

## Chapter 2

# Natural Sources of Nanoparticles

Nicolae Strambeanu, Laurentiu Demetrovici, and Dan Dragos

**Abstract** This chapter deals with the major natural sources of nanoparticles in the atmosphere: volcanic eruptions, desert surfaces, dust from cosmic sources located in the solar system or outside it. Details are given about the composition of very fine particles according to their type, the successive or parallel chemical transformations that can occur among them or when they meet the major components of the atmosphere (nitrogen, oxygen, carbon dioxide). The authors specify possible ways of evolution from the mineral kingdom to organic substances through nanoparticles originating from cosmic dust, based on suppositions that are provided in the literature of the field and accepted based on physical and chemical computational models.

### 2.1 Introduction

Earth, cosmic and weather-dependent phenomena on the planet produce particulate matter that is lifted in air through volcanic eruptions, air currents generated by storms or strong winds, the disintegration of meteorites entering the atmosphere or the accumulation of cosmic dust.

Hurricanes cause huge amounts of water to rise in the atmosphere from the surface of the planetary ocean. On evaporation, water releases both the saline and spore contents of algae and other unicellular organisms. Due to these complex phenomena which most of the time occur simultaneously, at different heights and distances, the atmosphere is constantly filled with nanoparticles that cause various reactions affecting the biosphere.

---

N. Strambeanu (✉)

Pro Air Clean Ecologic, 37, Vadul Crisului Street, 300613 Timisoara, Romania

e-mail: [ns\\_arana@yahoo.com](mailto:ns_arana@yahoo.com)

L. Demetrovici

Pro Air Clean Ecologic, Timisoara, Romania

D. Dragos

Department of Pharmacy, “Victor Babes” University of Medicine and Pharmacy, Timisoara, Romania

A very good example of nanoparticle sources is the eruption of Krakatoa on August 27th, 1883. The smoke column reached 80 km in height and the dust thrown into the ionosphere not only caused strange optical effects visible in North America and Europe, but also acted as a solar radiation filter, decreasing global temperature with about 1.5 °C in the next 2 years. In addition, the eruption threw a huge amount of gas into the atmosphere which later air currents carried around the planet, a phenomenon that led to an unprecedented elevation of acid concentration under the form of very fine drops in the cirrus clouds at high altitude. Acid rains were the obvious consequence everywhere in the world [1–7].

Another example is the Tunguska event [8–11], whose probable cause was the collision of a gigantic meteorite or comet fragment with Earth on June 30th, 1908. For several weeks after the event, luminescent yellowish green clouds that made reading possible even during moonless nights could be seen above Europe and North Africa, at the extremity of the troposphere [12–14].

Some authors [15, 16] hold that the northern lights are very bright optical phenomena seen on the night sky in the areas near the polar regions, caused by the interactions between the ionosphere nanoparticles and the solar wind particles, under the influence of Earth's magnetic field. In the northern hemisphere, the phenomenon is known as *aurora borealis*, as Galileo Galilei named it. The northern lights appear in September–October and March–April. In the southern hemisphere, *aurora australis* was seen for the first time by James Cook, in his failed attempt to reach the South Pole.

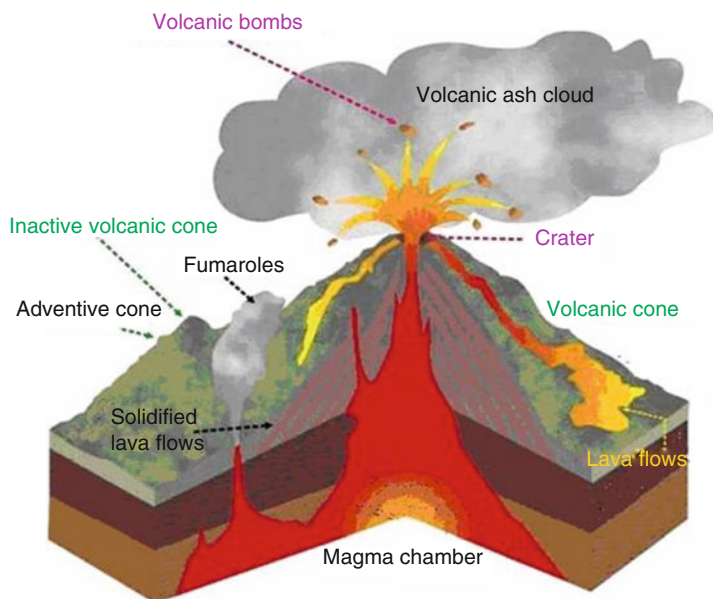
Auroras are not exclusive earthly events. They can also be seen on other planets of the solar system, such as Jupiter, Saturn, Mars and Venus. Although natural, they can be reproduced experimentally [16].

## 2.2 Volcanic Eruptions

Ash released during volcanic eruptions can reach temperatures over 1,400 °C and has a very complex structure consisting of solid and liquid particulate matter lifted by the hot gas current [17]. Following the paroxysmal phase of the volcano, as the ash spreads into the atmosphere, gas temperature lowers and gas composition changes; leading to the accumulation in deposit of particles either clusters through chemical reactions or based on electrostatic forces of attraction.

Volcanic gas emissions vary with thermodynamic and kinetic conditions (pressure, temperature, speed of reaction and diffusion, etc.) and the nature of magma (Fig. 2.1) [17]. Most volcanoes on Earth throw basaltic lava and erupt most frequently along the ocean ridges, at depth, having direct contact with the atmosphere only in several places of the world (Iceland and the Azores for the Atlantic Ridge).

Basaltic magma is rich in magnesium and iron and poor in silica. It generally has low viscosity and a reduced gas concentration consisting mainly of carbon dioxide and sulphur dioxide. Hydrogen sulphide (H<sub>2</sub>S) and hydrochloric acid (HCl) prevail in gas emissions (Table 2.1) [18–21].

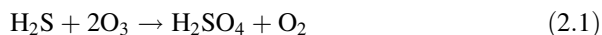


**Fig. 2.1** Intuitive representation of active and inactive volcanic phenomena [17]

**Table 2.1** Approximate composition of volcanic gas [18–21]

Component	H <sub>2</sub> O	CO <sub>2</sub>	SO <sub>2</sub>	H <sub>2</sub> S	COS	CS <sub>2</sub>	HCl	HBr	HF
% vol	50–90	1–40	1–25	1–10	10 <sup>−4</sup> –10 <sup>−2</sup>	10 <sup>−4</sup> –10 <sup>−2</sup>	1–10	10 <sup>−4</sup> –10 <sup>−2</sup>	<10 <sup>−3</sup>

As hydrochloric acid is highly soluble in water, it is quickly removed from the atmosphere through acid rains that usually start during eruptions, when water vapour condenses on cooled ash particles, in higher atmospheric layers. Hydrosulphuric acid has the same contribution, after it is oxidised by the ozone in the troposphere:



The hydrobromic acid (HBr) concentration is relatively low [22, 23]. However, its contribution, alongside hydrosulphuric acid oxidation, is significant for the direct decrease in both the ozone and the diatomic oxygen concentration, as it forms derivatives with the diatomic oxygen much easier than the hydrochloric acid:





There is little information about the hydrofluoric acid concentration eliminated by volcanoes in the atmosphere. In some cases (Laki 1783 or Mount Hudson 1990), hydrofluoric acid emissions were very high and contaminated the vegetation, killing animals and people. As with the other halogen acids, hydrofluoric acid spreads around the volcanoes through acid rains, so that excessive fluoride ions are one of the major causes of animal mortality on large areas, even a long time after the eruption. Fluoride intoxication becomes chronic and eventually lethal, if its concentration in the freshly grown vegetal matter exceeds 250 ppm [24].

The chemical composition of forming ash is easily identified if one studies the permanent emissions of latent volcanoes.

Dry fumaroles lack water and their temperature exceeds the critical temperature of water (374 °C). They contain nitrogen (N<sub>2</sub>), carbon oxide (CO), hydrogen (H<sub>2</sub>), methane (CH<sub>4</sub>), and sodium chloride vapour (NaCl), potassium chloride (KCl) and copper oxide (CuO). Through deposition on the edge of the crater, on the surface of the bombs thrown during eruption or under the form of ash, fumaroles generate particulate matter of halite (NaCl), sylvite (KCl), and tenorite (CuO) [17].

Acid fumaroles consist of hydrogen sulphide (H<sub>2</sub>S), sulphur dioxide (SO<sub>2</sub>), carbon dioxide (CO<sub>2</sub>) and water vapour. Their temperature is close to the critical temperature of water. They also contain iron chlorides (FeCl<sub>2</sub>, FeCl<sub>3</sub>), copper chlorides (CuCl, CuCl<sub>2</sub>) or iron oxides, mostly magnetite (Fe<sub>3</sub>O<sub>4</sub>), if acidity is not very high. In the presence of hydrogen sulphide (especially in submarine fumaroles), iron is found under the form of marcasite and pyrite (FeS, FeS<sub>2</sub>) [17].

Alkaline fumaroles are made of ammonium chloride (NH<sub>4</sub>Cl), ammonium hydroxide (NH<sub>4</sub>OH), in the presence of ammonia (NH<sub>3</sub>), in contact with water vapour. Ammonium chloride takes the form of micrometre or sub-micrometre particles. The temperature of these fumaroles is 100–400 °C.

Solfataras is a natural volcanic steam vent in which sulphur gases are the dominant constituent along with hot water vapours. The fumaroles releasing gases contain sulphur, hydrosulphuric acid (H<sub>2</sub>S) and or sulphur dioxide (SO<sub>2</sub>) and, in the presence of water vapour, sulphurous acid (H<sub>2</sub>SO<sub>3</sub>) and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), the latter being more stable. Realgar, orpiment (As<sub>2</sub>S<sub>3</sub>), ferrous, and copper pyrites, iron sulphate (FeSO<sub>4</sub>) and native sulphur resulted from vapour condensation have been identified as solid state of matter [17].

It must be specified that most metal and non-metal ores in Earth's crust were formed throughout the geological eras, because of volcanic activity. Consequently, any chemical element existing as such or in one of its combinations may be found in the atmosphere under the form of nanoparticles during eruptions or immediately after them.

## 2.3 Desert Surfaces of the Planet

Earth's large deserts are a major permanent source of nanoparticles which air currents lift in the atmosphere. The first observations about dust storms carrying dust from the Gobi Desert to the Yellow Sea coast were made in the fifth year of Di Xin of the Shang Dynasty (about 1150 BC) [25].

Dust storms seem to be the most important source of nanoparticles in the atmosphere. The long-range migration of both mineral dust and anthropogenic pollutants on the continents has been the focus of recent investigations which have revealed that about 50 % of aerosols in the troposphere are minerals originating from deserts [26] (Figure 2.2).

The chemical composition of very fine desert sand dust varies with origin and the anthropogenic activities developed in the adjacent areas that the air currents cross.

Analytical determinations of the particulate matter composition during a dust storm, performed in China and South Korea, reveal high silicon concentrations, aluminium, calcium and iron traces (Table 2.2). Many toxic substances like heavy metals (Hg and Cd) and PAHs (Polynuclear Aromatic Hydrocarbons) usually produced by coal burning have also been identified, but without specifying their origin in the stratospheric particle clouds which were the subject of the experiments [31, 32].

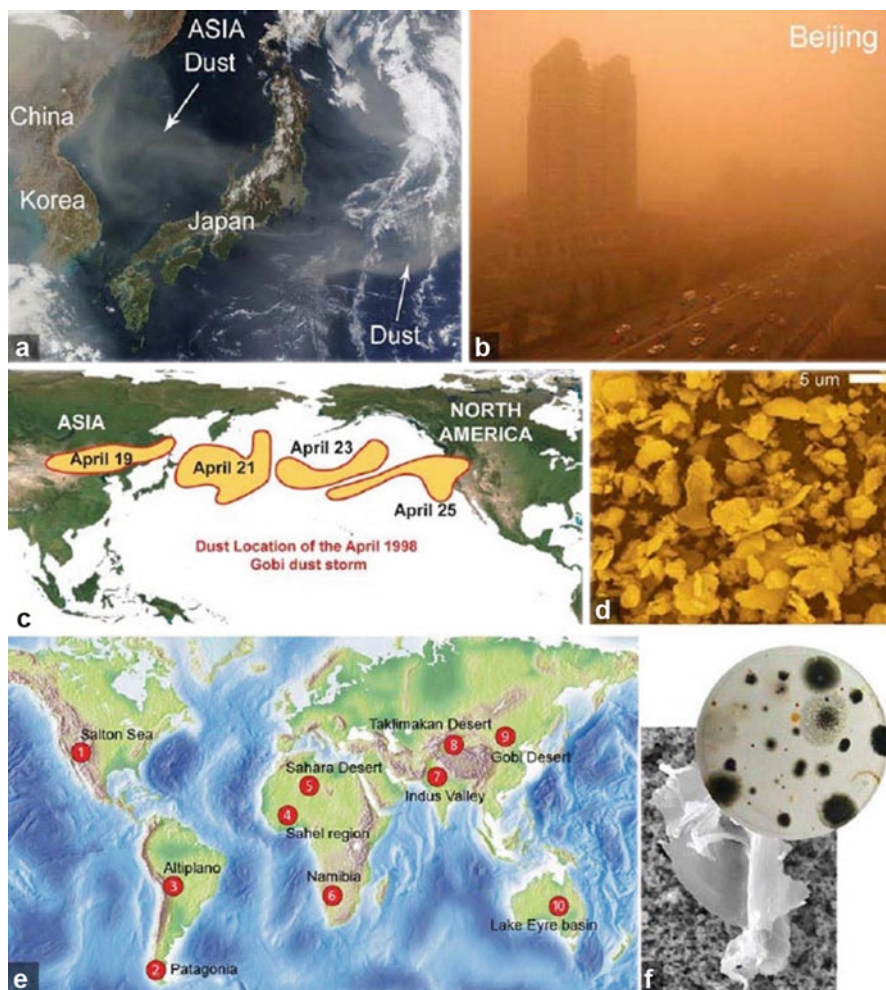
Recent simultaneous determinations conducted in the area around Xian, a city located at 400-m altitude, and at the summit of Mount Hua (2,060 m) during a massive atmospheric dust transport from the Gobi desert, have revealed sulphate, nitrate and ammonium ions of anthropogenic origin, besides a high carbon and organic nitrogen concentration, probably resulted from the atmospheric microbiological activity. The size of the wind-carried particles varied between 80 and 1,000 nm.

In the past decades, the type and behaviour of aerosols originating in Sahara have been studied intensively both in the Sahel region, in several archipelagos in the Atlantic Ocean, and Southern Europe.

Saharan dust contribution to  $PM_{10}$  was determined by gravimetric evaluation of Al, Si, Fe, Ti, nns (non-sea salt) Ca, nssNa and nss K oxides [33]. In most cases, the microcrystal content accounts for over 75 % of the oxide content identified as PM through measurements taken in Italy during Saharan-type dust storms, for several years. According to the multiannual means, the microcrystal content in Southern Italy atmosphere, expressed as  $PM_{10}$ , is  $5.42 \mu\text{g}/\text{m}^3$ , reaching a value as high as  $67.9 \mu\text{g}/\text{m}^3$  when air currents are strong. The amount of microcrystal aerosols and their contribution to  $PM_{10}$  indicate non-significant season dependence.

Optical measurements of particles, taken in parallel with composition measurements, show that within the 400–600-nm range, dust contains mostly soluble compounds of Fe, K and Co.

An estimation of the ionic balance of the atmosphere indicates that, on the one hand, the reactions involving anthropogenic acids and microcrystal particulates can play a major role in the sedimentation of nanoparticle systems; on the other hand,



**Fig. 2.2** Sand storms viewed at micro and macroscale. (a) Satellite images of the dust storm in mainland China over the Sea of Japan and the Pacific in April 2002. (b) Dust storm in Beijing [27]. (c) Approximate propagation of the dust cloud from a storm in the Gobi desert in April 1998 (models based on satellite photos) [28]. (d) Dust sample collected in South-Eastern Asia during a storm in the Gobi desert, on March 16th, 2001 [29]. (e) Ten major dust sources in the world [32]. (f) Bacteria collected from Sahara dust samples that reached North America [30]

**Table 2.2** Approximate composition of particulate matter in the Gobi desert, in China and Korea [31, 32]

Component	Si	Al	Ca	Fe
Nanoparticle content (% mass)	24–32	5.9–7.4	6.2–12	<1

they can influence the introduction of the mentioned substances in the cellular structures of living organisms [33].

Other studies conducted in the Cape Verde Islands [33] and the Island of Sal near the Senegalese coast [30], during fine particle advection caused by the Harmattan, were based on collecting fine dust samples on board of aircraft, at altitudes between 500 and 11,000 m. The results showed that while moving, the main cloud consisted of different particle currents, sedimented according to their mass (0.5–1 to 4–4.5 km altitude), based on statistical distribution.

Beyond 4,500 m, air opacity and  $O_3$  concentration decrease, which highlights the  $O_3$  reaction with sub-micrometre particles. The supposition is based on specific  $Al_2O_3$  concentrations containing up to  $54 \mu g/m^3$ , measured during very intense dust transport.

The same studies [34, 36] identified nanoparticles of compounds resulting from reactions of their components with anthropogenic aerosols, especially ammonium sulphate ( $NH_4HSO_4$ ). Samples collected at high altitudes were associated with air masses coming from Europe and travelling over North African desert areas. This hypothesis is much more plausible than that based on the great influence of local biomass combustion emissions, as the nitrate concentration did not increase. At high altitude, old pollution plumes resulted from fossil fuel combustion of possible North American origin were encountered.

The geochemical signature of dust particles resulted from the above-mentioned determinations was consistent with the previous results obtained in the area. According to these results, Si, Fe, and Ti concentrations were not changed, reflecting the soil composition faithfully, while the concentration of other elements like Ca and S increased from one decade to another, because of industrial activities developed in the African deserts [35].

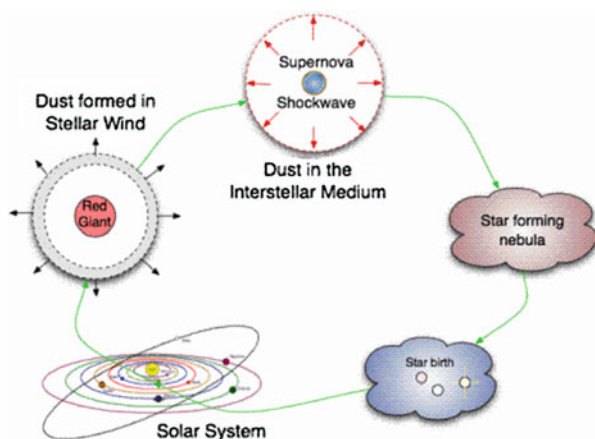
## 2.4 Cosmic Dust

The total influx of cosmic dust on Earth is about 40,000 t/year, of which the major fraction originates in the interplanetary dust cloud surrounding the Sun, the planetoids between Mars and Jupiter or the comets [37]. The components of the minor fraction can be classified according to their astronomic origin from beyond our solar system: interstellar dust, dust from meteorite clouds existing between the stellar systems (Ephemeris, Perseids, and Leonids) that the Sun and its planets cross periodically or those in the Kuiper Belt (30–50 AU far from the Sun) and the very large Oort cloud. Figure 2.3 gives a brief presentation of cosmic dust sources on Earth [37].

Regardless of their size, cosmic objects cross the space at high speed, sometimes over 150,000 km/h. As they approach the Earth, they slow down because of the friction with the atmosphere, which causes meteorites to burn up and give their characteristic glow. Smaller particles produce friction that reduces their speed through the atmosphere, but they do not burn up and finally reach the surface of the Earth.



**Fig. 2.3** Sources of cosmic dust on Earth [38]



Interplanetary dust composition and size were measured based on IR detection, during space missions like Pioneer 10 and 11, Giotto and Galileo. Similar measurements were taken under the EURECA programme, with satellites in circumterrestrial orbits situated at different distances. The studies conducted in the field were completed with data collected in the exosphere, at an altitude of 20–25 km.

This older or more recent research work reveals that cosmic dust consists of microparticles, nanoparticles and their aggregates. These are irregular-shaped and their porosity varies from spongy to compact. Their composition, size and physico-chemical properties are origin-dependent. For instance, the grains in dense matter interstellar clouds are covered in ice; consequently, they are much larger than dust particles in diffuse interstellar medium. Interplanetary dust particles (IDP) are usually the largest.

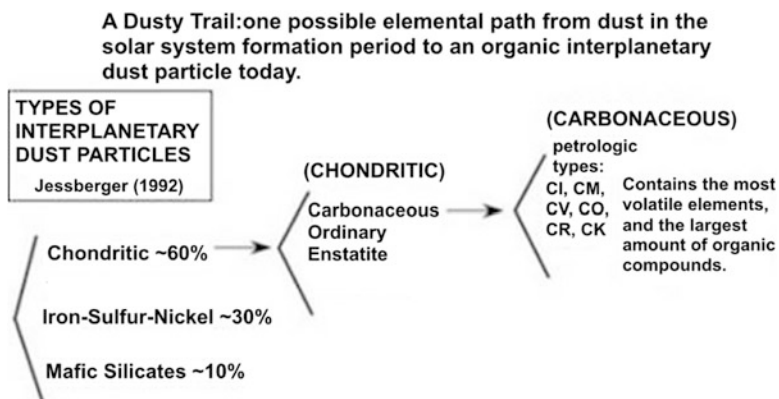
The largest fraction of the extra-terrestrial dust influx falling on Earth comes from meteorites in the 50–500  $\mu\text{m}$  size range, 2.0  $\text{g}/\text{cm}^3$  average density and 40 % porosity. The density of most IDP captured in the atmosphere ranges between 1 and 3  $\text{g}/\text{cm}^3$ , with an average of 2.0  $\text{g}/\text{cm}^3$  [38].

Interstellar dust clouds contain carbon monoxide, silicon carbide, amorphous calcium silicate, water ice and polynuclear aromatic hydrocarbons (PAH) or other simpler organic structures, while in diffuse interstellar medium carbon and silicon particles have been identified.

Comet dust differs in composition from dust resulted from asteroid disintegration. The former is closer to interstellar clouds, while the latter contain large amounts of silicon and iron [39–41].

A recent study [42] has identified the proportions of different element forms—hydrogen, oxygen, carbon, nitrogen—in comet dust samples collected during space missions. The relations between these elements provide information about the distance between the Sun and the place where comets were formed and what type of existence comets had (a high temperature is an indication that they passed close to the Sun).





**Fig. 2.4** A possible evolution path from the mineral kingdom to organic substances through cosmic dust nanoparticles [42]

It has also been revealed that cosmic dust contains organic substance complexes under the form of aromatic–aliphatic mixtures, which may be created spontaneously in the Universe, as shown in Fig. 2.4 [42].

Computational chemistry studies about complex organic molecules that forms the bases of life have led to the theory that such molecules might have been formed in the protoplanetary disc, in the nanoparticles that revolved around the Sun, before the formation of the Earth [43]. According to computer models, the process could be the same around any star that acquires planets through a mechanism similar to their formation around the Sun [44].

Other studies [45, 46] have revealed that under conditions similar to those in the interstellar medium, polynuclear aromatic hydrocarbons (PAH) change to amino acids and nucleotides through hydrogenation, hydroxylation or partial oxidation. The database for tracking PAH in the universe has been updated and enriched. According to very recent estimations, over 20 % of the carbon compounds can be tied up in PAH. It has even been asserted that PAH may have been formed only a short time after the Big Bang, are spread throughout the universe and can be associated with the formation of new stars and exoplanets [47].

Studies concerned with nanoparticle properties provide valuable information about planetary systems formation and the origin and role of water and organic substances in producing the first self-reproductive systems that have generated life.

## References

1. Aber JS (2006) Climatic controls of glaciations. ES 331/767 Ice age environments. Emporia State University, Kansas, USA. Course web site: <http://academic.emporia.edu/aberjame/ice/icehome.html>
2. Mandia A. Scott (2005) Possible causes for climate change, Smithtown Sciences Bldg

3. Houghton JT, Ding Y (2002) Climate change 2001: the scientific basis. IPCC. Int J Climatol 22(9):1144. <http://onlinelibrary.wiley.com/doi/10.1002/joc.v22:9/issuetoc>
4. Jones PD, Mann ME (2004) Climate over past millennia. Rev Geophys 45(2). <http://onlinelibrary.wiley.com/doi/10.1002/rog.v42.2/issuetoc>
5. Garrett C (1997) Volcanoes and climate change. <http://tiger.chm.bris.ac.uk/>
6. Robock A (1979) The little ice age: northern hemisphere average observations and model calculations. Science 206:1402–1404
7. Weber G (2005) Toba volcano, The Andaman Association
8. Gasperini L, Bonatti E, Longo G (2007) 100 years later, Tunguska remains mysterious. Terra Nova 19(4):245–251
9. Morgan J, Ranero CR et al (2004) Contemporaneous mass extinctions, continental flood basalts, and ‘impact signals’: are mantle plume-induced lithospheric gas explosions the causal link? Earth Planet Sci Lett 217:263–284
10. Yu A (2003) Ol’khovatov. Earth, moon and planets 93:163–173
11. Rubtsov V (2009) The Tunguska mystery. Springer, New York, NY
12. Verma S (2005) The Tunguska fireball: solving one of the great mysteries of the 20th century. Icon Books, Cambridge
13. Verma S (2006) The mystery of the Tunguska fireball. Icon Books, Cambridge
14. Las Heras A (2008) Enigma Tunguska. Editura Litera Internațional, București
15. Eather RH (1980) Majestic lights: the aurora in science, history, and the arts. American Geophysical Union, Washington, DC
16. Savage C (2001) Aurora: the mysterious northern lights. Sierra Club Books/Firefly Books, San Francisco, CA
17. Juravle D (2012) Geologia României, vol 1. Editura Universităţii, Iaşi
18. Symonds RB, Rose WI et al (1994) Volcanic gas studies: methods, results and applications. Rev Mineral 30:1–66
19. Symonds RB, Rose WI et al (1988) Contribution of Cl- and F-bearing gases to the atmosphere by volcanoes. Nature 334:415–418
20. Cadle RD (1980) A comparison of volcanic with other fluxes of atmospheric trace gas constituents. Rev Geophys Space Phys 18:746–752
21. Chin M, Davis DD (1993) Global sources and sinks of OCS and CS2 and their distributions. Global Biogeochem Cycles 7:321–337
22. McElroy MB, Salawitch RJ et al (1992) The changing stratosphere. Planet Space Sci 40:373–401
23. Bureau H, Keppler H et al (2000) Volcanic degassing of bromine and iodine: experimental fluid/melt partitioning data and applications to stratospheric chemistry. Earth Planet Sci Lett 183:51–60
24. Textor C, Graf HF, Timmreck C, Robock A (2003) Emissions from volcanoes (chapter 7). In: Granier C, Reeves C, Artaxo P (eds) Emissions of chemical compounds and aerosols in the atmosphere. Kluwer, Dordrecht
25. Tungsheng L, Xiongfei G et al (1981) Desert dust: origin, characteristics, and effect on man. Geological Soc Am 186:149–157
26. Shi Z, Shao L, Jones T, Lu S (2005) Microscopy and mineralogy of airborne particles collected during severe dust storm episodes in Beijing, China. J Geophys Res. p 301
27. USA today, 18361–18370, Sept 19 2005
28. Husar RB (2001) The Asian dust events of April 1998. J Geophys Res 2001:233–243
29. Buseck PR, Pósfai M (1999) Airborne minerals and related aerosol particles: effects on climate and the environment. Proc Nat Acad Sci 96:3372–3379
30. Taylor DA (2002) Dust in the wind. Environ Health Perspect 110(2):A80–A87, <http://www.ncbi.nlm.nih.gov/pubmed/?term=Taylor%20DA%5Bauth%5D>
31. Du Xiaodan (2007) Northern dust brings dirty skies in Shanghai. J Geophys Res
32. Chun Y, Cho H et al (2008) Historical records of Asian dust events (Hwangsa) in Korea. Bull Am Meteorol Soc 89:823–827

33. Wang GH, Zhou CB et al (2012) *Atmos Chem Phys Discuss* 12:21355–21397
34. Marconi M, Sferlazzo DM et al (2013) Saharan dust aerosol over the central mediterranean sea: optical columnar measurements vs. aerosol load, chemical composition and marker solubility at ground level. *Atmos Chem Phys Discuss* 13:21259–21299
35. Formenti P, Elbert WJ (2003) *J Geophys Res Atmos* 108
36. Goudie AS, Middleton NJ (2001) *Earth Sci Rev* 56:179–204
37. Zook HA (2001) Accretion of extraterrestrial matter throughout Earth's history. pp 75–92
38. Outreach site of Herschel Space Observatory. <http://sci.esa.int/herschel/>
39. Love SG, Joswiak DJ et al (1992) Densities of stratospheric micrometeorites. *Icarus* 111: 227–236
40. Humphreys W, Roberta M et al (1972) Spectroscopic and photometric observations of M Supergiants in Carina. *Astrophys J* 172:75
41. Donald D, Clayton W et al (1999) Condensation of carbon in radioactive supernova gas. *Science* 283:1290–1292
42. Donald D, Clayton W (2011) A new astronomy with radioactivity: radiogenic carbon chemistry. *New Astronomy Rev* 55:155–165
43. Starkey N (2013) Insight into the silicate and organic reservoirs of the comet forming region. *Gnocchi et Cosmochim Acta* 105:73–91
44. Kwok S, Zhang Y (2011) Mixed aromatic: aliphatic organic nanoparticles as carriers of unidentified infrared emission features. *Nature* 479:80–83
45. Moskowitz C (2012) Life's building blocks may have formed in dust around young sun. *Space.com*
46. Gudipati MS, Yang R (2012) In-situ probing of radiation-induced processing of organics in astrophysical ice analogs: novel laser desorption laser ionization time-of-flight mass spectroscopic studies. *Astrophys J Lett* 756(1). <http://iopscience.iop.org/2041-8205/756>
47. Hoover R (2014) Need to track organic nano-particles across the universe? NASA's got an app for that. <http://www.nasa.gov/ames/need-to-track-organic-nano-particles-across-the-universe-nasas-got-an-app-for-that/#.VC2hdmeSzSs>

Nanoparticles' Promises and Risks  
Characterization, Manipulation, and Potential Hazards  
to Humanity and the Environment

Lungu, M.; Neculae, A.; Bunoiu, M.; Biris, C. (Eds.)

2015, XIV, 355 p. 135 illus., 92 illus. in color., Hardcover

ISBN: 978-3-319-11727-0