COMPARATIVE PHYSICO-MINERALOGICAL STUDY OF ROMANITE AND
BALTIC AMBER; PRELIMINARY FT-IR AND XRD DATA

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Amber is fossilized resin that once exuded out of the bark or was produced in the heartwood of
different types of Conifers and certain flowering trees, particularly in hot weather. Many scientists
thought that time was important in the fossilization of resin to produce amber, this process beeing
estimated as taking from 2-10 milion years. But it appears that the types of sediment in which the
resin is deposited is much more important than time for amber formation, although it is not so clear
the effect of water and sediment chemistry on the resin (Ross, 1998).

This work presents some preliminary data of a larger project aiming to establish the local or
Baltic origin of the materials found in archaeological sites on the Romanian territory. The
complexity of the theme, making the object of a strong debate in the specialty literature, reveals the
necessity of using diverse analytical techniques, i.e. optical microscopy, infrared spectrometry (IR,
FT-IR), X- rays diffraction (XRD), nuclear magnetic resonance (NMR).

In Romania, a beautifull amber was exploted from the 19th century near Colţ (Buzău County), on the Sibiciu Valley. The resin-bearing strata belong to the Oligocene in the Eastern
Carpathian flysch. They are intercalated within the lower and medium part of the lower Kliwa
sandstone, having a thickness that is not constant (0.20-1.40 m). They consist of siliceous clay
always containing thin intercalations of bituminous shales (2-5 cm) and of preanthracite coal (1-2
cm). The paleobotanical and palynological researches on the amber-bearing formations give the age
as Upper Rupelian-Early Chattian (Ghiurca & Vavra, 1990). Having become a symbol of our
country, the crud, brown–reddish amber named romanite or rumanite was exposed at the Universal
Exposition in Paris, 1867. The systematical exploitation began in 1920, and between 1923 and 1925
more than 300 kg were extracted. By 1935 the exploration ceased. Between 1981 and 1986 the
Ministry of Mines and Oil organized a systematical exploitation, but the extracted material was lost
or became part of private collections (Ciobanu, Dicu 2005). Today amber of the Colţ area is not for
sale commercially. It is found in small amounts, retained more for scientific value. People continue
to look for amber along rivers after rain and regularly in the spring, but with less enthusiasm than
their ancestors. In order to expose the crude and processed amber objects, a special museum was opened in 1980 at Colți. Today it is a sad situation in Colți: the unique Amber Museum is in an advanced degradation stage and very few people practice amber processing.

Baltic amber or succinite is by far the earliest and wellknown of all fossil resins. Resin secreted by coniferous trees at least 40 million years ago was carried southwards by river from the Scandinavia and the present-day Baltic Sea and laid down in the Tertiary marine sediments known as blue earth. On the Sambian Peninsula (Russia) Baltic amber has been extracted from this deposit, from depth of 50 m, almost continually since the 17th century (Kosmowska-Ceranowicz, 2003). Poland has become one of the leading producers of amber jewelry in the past 30 years, processing some 200 tons annually (www.pan.pl).

The role of optical microscopy in the study of fossil resins is of prime importance. Apart from efficiency and commodity, it offers a precision grade comparable only with the chemical analyses and at the same time it allows detailed mineralogical investigations of the resins and of the host-rock. The observations have been marked up at the Faculty of Geology and Geophysics, Economic Geology & Metallogeny Laboratory, using a PANPHOT microscope transmitted light, to which a Nikon Eclipse E-400, 40 W has been attached, being thus possible to obtain microscopically images. The thin sections have been manufactured at the Sections Laboratory from the Mineralogy Department, using samples of romanite from Colți region and Baltic amber from Poland, Russia and Germany.

Diagenetic processes played a significant role in the creation of romanite (Kosmowska-Ceranowicz, 1999, Neacșu, 2006). One of the most important consequences is the appearance of an internal organization tendency, proved by its weak anisotropy; although in literature is mentioned the fact that amber does not present crystallization tendencies (Kucharska & Kwiatkowski 1977, Stout et al., 1995), the microscopic study on thin sections of romanite allowed the emphasizing of a light anisotropy with grey-yellowish to light-blue colors. The second consequence is represented by remineralizations in romanite, consisting in the substitution of organic matter by anhydrite and albite (fig. 1, 2). Having a novelty character, is the obvious presence on sections of two different romanite types: an older one, with distinct fissures, impregnated with organic material, and a recent one, light yellow, which borders the previous one and penetrates its fissures.

Baltic amber studied with this occasion revealed no anisotropy. A certain circular zonality of the inclusions’ disposal may be observed. If the fluid inclusions are very characteristic in many Baltic amber samples (fig. 6), in the case of romanite fluid inclusions had time to be emitted, due to a
longer exposure to sunlight, or/and to the influence of the temperature during the diagenesis. As a result of water and volatiles drastic elimination, microfissures can be also seen (fig.3).

Fig. 1 Neoformation albite surrounded by idiomorphic crystals in romanite NII 10x/0.25

Fig. 2 Organic spherules (pollen?) replaced by Albite albite crystals in romanite NII 20x/0.33

The microscopic study of romanite emphasized the presence of pollen of Sequoiapollenites type? from the European Tertiary, (fig. 4), of spores (of Osmundaceae?) and of wood vessels remains, free, cortex, all of them comprised by the resin. Ligneous tissue may be also observed in the sections from Baltic amber (fig.5). The microscopic study of amber revealed the identification of certain paleofossils of the Insects Class (fig.6) in Baltic amber.

Fig. 3 Polygonal cracks filled with organic material in romanite NII, 20x/0.33

Fig. 4 Sequoiapollenites ? in romanite, NII, 6x/0.18

Both X-ray diffraction and infrared spectroscopy studies have been made with equipments of Geological Institute of Romania. X-ray powder diffraction analyses was performed on a Bruker D8 Advance automated diffractometer equipped with a graphite-diffracted beam monochromator (Cu Kα radiation, λ = 1.54056 Å), at an operating voltage of 40 kV and a beam current of 40 mA. The patterns were collected using fixed 1° divergence and anti-scatter slits and a 0.6 mm receiving slit.
The records were made using an external Si standard (NBS 640b). They seem to indicate for romanite some internal organizing tendency confirmed by microscopically studies (Neacsu, 2006 and this paper). Some crystalline components may give rise to diffraction patterns and could have a genetic significance. Our data indicate oleandrine (one of several alkaloids found in the leaves of Nerium oleander) as a possible crystalline compound in romanite.
The infrared transmittance spectra were recorded with a Bruker Tensor 27 FT-IR spectrometer, using ATR accessory. The main technical specifications are: DTGS detector, KBr beamsplitter, spectral range 7,500 to 370 cm\(^{-1}\), resolution ± 1 cm\(^{-1}\), ± 2 cm\(^{-1}\) respectively, software OPUS. Baltic amber is further distinguished by a small transmittance near 890 cm\(^{-1}\) that indicates out-of-plane vibrational frequencies of an exocyclic methylene group (Beck et al., 1965). We do not find exocyclic groups (and aromatic compounds either) at the romanite samples. This fact proves a higher intensity of the alteration and fossilization processes which affected the resin from which romanite was formed; these processes might have acted on the organic substance, transforming it in simpler compounds. The 3700-3100 cm\(^{-1}\) region is different at romanite, indicating the lessening of free water proportion in comparison with succinite. Between 3000-2750 cm\(^{-1}\) peaks are approximatelly disposed in the same way: romanite presents two peaks with a maximum intensity at about 2924, 2866 cm\(^{-1}\), in comparison with those of succinite about 2924, 2867, 2848 cm\(^{-1}\), all for carboxyl groups. The transmittance range is evidently higher in the case of romanite, meaning that it has more carboxylic groups than succinite, probably because of a stronger oxidized process. The differences appeared in 1574 cm\(^{-1}\) band of Baltic amber with respect to 1591 cm\(^{-1}\) band of romanite are determined by the shift of asymmetry vibration frequencies for the carboxylic type groups, as function of the length of hydrocarbonated chains which come in resonance with (Teodor et al., in press).

Another discussion could appear in relation with intensity of the band at 1640 cm\(^{-1}\) assigned to the simple aliphatic unsaturation of the olefin group C=C; it could be compare with the intensity of the band at 1450 cm\(^{-1}\), assigned to the deformation of CH\(_2\) bonds to quantify the process of breakdown of C=C bonds (Moreno, 2000 in Shashoua, 2002). In the literature is mentioned that the breakdown of C=C bonds was related to the extent of maturation of amber from the liquid resin stage; the intensity of the two relevant bands were rationed and found to be lower for Baltic amber (0.35), but for romanite there is no information about it, although other studies have already advanced a higher maturation of romanite in comparison with succinite (Kosmowska-Ceranowicz, 1999, Neacșu, 2003 unpublished).
Conclusions

Light Microscopy analysis demonstrate that diagenetic processes played a significant role in the creation of romanite: its characteristic small surface cracks as a consequence of the lessening of free water proportion attest to this fact, in comparison with Baltic amber where a lot of fluid inclusions could be observed. It could see also remineralizations in Romanite, i.e. substitution of organic matter by anhydrite and feldspar. In other situation, the organic tissue was replaced by resin. The microscopic study seems to prove the crystallization tendency of romanite, raising thus the possibility of using X-ray diffraction as a diagnostic method for romanite. Regardless of the FT-IR technique applied, there are no notable differences between romanite spectra and Baltic amber spectra in the 3700-3100 cm\(^{-1}\) region. They appear in ‘Baltic shoulder’ region 1250-1150 cm\(^{-1}\) (Beck, 1965) but other differences could be found in order to clarify the geological origin of amber.

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