Ring crystals of osarizawaite from Whim Creek, Western Australia

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Abstract

Hexagonal ring crystals of osarizawaite, between 5 and 10 micrometers in diameter, are described for the first time. The rings are single crystals, of which the larger ones are made up of thin rhombohedral plates. The rings are believed to represent the outer rims of zoned tabular crystals of the alunite–jarosite group, from which the cores have been dissolved.

Introduction

At Whim Creek, Western Australia (lat. 20°50′S, long. 117°48′E) there is a stratiform Cu–Zn–Pb sulphide deposit that is oxidized to a depth of about 25 meters. The deposit outcrops as a gossan consisting largely of secondary hematite, goethite, and quartz, and with locally abundant malachite. Other secondary ore minerals, including carbonates, sulphates, phosphates, arsenates, vanadates, molybdates, and chromates, mainly of lead and copper, occur erratically, and mostly in microscopic amounts. One of these minerals is osarizawaite, $PbCuAl_2(SO_4)_2(OH)_6$, a mineral of the alunite–jarosite group, previously reported from Japan (Taguchi, 1961), Western Australia (Morris, 1962), Argentina (Cortelezzi, 1977), and Chile (Paar *et al.*, 1980).

Description of ring crystals

The mineral has so far been found in only one gossan sample from Whim Creek, where it occurs as spots of pale green efflorescence barely visible to the naked eye. Under the scanning electron microscope (SEM), the efflorescence is seen to consist largely of a multitude of tiny hexagonal rings. This is the first time, to my knowledge, that a mineral has been reported in this remarkable form, and a description is therefore warranted.

That the mineral is osarizawaite was established by X-ray powder diffraction, the pattern being essentially the same as that reported by Morris (1962) for analyzed osarizawaite. The composition, determined qualitatively by an energy-dispersive X-ray detector attached to the SEM, also conforms to osarizawaite. Finally, as is shown below, the orientation of the crystal faces is consistent with the crystal parameters of osarizawaite.

The osarizawaite rings occur in a variety of forms. The majority are thin, both in width and height, relative to their diameters (Fig. 1); a few have relatively wide walls surrounding a relatively small central hole (Fig. 2); a few consist of double rings (Fig. 3); and some have relatively high walls (Fig. 1). All the rings are hexagonal and fall within a fairly narrow size range, mostly between 5 and 10 micrometers in diameter. Some osarizawaite crystals also occur in the form of thin hexagonal plates. The thin rings are quite similar to beaverite–osarizawaite microcrystals recently reported by Paar *et al.* (1980). These microcrystals were described as "bowl-shaped crystal aggregates," but examination of the published SEM illustrations shows that some of them are probably ring crystals as well.

The faces on one of the larger crystals were measured by means of a stereographic plotting procedure (Hey, 1951, 1978), using SEM micrographs taken at two different angles. To obtain the required rotation for the two micrographs, a cluster of crystallites was mounted on the detent spindle stage designed by Bloss and Light (1973), and the entire assembly was mounted inside the sample chamber of the SEM. The projection protractor described by Fisher (1941) was very useful for the plotting procedure.

When the face normals were plotted on the stereographic projection, and the entire projection graphically rotated so that the face normals were symmetrically disposed about the center of projection, it was seen that the larger faces correspond to rhombohedral planes at an inclination of about 70° from the horizontal. Osarizawaite has been characterized as a
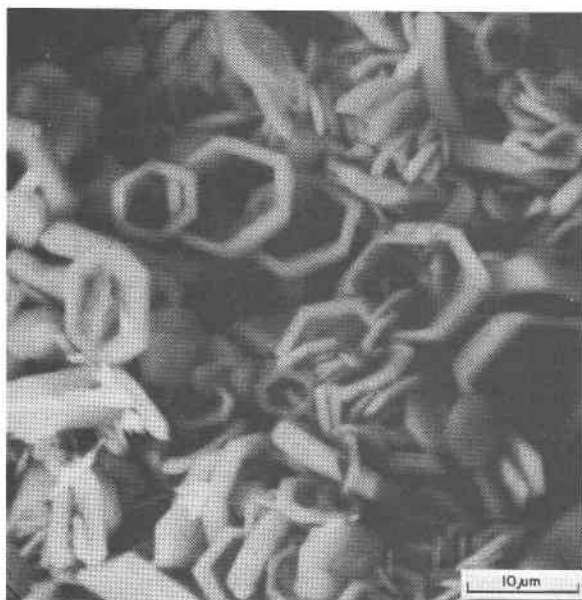
Fig. 1. Backscattered-electron SEM micrograph of osarizawaite, showing ring crystals of various sizes, as well as some hexagonal tablets.

Fig. 3. Backscattered-electron SEM micrograph of double-ring osarizawaite crystals.

rhombohedral mineral with $a = 7.05$ and $c = 17.23$Å (Taguchi, 1961). The rhombohedral faces $\{10\bar{1}1\}$ should be at an inclination of $\tan^{-1} (c/0.866a) = 70.5°$ from the horizontal. This is in good agreement with the observed inclination. The small facets terminating the tops and bottoms of the rings are too small for accurate measurement, but some seem to be basal
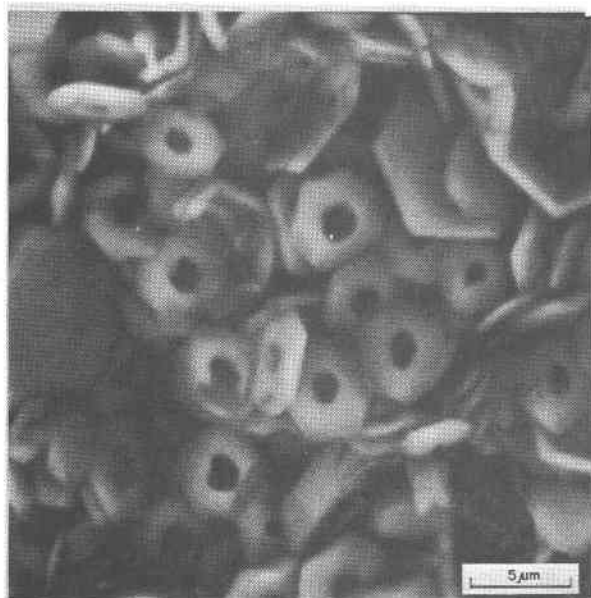

Fig. 2. Backscattered-electron SEM micrograph of wide osarizawaite ring crystals. Faint compositional zoning can be seen in several of the crystals.
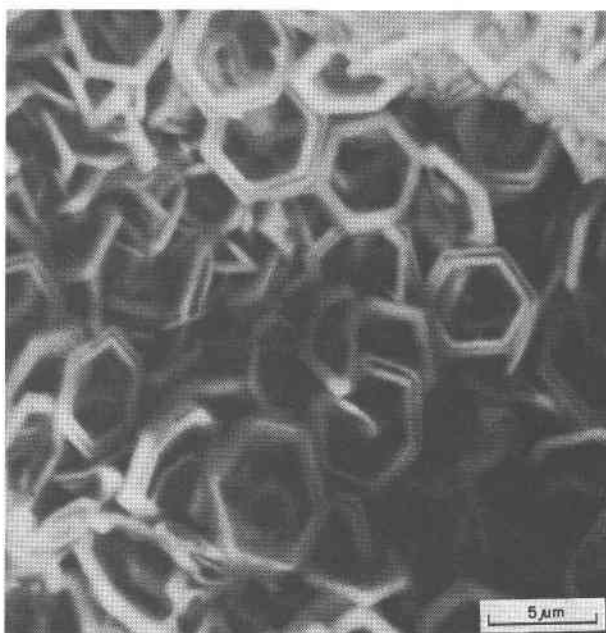
planes, while others appear to be rhombohedral. An idealized drawing of a ring crystal, assuming all faces to be rhombohedral ones of the form $\{10\bar{1}1\}$, and viewed along the c axis, is shown in Figure 4. Comparison with several of the larger crystals shown in Figure 1 indicates that the drawing is a reasonable approximation to the actual crystals.

Since all the observed crystal faces can be ascribed to the same general form, the ring crystals represent single crystals rather than twinned crystals such as those exhibited by geniculated rutile. This conclusion is supported by observations made on osarizawaite crystals in transmitted light. The ring crystals, when lying flat on the microscope stage, are completely black between crossed nicols, indicating that all faces have the vertical c axis in common. Crystal fragments, on the other hand, are appreciably birefringent.

Speculations on the growth of the crystals

A ring crystal can be regarded as an extreme variant of a hollow crystal. Hollow crystals have been reported for quite a wide range of substances, including some that occur as minerals, e.g. ice, NaCl, KCl, TiO_2, Al_2O_3, CdS, ZnO, ZnSe, ZnS, Sb_2S_3, Bi_2S_3, HgSe and HgTe. Hollow crystals reported in the literature generally take the form of hollow prisms, tubes, pyramids, and cones. In the literature on the
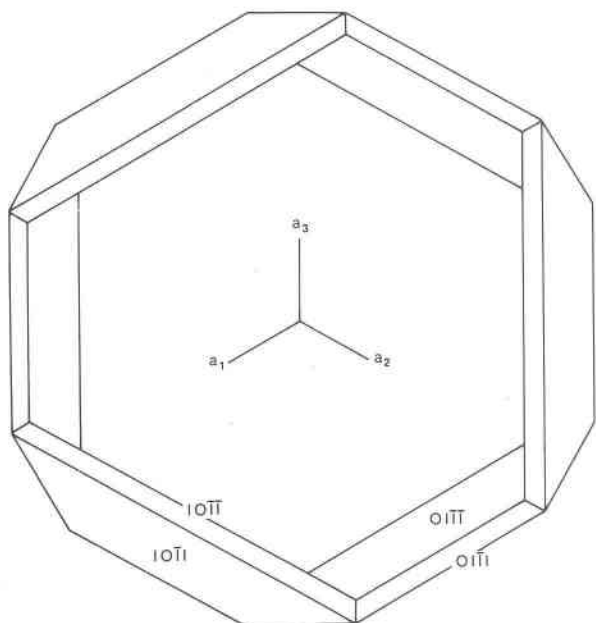
Fig. 4. Idealized drawing of osarizawaite ring crystal based on rhombohedral unit cell with $a = 7.05$ and $c = 17.23$Å. All the faces are rhombohedral ones of the form $\{10\bar{1}1\}$; c axis vertical.
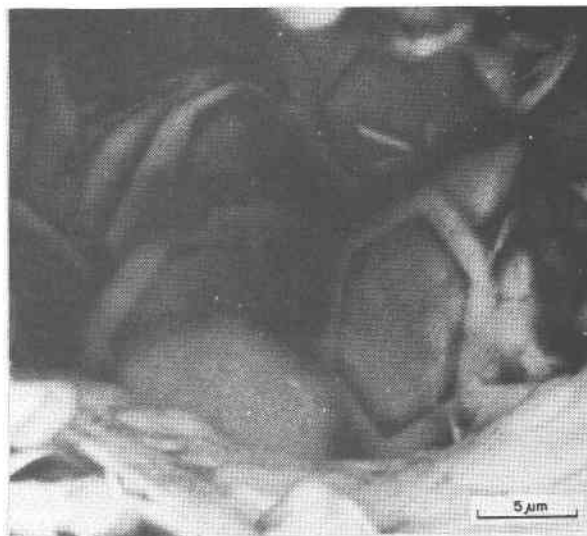

Fig. 5. Backscattered-electron SEM micrograph of osarizawaite crystals consisting of hexagonal rings enclosing tablets, separated by narrow gaps. In several of the crystals the tablet is slightly darker than the surrounding ring, which indicates a composition of lower average atomic number.

growth of hollow crystals, reviewed by Simov (1976), explanations for the growth mechanism are generally of two types, the one based on the form of the crystallization nuclei, and the other on a dislocation mechanism. A growth mechanism based on the form of crystallization nuclei, commonly used to explain hollow prismatic crystals, is one in which growth starts with a cluster of parallel whiskers growing from a substrate; as growth proceeds, the spaces between the whiskers are filled in to form solid walls. In the dislocation theory, a dislocation or group of dislocations develops in the seed crystal. Spiral growth then proceeds outward from the dislocation, resulting in a hollow cone or pyramid; at a later stage, growth may be arrested along the pyramidal directions, and proceeds along the prismatic directions.

The ring crystals described here appear to have developed in a different manner. Clues to their origin can be found in the existence of a few crystals in which the ring encloses a hexagonal tablet of apparently slightly different composition, with a narrow gap separating the two (Fig. 5). It is easy to imagine the tablet dropping out, leaving the outer ring intact.

Minerals of the alunite–jarosite group exhibit wide compositional ranges due to various substitutions, in both cation and anion positions (Botinelly, 1976). It is therefore plausible that, during supergene alteration, tabular crystals grew with concentric zones of different composition, depending on the activities of various possible substituting ions at the time of crystallization. When the composition of the supergene solutions changed so as to make one or more of the zones unstable, the unstable zones were dissolved away, leaving the relatively insoluble rims to be retained as rings.

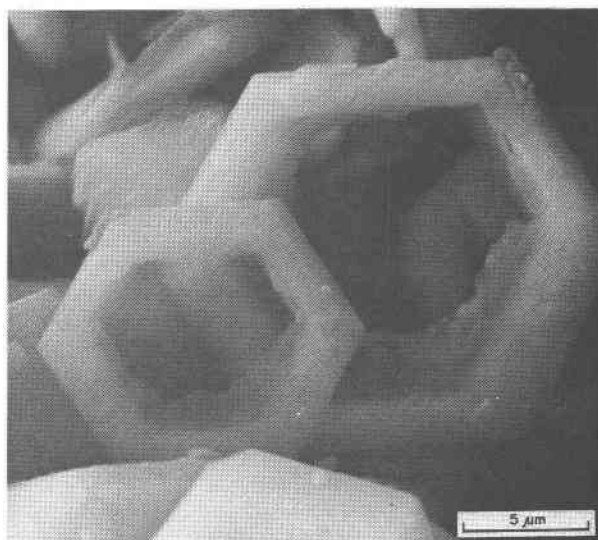Secondary-electron SEM micrographs of gold-shadowed crystals (Fig. 6) show that many of the

Fig. 6. Secondary-electron SEM micrograph of ring crystals (gold sputtered) showing thin diaphragms partly filling several of the rings.

rings are partly filled in by thin incomplete diaphragms not readily visible in the backscattered-electron micrographs. It is not immediately obvious whether these diaphragms represent unleached residua, or whether they represent later material that has been deposited after the cores were leached away.

In any case, it is quite evident that the ring crystals have developed as a result of a two-stage process: crystallization of a zoned crystal, followed by dissolution of one (or more) of the zones.

Acknowledgments

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