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Origin and geochemistry of agates in Permian volcanic rocks of the Sub-Erzgebirge basin, Saxony (Germany)

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ABSTRACT

Mineralogical and geochemical investigations of agates from Permian volcanic rocks of the Sub-Erzgebirge basin (Saxony, Germany) were made to constrain the genesis and characteristics of these spectacular forms of silica in acidic volcanic host rocks. Samples from the main agate occurrences of Chemnitz, Hohenstein-Ernstthal, St. Egidien and Zwickau were selected for detailed analyses.

The results of the study show that agate formation can be related to volcanic activity (Rochlitz ignimbrite) and the subsequent alteration of the volcanic rocks. Most agates originate from the infill of silica into cavities of lithophysae (high-temperature crystallization domains), which formed during cooling of welded ignimbrite. Agate formation temperatures of probably >150 °C were calculated from fluid inclusion and oxygen isotope studies, which indicate that the mobilization and accumulation of silica started already during a late phase of or soon after the volcanic activity.

The trace-element composition of chalcedony and macrocrystalline quartz in agates is different from that of quartz from magmatic or metamorphic rocks and pegmatites. Elements of the volcanic rock matrix (Al, Ca, Fe, Na, K) were released during the alteration processes and accumulated in the SiO_2 matrix of the agates. Extraordinary high contents of Ge (>90 ppm), B (46 ppm) and U (>18 ppm) were also detected, which can exceed the Clark concentration and sometimes the element concentration in the surrounding host rocks. In addition, chondrite-normalized REE distribution patterns of the agates show strong negative Eu-anomalies, enriched HREE as well as tetrad effects. These patterns are different from the REE patterns of the volcanic host rocks and point to fractionation processes during agate formation. The specific geochemical features indicate interactions of the host rocks with magmatic volatile fluids and heated meteoric water, and transport of SiO_2 and other elements both in aqueous solution and via stable fluorine (and chlorine) compounds such as SiF_4, BF_3, GeF_4, and UO_2F_2.

The results of cathodoluminescence (CL) microscopy and spectroscopy revealed a microstructure of the agates that is similar for all occurrences. Characteristic features are irregular internal textures and sector zoning in quartz as well as luminescence colours and spectra, respectively, which are caused by a typical high defect density (oxygen vacancies, silanol groups). According to these results, the formation of agates can be explained by crystallization via an amorphous silica precursor under non-equilibrium conditions.

1. Introduction

Agate is a spectacular and famous gemstone because of its wide variety of shape, texture and colour. Agates are banded chalcedony with the chemical formula SiO_2, but in detail, macrocrystalline quartz and/or quartzine can be intergrown or intercalated with chalcedony layers in agates (e.g., Godovikov et al., 1987; Blankenburg, 1988; Götze et al., 1998; Moxon and Rios, 2004). Moreover, opal-CT (Flörke et al., 1982) and moganite (e.g., Götze et al., 1998; Moxon and Rios, 2004) were identified as further silica phases in agate, and Moxon and Carpenter (2009) have identified cristobalite as possible agate precursor experimentally. In addition, agates often contain considerable amounts of mineral inclusions and water (1 to 2 wt.%) as both interstitial molecular H_2O and silanol groups (Flörke et al., 1982; Moxon and Rios, 2004). These facts demonstrate that agates are very complex products of nature. As a consequence, the formation history of agates may be very complex as well.

Although agates can be found in practically all rock types, the occurrence in volcanic rocks is the most abundant (Landmesser, 1984; Godovikov et al., 1987; Blankenburg, 1988; Götze, 2011). Most primary agate occurrences worldwide are related to SiO_2-rich (rhyolites,

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rhyodacites) and SiO_2-poor (andesites, basalts) volcanic rocks. In acidic volcanic rocks, agates mostly occur within spheroidal aggregates in the rock body: the so called lithophysae. However, agate formation in basic volcanics takes place in former vesicular cavities (Götze, 2011).

Several authors assume that the formation of volcanic agates is associated with late- or post-volcanic alteration or weathering of volcanic host rocks (especially of volcanic glass) (e.g., Walger, 1954; Harder, 1993; Holzhey, 1995; Pabian and Zarins, 1994; Götze, 2011). Evidence for the existence of rock alteration processes can be found in the chemical composition of the agates and the association with typical secondary minerals such as clay minerals, zeolites or iron oxides (Götze, 2011).

Nevertheless, the origin of agate remains incompletely understood. The discussions are controversial especially due to the fact that no one has unambiguously documented agate formation in real time and agates have never been successfully replicated in the laboratory. Pabian and Zarins (1994) concluded that a hypothesis concerning the formation of agates can only be developed by a complex consideration and evaluation of geological as well as mineralogical and geochemical data.

The favoured formation of agates takes place in volcanic rocks and therefore, agate occurrences are most likely connected with geological periods of volcanic activity. The oldest occurrence, the Warrawoona agate in Australia, has an age of 3.48 Ga and was found in metamorphosed rhyolitic tuffs (Moxon et al., 2006). Agates are also found in the one billion year old basalt hosts of the Lake Superior region in the USA and Canada. A widespread eruption of acidic volcanic lava and ignimbrites took place in Central Europe during the Permian (Rotliegend). As a result, at 280–320 Ma a number of volcanic rocks with numerous agate occurrences were formed in Germany (Thuringia, Saxony), and other European countries such as Poland, Czech Republic and France (Götze, 2011).

In the present study agates from Permian volcanic rocks of the Sub-Erzgebirge basin, Saxony, Germany were investigated, which is one of the most famous agate locations in Germany. An integrated mineralogical and geochemical study on selected agate material was carried out to provide data for the reconstruction of the geological and geochemical processes leading to the formation of agates in the acidic volcanic host rocks and the interpretation of their specific geochemical and mineralogical characteristics.

2. Geological setting

Samples for the present study originate from the Sub-Erzgebirge basin (also known as the Werdau-Hainichen trough — Prescher, 1987), which is the northern continuation of the Erzgebirge (Fig. 1). The basin extends from Hainichen via Chemnitz and Zwickau to Werdau with a SW–NE extension of about 60 km and a N–S extension of about 20 km and is bordered to the north by the Saxonian granulite massif and to the west by the Berga anticline (Walter, 1995). The area mainly consists of volcanic rocks as well as marine and terrestrial sediments of eroded material from the Variscan orogeny (Schneider et al., 1994; Schneider et al., 2014). The sedimentation areas of the Lower and Upper Carboniferous and the Rotliegend are related to the specific geodynamic regimes and represent different basin types. Several volcanic eruptions and tuff layers of Carboniferous to Permian age are intercalated between the different sediment cycles including rhyolitic to basaltic as well as lamprophyric rocks (Fischer, 1991).

The evolution of Permian volcanics in the Sub-Erzgebirge basin is related to anorogenic extension processes on the NW margin of the Bohemian Massif. The bimodal volcanic rocks are not genetically uniform but belong to two groups, called "upper" and "lower volcanics", which differ from each other in terms of age and geochemical composition (Seifert and Kempe, 1994). The volcanic rocks are associated with Late Variscan molasse sediments. Litho- and biostratigraphic investigations close to the Lower and Upper Rotliegend provide a Lower Rotliegend age for the sediments and the neighboring volcanics. According to Fischer (1991) and Schneider et al. (1994), the data correspond to an absolute age of about 289 to 294 Ma for both upper and lower volcanics. Results of recent SHRIMP measurements (288–298 Ma) confirmed these ages

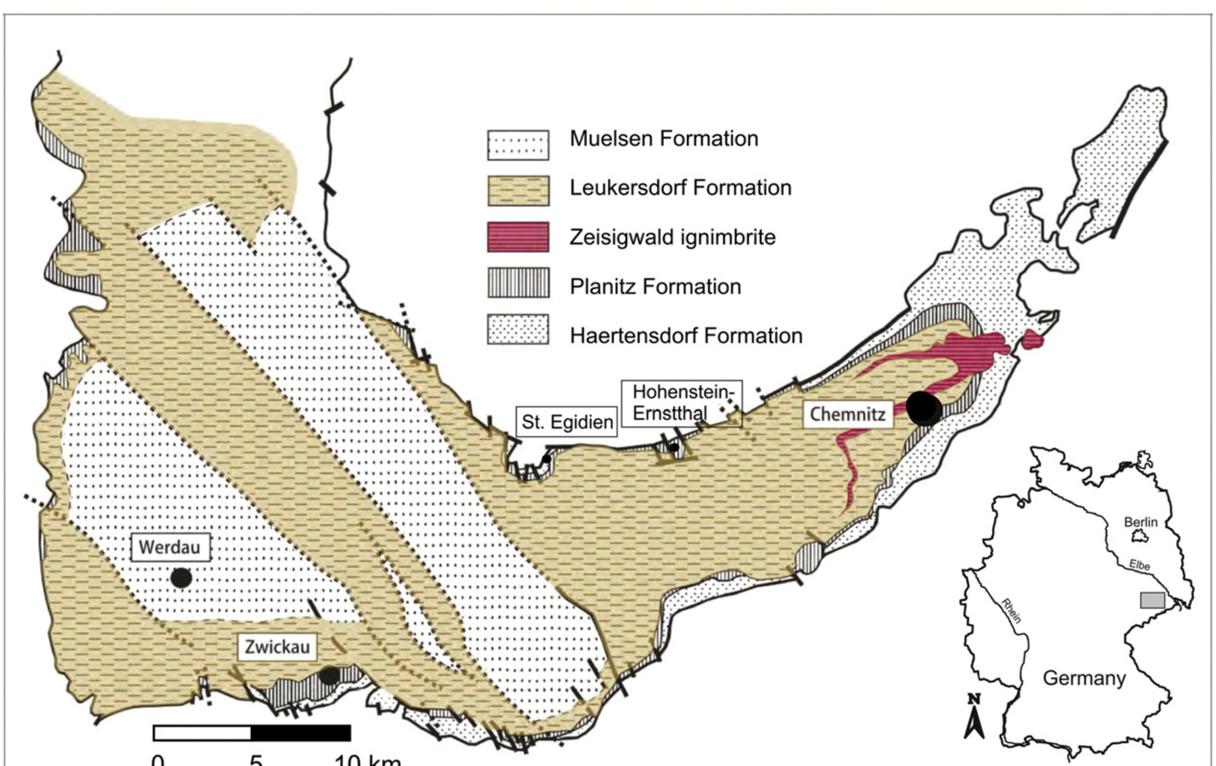

Fig. 1. Geological map (simplified) showing the Sub-Erzgebirge basin with the distribution of the different stratigraphic units (modified according to Schneider et al., 2014); the investigated samples from Chemnitz, Hohenstein-Ernstthal, St. Egidien and Zwickau all belong to the Rochlitz ignimbrite of the Planitz Formation.