## Agate

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Agate – a spectacular form of SiO2 and a famous gemstone – is commonly characterized as banded chalcedony. In detail, chalcedony layers in agates can be intergrown or intercalated with macro-crystalline quartz, quartzine, opal-C, opal-CT, cristobalite and/or moganite. In addition, agates often contain considerable amounts of mineral inclusions and water as both interstitial molecular H2O and silanol groups.

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## 1. Introduction

Agates belong to the most fascinating mineral objects in nature because of their wide spectrum of colors and spectacular morphologies. Therefore, they play a dominant role as gemstones and cut stone since antiquity. The name "*Agate*" can be dated back to ca. 350 B.C. (Theophrast) and was probably related to the discovery of agates in the river *Achates* (recently *Drillo*) in Sicily. Today, agate deposits and agate treatments are known from historical and recent sites all over the world<sup>[1][2][3][4]</sup>.

In general, agate occurrences are distributed around the world on all continents, and agates have already been formed very early in the Earth's history. The oldest known occurrence, the Warrawoona agate in Western Australia, was found in 3.48 Ga old metamorphosed rhyolitic tuffs<sup>[5]</sup>. More than one billion years old agates are also known from the basalts of the Lake Superior region in the USA and Canada.

A closer view reveals that agate occurrences are in particular connected with geological periods of strong volcanic activities such as huge basaltic lava flows or eruptions of acidic lava from Permian to Tertiary. Chemical and mineralogical analyses of the host rocks show that most global agate occurrences are related to both SiO<sub>2</sub>-poor (andesites, basalts) and SiO<sub>2</sub>-rich (rhyolites, rhyodacites) volcanic rocks (Figure 1a-d).

However, agates can also be formed by other processes and in other rock types. In different host rocks, hydrothermal vein agates occur in mm- and cm-sized fissures and veins (Figure 1e), but can also reach thicknesses of several dm and lengths of several hundreds of meters. In addition, agates of sedimentary origin have been found as irregular forms in stratigraphic sequences of carbonate rocks and clastic sediments (Figure 1f) including silicification of residues of animals and plants in the surface region of certain sediments and volcano-sedimentary units. Another common feature is the secondary deposition and redistribution of agates from primary deposits. Agates in clastic sediments (river gravel and marine sediments) are known from the surroundings of many agate occurrences worldwide (Figure 1g).



**Figure 1.** Compilation showing the different main agate types; (**a**) lithophysa (thunderegg) within the flow texture of the rhyolitic host rock from Nesselhof, Thuringia (Germany); (**b**) large thunderegg with agate from rhyolitic ignimbrite of St. Egidien (Saxony, Germany); (**c**) andesitic host-rock with both empty and agate-filled vesicles at the Rancho Coyamito (Chihuahua, Mexico); (**d**) finely banded agate from a trachyandesitic host-rock of Xuanhua (Hebei province, China); (**e**) hydrothermal vein agate in metamorphic host rocks (gneisses) from Röthenbach (Saxony, Germany); (**f**) sedimentary banded microcrystalline granular quartz from a clay seam in carbonate host-rocks from Dulcote (Mendip, Great Britain); (**g**) clastic agate pebble from river sediments of the Yangtze river near Nanjing (Jiangsu province, China); Scale bar is 5 cm.

## 2. Processes of agate formation

The processes of agate formation are complex and often involve multiple steps and can run under different conditions and involve divergent processes. Different analytical results provided a temperature range for agate formation between ca. 20 and 230°C.

The majority of agates can be related to mafic (basalts, andesites) and acidic (rhyolites, rhyodacites) volcanic host rocks. Many field observations and analytical results indicate that volcanic agates form in a late stage of volcanism or after solidification of the volcanic host rocks. Most of the silica necessary for agate formation is supplied by alteration processes of the surrounding volcanic rocks by heated meteoric water, hydrothermal/magmatic fluids and other volatiles such as CO<sub>2</sub> or F-complexes. In vein agates, SiO<sub>2</sub> derives from ascending hydrothermal-magmatic solutions, whereas silica in sedimentary agates is mostly accumulated by SiO<sub>2</sub>-rich pore solutions.

The transport of silica in the form of monomeric silicic acid  $H_4SiO_4$  or oligomers is predominantly realized by diffusion processes to cavities in the host rocks. In basic volcanic rocks, vesicular cavities form from included gases and liquids during the solidification of the lava, whereas in acidic volcanic rocks lithophysae (high-temperature crystallization domains) are formed above  $T_g$  in the cooling melt as host for the agates. Vein agates can be formed in fissures and veins within different types of host rocks, where a free movement of silica-bearing mineralizing fluids through a system of cracks is possible. In sedimentary rocks, formation of agates is often accompanied by replacement of pre-existing soluble minerals (sulfates, carbonates) by silica.

The accumulation and condensation of silicic acid result in the formation of silica sols and amorphous silica as precursors for the development of the typical agate structures. The process of crystallization often starts with the spherulitic growth of chalcedony or micro-granular silica continuing into chalcedony fibres. Macrocrystalline quartz crystallizes when the SiO<sub>2</sub> concentration in the mineralizing fluid is low.

The formation of the typical agate microstructure is most likely governed by processes of self-organization. Depending on the specific physico-chemical conditions (e.g., T, pH, SiO<sub>2</sub> concentration, trace-element contents), these crystallization processes may proceed in a very complex way and result in characteristic structures, SiO<sub>2</sub> phases, colors and inclusions. During agate genesis not only silica minerals are formed, but also numerous other mineral phases. The spectrum of paragenically formed minerals can significantly vary in dependence on the genetic type of agate. The most common minerals associated with agates are clay minerals, Fe-oxides/-hydroxides, minerals of the zeolite group and carbonates (especially calcite).

The complex processes of agate formation, often run under non-equilibrium conditions, result in a wide variety of peculiarities such as spectacular internal textures, "moss agates", "plume agates" or pseudo-stalactitic aggregations. Moreover, there are compelling indications for microbial activities that are sometimes involved in agate creation, at least in a very early state of formation. These specific features make agates a unique and spectacular product of nature.

## References

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