

## Defending Against the Sun – how minerals help.

The sun can have an impact on human skin at any time of the year. Most people get their highest exposure in the summer, depending on which hemisphere you are in, can be now, or 6 months from now. The skin is constantly being exposed to the air, solar radiation, pollutants, and other chemical insults. Daily exposure to sun and its solar radiation generates free radicals and other reactive oxygen species (ROS), which are the primary factors in skin damage. UltraViolet Radiation (UVR) is thought to be responsible for 80% of the factors leading to ROS damage to skin. UVR from sunlight is composed of three wavelength regions: UVC (absorbed by the ozone layer), UVB, and UVA. UVB is of the shorter wavelength, and its energy is absorbed in greater amounts by the epidermis and keratinocyte DNA. UVA is of the longer wavelength, and its energy penetrates deeper into the dermal layers. The primary mechanism through which UVR initiates possible damage to the human skin is via photochemical generation of free radicals and other ROS. Table 1 below lists the free radicals, free radical generators, and other ROS that are important to living organisms.



Table 1. **Reactive Oxygen Species (ROS)**

Free Radicals	Free Radical Generators (or other ROS)
<ul style="list-style-type: none"> <li>• Hydroxyl (OH<sup>•</sup>)</li> <li>• Superoxide (O<sub>2</sub><sup>•-</sup>)</li> <li>• Nitric Oxide (NO<sup>•</sup>)</li> <li>• Thyl (RS<sup>•</sup>)</li> <li>• Peroxyl (RO<sub>2</sub><sup>•</sup>)</li> </ul>	<ul style="list-style-type: none"> <li>• Peroxynitrite (ONOO<sup>-</sup>)</li> <li>• Hypochlorous Acid (HOCl)</li> <li>• Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>)</li> <li>• Singlet Oxygen (<sup>1</sup>O<sub>2</sub>)</li> <li>• Ozone (O<sub>3</sub>)</li> </ul>

*Poljsak B and Dahman R: Dermatology Research and Practice 2012)*

Human skin's normal protection against UVR damage is via melanin and enzymatic antioxidants, such as glutathione reductase, catalase, glutathione, superoxide dismutase, and ubiquinone, as well as antioxidants consumed via the diet (vitamins A, C, and E, and others). In addition, sunscreens offer protection against UVR, as well as the use of exogenous antioxidants taken orally or via topical application. When the amount of UVR generated ROS overpowers the body's protective substances (exogenous and endogenous), the resulting oxidative stress leads to skin damage. Severe oxidative stress will eventually cause cell damage and death. The effects of UVR have been well studied and the effects of visible light on skin have been much less studied. A study by Liebel F, et al, [Journal of Investigative Dermatology (2012) 132, 1901-1907] examined the irradiation of skin via visible light. The spectral distribution of solar energy at sea level is comprised of approximately 3-7% UVR (290-400 nm), 44% visible light (400-700 nm), and 53% infrared (IR) radiation. UV radiation can rapidly deplete the endogenous skin enzymes and antioxidants, such as glutathione reductase, catalase, glutathione, and so on, inducing proinflammatory cytokines and matrix metalloproteinases (MMPs) in skin cells, such as keratinocytes and fibroblasts. When activated in this way, MMPs lead to collagen destruction (major structural component of the skin), and inhibition of collagen synthesis. The induction of proinflammatory cytokines leads to overall skin inflammation (sunburn being one of the results of the inflammatory process), and is an important factor in the photo aging of the skin. It has also been seen that IR radiation causes oxidative stress to the skin, leading to increased MMPs. Additional studies (Cho, et al., J Dermatol Sci, 2008, 50:94-101) observed that IR unregulated MMP-1 expression in the dermis of 80% of the tested individuals.

The Liebel study was designed to examine the impact of sunlight (visible light, 400-700 nm) on the skin. It is important to note that commercial sunscreens are only able to block UVR at wavelengths up to 380 nm, so the skin is not protected at all by topical sunscreens against visible sunlight. This in vitro study showed that visible light induces significant ROS production, leading to the release of proinflammatory cytokines and MMP expression.

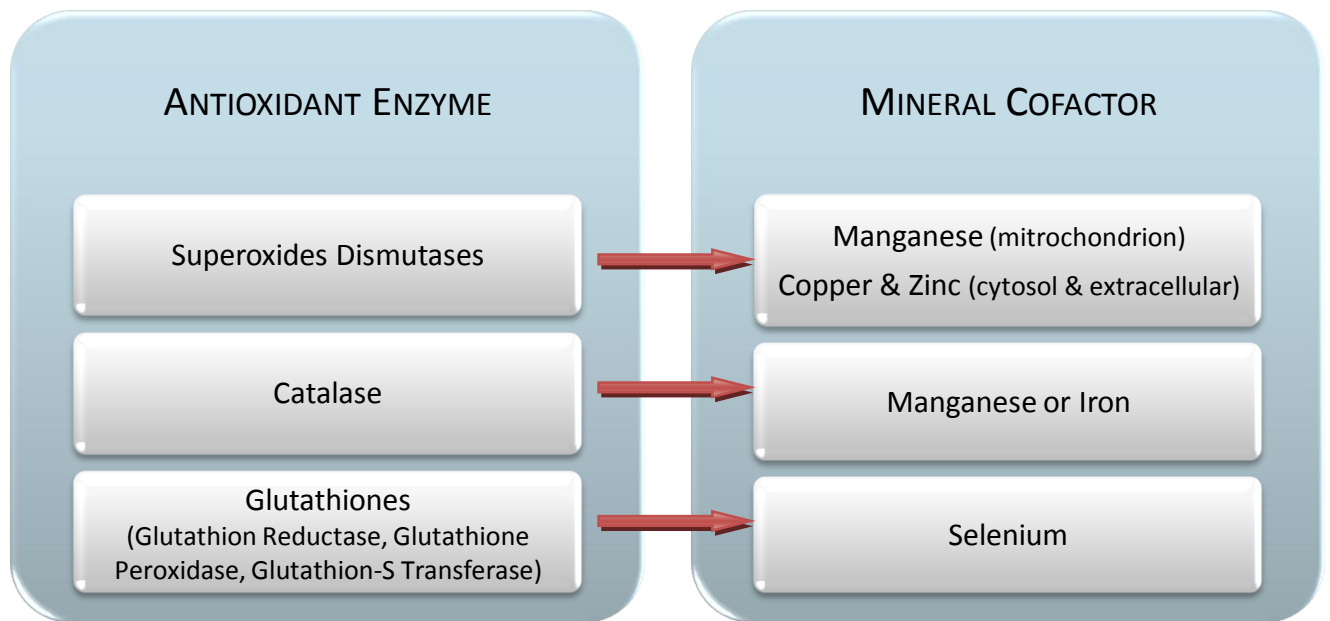
This study goes on again to examine the effect of visible light on human subjects, and the findings were supportive of the in vitro results. In addition, the use of UVA/UVB sunscreens were shown to be ineffective in protecting the skin from free radical generation in the human subjects. However,

the addition of antioxidant combinations to the topical sunscreens was found to decrease the amount of free radicals generated by visible light.

The damage to the skin that can come from oxidative stress induced by overexposure to the sun is indisputable. When the skin’s protective factors are overwhelmed by the different spectral ranges of solar energy, the skin is damaged in a variety of ways. Dryness, premature aging, and certain skin cancers can ensue.

The oxidative stress fighters against sun damage include a variety of endogenous and exogenous antioxidants. Melanin and enzymatic antioxidants, as well as nutrition intake of certain antioxidants are the protectors against the sun. There are important mineral components to these enzymatic antioxidants (Table 2.).

Table 2.



All of these mineral activated antioxidants have been shown to play roles in fighting against the various free radicals and other ROS generated by solar energy. Some of these minerals or enzymes have been incorporated into topical sunscreen/antioxidant creams or lotions as a means to protect against the potential harm from overexposure to solar energy. In addition, it has been shown that the nutritional intake of these minerals can help boost the levels of their associated antioxidant enzymes.

In order for these minerals to have any nutritional benefit, they need to be taken in a form that is of good bioavailability. Albion has had clinical studies done on these important trace minerals that demonstrate their physiological impact.

The following study abstracts clearly demonstrate the effectiveness of the Albion forms of manganese, copper, zinc, selenium, and iron:

### **Longitudinal Changes of Manganese-Dependent Superoxide Dismutase and Other Indexes of Manganese and Iron Status in Women**

Davis CD and Greger JL.

Am J Clin Nutr; 1992;55:747-52.

#### **Abstract**

The effect of dietary factors on manganese-dependent superoxide dismutase (MnSOD) activity in humans has not been studied. We longitudinally evaluated changes in MnSOD activity and other indices of manganese and iron status in 47 women during a 124-d supplementation study. Subjects received one of four treatments: placebo, 60 mg iron, 15 mg manganese, or both mineral supplements daily. Manganese supplementation resulted in significant increases in lymphocyte MnSOD activity and serum manganese concentrations from baseline values but no changes in urinary manganese excretion or in any indices of iron status. Oral contraceptive use and the stage of the menstrual cycle did not confound the use of lymphocyte MnSOD activity or serum manganese to monitor manganese status, but fat intake affected both indices. This work demonstrated that lymphocyte MnSOD activity could be used with serum manganese concentrations to monitor manganese exposure in humans.

### **A Bioavailability Study Comparing Two Oral Formulations Containing Zinc (Zn bis-glycinate vs. Zn gluconate) After a Single Administration to Twelve Healthy Female Volunteers**

Gandia P, Bour D, Maurette JM, Donazzolo Y, Duchène P, Béjot M, Houin G.

Int J Vitamin Nutr Res; 2007; 77(4): 243-8.

#### **Abstract**

As the current nutritional zinc intake frequently falls outside the Dietary Reference Intake (DRI) and as zinc is an essential trace mineral involved in the function of many enzymes, zinc supplementation has been recommended to prevent or treat the adverse effects of zinc deficiency. The aim of the present study was to compare the oral bioavailability of zinc bis-glycinate (a new formulation) with zinc gluconate (reference formulation). A randomized, cross-over study was conducted in 12 female volunteers. The two products were administered orally at the single dose of 15 mg (7.5 mg x 2), with a 7-day wash-out period between the two tests. Serum concentrations of zinc were assayed by a validated inductively coupled plasma optical

emission spectrometry (ICP-OES) method and C(max), T(max), and areas-under-the-curve (AUCs) were determined. The comparison between the two treatments was performed by comparing the C(max), AUC(t), and AUC(inf) using an analysis of variance followed by the calculation of the 90% confidence intervals of the ratio test/reference. Bis-glycinate administration was safe and well tolerated and bis-glycinate significantly increased the oral bioavailability of zinc (+43.4%) compared with the gluconate.

### **Copper Supplementation Effects on Erythrocyte Superoxide Dismutase Activities in Middle Aged Men and Women**

Robert A DiSilvestro , Elizabeth Joseph , Wenyi Zhang , Young Min Kim and Ni Sun  
FASEB J; 2007;21:698.8

#### **ABSTRACT**

Based on the current RDAs for copper, which fall below older recommendations, fewer people show inadequate copper intake than previously proposed. However, 8 week copper supplementation (2 mg copper as copper glycinate per day), in middle aged adults (N=35), consistently raised values for erythrocyte activities of the copper enzyme superoxide dismutase. Placebo had no effect. The copper supplementation-induced changes in erythrocyte superoxide dismutase activities correlated with changes in two plasma copper enzyme activities, ceruloplasmin and diamine oxidase. These results suggested that in this population, copper intake was not typically high enough to maximize copper enzyme activities. A number of possible practical health consequences of this behavior were investigated, but none of the measures were altered by copper supplementation. For example, copper supplementation did not significantly alter plasma cholesterol related parameters, though changes in HDL cholesterol correlated with final superoxide dismutase values in both the copper and placebo groups. Copper supplementation did not alter C-reactive protein, homocysteine, and LDL oxidation based on ELISA analysis. LDL oxidation, when measured by lag time ex vivo, had previously shown a relationship to copper status. Values for the ELISA measure may be slow to change since they were not affected by 8 weeks of 400 IU/day of vitamin E supplementation (plasma vitamin E did rise). A number of previous studies had shown vitamin E supplementation to affect LDL oxidation lag time. In summary, copper supplementation can readily raise copper enzyme activity readings in middle aged adults, but the practical health consequences remain unclear.

### **Selenium Glycinate Supplementation Increases Blood Glutathione Peroxidase Activities and Decreases Prostate-Specific Antigen Readings in Middle-Aged US Men**

Zhang W, Joseph E, Hitchcock C, DiSilvestro RA.  
Nutr Res. 2011 Feb;31(2):165-8.

#### **Abstract**

Two concepts are often currently applied to selenium in adult men in the United States: • Intake is generally enough to maximize blood glutathione peroxidase activities. • In such men,

selenium supplementation does not reduce risk of prostate cancer. In contrast to these concepts, 30 healthy middle-aged men were studied to test the following hypothesis: 6-week supplementation of 200 µg of selenium as glycinate can raise activities of 2 blood selenium enzymes and lower a marker of prostate cancer risk. The hypothesis was confirmed, in that selenium supplementation raised activities for erythrocyte and plasma glutathione peroxidase as well as lowered values for plasma prostate-specific antigen. The enzyme activity increases were not extremely large, but based on a chicken study, changes in blood glutathione peroxidase activities can reflect bigger changes in the prostate. Placebo treatment did not duplicate the selenium effects in 30 other men. In conclusion, this study suggests that US middle-aged men may not typically consume optimal amounts of selenium.

### **Relative Effectiveness of Iron Bis-Glycinate Chelate (Ferrochel®) and Ferrous Sulfate in the Control of Iron Deficiency in Pregnant Women**

Szarfarc SC, de Cassana LM, Fujimori E, Guerra-Shinohara EM, de Oliveira IM.  
Arch Latinoam Nutr. 2001 Mar;51(1 Suppl 1):42-7.

#### **Abstract**

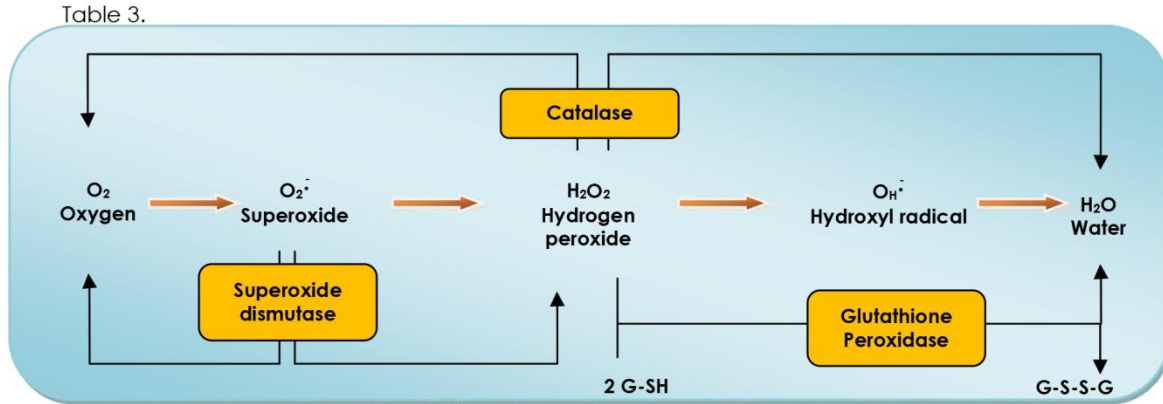
The relative effectiveness of daily supplementation of iron deficiency during pregnancy using 15 mg/day of iron from iron-bis-glycinate chelate (71 pregnant women), or 40 mg iron from ferrous sulfate (74 pregnant women) was evaluated by measuring hemoglobin, transferrin saturation and serum ferritin, at the beginning of the study (< 20 weeks of pregnancy) and at 20-30 weeks and 30-40 weeks thereafter. Ingestion for 13 weeks or more was considered adequate. Seventy three percent of the Ferrochel consuming group and 35% of the ferrous sulfate consuming group were considered to have taken the treatment adequately. The decrease in levels of all the measured parameters was significantly less pronounced in the group that consumed Ferrochel in spite of the lower treatment dose. Iron depletion was found in 30.8% of the women treated with Ferrochel and in 54.5% of the women than consumed ferrous sulfate. Of the factors responsible for non compliance taste was reported in 29.8% of the ferrous sulfate consumers and none in the groups that consumed Ferrochel. It is concluded that daily supplementation with Ferrochel was significantly more effective, in spite of the lower dose, than supplementation with ferrous sulfate.

### **Summary**

The enzyme antioxidant systems, which rely on key trace mineral cofactors for their activity, play critical roles in helping our skin fight against the damaging effects of solar radiation.

Super oxide dismutases (SOD) are enzymes that catalyze the dismutation of the free radical superoxide (O<sub>2</sub><sup>-</sup>) into oxygen and hydrogen peroxide. There are three forms of SOD present in man. SOD 1 (in the cytoplasm) and SOD 3 (extracellular) contain copper and zinc. SOD 2 (mitochondrial) contains manganese. The catalase enzymes, which utilize manganese and sometimes iron, is responsible for taking the ROS hydrogen peroxide, and converting it to water and oxygen.

The various glutathiones (including peroxidase and reductase), rely on selenium, and they are involved in fighting oxygen reactive species, like hydrogen peroxide and the hydroxyl radical (see table 3).



The bottom line is that to ensure that the human skin has the weapons to help fight against the dangers of solar energy, the body needs all of the trace mineral dependent enzyme antioxidants it can manufacture. To do that, it needs to take in bioavailable forms of manganese, zinc, copper, and iron.

Albion makes all of these trace minerals in proven bioavailable forms.

