Paleoluminescence Laboratory

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The laboratory uses methods and equipment developed at the Physics Department. They are subject to three Bulgarian inventions, and one Canadian patent of our laboratory's team. Some of the devices developed, and used by the laboratory have no analogues abroad, others are subject to numerous attempts of coping or modifing by other laboratories around the world.

The laboratory was created in 2001. In 2005 and 2006, a PhD student from the University of Bologna, Italy was trained for six months here within the European exchange program ERASMUS.

Scientific fields and experiments:

Study of global climate changes in the past.

The main activity of the laboratory is the study of global climate changes in the past, and solar influences on them. Until recently, variations of solar radiation reaching the surface of the Earth (insolation), could only be calculated theoretically from orbital variations of Earth's orbit, causing a change in the distance from any point on the Earth's surface to the Sun, resulting in a change in the amount of solar radiation reaching the Earth's surface. But their calculations require many incorrect assumptions, leading to significant inaccuracies in the results (50% of the variation in the theoretical curves do not match this in the experimental records).

Therefore the team of our laboratory was developed an indirect index of insolation (Figure 10), which is obtained from measurements of the distribution of the luminescence of the organic acids in flowstone calcites along the growth axis of their crystals (Figures 10, 11,12). Absolute dating of these calcites allows measurement records of insolation (Figure 10) in the last 250,000 years. So far these are the only experimental records of insolation. They are widely used in studies of global climate change in the past.

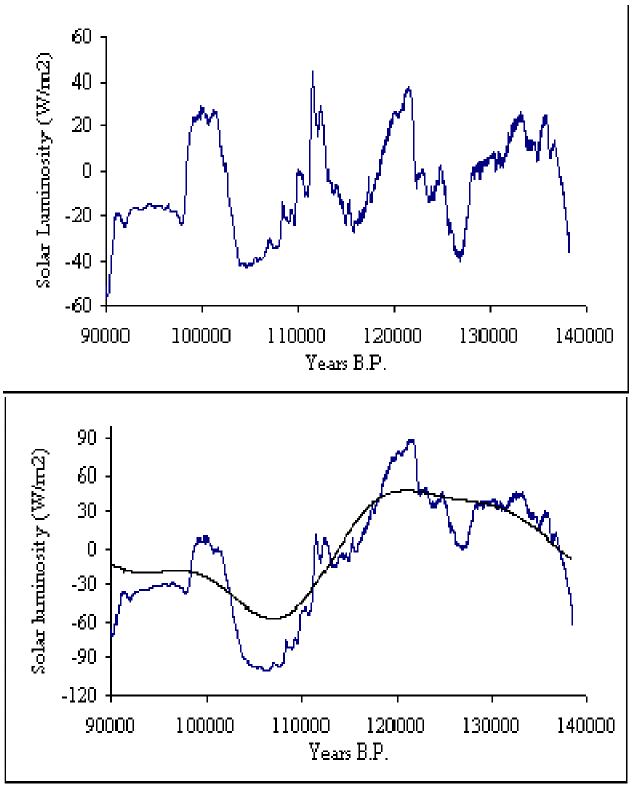

Figure 10. Variations of the solar luminosity (above) derived from a luminescent record of solar insolation in flowstone calcite from South Dakota, USA (below).

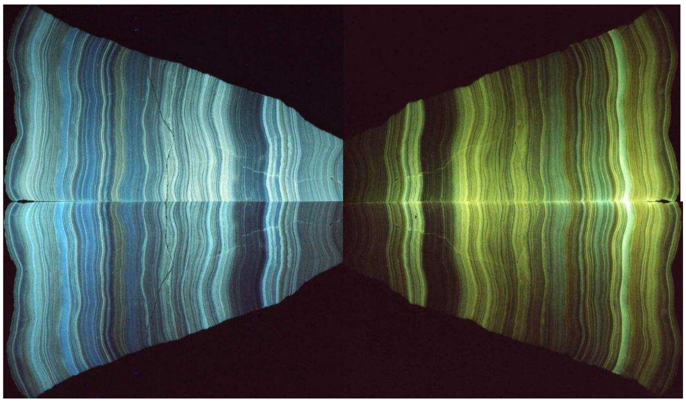

Figure 11. Fluorescence (left) and phosphorescence (right) of a crossection of a flowstone calcite from South Dakota, USA allong its growth axis. Records on Figure 10 are obtained from a part of this sample. (photo by Dr. Yavor Shopov)

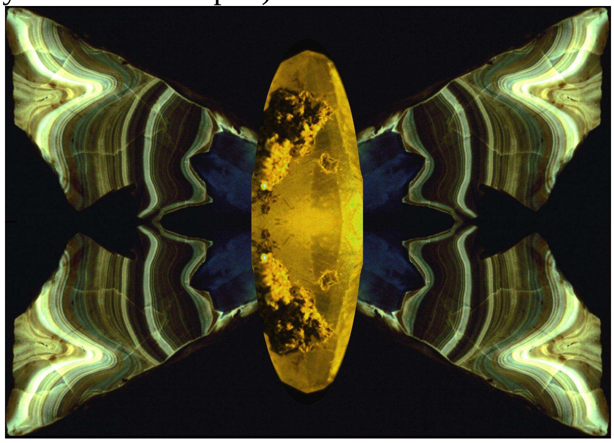

Figure 12. Phosphorescence of a crossection of a flowstone calcite, after ultraviolet (UV) irradiation with a pulsed xenon lamp. (photo by Dr. Yavor Shopov)

Study of regional climate changes.

An important activity of the laboratory is the study of regional climate changes using flowstone calcites as natural climatic stations. For this purpose, the laboratory has developed indirect indices of annual temperature and annual rainfall, which are obtained from measurements of the distribution of the luminescence of the organic acids in flowstone calcites.

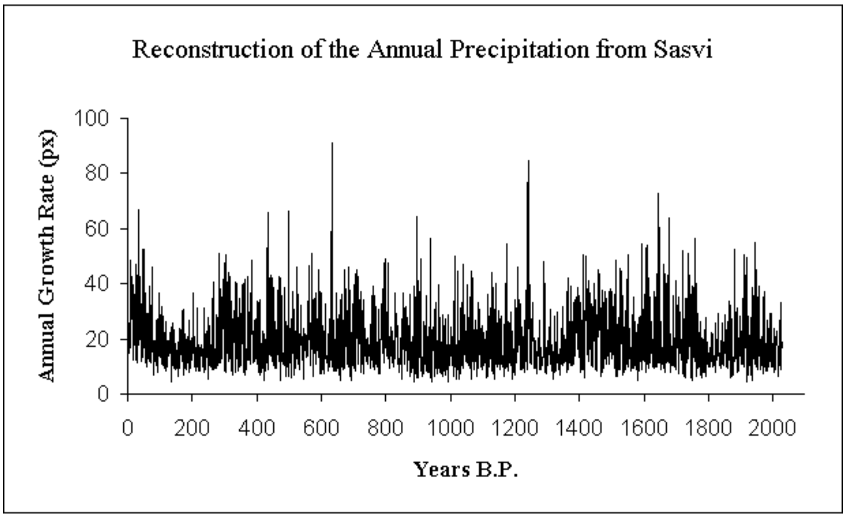

Figure 13. Reconstruction of the variations of the annual growth rate of a flowstone calcite, which is proportional to the average annual rainfall in the area of Trieste, Italy over the last 2028 years.

Reconstructions of records of the indirect index of annual rainfall in the past are derived from microphotographs of the distribution of fluorescence of organic acids in flowstone calcites along the growth axis of their crystals, to visualize their annual growth layers. The resulting photographs of fluorescence (Fig. 14) allow for measuring the annual growth rate of crystals, which is proportional to the average annual rainfall in the area from where the sample was taken (Fig. 13). These annual layers are also used to date records, and were first observed by the head of the laboratory.

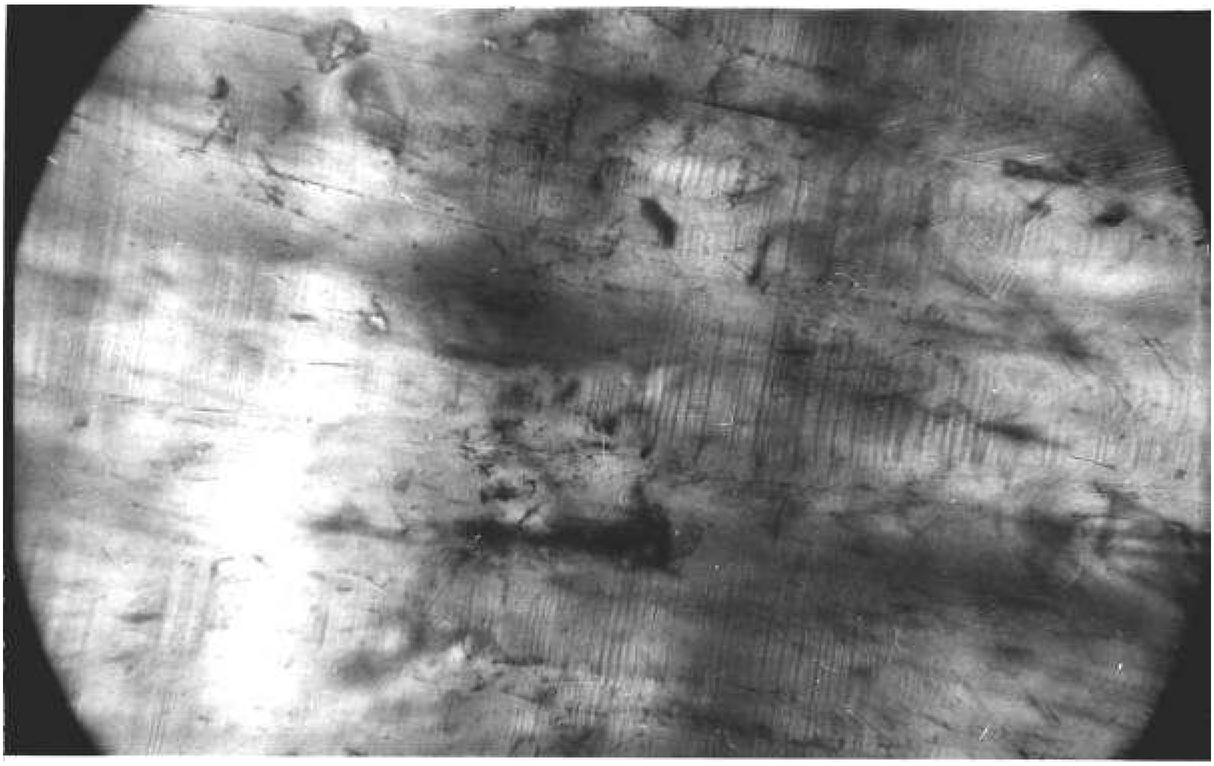

Figure 14. Annual layers of distribution of fluorescence of organic acids in flowstone calcite from the region of the village Bosnek, Pernik. (photo by Dr. Yavor Shopov)

Using luminescence for search, field and laboratory diagnostics of minerals, oil and gas

Part of the research of our laboratory is dedicated to using luminescence for search, field and laboratory diagnostics of minerals, oil and gas. This includes:

a. Development of a new method, techniques, and apparatus for registration of luminescence of minerals and its spectrum in the field conditions.

The known method for the search of minerals by their luminescence in field conditions uses portable continuous UV sources to observe only fluorescence of minerals. The disadvantage of this method is the low brightness of the sources and the inability to observe phosphorescence of minerals and its attenuation. For observing and registration of these phenomena we developed a new method "Impulse photography luminescence". For the use of this method in field conditions we developed and patented a fundamentally new equipment, that can record images of fluorescence or phosphorescence separately or together. We proposed a new system for field diagnostic of minerals using luminescence which led to finding deposits of many new minerals for Bulgaria.

With the development of the new technique "Time-resolved photography of phosphorescence", field studies and registration of phosphorescence attenuation and the color change of phosphorescence with time in the presence of several luminescent centers in the sample became possible. This appeared to be particularly useful to distinguish phosphorescence of inclusions of oil and natural gas (Figure 15) from that of humic and fulvic acids (Figure 11) in calcite under field conditions, which can be used for oil survey.

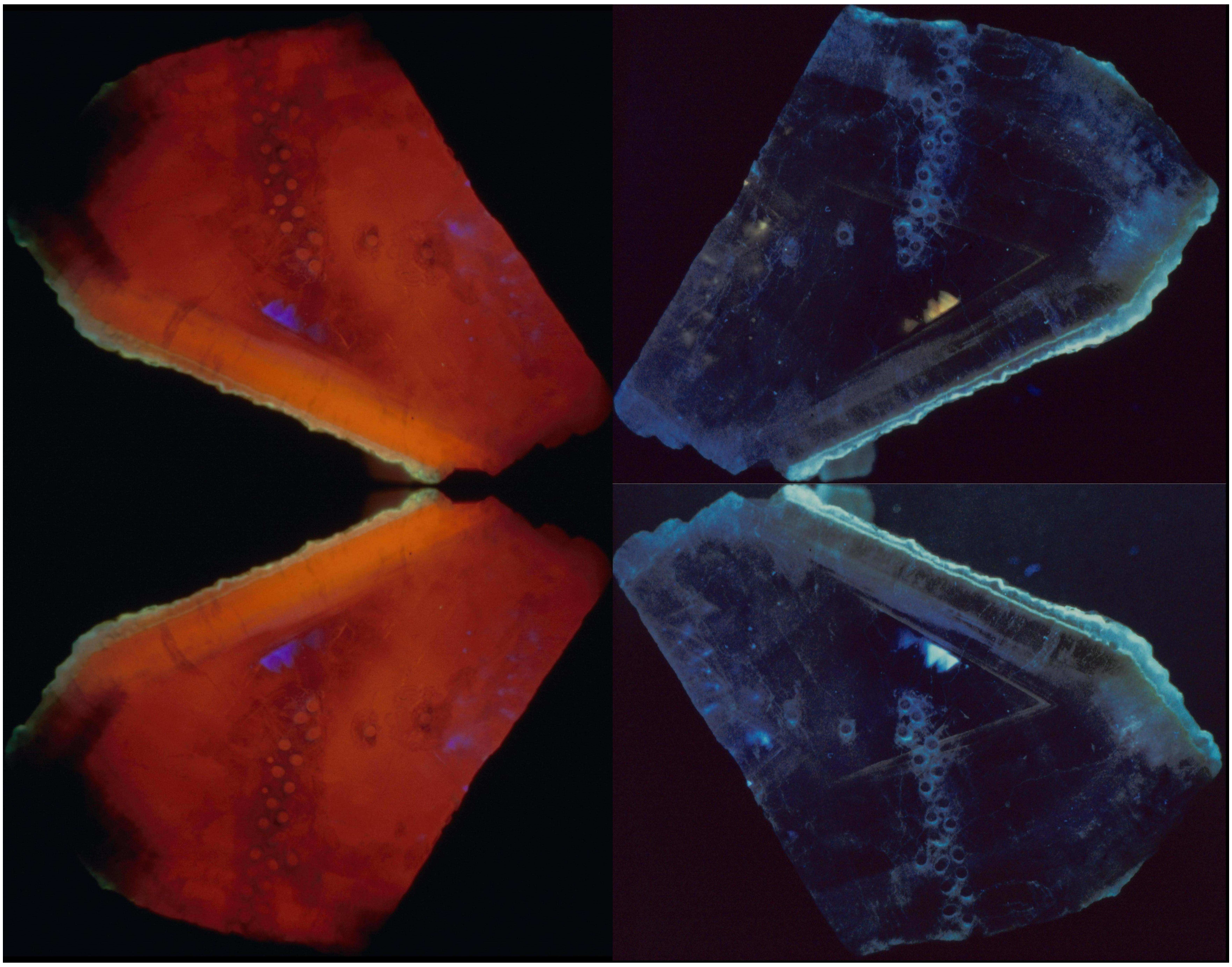

Figure 15. Phosphorescence (left) and fluorescence (right) of a calcite crystal from Carlsbad, USA under irradiation with long-wave UV (right, above) and short-wave UV light (right, below). Blue-violet phosphorescence is due to inclusions containing petroleum hydrocarbons, indicating the presence of oil fields in immediate vicinity. (photo by Dr. Yavor Shopov)

b. Research on the spectra of the luminescence of the minerals in the laboratory

The diagnostics of minerals by their luminescence sometimes requires a detailed study of the spectra, the nature and properties of their luminescence by selective excitation with laser emission with different wavelengths. This is achievable only in laboratory conditions. At such measurements Raman spectra of the samples are obtained as well, which are very effective for diagnostics of microscopic mineral agregates and inclusions.

Studies of records of contamination and migration of toxic metals and of groundwater acidity.

The luminescence of some samples flowstone calcite is induced by toxic elements. Some of them even have annual zonality (Figure 15) due to variations in the acidity of the groundwater, which causes variations in the solubility of some toxic elements such as uranium, lead, etc.

On Figure 16 is shown fine zonality of the fluorescence in a flowstone calcite upon irradiation with short-wave UV (left) due to uranium impurities. Fine fluorescent zonality upon irradiation with long-wave UV (right) is due to impurities of rare earth elements in the same sample.

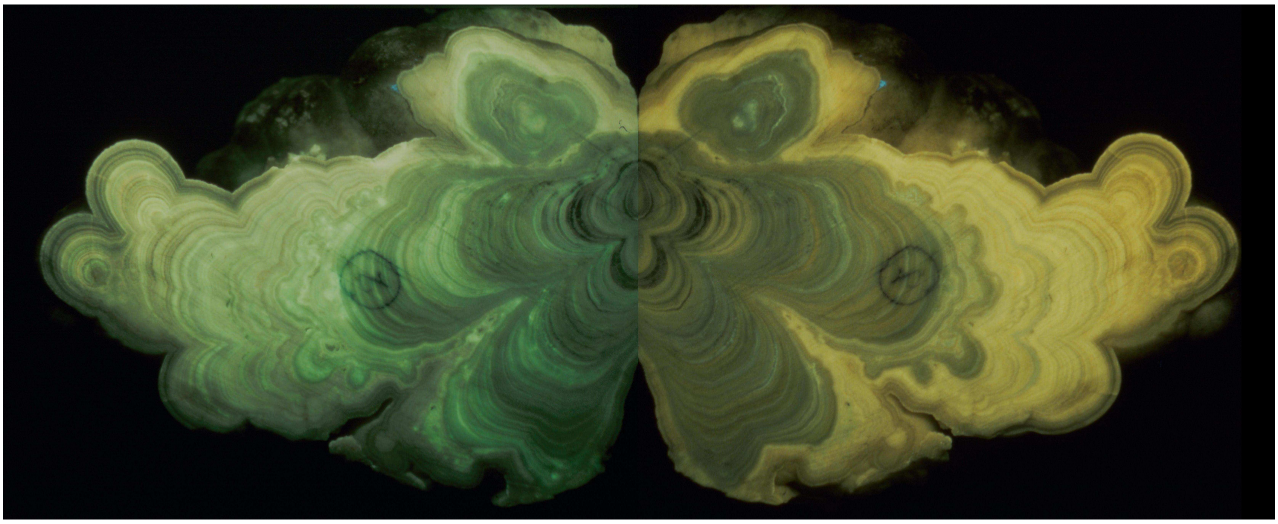

Figure 16. Fluorescence of a crossection of a flowstone calcite from Irkutsk, Russia at irradiation with short-wave (left) UV (SWUV) and long-wave UV (LWUV) light (right). Green fluorescence is due to the impurities from uranium ions. (photo by Dr. Yavor Shopov)

Dating of fluorescent records

Luminescent records required development of a new dating method due to lack of any dating method with the precision corresponding to their high resolution and precision. The apparent annual cyclicity of records allows calculating the average annual growth rate of the flowstone by determining the average annual period (in pixels) using time series analysis. This procedure was set at the base of a fundamentally new dating method called "Autocalibration dating."

Autocalibration dating of time series with unknown uneven time step uses time- frequency mathematical spectral analysis or Fourier transformation to determine the mean time step of the time series and to determine the time interval from the beginning to the end of the time series. If the beginning of the time series is known it can be dated using its thus obtained duration. The method is applicable to the dating of any natural materials with cyclic structure and was recognized for invention. So far this is the only dating method based entirely on a numerical method.

The basis of this method is the annual bands of luminescence (Figure 14) observed for the first time by the head of the laboratory. Therefore Prof. S.E. Lauridzen from the University of Bern, Norway named this phenomenon which found wide application to reconstruct the environment in the past after the name of Y. Shopov ("Shopov- bands") (see http://www.karstwaters.org/conduit/vol4no2.htm) and called one of the sessions of the international conference in Bergen "Shopov- bands and other high- resolution stratigraphic information" (http://www.karst.edu.cn/igcp/igcp379/1997/part2-1.htm).

Distinctive and representing interest experiments:

Paleoclimate records with extra high-resolution which are measured by our laboratory are of particular interest. One of the methods developed at our laboratory (Laser Luminescent Microzonal Analysis) allows for easy variation of the resolution of the obtained records by varying magnification of the optical system. Reconstructions of variations of paleo temperature and solar activity (more precisely insolation) with extremely high-resolution (Figure 17) are measured with this method.

Studies of the cycles of the variations of the solar insolation in the record of Fig. 17 have shown that it recorded even the changes of solar radiation with period of 27 to 30 days, which are caused by the rotation of the Sun around its axis (Fig. 18, above). The cycles of the variations of the solar insolation in the record shown in Fig. 17 coincide with those of the variations of the total solar irradiance (called) "solar constant" measured from space (Fig. 18).

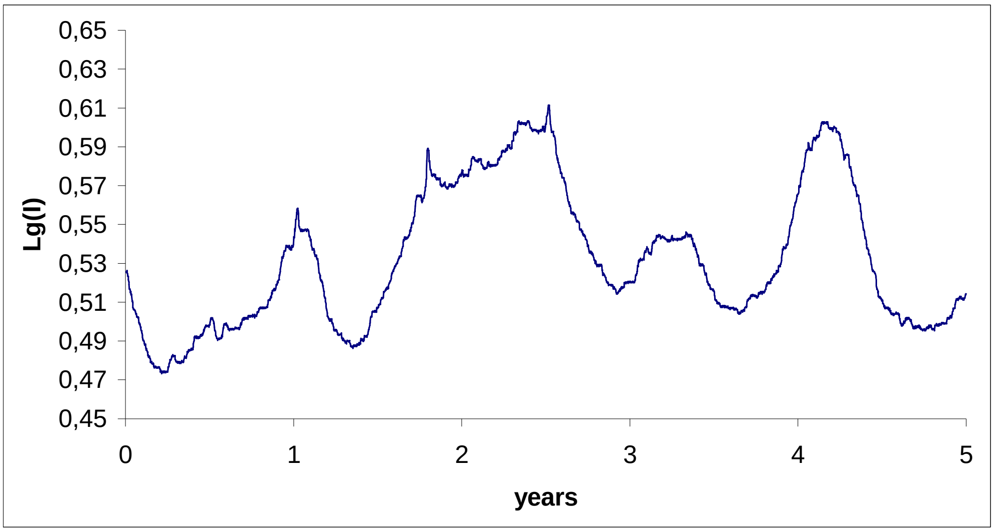

Figure 17. Luminescent record of solar insolation about 1000 years ago in flowstone calcite, with very high resolution (12 hours = 2px per day) by (Shopov & Stoykova, 2010).

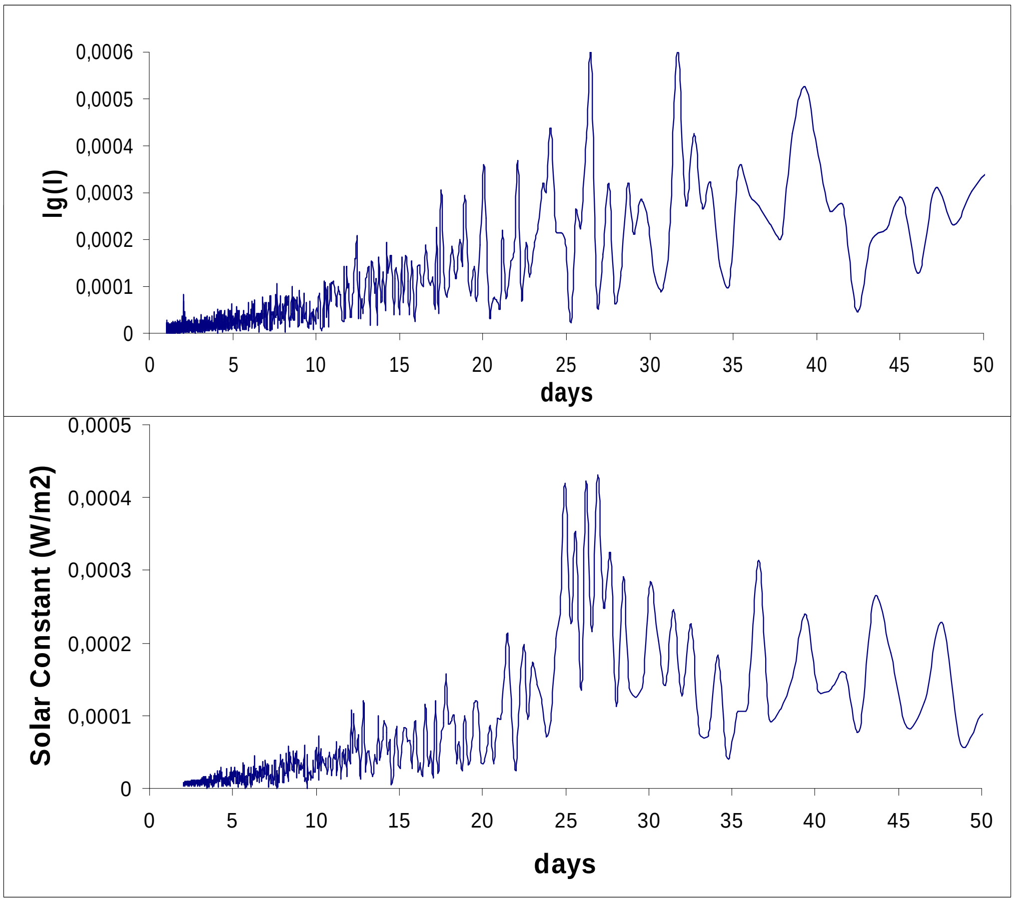

Figure 18. Cycles of the solar insolation variations in the record of Fig. 17 (above), and of variations in the solar constant for the past 50 years (below) by (Shopov & Stoykova, 2010).

Stoykova D. A., Y.Y. Shopov, L.T.Tsankov, C.J. Yonge (2008) Origin of the Climatic Cycles from Orbital to Sub-Annual. *Journal of Atmospheric and Solar-Terrestrial Physics*, **v. 70**, pp. 293–302

Shopov Y., D. Stoykova (2010) Cycles of the Solar Wind Flux at the Front of the Earth's Magnetosphere. *AIP Conf. Proc.* **v. 1356**, pp. 192-203; doi:10.1063/1.3598105