Quaternary International xxx (2017) 1–10

Contents lists available at ScienceDirect

Quaternary International

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

A novel approach in the mineralogy of Carpathian mahogany obsidian using complementary methods

Zsolt Kasztovszky [a, *], Károly Lázár [a], Viktória Kovács Kis [a], Adél Len [b, c], János Füzi [b, c], András Markó [d], Katalin T. Biró [d]

[a] Centre for Energy Research, Hungarian Academy of Sciences, 1121 Budapest, Konkoly-Thege Miklós út 29-33, Hungary
[b] Wigner Research Centre for Physics, Hungarian Academy of Sciences, 1121 Budapest, Konkoly-Thege 29-33, Hungary
[c] University of Pécs, Faculty of Engineering and Information Technology, 7624 Pécs, Boszorkány Street 2, Hungary
[d] Hungarian National Museum 1088 Budapest, Múzeum krt. 14-18, Hungary

ARTICLE INFO

Article history:
Received 9 May 2017
Received in revised form
14 December 2017
Accepted 17 December 2017
Available online xxx

Keywords:
Carpathian obsidian
Mahogany obsidian
Prompt Gamma Activation Analysis
Small Angle Neutron Scattering
Mössbauer spectroscopy
Transmission electron microscopy

ABSTRACT

Carpathian obsidians can have various macroscopic features. They are typically black or grey and their transparency ranges from clear to opaque. The Tolcsva source, very rarely, can yield brown or red ('mahogany' type) obsidian. Archaeological, as well as geological pieces of mahogany obsidian were previously identified and characterised using Prompt Gamma Activation Analysis (PGAA). In 2007, the exact location of the red variant's outcrop was identified on the Szokolya hill (Tolcsva). The aim of this study was to better understand the possible reasons for the colouring of red obsidian. A novel approach was applied, using multiple methods for the analysis of the samples. For comparison, other Carpathian type, namely black obsidian from Tolcsva, and red obsidian from Bogazköy (Anatolia) were also studied.

Besides the PGAA measurements of the bulk elemental composition, Mössbauer spectroscopy and transmission electron microscopy (TEM) were used to study the samples in order to identify the presence of ferrous or ferric iron. With the help of Small Angle Neutron Scattering (SANS), the bulk nanostructures of the samples have been investigated and their surface or volume fractal dimensions have been determined. Black obsidians showed isotropy, while mahogany samples displayed a considerable anisotropy in the bulk pore orientation. According to our results, a large amount of the iron is dominantly located in different phases in the case of mahogany and black obsidians. Based on the summarised results, the differences between the red and black variants can be also explained by the different oxidation states of the Fe-ions, which may explain the colour difference.

1. Introduction

Besides the most widely spread black obsidian, some varieties with different colour are reported worldwide, e.g. green or grey-green from Patagonia (Stern, 2017), green or light green with gold hue from Sierra de las Navajas, Mexico (Donato et al., 2017). The relationship between the macroscopic features, i.e. the colour and the geochemical features of green obsidian from Mexico has been already investigated using various analytical techniques (Donato et al., 2017; Tenorio et al., 1998). Our present study focuses on rare "mahogany" obsidian that can be found near Tolcsva, Hungary.

In the continental part of Europe, obsidian sources are found only in the North-Eastern part of the Carpathian Basin, mostly in the Tokaj-Prešov Mountains. In the 1970s and 1980s two main variants were distinguished (Williams and Nandris, 1977; Williams-Thorpe et al., 1984; Biró et al., 1986).

The obsidian pieces found in North-East Hungary and East Slovakia can be classified into three macroscopic groups (Rosania et al., 2008). In the northern part of the region transparent or translucent obsidian occurs at several Slovakian outcrops, occasionally in relatively large nodules (e.g. Viničky, Brehov). In Hungary, between the villages of Mád and Erdőbénye, pieces of grey or greyish banded variants can be collected, and in the Tolcsva environs, non-transparent homogenous black obsidians are found in the form of nodules up to the size of a fist.

* Corresponding author.
E-mail addresses: kasztovszky.zsolt@energia.mta.hu (Z. Kasztovszky), lazar.karoly@energia.mta.hu (K. Lázár), kis.viktoria@energia.mta.hu (V. Kovács Kis), len.adel@wigner.mta.hu (A. Len), fuzi.janos@wigner.mta.hu (J. Füzi), marko.andras@hnm.hu (A. Markó), tbk@hnm.hu (K.T. Biró).

https://doi.org/10.1016/j.quaint.2017.12.028
1040-6182/

The transparent, so-called Carpathian I or C1, obsidian is similar to the raw material of the archaeological artefacts found in vast regions of Central Europe. The largest and best quality geological samples can be collected in South-East Slovakia, at the localities Brehov and Viničky. In the southern part of the 'obsidian region', in the central and southern parts of the Tokaj-Prešov mountains, two main macroscopically different types were distinguished among the non-transparent Hungarian or Carpathian II variants: C2T (Tolcsva) and C2E (Mád-Erdőbénye) types, respectively (Williams-Thorpe et al., 1984; Biró et al., 1986). C2E is typically grey, often with striped pattern while the homogenous black coloured variant (C2T) is known from the southern slopes of the Szokolya hill at Tolcsva. The geographical locations of the main Carpathian obsidian sources can be seen in Fig. 1a and b.

The occurrence of red (or mahogany) obsidian in the Tolcsva region was reported in the 19th century (Szabó, 1867, 1876), but the precise geographical position of the source remained unknown until the modern field studies.

In the archaeological collections, the first piece of mahogany obsidian was spotted among the finds of the Arka Upper Palaeolithic (Epigravettian) settlement (Biró 1984; Biró 2002). Later on, the occurrence of this variant was identified in several Gravettian and Middle Palaeolithic assemblages, not only from the vicinity of the Tokaj-Prešov mountains, but also from localities lying more than 100 km to the west (Biró et al., 2005). A piece of mahogany obsidian from the archaeological site Arka (Inv. nr. Pb 63.264 in the Palaeolithic Collection of the Hungarian National Museum) is shown in Fig. 2.

In 2007, it was possible to re-identify the source of mahogany obsidian on a little hill near Tolcsva (Fig. 3). The surrounding region supplied, nevertheless, only the common C2T type black obsidian. The purpose of the current analyses is to better understand the specific and rare phenomenon of appearance of Carpathian „mahogany" obsidians. Since the mahogany obsidian occurs together with the black variant, it raised several questions: why this special tint appears, whether it is related to chemical composition and whether it has any consequences on provenance studies applying geochemical methods.

2. Locality and lithology of analysed samples

„Red" obsidian occurs on a very small area within the so-called Carpathian sources. It can be collected, in a secondary deposit on the slopes of the Szokolya hill near Tolcsva, which is abundant in obsidian of the „normal" type: black, non-transparent, belonging to the well-known Carpathian 2T (Tolcsva variant) obsidians. The modern geological map (Fig. 4) of the region puts the findspot into the Miocene (Upper Sarmatian-Lower Pannonian) Erdőbénye formation with rhyolite tuff (possible bedrock for the obsidian) and various hydrothermal and limnic siliceous rocks, also used as raw material by the prehistoric population.

In a previous study (Biró et al., 2005), Prompt-gamma Activation Analysis (PGAA) of several mahogany obsidian archaeological artefacts and a single geological sample collected from a stream deposit near Tolcsva was published. The occurrence of reddish-brown obsidian has occasionally been reported from other obsidian source regions, too (e.g. a voluminous outcrop in Büyüksulata, Turkey (Heide et al., 1996). A sample originating from the Anatolian quarry near Bogazköy which exhibits the mahogany tint was also analysed in the present study.

3. Methods

In the current work, PGAA measurements of four black and five mahogany obsidian samples from Tolcsva, as well as measurements of one mahogany obsidian sample from Bogazköy are discussed.

In addition to the PGAA study, Transmission Electron Microscopy (TEM), Mössbauer spectroscopy (MS) and Small Angle Neutron Scattering (SANS) studies have been performed on one mahogany and one black obsidian from Tolcsva, as well as the one mahogany obsidian from Bogazköy. The specimens analysed with different methods have been prepared from the same parent obsidian sample, in case of both the mahogany and black obsidians from Tolcsva, as well as the mahogany one from Bogazköy with the exception of black obsidian sample used for SANS. All the analysed samples were geological pieces from the Lithotheca collection of the Hungarian National Museum. In Table 1, we summarize the analytical studies that are discussed in this work.

3.1. Prompt-gamma Activation Analysis (PGAA)

Prompt-gamma Activation Analysis (PGAA) is a bulk panoramic elemental analytical method based on the radiative capture of thermal or cold neutrons, i. e. the (n,γ) reaction. The sensitivity of PGAA for the different elements primarily depends on the neutron absorption cross-sections of the atomic nuclei. PGAA is sensitive for most major geochemical elements, and also for some traces, principally for B, Cl, Nd, Sm and Gd. Since neutrons can penetrate through a few cm thick sample, the composition data provide average values for the irradiated volume (Kasztovszky et al., 2008).

The PGAA measurements have been done at the Budapest Neutron Centre. The upgraded Budapest PGAA facility is described by Szentmiklósi et al. (2010). The samples from Tolcsva have been measured in 2015, while the sample from Bogazköy was analysed in 2004, using the external horizontal cold neutron beam of 9.6×10^7 cm^{-2} s^{-1} thermal equivalent flux. The samples of a few cm^2 area and around 5–10 mm thickness were placed in the beam of 44 mm^2. They were irradiated for 1400–3600 s, depending on the sample size, in order to achieve the statistically significant counts in the spectra. The determination of the elemental concentrations has been done using the k_0-method. The standardisation of the PGAA method and the calculation of concentrations are discussed by Révay (2009). The applicability of the PGAA method to the analysis of obsidians was verified through measurements on JR1 and JR2 international geological reference samples (Kasztovszky et al., 2008, 2017).

3.2. Transmission electron microscopy (TEM)

The purpose of the TEM investigations was to perform structural and chemical analyses on the nanometre scale. Two sample preparation methods were applied. 1.) A small amount of obsidian was gently crushed under ethanol to produce electron transparent pieces and a droplet of the resulting suspension was deposited onto a lacey carbon coated Cu grid (TedPella). 2.) A small glass shard was embedded into a 2 mm × 2 mm Ti window (Technoorg) and after mechanical polishing down to ca. 40 μm of thickness it was thinned with Ar ion bombardment until a hole was formed. The areas in the proximity of the hole are perfect for TEM analysis.

Selected area electron diffraction (SAED) patterns and chemical analyses were performed using a Philips CM 20 transmission electron microscope (TEM) with a LaB_6 cathode, equipped with a Bruker Xflash 5030T energy-dispersive spectrometer (EDS). For chemical analyses, a 55 nm spot size and counting times of 100 s were used. SAED patterns were taken from areas of ca. 250 nm of diameter and each area subjected to SAED was subsequently analysed chemically. High resolution TEM (HRTEM) was carried out on a JEOL 3010 UHR with a LaB_6 cathode, with point resolution 0.17 nm, equipped with Gatan Imaging Filter Tridiem, and processed with Digital Micrograph (Gatan).

Please cite this article in press as: Kasztovszky, Z., et al., A novel approach in the mineralogy of Carpathian mahogany obsidian using complementary methods, Quaternary International (2017), https://doi.org/10.1016/j.quaint.2017.12.028