International Journal of Coal Geology 132 (2014) 6–12

Contents lists available at ScienceDirect

International Journal of Coal Geology

journal homepage: www.elsevier.com/locate/ijcoalgeo

Blue-fluorescing amber from Cenozoic lignite, eastern Sikhote-Alin, Far East Russia: Preliminary results

Igor Yu. Chekryzhov *, Victor P. Nechaev, Valery V. Kononov

Far East Geological Institute, 159 Pr 100-let Vladivostoku, Vladivostok, Russia

ARTICLE INFO

Article history:
Received 3 April 2014
Received in revised form 11 July 2014
Accepted 13 July 2014
Available online 1 August 2014

Keywords:
Blue amber
Paleogene lignite
FTIR
Volatiles
Wildfire
Perylene

ABSTRACT

Blue and greenish-yellow, in addition to ordinary yellow-orange amber, has recently been found in a lignite seam in the Zerkal'nenskaya depression, Primorsky Krai, Russia. The amber is associated with abundant charcoal and fusain fragments in the host rocks. Its FTIR spectra indicate the presence of significant quantities of volatile matter, including free hydroxyl groups and carbon dioxide. Both CO_2 and OH^- contents are greater in the greenish-yellow and blue hard varieties, suggesting rapid heating, possibly from a wildfire, followed by rapid cooling in water as a causative agent of amber hardening and extreme polymerization. This process and the following amber deposition in the reduced environment might produce the fluorescent aromatics that have been previously suggested and confirmed by this study as the blue glow main cause.

1. Introduction

Amber, a gem that originates from fossilized plant resin, is widely distributed throughout the world, mostly in Cenozoic and Cretaceous sediments, and less commonly in older marine deposits. However, concentrations of commercially-valuable amber are quite rare. The largest amber deposits are located in the southeastern Baltic regions. Amber is characterized by a wide spectrum of colors, mainly yellow, red, brown, and orange. A blue variety is one of the most uncommon and valuable on the market. This variety is unusually luminous under normal sunlight, more brightly blue fluorescent under ultraviolet light, and appears yellow or brown under artificial light. Famous deposits of blue amber are located along the Atlantic coast of Central America, the largest of which is exploited at the El Cacao Mine, Dominican Republic (Iturralde-Vincent, 2001). The Dominican amber originated from angiospermous (Hymenaea) resin (Iturralde-Vincent, 2001; Langenheim and Beck, 1965). Its blue glow was determined to have been caused by the presence of perylene, as suggested by optical absorption, fluorescence, and time-resolved fluorescence measurements (Bellani et al., 2005). Another well-studied deposit containing both common and blue amber varieties of Albian age was described at the El Soplao site, northern Spain (Menor-Salván et al., 2010; Najarro et al., 2009). This amber is Cupressaceae in origin. Causes of its blue color were not determined.

Small pieces of blue amber have recently been found in a lignite bed from the Voznovo Formation, which is situated in the Zerkal'nenskaya depression, eastern Sikhote-Alin, Far East Russia (Figs. 1 and 2). This paper presents the first description of these pieces, including results of our field observations, Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy, as well as fluorescence and fluorescence excitation measurements. Some paleontological data that have been already published (Pavlyutkin et al., 2011) are also discussed.

2. Geological outline

The Voznovo Formation consists of volcano-sedimentary deposits (primarily mudstone, sandstone, tuffaceous mud- and sandstones, and tuff) and includes a lignite bed that is up to 2 m thick. The section studied at an active open-pit mine and from cores of coal exploration boreholes is shown in Fig. 1.

The age of the upper part of the formation that overlies the lignite bed is Early Oligocene, according to the most recent paleobotanical data (Pavlyutkin et al., 2011), while K–Ar dating of the underlying Suvorovo Formation basalt was determined to be Eocene (45.8 ± 1.1 Ma, Otofuji et al., 1995; 47.3 ± 1.21 Ma, Okamura et al., 1998). All of the deposits of the Voznovo Formation are considered to be continental in origin. Nevertheless, recent work suggests that some of them might be accumulated in the brackish-water environment. Significant Na_2O/Al_2O_3 elevations determined by XRF analyses below and above the lignite bed confirm this suggestion (Fig. 1), while low Na_2O/Al_2O_3

* Corresponding author. Tel.: +7 908 4485166.
E-mail addresses: chekr2004@mail.ru (I.Y. Chekryzhov), vnechaev@hotmail.com (V.P. Nechaev), kononov46@mail.ru (V.V. Kononov).

http://dx.doi.org/10.1016/j.coal.2014.07.013
0166-5162/

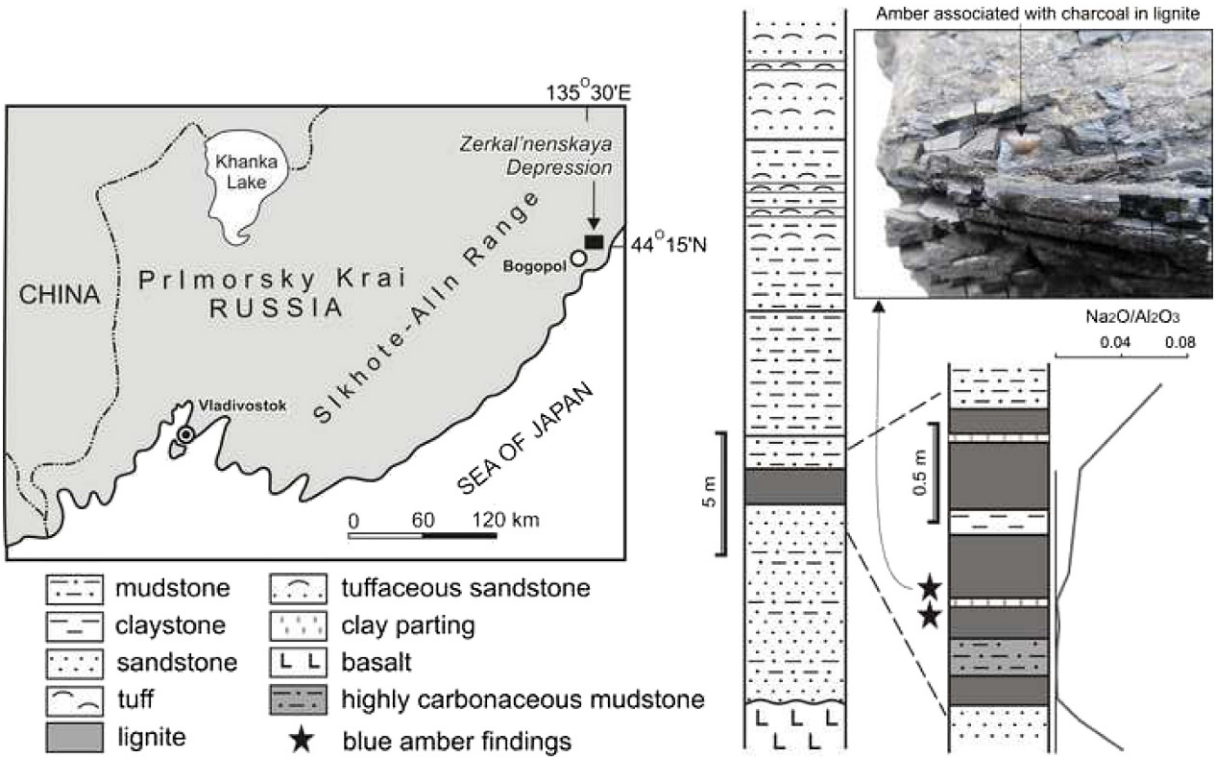

Fig. 1. Location of the Voznovo lignite deposit, its lithological column with Na_2O/Al_2O_3 variations in the rocks along the section, and photograph showing the occurrence of blue amber with charcoal in the lignite.

values suggest that the amber-bearing sediments themselves were deposited in the fresh-water environment.

3. Methods

The Voznovo amber was studied under reflected and transmitted white and UV light using a Zeiss Stemi DV4® optical microscope equipped with a Nikon Coolpix 4500® camera and Multispec® UV lamp. Surface features and inorganic geochemistry were examined using a JSM-6490LV scanning electron microscope equipped with EDS INCA Energy, X-max and VDS INCA Wave applications. In addition, Fourier Transform Infrared Spectroscopy was used with the help of a Nicolet 6700 spectrometer (Thermo Scientific, USA) using potassium bromide (KBr) disks prepared from powdered samples (3 mg) mixed with dry KBr. All these works were undertaken at the Far East Geological Institute (FEGI), Vladivostok, Russia. Fluorescence and fluorescence excitation experiments were performed at room temperature using a RF 5301 (Shimadzu) spectrofluorimeter at the Institute of Chemistry, Vladivostok, Russia.

4. Results

4.1. Amber findings

Amber is widely distributed in the Voznovo lignite. It commonly forms small (up to 0.5 cm), irregularly-shaped and friable clasts that are yellow and yellow-orange in color (Fig. 2f). Much harder pieces of amber are rarer, larger (up to 1–2 cm in size), and appear blue (under reflected sunlight and, more brightly, under ultraviolet light) and greenish-yellow in color (Fig. 2a–e). Some of them contain abundant wood microfragments (Fig. 2d). Both blue and greenish-yellow hard amber pieces were concentrated directly below and above the clay parting in the lower part of lignite seam (Fig. 1). The amber-bearing lignite, carbonaceous mudstone, and sandstone are characterized by abundant fragments of charcoal and fusain (photo in Fig. 1). The blue amber has been found in highly carbonaceous mudstone and lignite only, while sandstone contains only friable yellow amber inclusions.

4.2. Paleobotanical data

The plant fossil assemblage of the Voznovo Formation is dominated by gymnosperms (Pavlyutkin et al., 2011). Among them, 45 species belonging to three orders, namely Ginkgoales, Pinales, and Cupressales including five families were identified. The Pinaceae family, which is a well-known source of resin and amber (Tappert et al., 2011, 2013), is represented by 31 species. The Cupressaceae family plants, also well-known sources of resin and amber (Menor-Salván et al., 2010; Tappert et al., 2011, 2013), are represented by *Thuja nipponica* Tanai et Onoe and Cupressaceae sp. Araucariaceae is represented by a single pollen grain. Fossil angiosperms of the Hymenaea family, which is the source of Dominican amber (Iturralde-Vincent, 2001; Langenheim and Beck, 1965), have not been found at all.

4.3. Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is commonly applied in the amber and resin studies to identify their hydrocarbon structure and origin (Langenheim and Beck, 1965; Najarro et al., 2009; Poinar and Mastalerz, 2000; Tappert et al., 2011, 2013; and many others). In this study, it was used for the same purpose, focusing on differentiating the color varieties of the Voznovo amber.

Fig. 3 shows the FTIR spectra of the three studied samples from lignite of the Voznovo Formation: blue (two spectra determined for different parts of the same sample) and greenish-yellow hard ambers, and yellow-orange friable amber. In addition, it presents the spectra of reference materials (water, carbon dioxide, perylene, conifer resin, and amber from the three well-studied locations) for comparison (Hudgins and Sandford, 1998; Khanjian et al., 2013; Najarro et al., 2009; Smith, 1982; Tappert et al., 2011). As shown, all of the Voznovo samples are characterized by infrared spectra basically similar to each