

Manganese rosettes—a special form of manganese dendrites

by Ulf Thewalt and Gerda Dörfner (Gerstetten, Germany)

About the Term “Dendrites”

The term “manganese dendrites” is frequently encountered in the literature to describe more or less delicate, flat deposits of manganese oxide minerals. This refers to

(1) tree-like forms (dendron = tree, Greek; that is, structures with a central stem) (Fig. 1).
(2) ring-bound, rosette-shaped manganese oxide deposits; in a sense, small trees without trunks.

(3) individual “moss-like” structures, such as those that also appear as “branches” in (1) and (2) (Fig. 3).

This note focuses on objects of type (2), which are referred to here as manganese rosettes. The diameters of the manganese rosettes range from sub-millimeter to centimeter sizes. The limestone slabs of the White Jurassic in the Solnhofen area (Franconia, Germany) are known for the occurrence of particularly well-developed specimens of manganese dendrites and rosettes. Upon closer inspection, similar—albeit less conspicuous—deposits of manganese minerals can be found in many locations throughout the White Jurassic region of southern Germany. It is also evident that manganese dendrites and manganese rosettes are not limited to limestone. Finally, it is worth noting that two- and three-dimensionally developed manganese dendrites and rosettes can even be observed in agate and opal from certain localities.



Opal and chalcedony with manganese dendrites. Waldkirchen, Lower Austria, Austria.
Width: 10 cm. Anton Rauscher Collection. Photo by Andreas Riepl.

A Closer Look at Manganese Rosettes...

In the following, we present and discuss photographs of manganese rosettes originating from limestone quarries in the Ulm area (Württemberg, Germany). Most of these quarries are now closed. We compiled the material for this note more than two decades ago. Finally, we outline the current understanding of the formation of manganese rosettes and dendrites.



Fig. 1: Manganese dendrites in the strict sense. Their central stems suggest that they formed through the infiltration of coloring material along the stems and that the coloring material originated from outside the slab.

However, the matter is more complicated. Manganese rosettes, at any rate, cannot have formed in this way! After all, they have no “supply channels” and are not located at the edges of the slabs.

Abandoned quarry on the B28 near Zainingen. Width: 18.5 cm.

The photos in this article were taken by the authors except otherwise stated.



**Fig. 2: Manganese rosettes. Abandoned quarry on the B28 near Zainingen.
Width: 10.2 cm.**



Fig. 3: Stem-like manganese dendrites. Beautiful examples could be found in all the quarries in the Ulm area. The specimen shown comes from the abandoned quarry near Blaustein-Herrlingen. In aggregates of types (1) and (2), such stem-like structures can often be recognized as closely packed structural elements. Width: 4.9 cm.

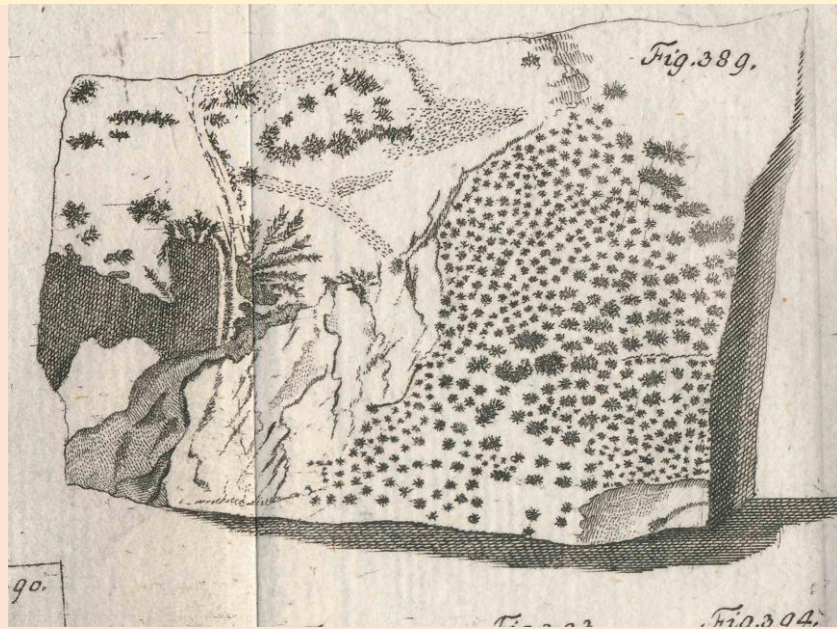


Fig. 4: This copperplate engraving is from LINNÉ's **System of the Mineral Kingdom** (Figure 389). LINNÉ writes: "*Pseudoasteroit ... It is actually a subspecies of the dendrite, with which it also shares the manner of its formation, and is so named when the small tendrils and branches lying on the surface of the stone form a circular pattern ...*"

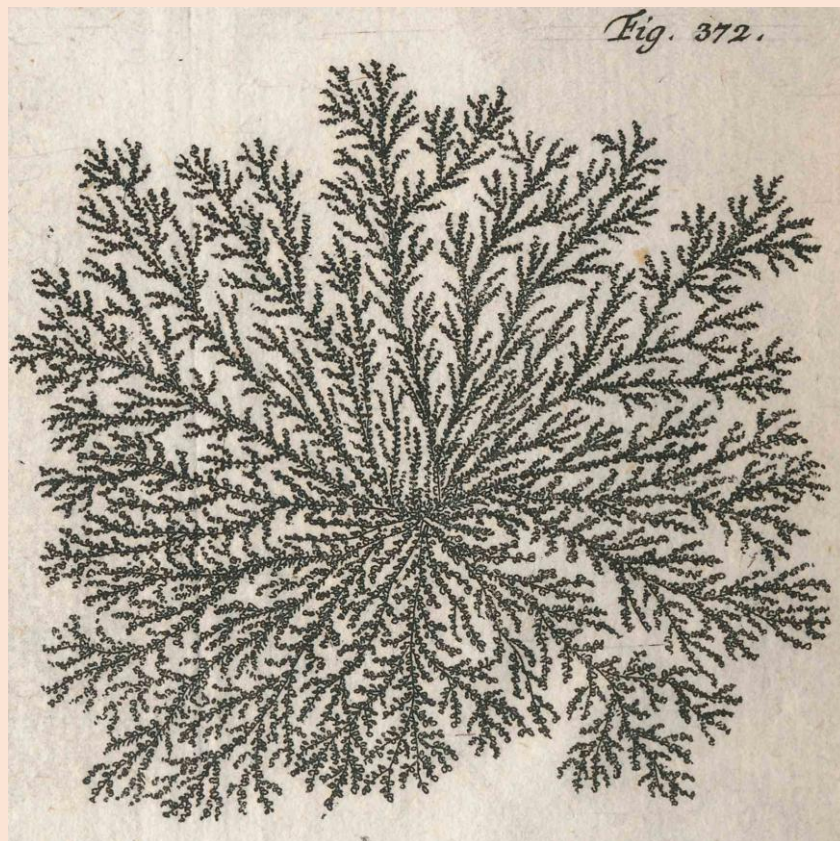


Fig. 5: "Dendritic Rose": Figure 372 from LINNÉ's *"System of the Mineral Kingdom"*. Original text: "*They are called ... dendritic roses when the fine shoots, with even finer twigs and leaf tips, radiate from a central point toward the entire circumference.*"



Fig. 6: This piece of limestone with manganese rosettes could almost have served as a template for Fig. 4. It comes from the Wager-Fischer quarry near Söhnstetten. Width: 11.2 cm.



Fig. 7: Manganese rosettes: Enlarged detail from Fig. 6.
Image width: 1.6 cm.

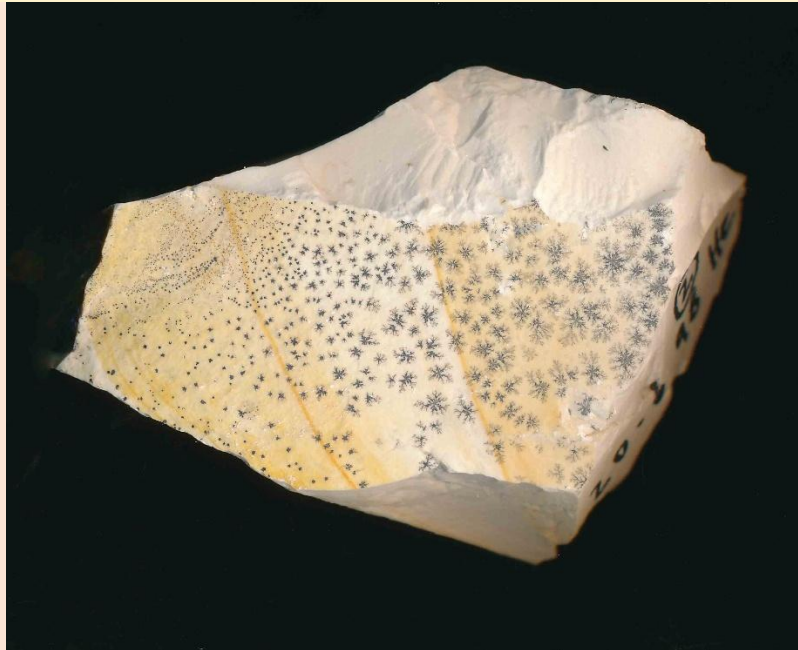


Fig. 8: The size of the manganese rosettes increases from left to right in this specimen. This suggests temporal and/or spatial changes in the reaction conditions during the formation of the rosettes. The rosettes here are particularly delicate in form.

Source: abandoned quarry near Blaustein-Herrlingen. Width: 5.2 cm.

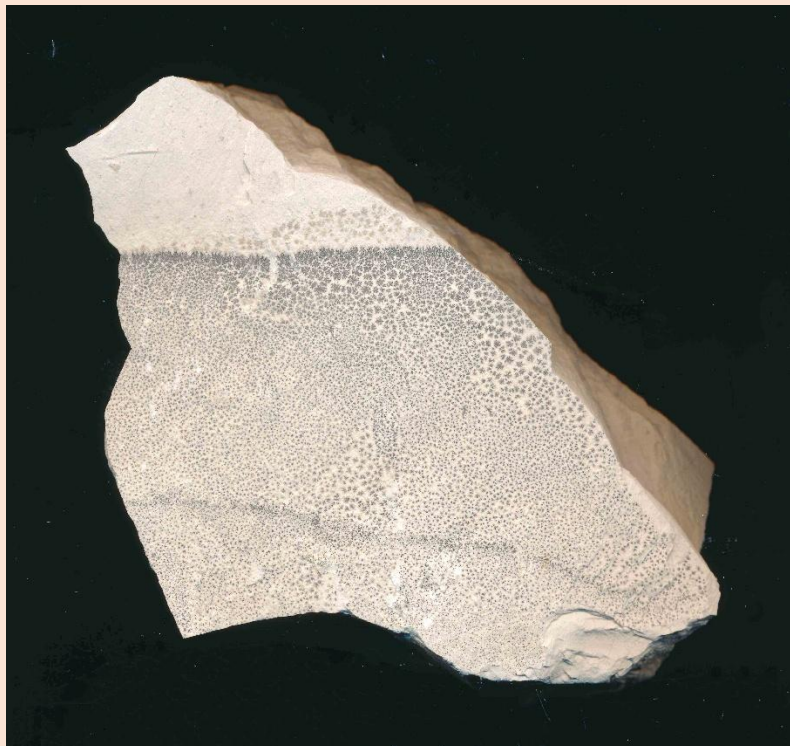


Fig. 9: The most common form of manganese rosettes: small, roundish, and unremarkable. Although they may be closely spaced, they clearly seem to avoid contact with one another (THEWALT, 2015).

Found at the Merkle Quarry near Gerhausen. Width: 11.4 cm.



Fig. 10: The structural principle—no contact with neighboring rosettes—is also clearly evident in this pattern.

Source: Abandoned Reischl quarry in the Little Lauter valley near Blaustein. Width: 2.2 cm.



Fig. 11: Manganese rosettes on fossils. In this example, they formed in the joint between the shell—composed of preserved original calcite from a Terebratulid—and the surrounding limestone sediment.

Source: abandoned quarry near Blaustein-Herrlingen. Image width: 4.3 cm.

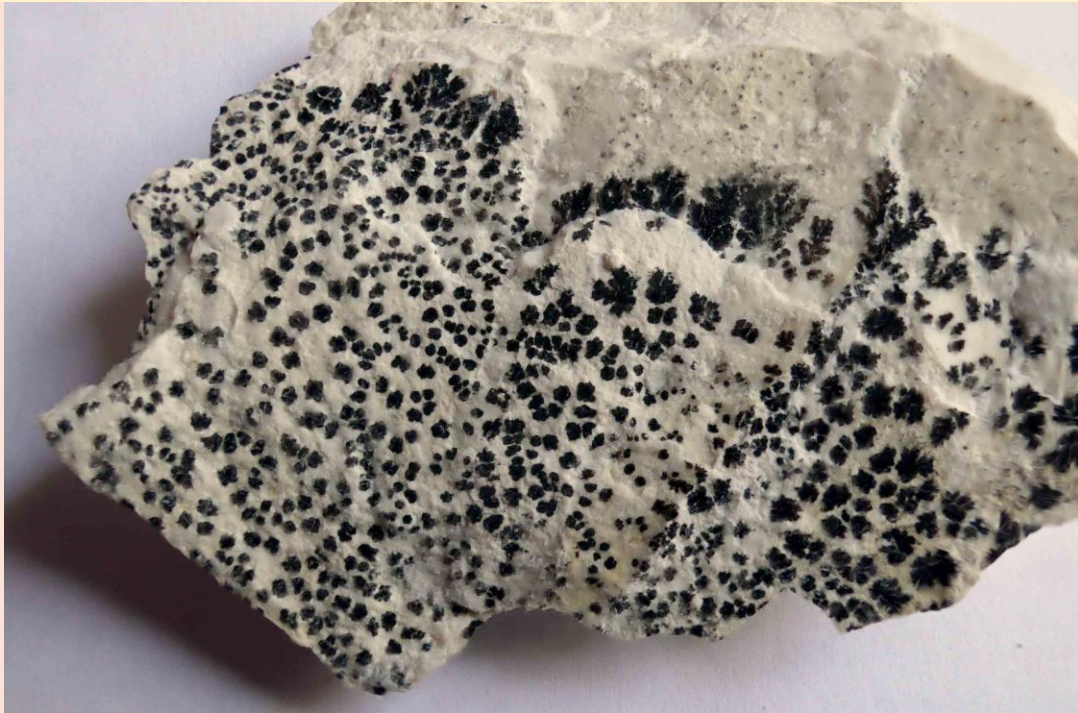


Fig. 12: Manganese rosettes that look like inkblots.
Source: Abandoned quarry in the Schammen valley near Blaustein. Width: 4.2 cm.

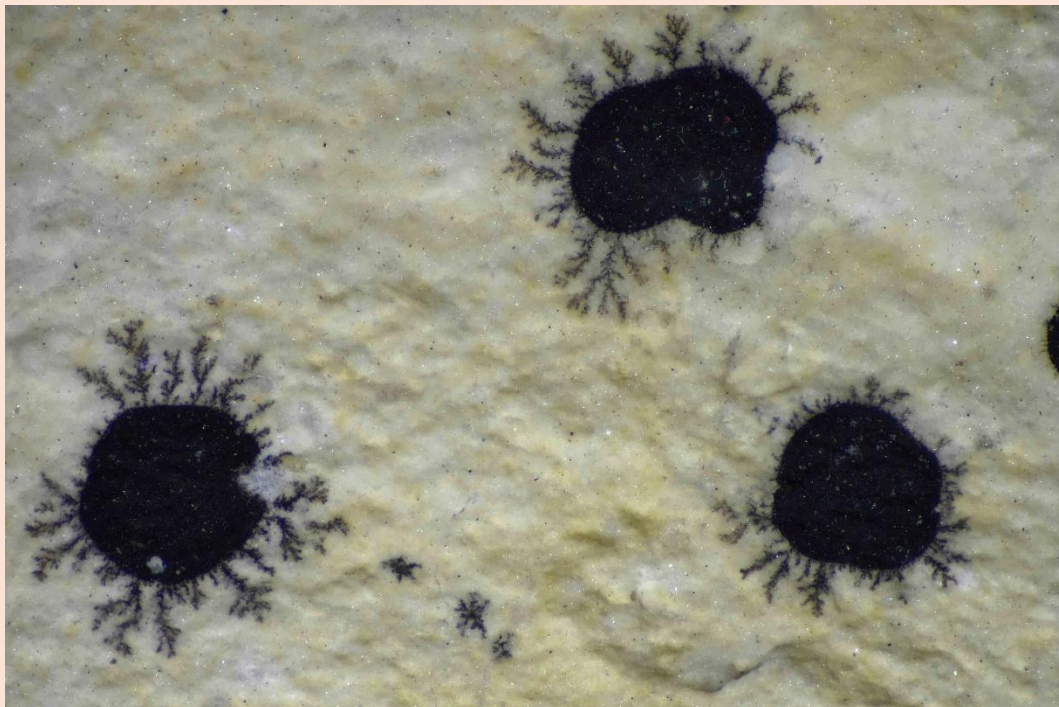


Fig. 13: Detail from Fig. 12. Upon closer inspection, it becomes clear that the figures are by no means clumsy: delicate growths emerge from the central “blobs.” There were evidently two growth phases corresponding to different reaction conditions.

The resulting structures bear a striking resemblance to the famous “Apple Man,” arguably the best-known figure in fractal geometry.

Source: Abandoned quarry in the Schammen valley near Blaustein. Image width: 0.5 cm.



Fig. 14: Even in the early stages of their formation, as shown here, manganese rosettes can exhibit their typical branched structure. Merkle Quarry near Gerhausen. Image width: 1.6 mm.



Fig. 15: In almost all of the manganese oxide aggregates shown, the majority of the coloring material is no longer present (lost during the preparation of the specimens, while lying outdoors, or because it adheres to the other half of the split stone). In the larger rosettes shown in this figure, however, it is still present: small, metallic-luster crystals of one or more manganese(IV) oxide compounds.



Fig. 16: A directed, time-varying flow of an aqueous solution evidently played a role in the formation of these manganese rosettes, similar to Fig. 8. The specimen comes from the abandoned quarry in the Schammen Valley near Blaustein. Width: 10.6 cm.



Fig. 17: As mentioned earlier, manganese dendrites (in the narrower sense) are found at the edges of the limestone shards and rosettes in the central areas. In this specimen, dendrites have also grown in the interior. This is likely related to the specific pattern of transport pathways for the oxide particles during the formation phase of the dendritic structures. Also noteworthy: Iron dendrites had formed in several places near the manganese dendrites—recognizable by their brown color. However, they are poorly preserved. Similar iron dendrites can also be seen in Fig. 1. Origin: abandoned quarry near Blaustein-Herrlingen. Width 12 cm.

The construction principle:**No crossing branches!****Avoid contact with neighboring branches as much as possible!**

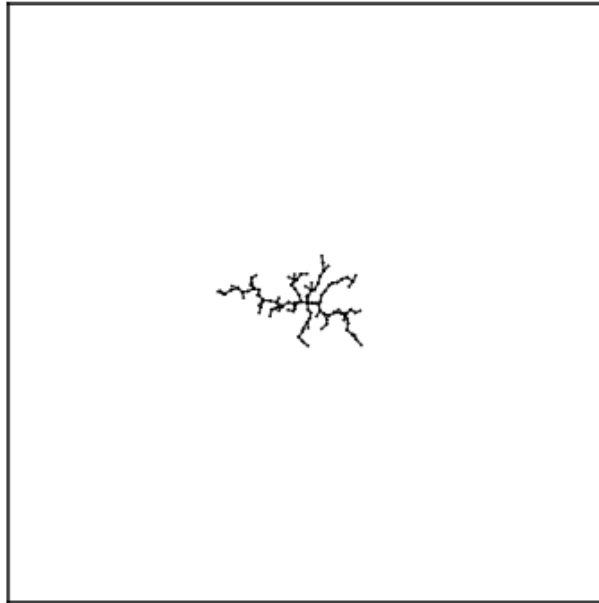
An examination of the illustrations presented shows that the branches and lateral branches of the rosettes (as well as the dendrites) do not cross each other. This applies both to branches belonging to the same rosette and to branches of adjacent rosettes in the area between the rosettes (THEWALT, 2015). Proposals for a formation mechanism of Mn rosettes are therefore acceptable if they can explain how crossings are avoided.

On the Formation of Manganese Rosettes (and Dendrites)

This question concerns (1) the formation of the patterns and (2) the relevant chemical reactions. The first point, in particular, has long been the subject of debate. What is likely the first realistic proposal comes from the Dutch sedimentologist L. van STRAATEN (1978). An important step forward came around 1980 with the realization that the diffusion of particles (in our case, tiny particles of manganese oxide minerals) and their irreversible aggregation naturally explain the shape and growth of the structures (WITTEN & SANDER, 1981). The relevant concept of “diffusion-limited aggregation” (DLA) can be implemented surprisingly easily on a PC. To put it simply: The growth of a manganese rosette can be visualized on a screen. Fig. 18 shows two snapshots of such a simulation. An overview of DLA can be found on Wikipedia. It is also worth noting the program “Particularly Stuck” (BROCKMANN, 2017), which is available online and can be operated interactively on a PC, as well as the collection of Python programs for “modeling complex systems” by H. SAYAMA (2015), which can be downloaded from the Internet. This collection also includes the source code for a DLA program.

Now for the chemical aspect. There is consensus in the relevant publications that Mn^{2+} cations dissolved in water are oxidized by elemental oxygen from the air to form black, poorly soluble Mn(IV) compounds. However, the details remain unclear. Do manganese-oxidizing bacteria possibly play a role in this process? What exactly are these structures—the “particles of oxidic manganese minerals” postulated in the previous section? Questions regarding the origin of the reactants (Mn^{2+} and O_2) and their transport to the reaction centers are comparatively easy to answer.

20 moving particles, 5000 cycles,
108 particles used for producing the rosette



20 moving particles, 20000 cycles,
1293 particles used for producing the rosette

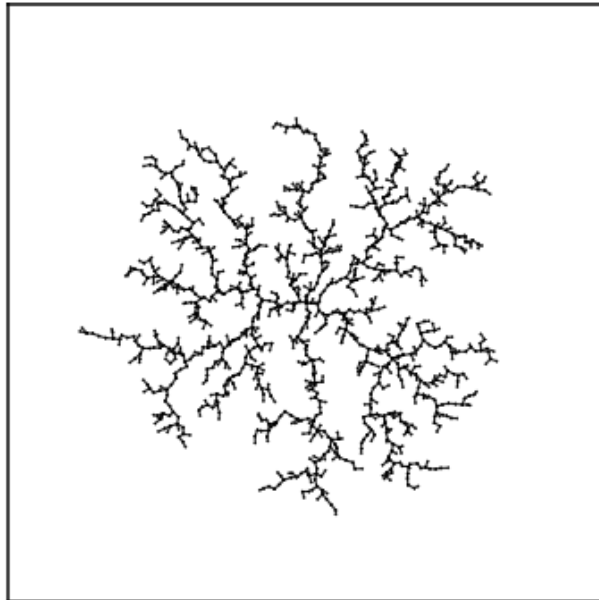


Fig. 18: Computer simulation of the formation of manganese rosettes from given particles. The center of the screen is chosen here as the starting point of the rosette. It acts, in a sense, as a seed crystal. When a particle, while wandering around (Brownian motion), comes close enough to it, it docks onto it, becomes stationary, and thus becomes part of the rosette. The rosette then consists of two building blocks. The process—docking onto the existing rosette—repeats itself: it continues until there are no more particles to add. Here are two snapshots of a growing rosette.

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