Oxygen – a premier class element

published in Beauty Forum 2021 (2), 42-44

We inhale it and egest the largest part of it in the form of carbon dioxide and water. It is transparent and without any scent. There is talk of oxygen: a colourless gas that only appears bluish when seen from the outer space and that we all seem to know.

Oxygen (O) is the most frequent element in the geosphere (up to 16 km depth) and in the earth crust (up to 35 km depth) where, unlike the diatomic gaseous O_2 in the air, it forms a compound with other elements.

Oxides

Whenever oxygen is bound with a single other element, we speak of oxides (table 1).

Table 1: List of oxides

Bound element	Oxygen compound	Common name
Hydrogen (H)	Hydrogen oxide, H_2O	Water
Aluminium (Al)	Aluminium oxide, Al_2O_3	Aluminium oxide
Iron (Fe)	Iron oxide, Fe_2O_3	Rust
Silicon (Si)	Silicon dioxide, SiO_2	(Quartz)-sand
Nitrogen (N)	Nitrogen dioxide, NO_2	Nitric oxide
Carbon (C)	Carbon dioxide, CO_2	Carbon dioxide
Sulphur (S)	Sulphur dioxide, SO_2	Sulphur dioxide
Magnesium (Mg)	Magnesium oxide, MgO	Magnesia

When further elements participate in the compound, there are often substances involved that form entire mountain ranges (table 2).

Table 2: Oxygen compounds with additional elements

Bound element	Oxygen compound	Common name
Calcium (Ca), carbon (C)	Calcium carbonate, $CaCO_3$	Limestone, Chalk, Marble
Calcium (Ca), magnesium (Mg), carbon (C)	Calcium magnesium carbonate, $CaMg(CO_3)_2$	Dolomite
Calcium (Ca), sulphur (S)	Calcium sulphate, $CaSO_4$	Gypsum, Anhydride
Aluminium (Al), silicon (Si)	Aluminium silicate, $Al_2(SiO_3)_3$	Clay

Further oxygen compounds

While water in the form of a liquid oxide presumably is the most frequent cosmetic ingredient, the group of solid oxides comprises many pigments for decorative purposes – as for instance iron oxides (red, brown, black) and titanium dioxide (white). Calcium sulphate can be found in hardening masks and modelages. Sand, bentonite and iron oxides are the main ingredients of mineral clay and healing earths used as (cleansing) masks or for physiotherapeutic applications.
Despite of the discussions around aluminium, basic aluminium acetate is a widely used astringent in the medical field. It should be said however that the term is somehow misleading since the mineral clay, as mentioned above, is no longer existent but is a matter of aluminium salts that form with the reaction of aluminium oxide with acetic acid (acetates) or tartaric acid (tartrates).
Both are organic carboxylic acids that contain oxygen besides carbon and hydrogen. These carboxylic acids belong to a multitude of organic oxygen compounds. The most important are the following:

- alcohols, as for instance ethanol (ethyl alcohol), isopropyl alcohol (frequent alternative for disinfecting purposes), benzyl alcohol (preservative) and glycerine (component of the NMF),
- aldehydes and ketones, which comprise many odorous substances such as citronellal (lime) and muscone (musk),
- carboxylic acids, such as acetic acid, citric acid, salicylic acid and essential fatty acids (linoleic acid, α-linolenic acid, etc.), as well as the
- compounds among each other – as for instance ethers (“ether“ of 2 x ethyl alcohol) or esters (of alcohol and carboxylic acid). Main ingredients of the herbal oils and animal fats are triglycerides, or in other terms, esters formed of glycerine and three carboxylic acids.

Alcohols, carboxylic acids and carboxylic acid esters are frequently found in cosmetic products and serve as solvents, spreading agents, acid-peeling agents, consistency agents, fattening components and active agents.
The number of oxygen compounds in living organisms still is increasing, if other elements are added as for instance nitrogen occurring in amino acids, peptides and proteins, or phosphor and trace elements.
Oxygen-free compounds, such as carbohydrates – an example here is squalene that occurs in the human sebum – rather are an exception or exist in combination with anaerobic microorganisms, in other words microorganisms living in oxygen-free conditions. The methane formation in the stomachs of ruminants can be mentioned as an example here.

Oxidation

Oxygen is a very reactive element that fortunately requires a certain amount of activation energy (high temperature, matches, or radiation) in order to convert combustible, or in other words, oxidisable substances in an accelerating chain reaction. Without such a threshold the world around us would be impossible since everything would burn immediately respectively be oxidised immediately.
During these oxidation processes energy is generated that not only is used in power plants to produce electricity and in cars for the locomotion but also in our body for the maintenance of body temperature and the provision of mechanical energy in the muscles. There are specific organelles in the human cells for this purpose – they are called mitochondria. The most important oxidation processes in mitochondria are:

- degradation of acetyl-coenzyme A in the citric acid cycle,
- degradation of fatty acids by means of ß-oxidation, and
- glucose oxidation.

In analogy to the fuel cell the oxidations are biochemically controlled. The individual reaction steps are catalysed by enzymes (oxidoreductases), or in other words, implemented with the lowest possible amount of activation energy. In this process also radical reactions take place. End products are carbon dioxide, which is exhaled, as well as water and oxidised organic compounds whereas the major part of them is excreted via faeces and urine. The urea contained in the urine links the carbon dioxide to the waste product called ammonia.
Outside of the mitochondria the uncontrolled radical oxidations can be harmful. That is why the cells of organisms are protected by antioxidants such as vitamin C (ascorbic acid) and vitamin E (tocopherol). Within the skin barrier the protective functions are assumed by the amino acids of the Natural Moisturizing Factor (NMF) and several peptide structures that, in particular, are effective against oxidising atmospheric radicals such as nitrogen oxides.
In the so-called “free“ nature the simultaneous impact of oxygen and energy-rich (UV) radiation generates a multitude of harmful substances. Just to mention some examples:

- the photochemical oxidation of herbal or anthropogenic carbohydrates into peroxyacetyl nitrate (PAN), a component of atmospheric smog,
- the impact of ozone consisting of 3 oxygen atoms (O_3) on organic compounds,
- the formation of allergenic peroxides from essential oils, as for instance ascaridol from tea tree oil, or
- the peroxidation of unsaturated acids; in this process cleaving products are formed (aldehydes) causing the rancid smell of oils and fats.

ROS and free radicals

Particularly aggressive besides the ozone (O_3) and the energy-rich singlet oxygen ($^1O_2$) are peroxide anion (O_2^{2-}), hydroxyl radical (HO•) and the hyperoxide anion alias superoxide anion (O_2^-). They belong to the group of ROS (Reactive Oxygen Species). The organic hydroperoxides (R-OOH), peroxy radicals (R-OO•) and alkoxy radicals (R-O•), all resulting from uncontrolled reaction with organic compounds, also are very reactive and harmful. In order to avoid their formation and to protect against them, food, cosmetic products and many other objects of our daily life are supplemented with antioxidants. The basic principle is to react with the ROS before the substances to be protected are reacting. The antioxidants are consumed in the process, though.
With sun protection products the cosmetic industry adopts another strategy. Before radicals can form, the radiation is transferred into heat by means of UV filters.

Oxidative effects on the skin

Lipid- (“lipid peroxidation") or protein damages ("protein oxidation") in the skin can trigger inflammatory- and aging processes, DNA damages as well as skin alterations up to carcinoma. Visible symptoms are age spots consisting of oxidised protein lipid complexes (lipofuscin) or sugar protein agglomerates (Ad-

vanced Glycation Endproducts [AGE]). In the case of AGE the carbohydrates react with the amino acids and proteins and form so-called melanoidins in a concomitant oxidation process.
With a normal physiological metabolism and in the case of immune responses the body itself utilizes the aggressive ROS molecules. Just to mention hydrogen peroxide (H_2O_2) as an example which the body uses for specific biochemical reactions in an enzyme-controlled process. Surplus hydrogen peroxide is degraded into water and oxygen by the enzyme catalase (CAT) and into water by the selenium-containing glutathione peroxidase (GPX). In this way damages to the organism are avoided unless there are enzyme deficiencies.
The visible consequence of an existing enzyme deficiency for instance is vitiligo (skin depigmentation). In this particular case non-degraded hydrogen peroxide affects the melanin and the melanin formation process of the body. Large areas of the skin then remain unpigmented. A similar effect can be observed during the bleaching process of skin and hair by means of hydrogen peroxide.
Also the skin flora has specific enzymes to oxidise and degrade the lipids. In this process, among other substances, also short-chained carboxylic acids are formed that build up the protective acid mantle of the skin and reduce the pH level.

Oxygen in therapeutic applications

The oxygen multistep therapy[1] developed by Manfred von Ardenne consists of an inhalation of pure oxygen or an increase of the oxygen content in the respiratory air after the oral intake of a mix of vitamins which is then followed by a mental and physical training. The so improved availability of oxygen in the arteries is supposed to accelerate the healing processes in various indications. It should however be mentioned that statistically backed proofs of efficacy (POE) are not available.
Reactive oxygen compounds have aseptic effects in the case of infections of the skin surface and against mycoses. Benzoyl peroxide to treat acne symptoms and ozonised herbal oils are some examples in this context.
Low concentrated hydrogen peroxide solutions are used for the surface disinfection of larger objects. They also are effective substances in the fight against mould. In this process highly reactive nascent (monoatomic) oxygen is released. Frequently used oxygen-releasing compounds are potassium permanganate, which is used as a fast acting remedy in the case of fungus- and other skin infections, as well as alkaline hypochlorite solutions (oxidative cleaners).
Cosmetic high frequency devices generate low amounts of ozone and nitrogen oxides that have disinfecting effects in the cleansing of acne comedones or during the treatment of inflamed skin areas. A UV light emitting quartz lamp generates ozone in cosmetic vaporizers (Vapozon).

Other interesting facts

Intramolecular oxidations are the active principle in explosives. The devastating explosion in the Beirut Harbour in August 2020 was caused by ignition of the salt-like ammonium nitrate (NH_4NO_3). In this process the oxygen-rich nitrate moiety (NO_3^-) oxidises the ammonium group (NH_4^+) in a kickback reaction with forming gaseous water (H_2O), nitrogen (N_2), and oxygen (O_2).
Since, from a physical point of view, the oxidation always is linked to an electron transfer from a substance to be oxidised to the oxygen, we generally also speak of oxidation when in one way or other, electrons are withdrawn from a substance. Just to mention an example: Silver turns black after reacting with sulphur compounds; in this process the elementary silver (Ag) is “oxidised“, releases an electron and is transferred into an ionic silver compound (Ag^+).
During the photosynthesis of plants that produce oxygen from water, the oxidation of the oxygen (O^{2-}) in the water into gaseous oxygen (O_2) occurs while releasing electrons.

Dr Hans Lautenschläger

[1] Wolfgang Schnizer, Birgit Siebert, Jürgen Kleinschmidt und Reinhard Erdl, Deutsches Ärzteblatt 1985 (82), 27: 2026-2030