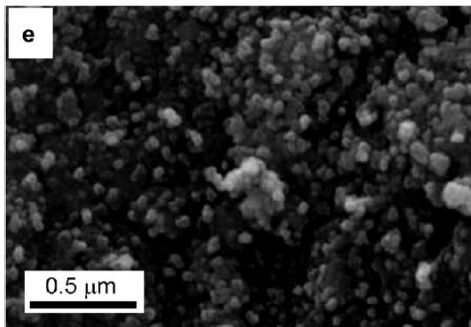
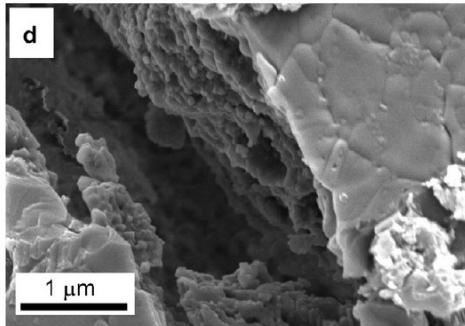
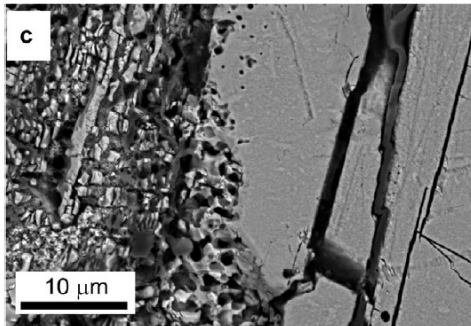
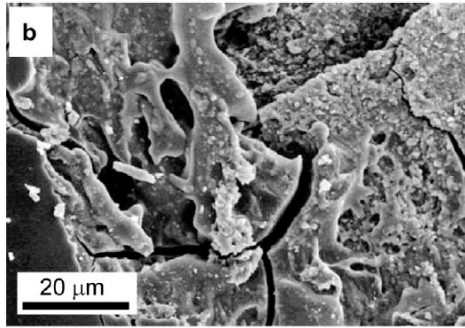
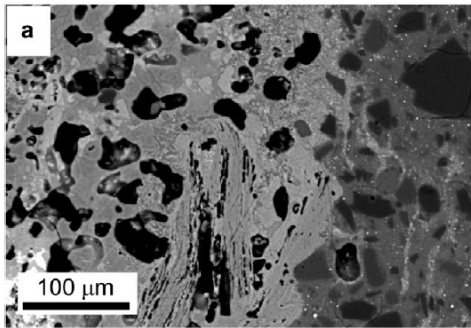


Figure 4 Explosions of 75 g were recorded at nearest 3C geophones (A, 1 of Fig. 3) in 500 m distance (compiled from Labak et al., 2005). Depending on different ambient noise conditions, the signal was either recognized (top), or masked completely (bottom).



Microstructures of experimental slipping zones. (a) Experimental pseudotachylyte produced by frictional melting of tonalite. A large biotite grain (pale gray in colour) in the wall rock to the left undergoes to selective melting resulting in lattice breakdown, biotite dehydration and formation of vesicles (black in color). The Fe-rich melt from the biotite is mingled in the friction melt (20 MPa normal stress, 1.3 m/s slip rate and 3 m of slip, BSE-SEM image, Di Toro et al., 2006a,b).

(b) Silica gels decorating the sliding surface of deformed novaculite (112 MPa normal stress, 3.2 mm/s slip rate, 1.7 m of slip SEM image, Goldsby and Tullis, 2002: photo courtesy of David Goldsby).

(c) Decarbonation products and porous microstructure in deformed Carrara marble (100% calcite). The slip surface is located 50 mm to the left (10 MPa normal stress, 6.5 m/s slip rate, slip 13.45 m. BSE-SEM image).

(d) Sliding surface of dolomitic marble. The sliding surface has a pavement of euhedral grains about 100 nm thick of Mg-rich calcite. The pavement covers a 25e40 mm thick layer made of nanoparticles of periclase and lime (10 MPa normal stress, 6.5 m/s slip rate, slip 19.5 m. BSE-SEM image).

(e) Sliding surface on limestone made of nanoparticles of probable calcite. Experimental conditions aimed at investigate flash heating and weakening (3 and 5 MPa normal stress, 0.3 m/s slip rate, slip 4 cm. SE-SEM image, Tisato et al., in press).

2.3. Carbonate decomposition and nanopowder lubrication

Han et al. (2007a, 2010) showed that decarbonation of both calcite and dolomite marble occurred when samples were deformed at moderate normal stress (~ 10 MPa) and relatively high slip velocity (>0.1 m/s). In these experiments, the total slip was of the order of meters, so longer than those reported in Section 2.2. They measured an increase in CO_2 concentration that accompanied strong dynamic weakening and concluded that thermal decomposition of the carbonates occurred. Observations of the slip surfaces after the experiments demonstrated the presence of very fine-grained (<1 μm) powders of lime (CaO) and portlandite ($\text{Ca}(\text{OH})_2$) (Fig. 3c and d). Experiments run on pre-decarbonated samples also showed strong weakening, so it was concluded that the weakening was not caused by increased fluid pressure due to the release of CO_2 but rather by nanopowder lubrication, a well-known phenomenon in tribology (e.g. Heshmat, 1991, 1995; Worniyoh et al., 2007). Han et al. also performed a number of slide-hold-slide tests which demonstrated that the nanopowders coating the sliding surface rapidly restrengthen during short periods (as short as 4 s) of no sliding.

Earthquakes occur because rock strength (and friction) decreases with increasing slip and slip rate (Rice, 2006). Most theoretical, field and experimental studies suggest that during seismic slip a large percentage of the total mechanical work is converted in to heat, which is restricted to a relatively narrow band within and adjacent to a thin (often <1 mm thick) slip zone (Sibson, 2003; Chester et al., 2005; Rice, 2006; Pittarello et al., 2008). Within the slip zones of carbonate-bearing faults, the temperature rise due to frictional heating may lead to flash heating and weakening at asperity contacts, expansion or vaporization of pore fluids, decarbonation of CO_3 -bearing minerals (calcite, dolomite, siderite, etc.), and production of nanoparticles (De Paola et al., 2011; Han et al., 2007a,b, 2010; Sulem and Famin, 2009; Tisato et al., 2012). Expansion or vaporization of pore fluids may increase fluid pressures to supra-lithostatic values, leading to a reduction in effective normal stress across the fault (Hubbert and Rubey, 1959; Sibson, 1973; Lachenbruch, 1980; Rice, 2006). Other weakening effects may occur in the slip zone with the production of ultra-fine-grained decomposition products (e.g. <1 μm particles of lime (CaO) and hydrated lime ($\text{Ca}(\text{OH})_2$) from pure limestone protoliths or more stable periclase (MgO), magnetite (Fe_3O_4) and magnesioferrite (MgFe_2O_4) from impure limestone and dolostone protoliths) that has been correlated with a dramatic reduction in frictional strength observed in high-velocity rock deformation experiments (Han et al., 2010, 2011; De Paola et al., 2011; Tisato et al., 2012).

Micro-, Nano- and Picoearthquakes: Implications for Fault Friction and Fault Mechanics

Micro-, Nano- and Picoearthquakes: Implications for Fault Friction and Fault Mechanics

By William L. Ellsworth ¹ and Kazutoshi Imanishi ².

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The deployment of instrumentation within seismically active crustal rocks in deep boreholes and mines has opened a new window for the study of the earthquake source. Advances in both sensors and high-temperature electronics enable recording of seismic waves over a very broad frequency spectrum (D.C. to several KHz) and amplitude spectrum (Earth noise floor to several g acceleration) in these challenging underground environments.

By reducing the distance between source and receiver to a few hundred meters or less, it becomes possible to observe dynamic processes on space and time scales that approach those of laboratory experiments.

Using deep borehole seismometers in the main hole of the San Andreas Fault Observatory at Depth (SAFOD) and in the Long Valley Exploratory Well (LVEW) in the center of Long Valley Caldera, CA, we have observed earthquakes at the lowest limit of magnitude detection

The smallest events have source dimensions < 1 m, indicating that if there is a minimum earthquake size, it must lie at lower magnitude and spatial scales. Mean displacements in the smallest events are on the order of 100 microns, suggesting that the displacement weakening distance is smaller still. The rate of fault weakening can be studied using the earliest part of the P-wave arrival.

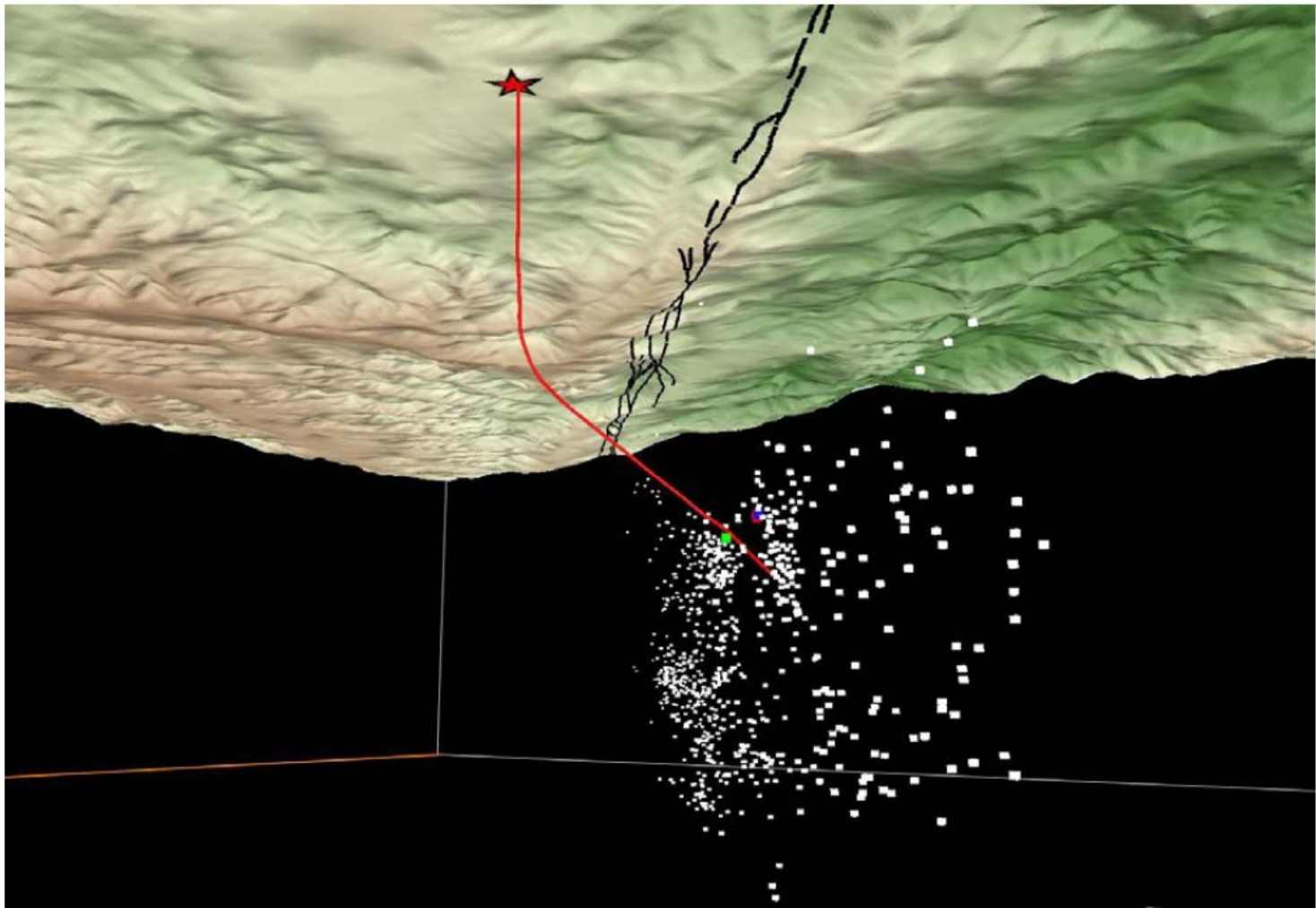
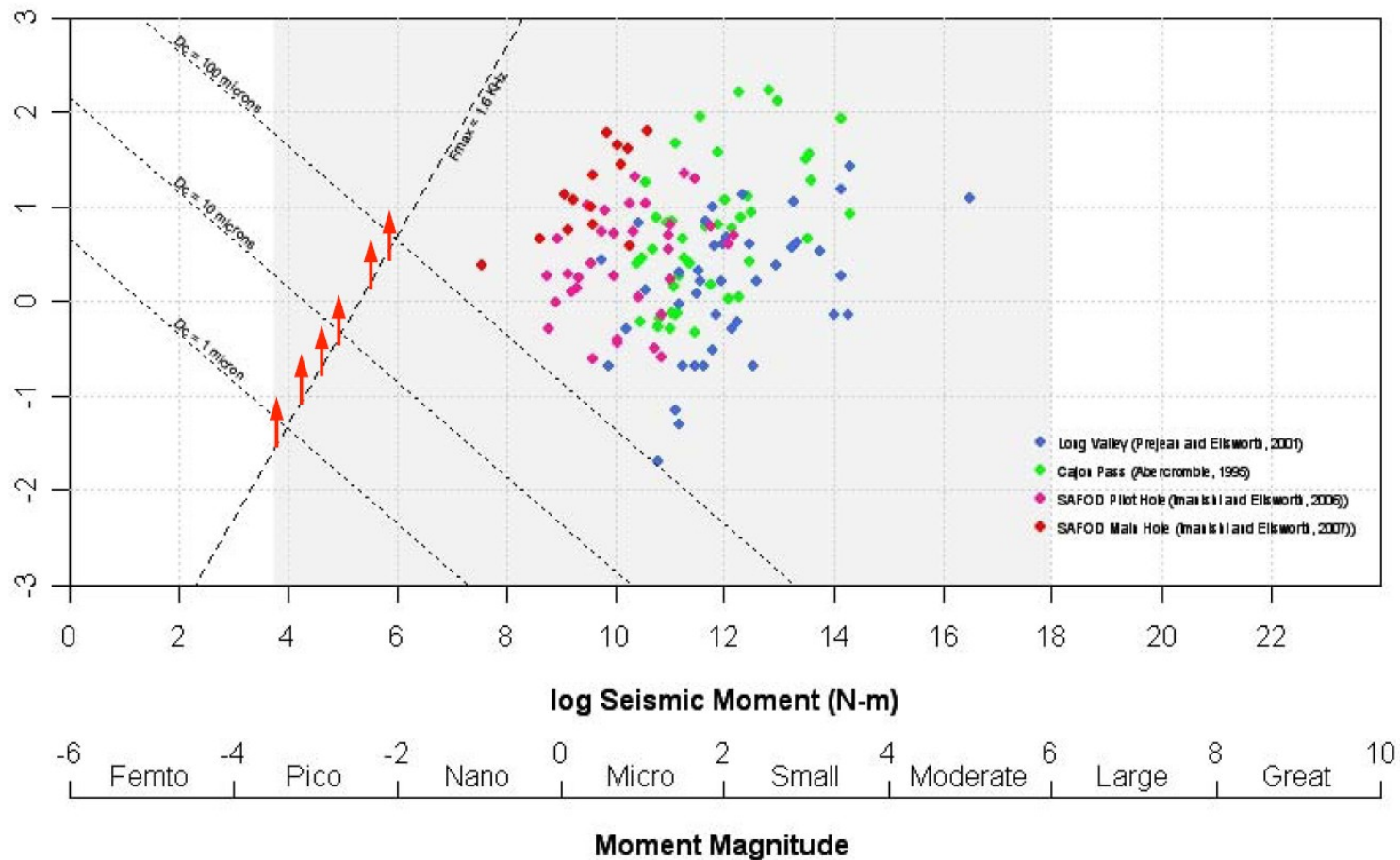


Figure 1. The San Andreas Fault Observatory at Depth Main Hole (red star) follows a diagonal path from the Pacific to North American Plate, intersecting the seismically active fault (squares) at approximately 3 km depth. View is from below, with the surface trace of the fault (black) and surface topography shown. The SAFOD target earthquakes include the “San Francisco” (red), “Los Angeles” (blue) and “Hawaii” (green) repeating earthquakes. Illustration by Luke Blair (USGS).



Study of Nanocrystals in the Dynamic Slip Zone

Slickensides are smoothly ground or polished surfaces produced by the relative frictional motion of the rocks on the opposite sides of the fault plane. The grooves and stepped topography of these surfaces give an insight into the kinematics of the motion of the blocks of the rock (Allaby, 1990). The slickensides revealed in the zones of paleoseismic events allow correlating their origin to the seismic cycle (Pover and Tullis, 1989).

Typically, slickensides are formed at a slip rate exceeding 1 m/s, when a coefficient of friction of the sliding rocks decreases by at least an order of magnitude. This phenomenon develops due to the formation of an intermediate layer between the blocks, which is low resistant to shear. This layer is supposed to be a product of the grinding of the rocks into a **gouge of nanoparticles** (Han et al., 2011; Di Toro et al., 2011), or a fluid saturated mineral assembly (Wang and Manga, 2010), or a mineral melt in the zone of friction (Fialko and Khazan, 2005; Nielsen et al., 2008).

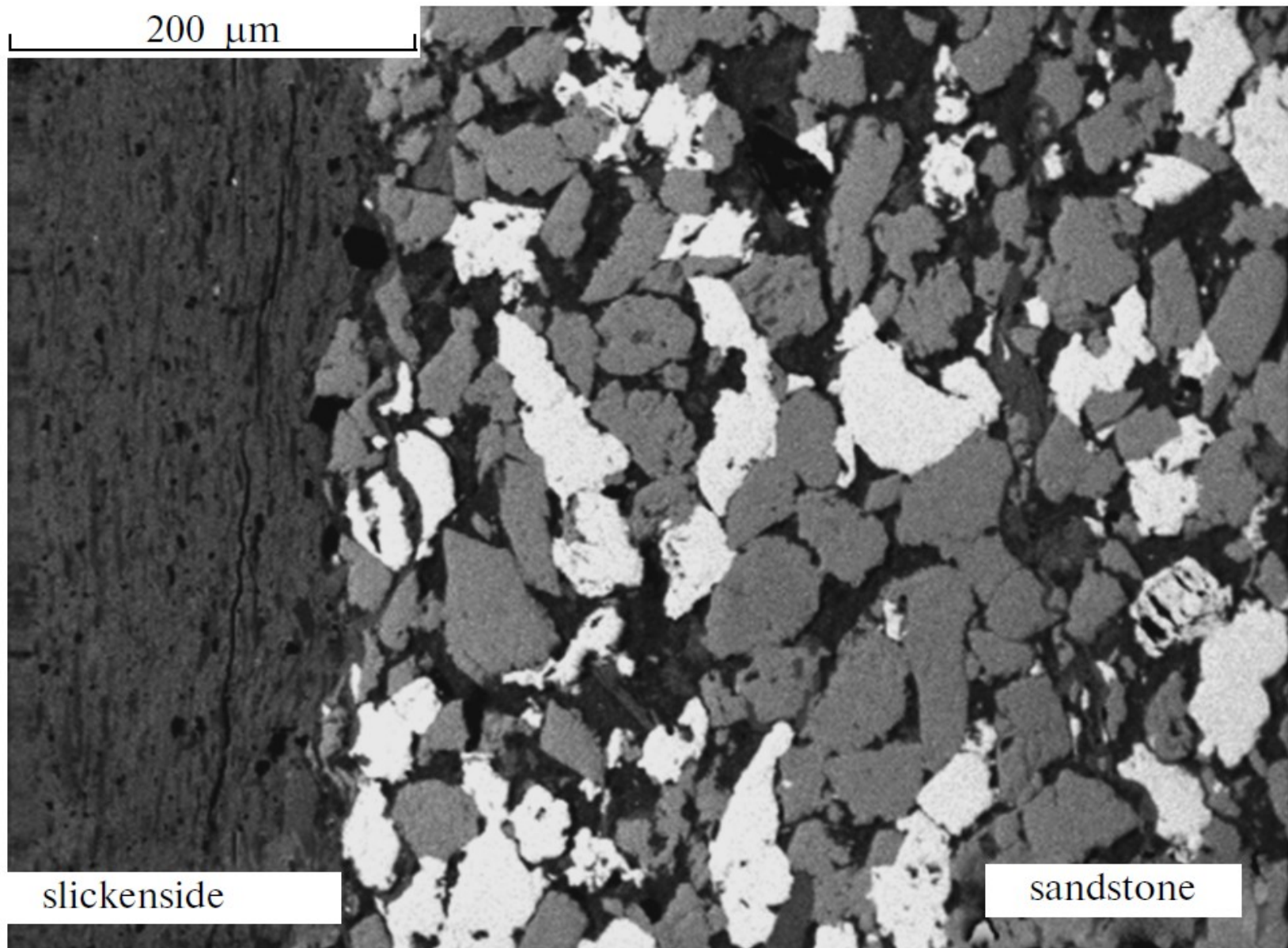


Fig. 1. Electron microscopy image of the surface of PV-364 specimen in Si line.

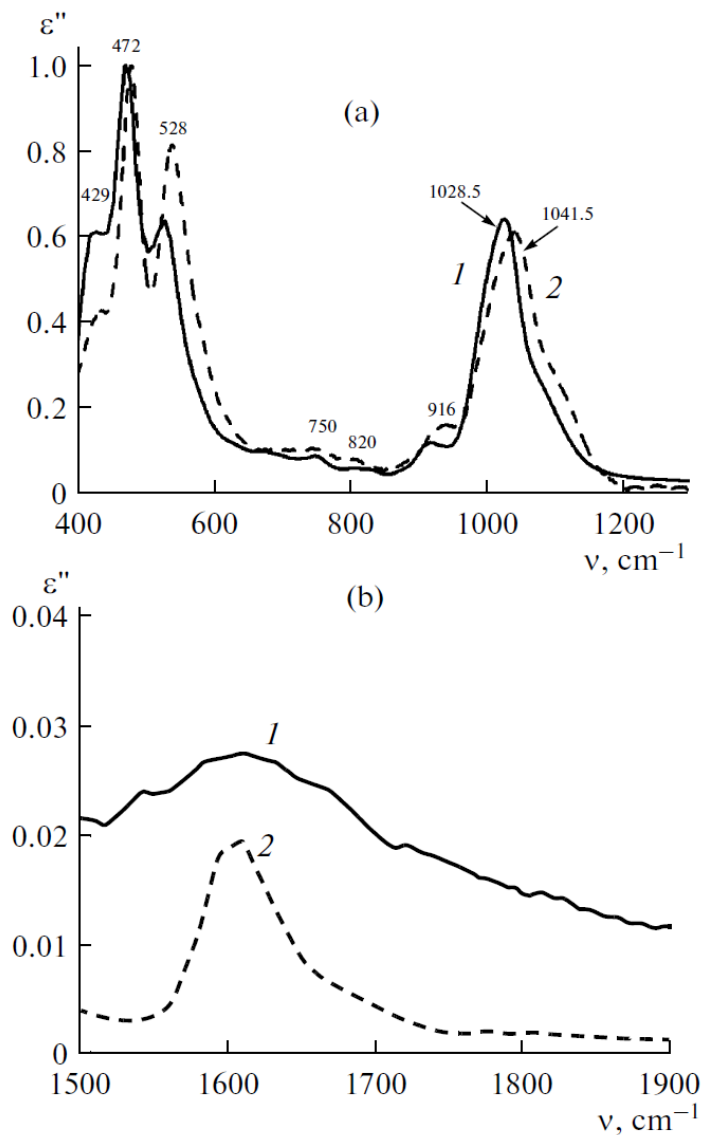


Fig. 3. The IR absorption spectra $\varepsilon''(\nu)$ (1) in the slickenside and (2) in montmorillonite in the frequency bands of (a) 400–1300 cm^{-1} and (b) 1500–1800 cm^{-1} . The arrows indicate the peak frequencies of valence vibrations assigned to SiOSi in the spectra from montmorillonite and slickenside.

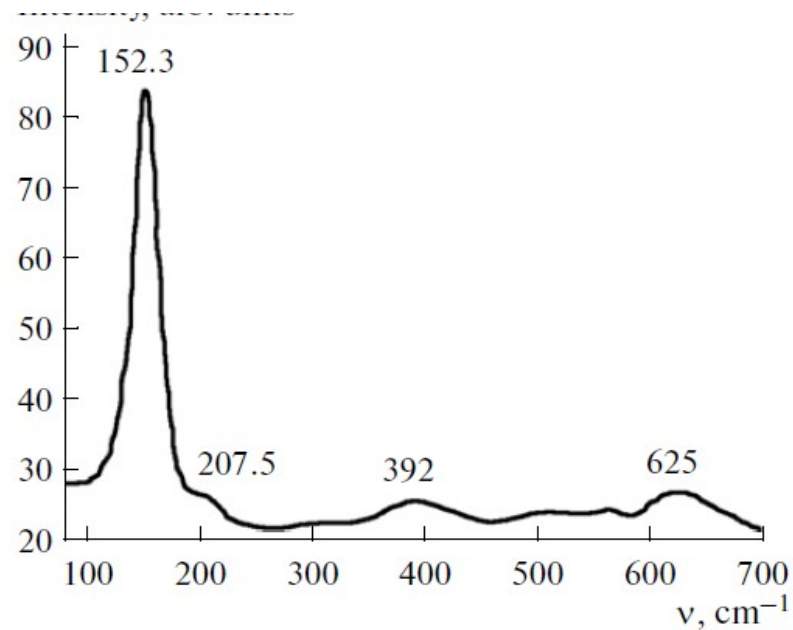


Fig. 4. The Raman spectrum from the slickenside.

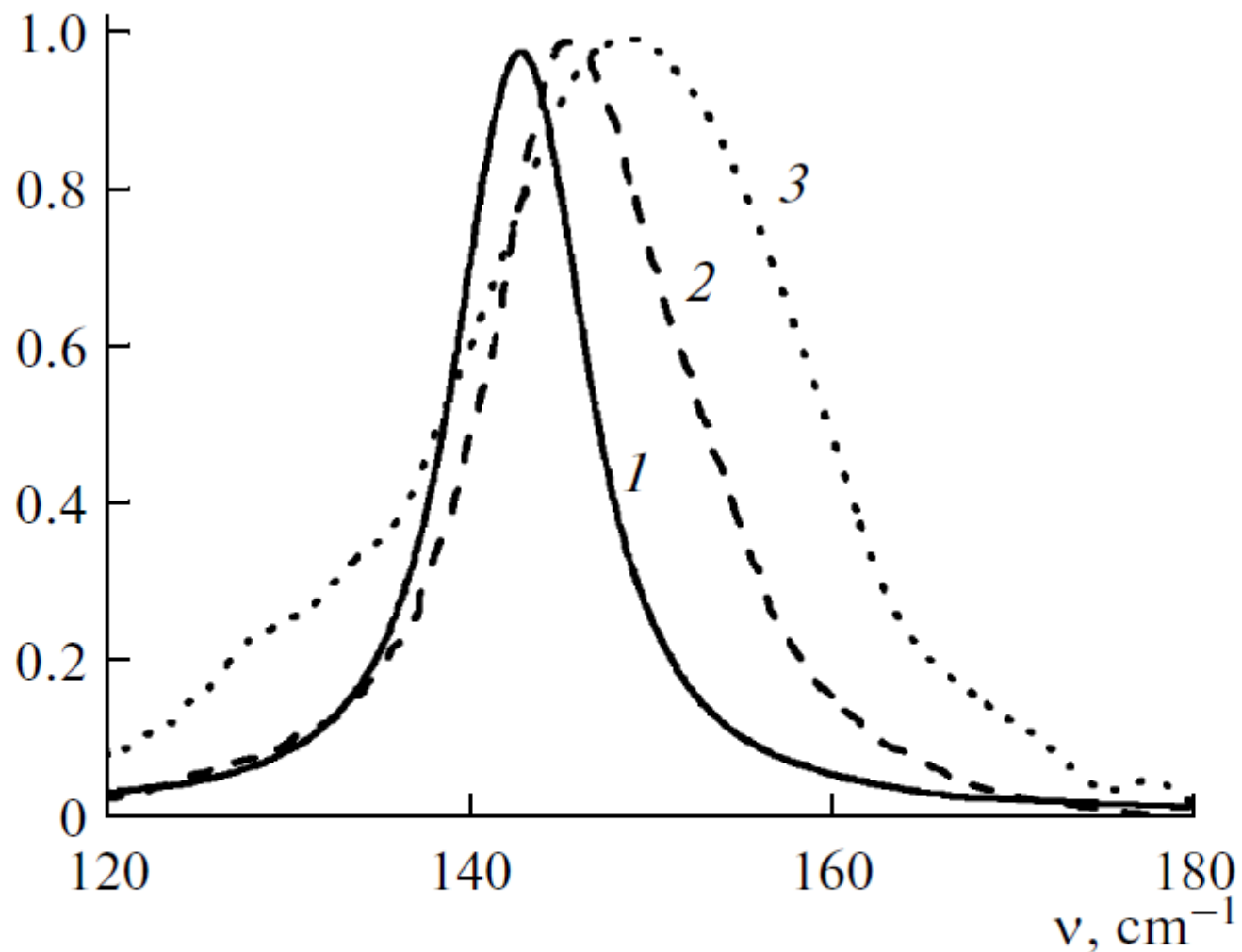
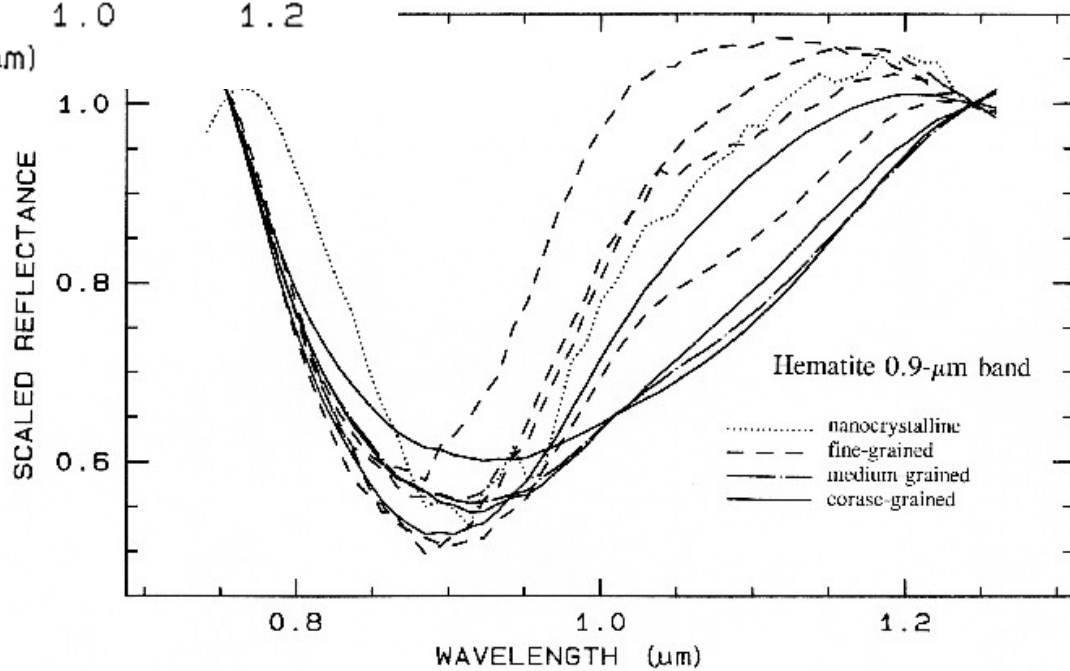
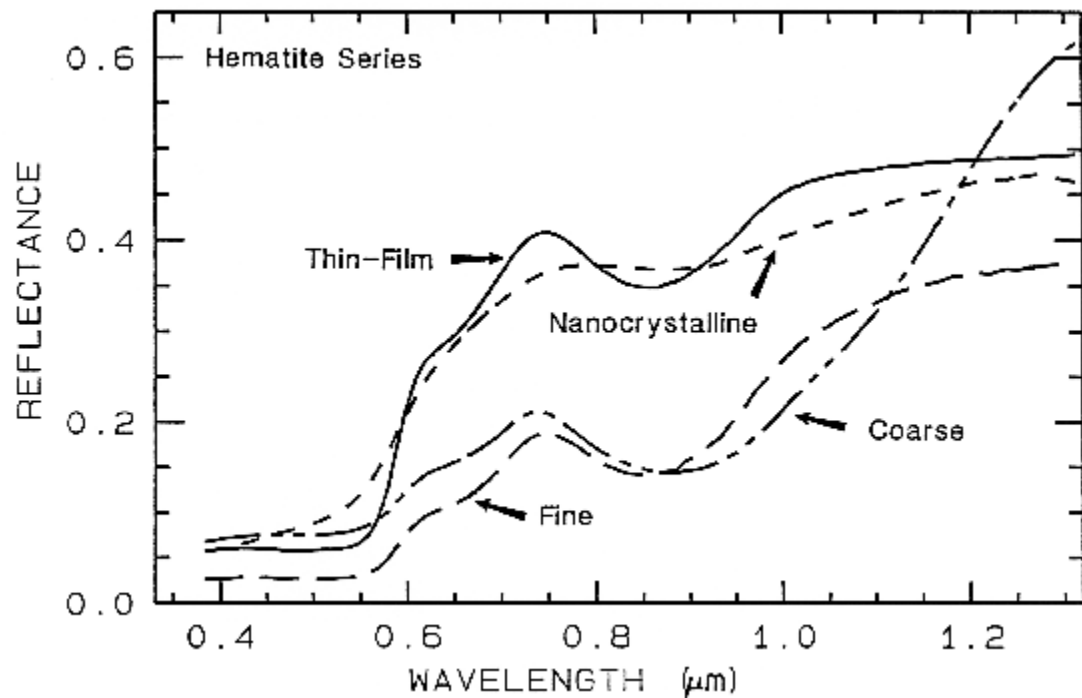


Fig. 7. The vibration band assigned to the crystalline lattice of anatase in the Raman spectra from (1) the macroscopic crystal, (2) the bulk of sandstone, and (3) the slickenside.

The IR and Raman spectroscopy showed that the slickenside on the surface of arkosic sandstone and the bulk of the sample at a depth of 3 mm from the surface have a different mineral composition. The slickenside is composed of the crystals of montmorillonite and anatase, which have an average linear size of ≈ 15 and 3 nm, respectively.

Besides montmorillonite, also beidellite, nontronite, quartz, anatase, and plagioclase are identified in the bulk of the sandstone. The average size of the nanocrystals of anatase in the bulk of the specimen is about 8 nm.



NANO FOSSILS

Nanobacterial fossils and grainy textures have been described in the geological record (Camoin et al., 1999; Folk, 1993; Vasconcelos et al., 1995), as well as in the Martian meteorite ALH84001 in association with carbonate globules (McKay et al., 1996).

These micro sedimentary structures were initially considered as possible evidence for past life, leading to a still-unresolved debate concerning both the significance of the grainy texture and the existence of microbes measuring <200 nm (Nealson, 1997).

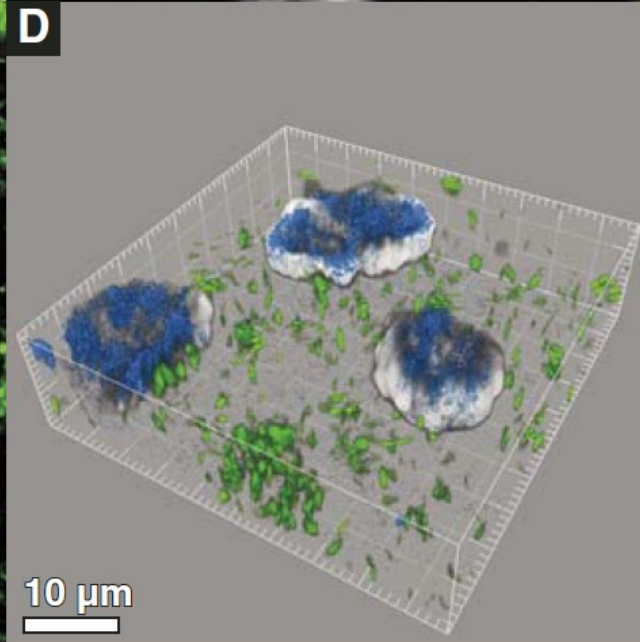
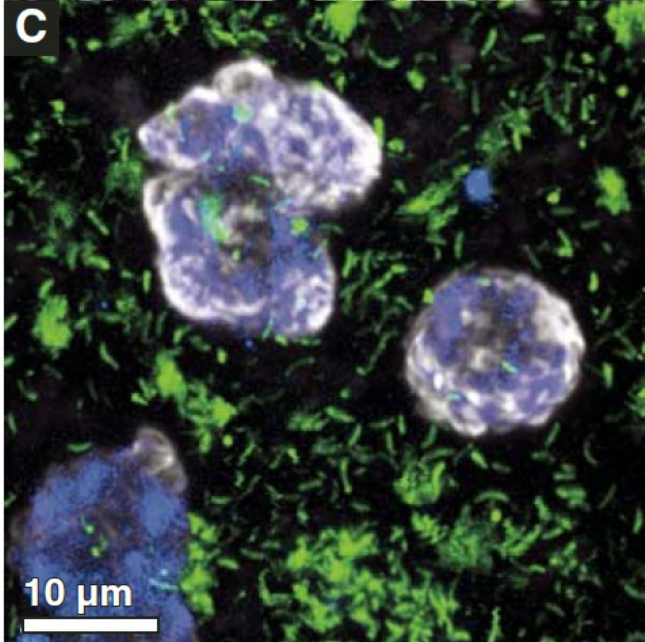
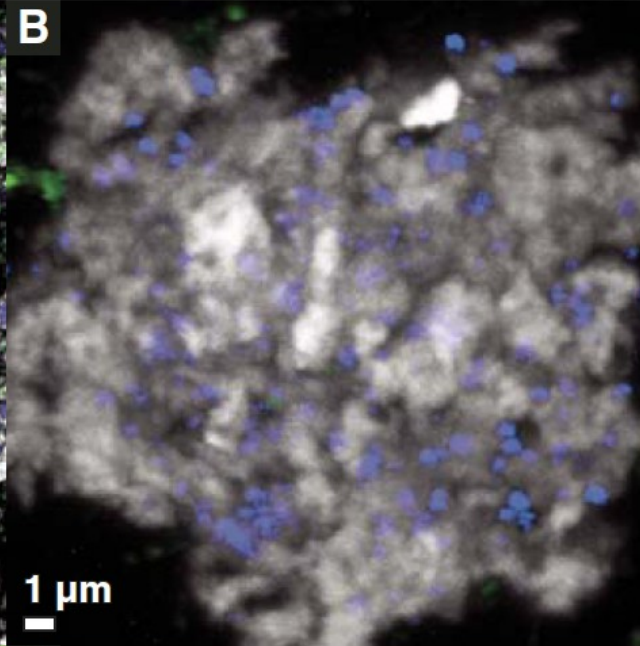
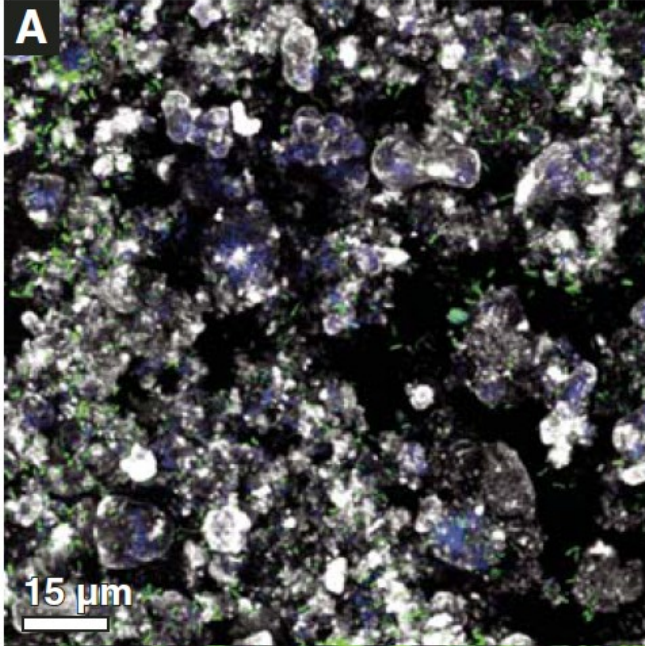
In addition, nanoforms and grainy texture have been observed in modern natural environments, as well as in laboratory culture experiments, in the presence of sulfate-reducing bacteria (SRB), which mediate carbonate formation (van Lith et al., 2003a; Vasconcelos and McKenzie, 1997; Warthmann et al., 2000).

Imaging Techniques

Confocal laser scanning microscopy images of culture experiment inoculated with *Desulfovibrio brasiliensis*. Sample was stained to visualize relationship among minerals (blue), bacterial cells (green), and extracellular polymeric substances (EPS) (white).

A: Overview of the culture experiment. **B:** Nanosize minerals nucleating in EPS aggregate.

C: Mineral globules enveloped within EPS surrounded by bacteria. **D:** Section through threedimensional reconstruction of image C. Note that bacterial cells are not included within globular structures.



 Bacterial cells

 Minerals

 EPS

In the specific case of microbial dolomite formation in laboratory experiments, we have demonstrated that nanobacteria-like particles represent mineral nucleation and growth within EPS

Similar structures present in the geological record may have been formed through a similar process

A close association between SRB (Sulphate Reduction Bacteria) and precipitation of lithified laminae has been documented in modern microbial mats, which are regarded as possible analogues for Precambrian stromatolites

Many of the current models predict that SRB induce carbonate formation through the excretion of metabolites, which increase the alkalinity and pH of the water solution (Castanier et al., 1999).

Paleoenvironmental Application of Calcareous Nannofossils

Biostratigraphers primarily use benthic foraminifera and palynological assemblages for paleoenvironmental reconstruction; calcareous nannofossils and planktonic foraminifera for detailed age dates.

Preliminary research comparing modern to Miocene coccoliths indicates that broader application of calcareous nannofossils may be possible. Ocean depth preferences of the modern calcareous nanoplankton can be extrapolated to the fossil record, if we assume that morphological variability can imply habitat.

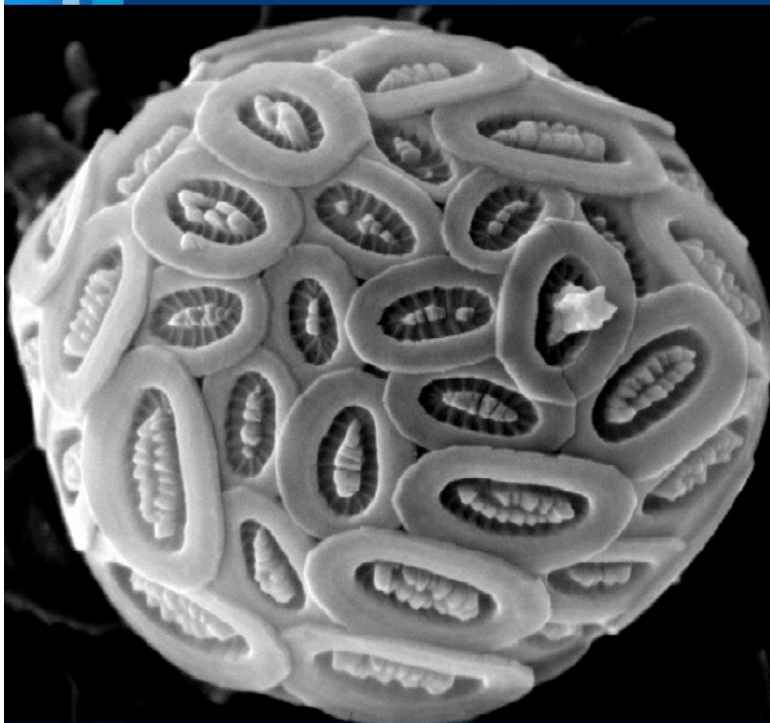
The morphological variability between coccoliths of extant calcareous nanoplankton species and the Miocene species, *Minylitha convallis*.

The morphology of the coccoliths of *M. convallis* remains constant through time, with overall low intraspecific variability in all samples, indicating that it may have lived in the deep photic zone. Following this assumption, greater relative abundance of *M. convallis*, like that of the modern deep photic zone species, should indicate a highly stratified paleo-ocean, deep nutricline, and warmer climate, whereas reduced abundance relative to other calcareous nanoplankton species should indicate a cooler climate and shallow nutricline.

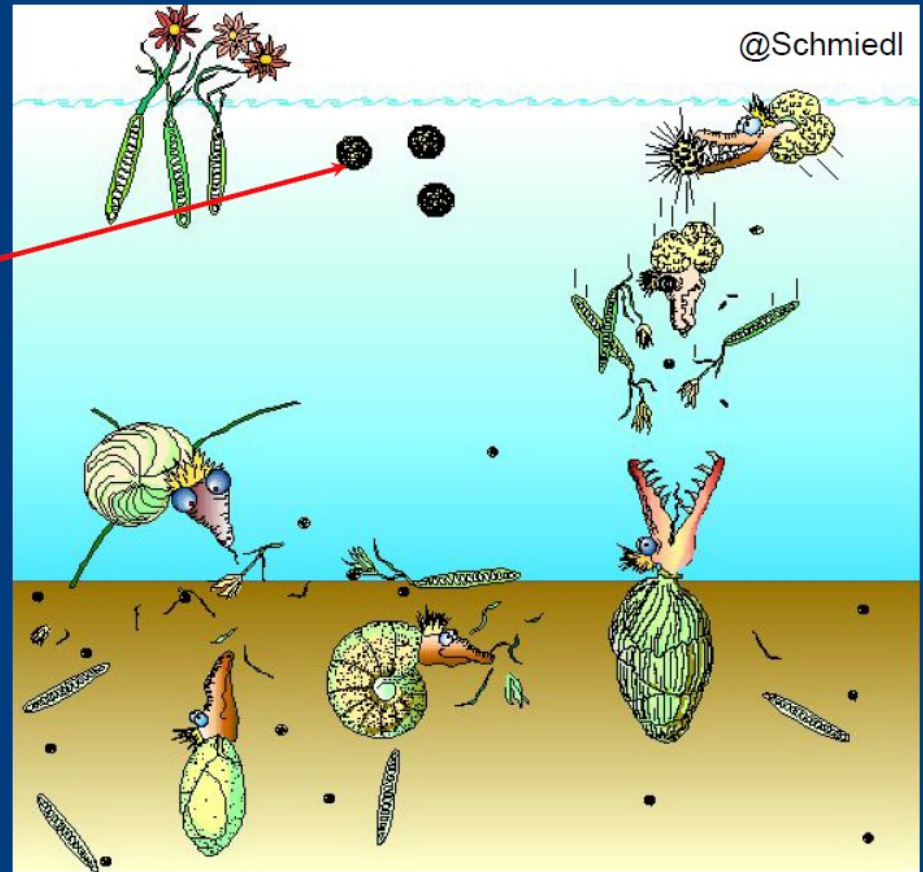
What are calcareous nannoplankton?



Calcareous nannoplankton = unicellular, marine gold brown algae (phytoplankton)



Syracosphaera molischii



@Schmiedl

Calcareous nannoplankton overview

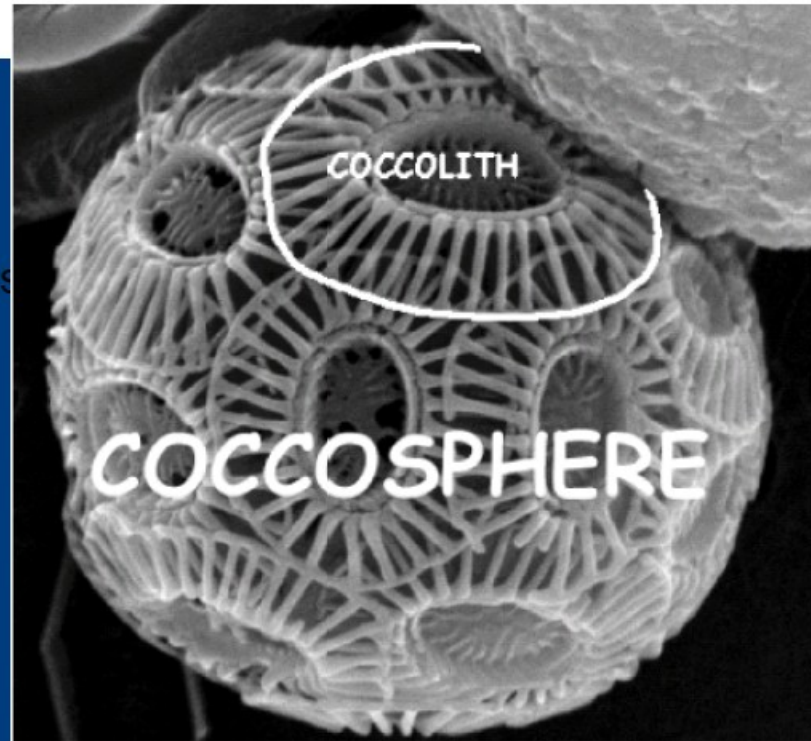


Coccolithophore - the organism, including the cell and external coccoliths (living cell).

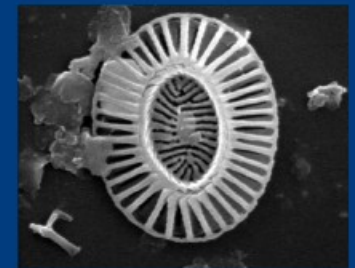
Coccosphere - ~ spherical layer of coccoliths surrounding the cell.

Coccolith - the individual calcareous plate (CaCO_3).

After death coccospheres collapse and the coccoliths contribute substantially to sediments, e.g., Upper Cretaceous calks.



Coccosphere



Coccolith

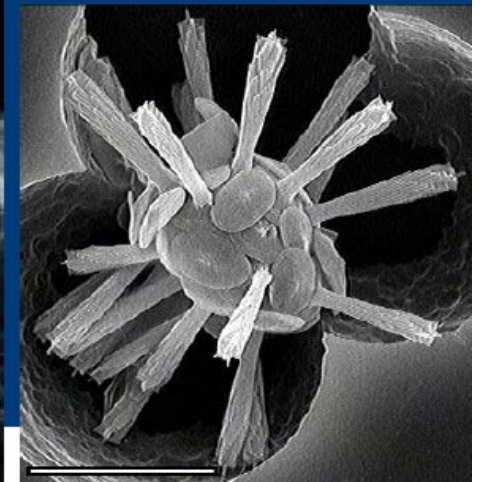
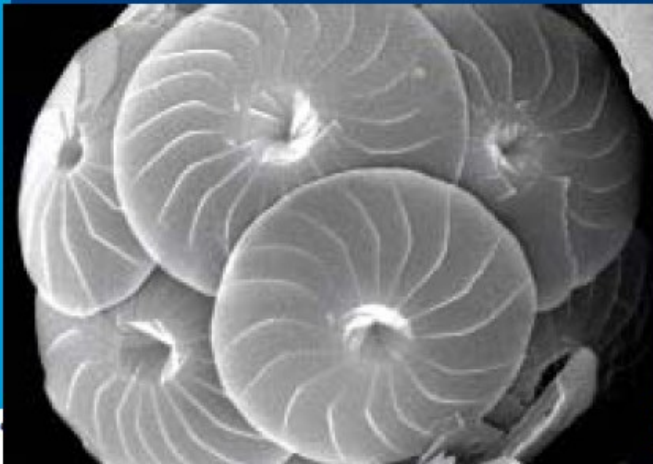
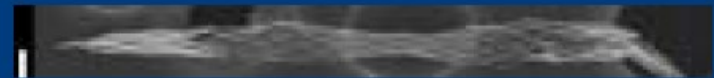
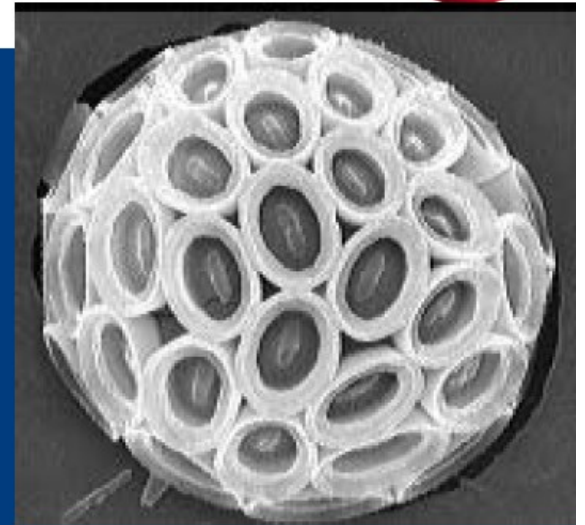
Coccolithophore morphostructure

Secreted coccoliths composed of calcium carbonate

Function unknown/unconfirmed

Sound taxonomy based on the morphostructure of the coccoliths

Here use structure, morphology to extract information (from extant to fossil)



Present is the key to the past - applicability of extant coccolithophores to fossil record

Biostratigraphy

*Paleoceanographic interpretation

- Stratification
- Depth (shelf, open water, within water column)



Purpose/Methodology

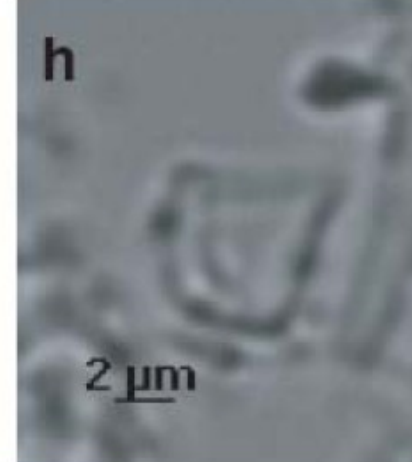
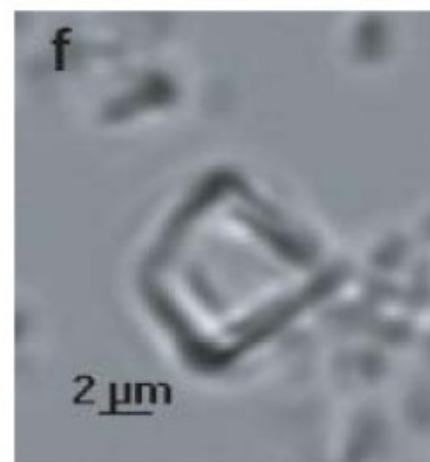
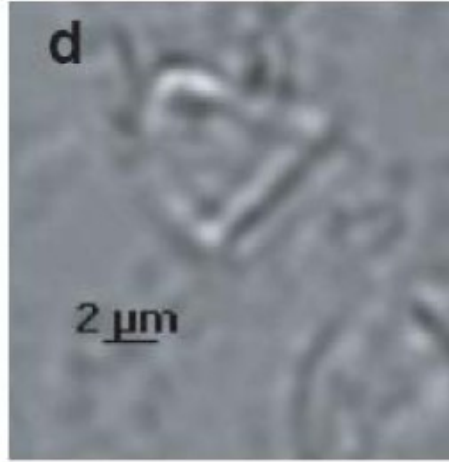
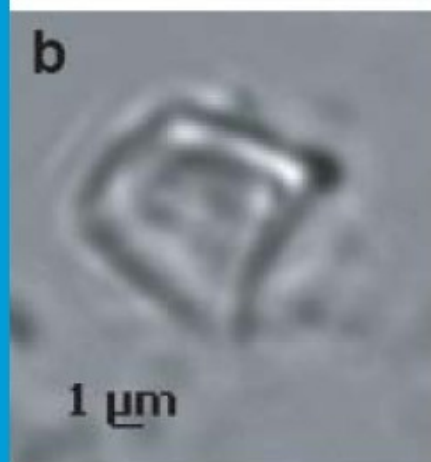
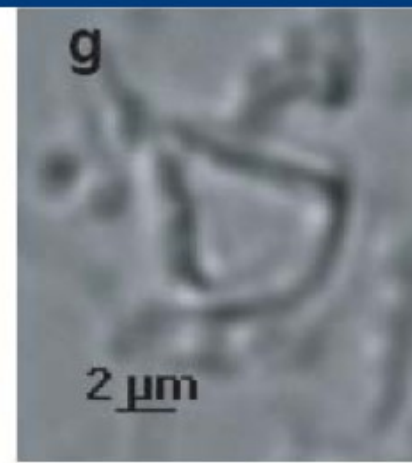
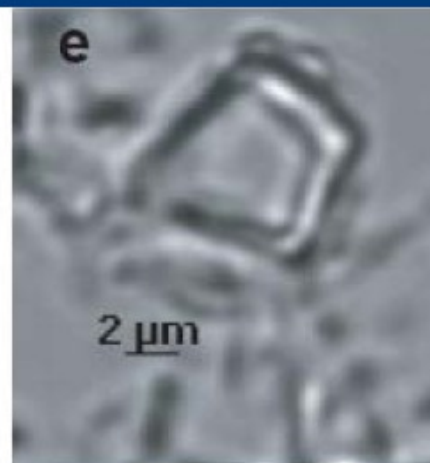
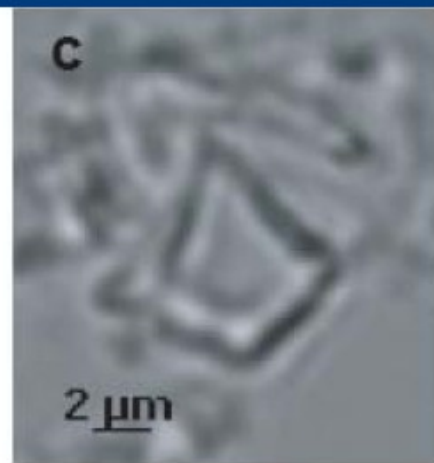
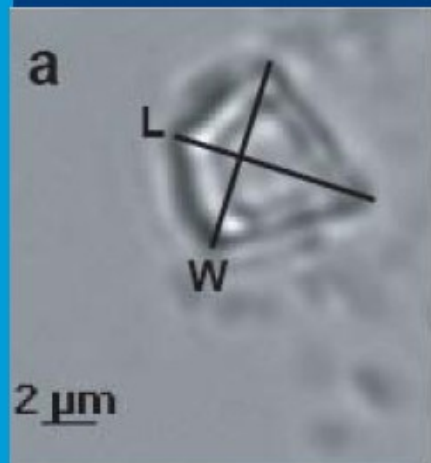
Document intra- and interspecific variability in the coccolithophores from the shallow and deep photic zone in the southern Indian Ocean

- Quantitative measurements
- Morphological analysis

Apply model to fossil record by establishing intraspecific variability in fossil record

- Interpret paleo-habitat of species
- Extrapolate paleoceanographic conditions

Minylitha convallis

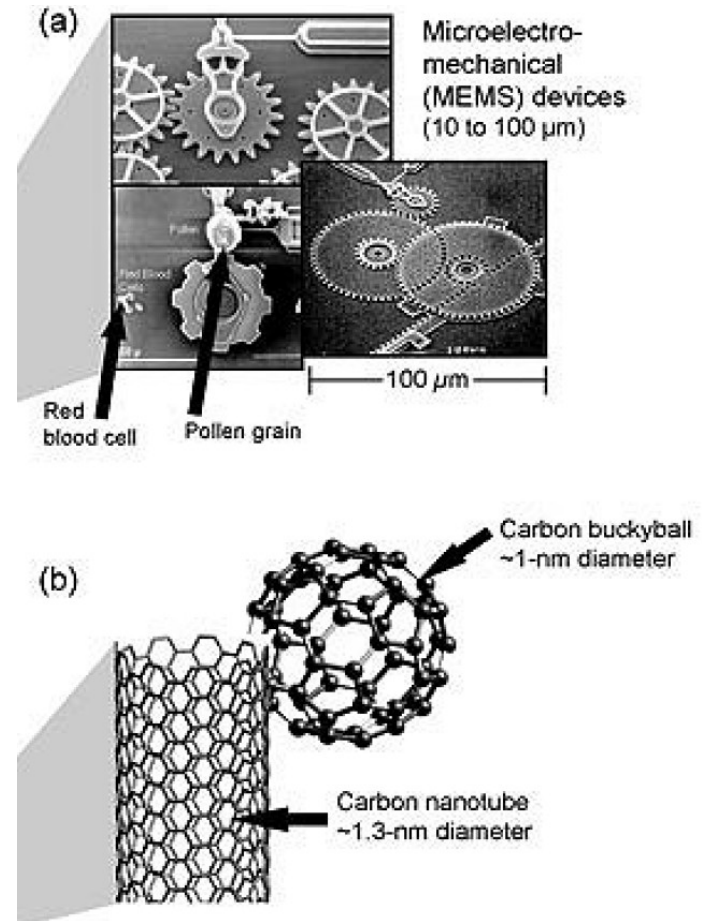


Nanotechnology Applications in Petroleum Reservoirs

- Nanotechnology-enhanced materials that provide strength and endurance to increase performance and reliability in drilling, tubular goods, and rotating parts.
- Improved elastomers, critical to deep drilling and to improve drilling in high-temperature/high-pressure environments.
- Designer properties to enhance hydro-phobic or hydrophilic behavior, to enhance materials for waterflood applications.
- Nanoparticulate wetting carried out using molecular dynamics, which shows promise in solvents for heterogeneous surfaces and porous solids.
- Lightweight, rugged materials that reduce weight requirements on offshore platforms, and more-reliable and more-energy-efficient transportation vessels.
- Nanosensors for improved temperature and pressure ratings in deep wells and hostile environments.
- New imaging and computational techniques to allow better discovery, sizing, and characterization of reservoirs.
- Nanosensors deployed in the pore space by means of “nanodust” to provide data on reservoir characterization, fluid-flow monitoring, and fluid-type recognition.
- Small drill-hole evaluation instruments to reduce drilling costs and to provide greater environmental sensitivity because of less drill waste.

Nanotechnology Applications in Petroleum Reservoirs

A buckytube, or nanotube, is an elongated cylinder of carbon atoms having a diameter a bit more than one nm and a length ranging from one μm to several millimeters. A nanotube also can contain process-activated molecules. Similar to a buckyball's behavior, the reaction of a nanotube offers a host of possibilities that may provide diagnostic information about reservoir flow and connectivity.



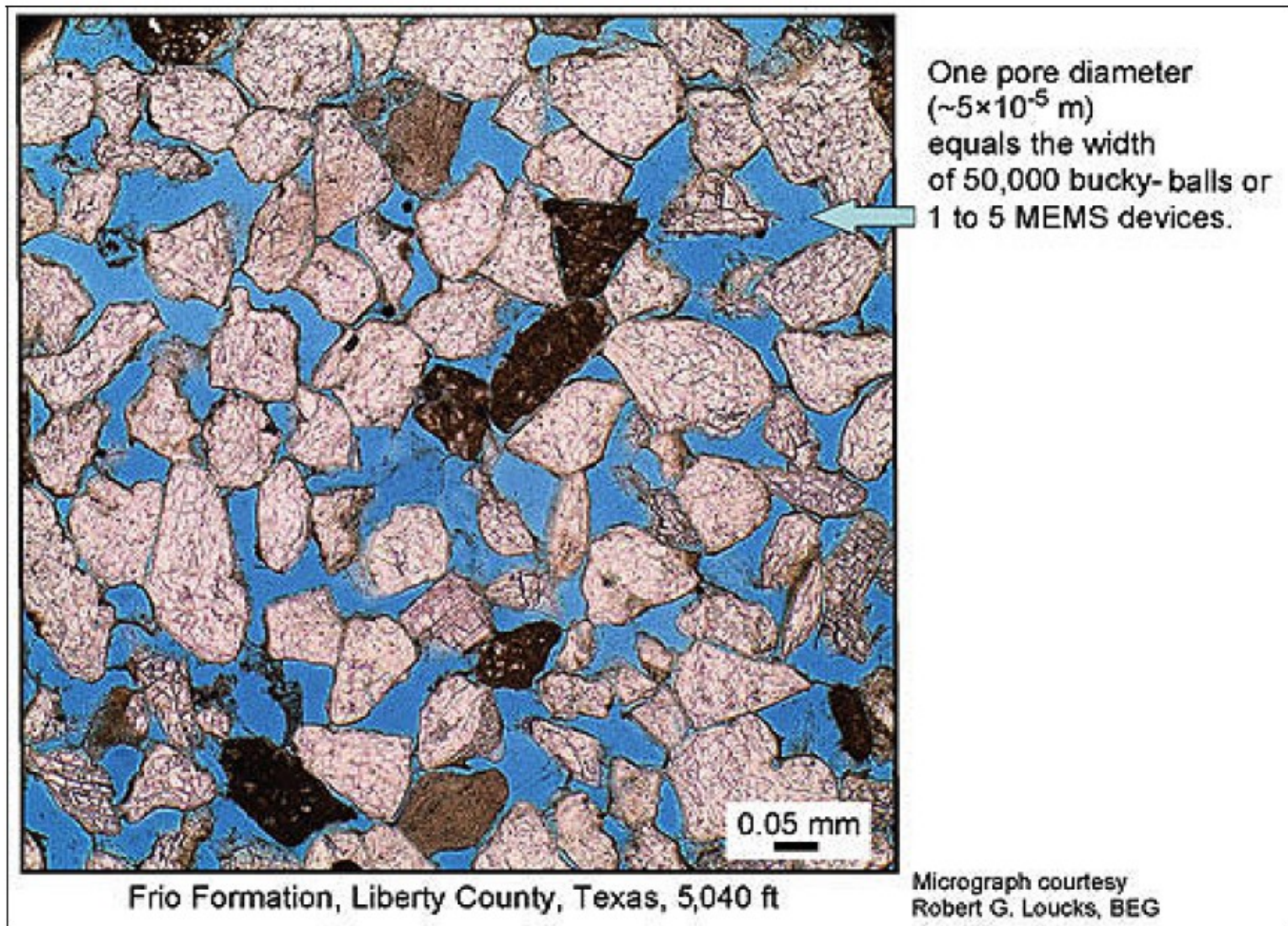


Figure 2. Thin section photomicrograph of Frio reservoir comparing pore dimensions with sizes of nanodevices. Porosity of reservoir interval ranges between 20 and 30 percent.

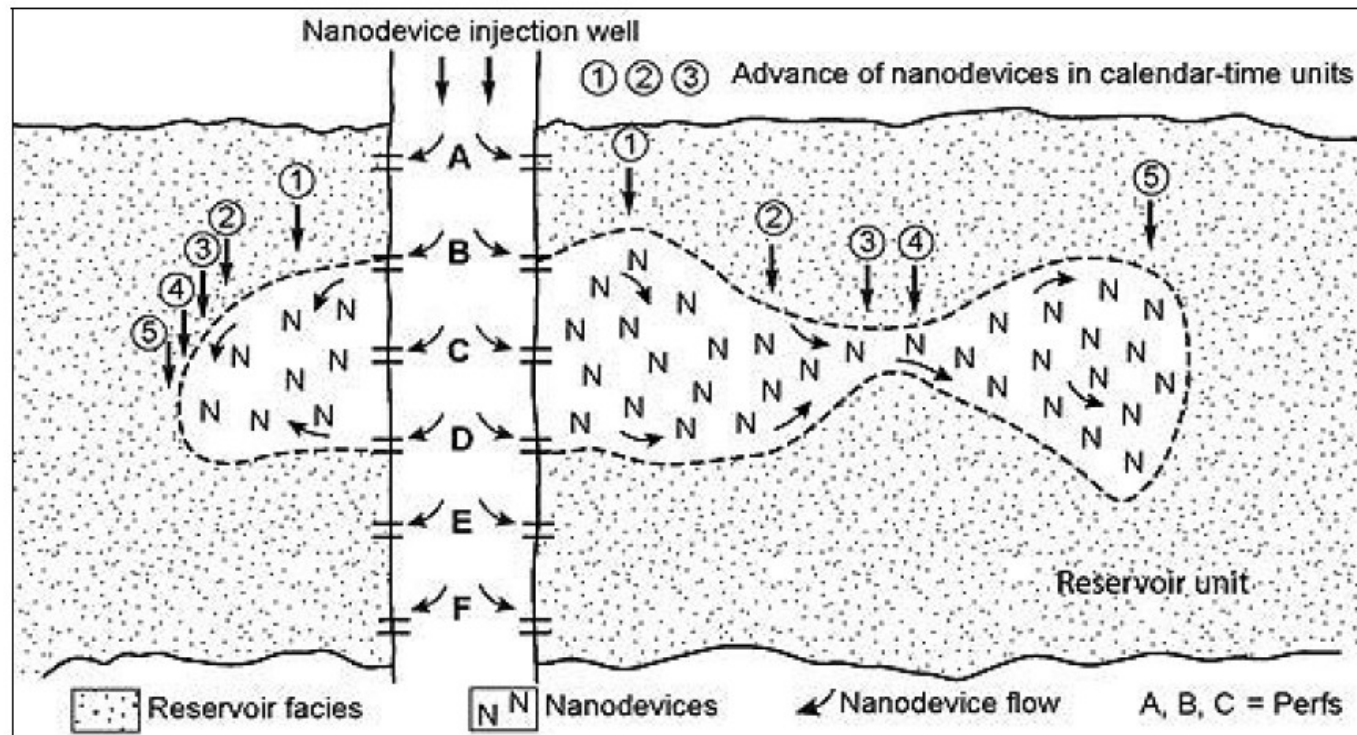


Figure 3. One concept for use of nanotechnology in reservoir characterization. Nanodevices (N) are injected in perfs A through F and move through a reservoir. At calendar-delay times of 1, 2, 3, 4 and 5 time intervals, spatial distribution of the nanodevices is measured by EM or seismic methods to determine their XYZ coordinates, allowing inferences to be made about fluid-flow paths, compartment boundaries and reservoir connectivity.

Because nanotubes can be designed to become efficient electrical conductors, electromagnetic (EM) measurements may be the branch of geophysics that first develops applications of nanotechnology in reservoir characterization

Nanocatalysts for the Production of Hydrocarbon-Based Fuels

Nanomaterials like zeolite and nanostructured metal oxides have been applied for a long time on an industrial scale for the decomposition of long-chain hydrocarbons in crude oil refining. With growing scarcity of global oil reserves the far greater amount of coal will regain importance as a source for liquid fuels and chemical raw materials in future. Up to now, the known technical methods for coal liquefaction failed due to lacking economic efficiency. Improvements of methods, inter alia in the field of nanostructured catalysts, can help increase the efficiency of coal hydrogenation considerably. Interest in coal liquefaction is currently observed especially in China, where several pilot plants are going to be installed. A long-term development goal is the low-cost production of synthetic Diesel and fuel petrol from natural gas or biomass gasification using nanooptimized catalysts.

Nanofluids and nanomaterials for drilling

Nanotechnology has opened the door to the development of a new generation of fluids defined as “smart fluids” for drilling, production and stimulation related applications.

Thanks to the exceptionally high surface to volume ratio, nanofluids and nano-based additives exhibit major interaction with the surrounding environment even at very low concentrations. Such smart fluids will further enhance drilling by adding benefits such as wettability alteration, advanced drag reduction and sand consolidation (Chaudhury, 2003; Wasan and Nikolov, 2003).

Petroleum laboratory has developed an advanced fluid mixed with nanosized particles and superfine powder that significantly improves the drilling speed and can eliminate formation damage in near wellbore zone (Esmaeili, 2009).

The use of two different types of polysilicon nanoparticles in oil fields to enhance water injection and improve oil recovery (Ju and Fa, 2009). Reportedly, one nanometer-scale polysilicon material could change the wettability of porous surfaces of sandstone and consequently affect the flow of water and oil when injecting a suspension of nanoparticles in an oil reservoir (Ju and Dai, 2002).

Anti-wear coating

- Goal is to increase durability in moving parts
- Increased durability gives added toughness, a longer life span, and a lower equipment cost over time
- Coating is usually sprayed on and will bond with the host material.
- Drilling materials need advances to be able to reach hard to get oil reserves

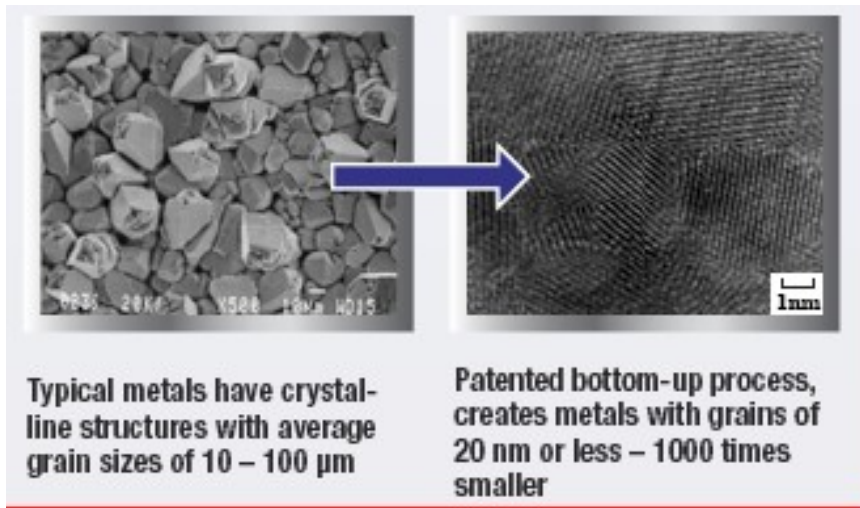
Nanovar

- Produced by Integran
- Can be put on most any composite metal
- Coatings custom made for situation and material being applied to



Nanovar

- Much denser than metal on an atomic level
- Provides strength, hardness, and thermal resistance which are three things needed in oil drilling in the future to reach reserves

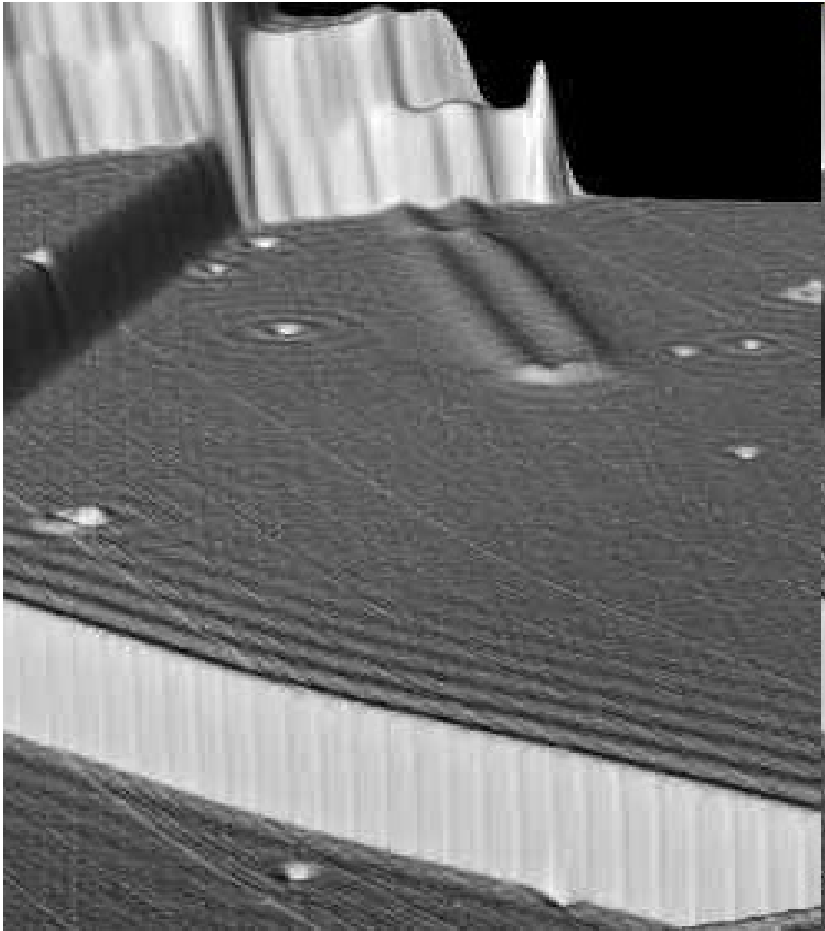


Anti-corrosion

- Long lasting coatings are needed to protect under sea pipes from sea water
- Coatings used on rigs and other platforms to prevent rust and corrosion that can cause safety issues
- More environmental friendly than anti-corrosion paints and cheaper



Anti-corrosion



- Metal surfaces are imperfect
- Surface penetration from the coating is vital to performance
- Nanocoatings can be custom made and outperform traditional coatings in this aspect

Nanofluids - lubricants

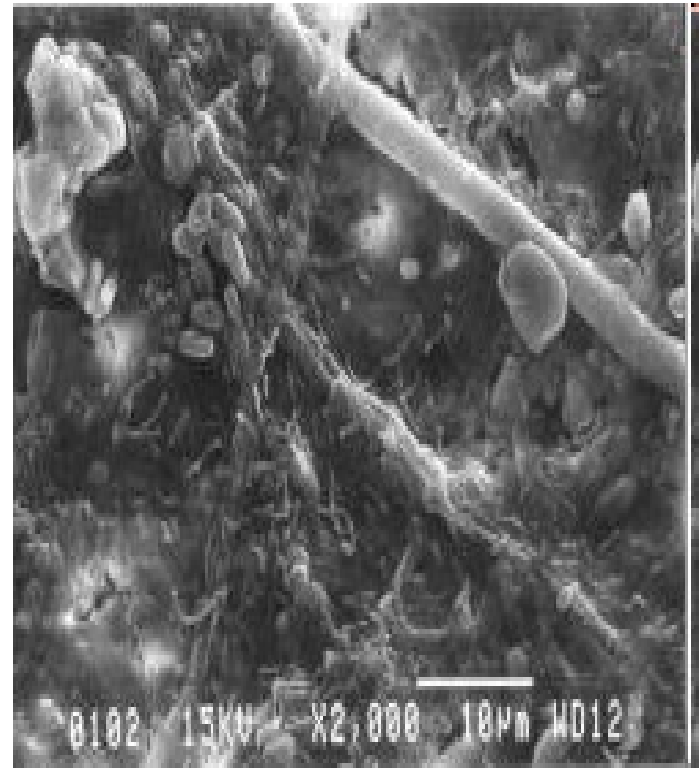
- Suspensions of nanoparticles in fluids that enhance its properties
- Main advantage in the oil and gas field is the enhanced thermal properties (performs well at high/low temperatures, transfers heat well, insulates well, etc)
- Highly customizable to the desired situation

Nanofluids – drilling mud

- Nanofluids used in drilling mud is being looked at as a solution to ultra deep drilling fluid
- Nanoparticles added at a low weight percentage can have a big impact in the fluid
- The suspension of nanoparticles can provide enhanced stability against sedimentation along with better thermal, mechanical, electrical, and magnetic properties
- Customizable for the situation and geography/region
- Improvements will enable access to deeper, hotter regions in high grade formations where oil cannot currently be reached

Anti-fouling

- Big issue in the marine industry
- These bacteria and plants can increase a ships fuel costs by 40%
- Environmental concerns about current anti-fouling paints



Anti-fouling

- AMBIO project is seeking a nanocoating solution that eliminates fouling
- Focuses on how microorganisms attach to the surfaces of ships
- Seeks to combine a low drag silicon coating with carbon nanotubes



Wrap-up

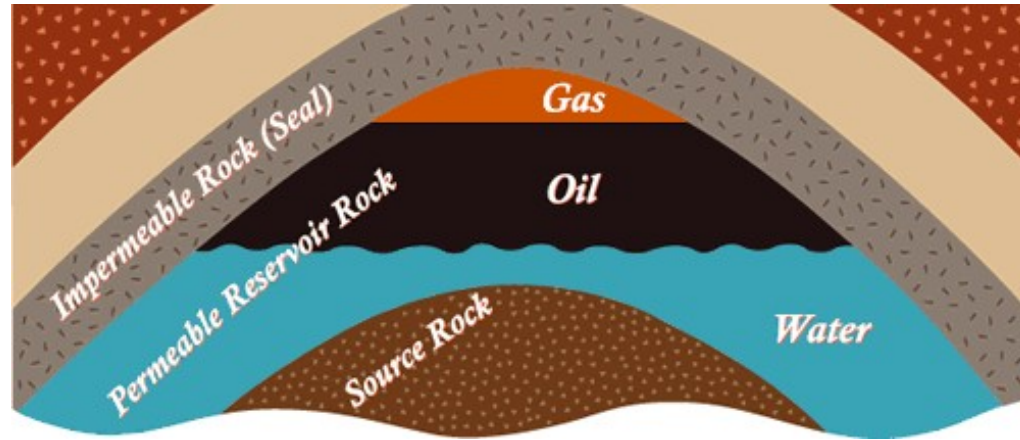
- Still a lot of development occurring in this field
- Development slowed by competing companies. No free flow of information
- Will be greatly important as we seek harder to reach oil and gas reserves

Reservoir Surveillance

- Purpose: To increase knowledge about oil wells in an attempt to recover more oil from wells
- Rice University is working on “nanoreporters”
- Made up of hundreds of millions of carbon clusters
- Each reporter is approximately 30,000 times smaller than a human hair



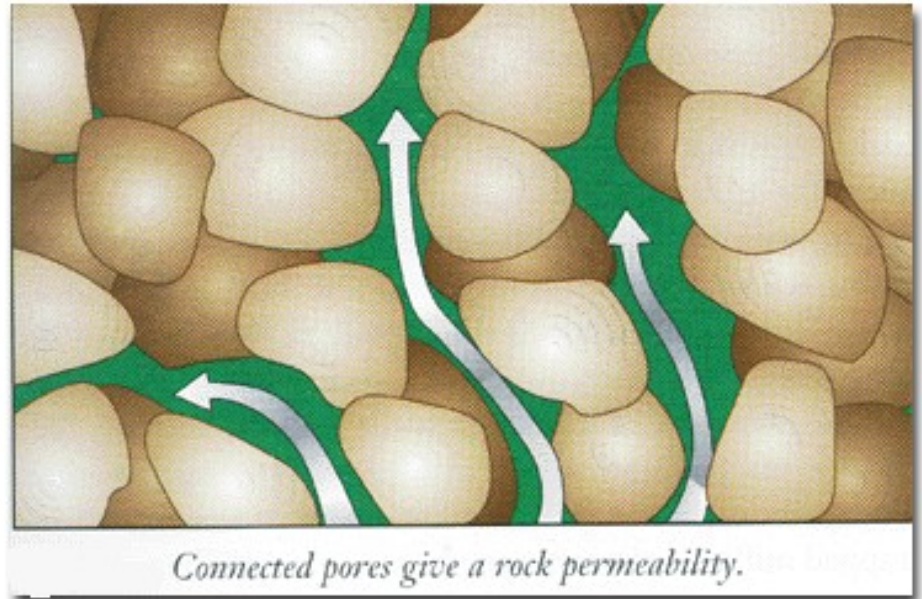
Reservoir Surveillance



- These “reporters” are designed to change their molecular makeup depending on what they encounter – water, petroleum, hydrogen sulfide, etc
- They are also given tags, similar to barcodes, that can tell scientists how long they have been underground

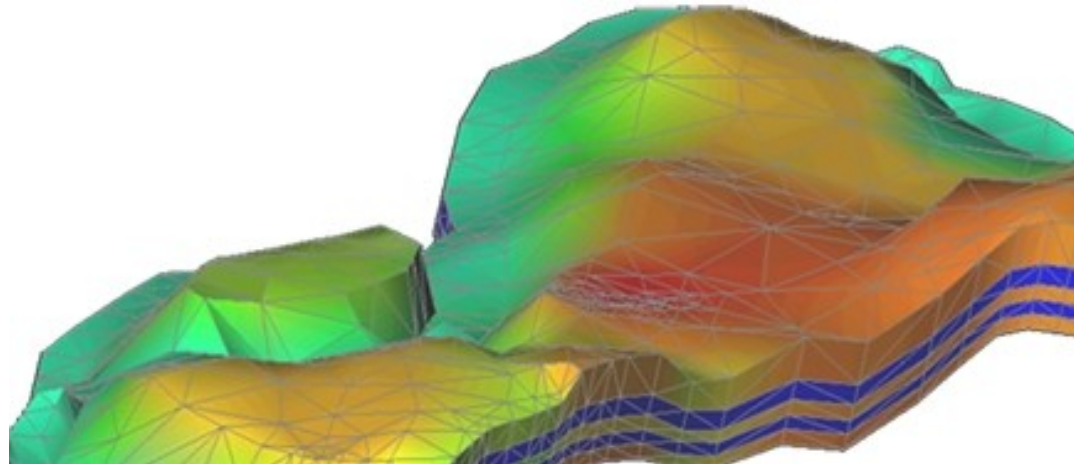
Reservoir Surveillance

- Lastly, they are being designed to be able to report properties about the material that they are currently near
- With the ability to report temperature and pressure, they can relay valuable information to scientists



Reservoir Surveillance

- How does this increased knowledge help?
- With a better idea of the physical properties of an oil reservoir, operators will have a much easier time finding and recovering oil
- This would also allow easier placement of Enhanced Oil Recovery (EOR) chemicals such as emulsifier and foamer



Nanorobots

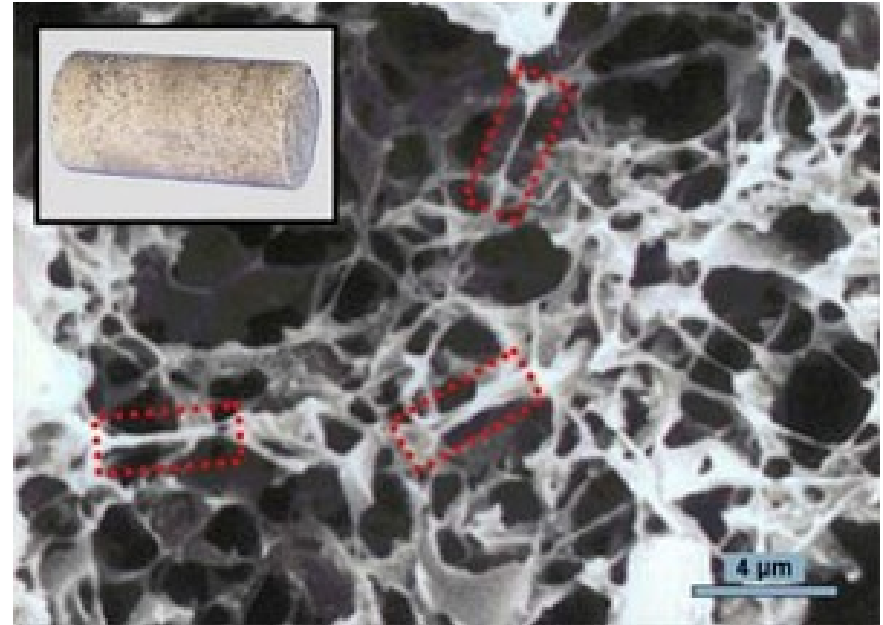
- Another new technology that may have an impact on the oil and gas industry is nano-robots. The EXPEC Advanced Research Center has been looking into this new technology
- They have coined the phrase resbots, or reservoir robots
- These resbots are designed for a similar purpose as the nanoreporters; however, they are proving to be difficult due to their larger size



Resbot lead technologist Mazen Kanj illustrates that one drop of solution contains more 600 billion Resbots. One milligram of the dry material holds 6 trillion Resbots.

Nanorobots

- In order for any particle to move through an oil reservoir, it must be able to pass through tiny pores in the rock
- In order for resbots to be able to pass through them, EXPEC ARC had to manipulate the physical and chemical properties of the resbots until they were able to pass through the pores



Reservoir rock holds oil in tiny pores connected by “pore throats,” outlined in red, which are even smaller than the pores. Nanorobots must be small enough to pass through the pore throats.