Journal of African Earth Sciences 97 (2014) 99–108

Contents lists available at ScienceDirect

Journal of African Earth Sciences

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

Occurrence of dendritic agate from Dereyalak village (Eskişehir) – NW of Turkey and its relationship to sepiolite nodules in the region

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ARTICLE INFO

Article history:
Received 18 June 2013
Received in revised form 17 April 2014
Accepted 28 April 2014
Available online 9 May 2014

Keywords:
Dendritic agate
Replacement
Sepiolite nodule
Magnesite
Dereyalak village
Eskişehir

ABSTRACT

This study presents the geology and mineralogy of the agate nodules that occur in the Pliocene polymictic conglomerates, northwest of Dereyalak village, Eskişehir, northwest Turkey, and their relationship to sepiolite nodules. The host-rock of the agates is a layer 5–25 m thick with an outcrop length of more than 1.5 km. This host rock consists of well-rounded pebbles, mainly composed of opal, ultramafics, sandstones, limestones and volcanics. The conglomerates unconformable overlie an Upper Cretaceous ophiolite complex. This tectonic contact, which trends E–W, is accompanied by another NE–SW-trending major fault. Most of the agate nodules are present along these fault zones.

The mainly white and black agate nodules range from 5 to 30 cm in diameter and show a zoned macrostructure. The transparent core is surrounded by a translucent white zone, which, in turn, is surrounded by a zone rich in black dendrites. An opal-rich zone is present nearest the outermost rim. XRD analyses revealed alpha quartz (chalcedony), opal-CT (pseudocrystalline cristobalite), opal-C (pseudocrystalline tridymite) and moganite as the main mineral constituents of the agates. Under polarised light, the predominance of microcrystalline, fibrous quartz ("chalcedony") is observed. The black colour and fabric of the third, outer zone is due to the presence of black pyrolusite and manganite dendrites. SEM images also show different textures in agates that confirm the presence of a zoned structure in the dendritic agates.

Nodular sepiolite (Meerschaum) is well known and has been exploited for centuries in Eskişehir region. Major sepiolite nodule deposits are mainly observed northeast and east of the Dereyalak region. The field observations and the mineralogical data, including comparison between the internal texture of agates and sepiolite nodules and additional geochemical analyses, suggest that the Dereyalak dendritic agates could have formed by sepiolite replacement by low-T silica-rich hydrothermal solutions that most likely circulated along the fracture systems.

Contents

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http://dx.doi.org/10.1016/j.jafrearsci.2014.04.028
1464-343X/

1. Introduction

The quartz gemstone family (quartz, agate, and jasper) are some of the more abundant minerals and have been commonly used as gemological objects since ancient times. From this family, agates present one of the more spectacular examples of autonomous pattern generation in nature. Agates have a cryptocrystalline structure formed from microscopic particles, mainly fibrous and partially granular silica particles, which are mainly chalcedonic silica components (Taijing and Sunagawa, 1994; Wang and Merino, 1995). Thus, the agates are classified as a variety of microcrystalline quartz minerals (Flörke et al., 1982; Moxon, 1996).

Despite world-wide agate distribution and numerous investigations (e.g., Fallick et al., 1985; Flörke et al., 1982; Landmesser, 1984; Landmesser, 1988a,b; Harris, 1989; Heaney, 1993; Wang and Merino, 1990; Taijing and Sunagawa, 1994; Merino et al., 1995; Harder, 1993; Heaney and Davis, 1995; Götze et al., 1999, 2001; Moxon, 2002; Petrǎnek, 2004), the process of formation of agate is not yet completely understood (Moxon, 1996; Götze et al., 1999, 2012). Discussions involving the origin of agate are controversial because agates have never been successfully replicated in the laboratory (Götze et al., 2001). Agates are present in acidic and basic volcanic rocks, and they either form during hydrothermal processes or in sedimentary/diagenetic environments, each of which produce agates with its own set of characteristics and can be observed on every continent (Moxon, 2002; Moxon et al., 2006).

Of the thousands of agate locations in the world, several locations are considered to be "classical". The countries with these "classical" agate locations are Brazil, Uruguay, Argentina, Germany, Mexico, Morocco, England, the U.S.A. (Oregon, Washington, Montana), Scotland and Turkey (Moxon, 1996; Hatipoğlu and Dora, 2000; Zenz, 2005; Pertille et al., 2013). While there are many agate deposits with economical reserves located in various regions of Turkey, only a few of them are well-understood in terms of their origin. In central Turkey, a famous agate deposit with a distinctive gem quality is documented in the Çubuk area of the Ankara region (Hatipoğlu and Dora, 1998, 2000). These agates were hydrothermally deposited in various volcanic host rocks in the Çubuk region (Hatipoğlu et al., 2011). In the northwest part of central Turkey, the Dereyalak district of the Eskişehir region is another important location for finding the dendritic agate in volcanogenetic conglomerate host rocks.

There are only a limited number of studies (e.g., Arzoğulları, 2007; Çalık and Arzoğulları, 2009; Paralı et al., 2011) of the Dereyalak dendritic agates. Therefore, little is known about these agates in terms of their mineralogy, petrography and distribution. To address this knowledge gap, this study investigated the mineralogical and geochemical aspects of the dendritic agates in the vicinity of Dereyalak village and their potential as a new local gemstone resource. The scope of this paper is to describe (1) the field aspects of the agates, (2) the detailed petrography and mineralogy of representative agate samples, (3) the silica source and method of deposition, and (4) the relationship between the sepiolite nodules in the region and the agate.

2. Methods

The methods used to study the properties of the Dereyalak dendritic agate samples were as follows:

X-ray powder diffraction analyses were performed to powder crushed and milled from the dendritic agate sample. The X-ray powder diffraction patterns of the samples were obtained using a Philips PW-1430 XRD with Cu tube and a monochromatic graphics. Random amounts of finely powdered agate samples were scanned between 5° and 70° 2θ. The XRD patterns were obtained in the laboratory of the Geology Engineering Department in İstanbul University.

The samples were analysed using a Jeol/JSM-6335F/INCA-EDS scanning electron microscope (SEM) at various magnifications up to 50,000×. The SEM investigations were carried out in the TUBİTAK-Marmara Research Centre. Thin sections of the samples were analysed using a BX 51 Olympus polarising microscope. These observations were made in the Department of Geological Engineering of Çanakkale Onsekiz Mart University.

The chemical contents of the dendritic agate sample were performed, certificated with the code number "IZ12279832", under contract by the accredited ALS Chemex Laboratory, Canada, using ICP-MS (inductively coupled plasma mass spectrometry) for major oxides and ICP-AES (inductively coupled plasma atomic emission spectroscopy) for trace and REE elements according to their Code ME-ICP06 and ME-MS81 (Table 1). The ICP-AES (inductively coupled plasma atomic emission spectroscopy) analyses for major oxides were done by the samples underwent a $LiBO_2$ (lithium metaborate)/$Li_2B_4O_7$ (lithium tetraborate) fusion and were dissolved in 100 m of 4% nitric acid/2% hydrochloric acid. The ICP-MS analyses for REE and incompatible elements were done by $LiBO_2$ fusion and subsequently dissolution in 100 ml of 4% HNO_3/2% HCl_3. This procedure was applied for Ag, Ba, Cr, Co, Cs, Ga, Hf, Mo, Nb, Ni, Pb, Rb, Sn, Sr, Ta, Th, U, V, W, Y, Zr, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. The precious and base metals 2 + (Mo, Pb, Zn, Ni, As, Cd, Sb, Bi, Ag, Au, Hg, Tl, Se) were digested in aqua regia and also analysed by ICP-AES. Loss of ignition (LOI) was determined by weight loss after ignition at 1000 °C.

3. Results and discussion

3.1. Geological setting of the Dereyalak dendritic agate deposits

The study area, which measures approximately 48 km^2, is located 45 km southwest of the city of Eskişehir (Fig. 1). The geologic units in the study area range in age from Mesozoic to Quaternary. These units, listed from oldest to youngest, consist of Triassic (Gözler et al., 1996) İnönü metamorphics (metaquartzite), an Upper Cretaceous ophiolitic unit (mainly serpentinite), a Pliocene (Gözler et al., 1996) volcanogenetic sedimentary sequence (volcanogenetic conglomerate, volcanogenetic sandstone, and basalt), and Quaternary alluvium (Fig. 1).

The basement in the study area, the Triassic İnönü metamorphic unit, consists of metabasic rocks and metaquartzite. Calcschist also