

ZIRCONIUM FROM THE REGION OF POÇOS DE CALDAS

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ABSTRACT

Zircon occurs as single crystals, in crystal groups, and in botryoidal intergrowths with fibrous, radial zirconium oxide in the region of Poços de Caldas, Minas Gerais, Brazil. The forms noted are: $p\{111\}$, $a\{100\}$, $m\{110\}$, and $x\{311\}$. The amorphous zirconium oxide is believed to have been formed by precipitation from hot, ascending solutions that obtained their zirconium through the destruction of primary zirconium silicates (chiefly rosenbuschite, astrophyllite, and eudialyte). Much of the zircon appears to be later than the zirconium oxide and is believed to have resulted from the interaction of silica-bearing solutions with the oxide.

INTRODUCTION

This study is based on materials personally collected at Cascata, São Paulo and Poços de Caldas, Pocinhos do Rio Verde, in Minas Gerais, and in neighboring regions, and also on specimens in the Department



FIG. 1. Index map of Brazil, showing location of the Poços de Caldas region.

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of Mineralogy and Petrography of the University of São Paulo, Brazil. Additional study material was kindly donated by colleagues. Figure 1 shows the area in which the deposits occur. The specimens were obtained almost entirely from the following localities in the mineralized area: Córrego do Quartel, Serrote, Quirinos and Triângulo (Cascata); Campinas, Pouso Alegre, Campo do Alemão (Taquari), Coqueiro and Retiro dos Coqueiros, all in the region of Pocinhos do Rio Verde and Parreiras.

Our chief concern has been to study the principal forms of zircon and zirconium oxide and the general aspect of their complex occurrence. Special attention was given to chemical analyses. The discussion of the origin is based on the mineral relationships and the geology. It is not yet possible to draw conclusions as to the true chemical nature and structure of some of the minerals in the veins. The identification of these minerals will depend on x -ray studies now in progress in our department, for there is no chemical means for their determination.

PREVIOUS WORK

Because of the varied and important rôle played by these deposits of zirconium oxide and silicate, the Poços de Caldas region has been extensively and intensively studied both by foreign and Brazilian geologists. Worthy of attention are the works of Derby (5), Machado (15), Coburg (18), Hussak and Reitinger (14), Silva (19), Guimarães (10), Barbosa (1, 2) and Teixeira (20).

In Derby's work (5) no particular attention was paid to the problem of the zirconium; his interest was especially in the rocks that occur in the highland of Poços de Caldas, but he made a passing reference to large crystals of zircon from the region of Parreiras, and intimated that a zircon syenite or a variety of zircon foyaite might be the source rock of the zirconium minerals. He pointed out, however, that zircon had not been noted in any of the foyaite found in Brazil up to that time.

Machado (15), in describing the rocks of the region, noted the presence of the complex zirconiferous silicates—lâvenite and eucolite or eudialyte without mentioning zircon as one of the rock constituents.

Coburg (18) studied the crystallography and described some forms of zircon: $p\{111\}$, $m\{110\}$ and $a\{100\}$, which he encountered on scattered crystals in the sands of the River Verdinho. He called attention to the similar relations which exist between the zirconiferous deposits of the Poços de Caldas region and those of Norway, where augite nepheline syenites also occur.

Hussak (13) reported the discovery of the source rock of zircon when, while examining a specimen of decomposed augite syenite, he found hundreds of zircon crystals. He described, in addition to the idiomorphic

crystals of zircon, honeycombs of dark gray, black, and reddish-brown material. The chemical analysis of these honeycombs showed a high content of zirconium oxide (97 per cent). He suggested that the honeycombs might be a secondary decomposition product of zircon, which would be the most likely primary mineral of zirconium. Zircon would be transformed by a loss of SiO_2 into the oxide of zirconium encountered in the "combs."

Hussak and Reitinger (14), who studied in a detailed manner a large number of "combs," came to the conclusion that the percentage of SiO_2 varies within wide limits. This discovery suggested the hypothesis that the zirconium oxide "combs" might have originated from zircon. They showed that the percentage of silica varied between 2 and 15.5 per cent. They described the "combs" as being of fibrous-radial structure, which, when broken, fell into polyhedral pieces with smooth surfaces and poorly developed faces. They concluded, moreover, that the fibrous material, which contained more than 97 per cent ZrO_2 , had nothing to do with the baddeleyite described by Hussak in jacupiranguite from the region of Jacupiranga, São Paulo, Brazil.

Silva (19) states that the zirconium ore must have originated from a magmatic concentration of zirconium silicate in the nepheline rocks of the region. Later, through metasomatism the complex oxides of the ore, called "caldasite," must have been formed.

Djalma Guimarães (10), suggests a hydrothermal process at high temperatures and in an oxidizing medium as being responsible for the botryoidal masses of ore which occur in the region. He believes the "caldasite" was formed by hydrothermal metamorphism which brought about metasomatic replacement in the nepheline rocks.

Barbosa (1, 2) called attention to the presence of ore veins in the highly decomposed nepheline rocks. He concluded that all the zirconium comes from the alteration of these rocks—phonolites and foyaites. He, like Machado previously, pointed out the presence of zirconiferous silicates in the nepheline rocks and said that the zirconium ore must have begun to form soon after the extrusion of the last sheet of phonolitic lavas, which were rich in acid and alkaline solutions. As a result of several analyses, he thought that the zirconium oxide and the zircon were formed at the same time, and that both were of primary origin.

Teixeira (20), in referring to the occurrence of zirconium minerals, considered them as unique in their characteristics. In dealing with their genesis, he classified the deposits as of hydrothermal origin. The nepheline rocks of the region must have been attacked by alkaline solutions, after the eruptive period, with resultant solution of the zirconium of the zir-

coniferous silicates (eudialyte, rosenbuschite, l avenite) and later deposition of zirconium oxide in fractures.

MINERALOGY

Zircon

The zircon crystals occur as idiomorphs of various sizes—from microscopic up to individuals 4.5 cm. in width. In addition to irregular crystal groups, and less common parallel ones, isolated crystals are also encountered. In reflected light they are dark brown, reddish brown, green, greenish, greenish brown, or light green, and usually of adamantine brilliancy. Bi-colored individuals also occur. On the cleavage faces of polished crys-

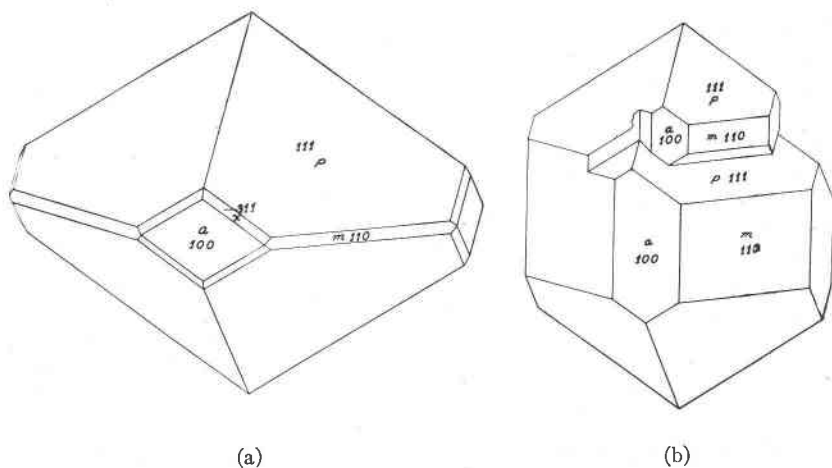


FIG. 2. (a) Zircon crystal of typical habit, showing most complex development.
(b) Parallel growth of two zircon crystals of typical habit.

tals color zones of varying widths are accentuated. On these faces the crystals show various iridescent colors. In transmitted light they are strongly colored. Internally they are fractured and full of cavities. The commonest habit is pyramidal. Such crystals may be simple, with $\rho\{111\}$, or with $\rho\{111\}$ and $a\{100\}$, which are sometimes equally developed so that the crystal resembles a dodecahedron. Other combinations include: $\rho\{111\}$ and $a\{100\}$ with predominant development of $\rho\{111\}$; $\rho\{111\}$, $m\{110\}$ and $a\{100\}$, the most common combination; $\rho\{111\}$, $m\{110\}$, $a\{100\}$ and $x\{311\}$, less common (Fig. 2a). The crystals of pseudododecahedral habit are found in the Campo do Alem ao (or Taquari) deposit. They are green and occur in veins of varying width, together with masses of microcrystalline zircon.

The largest crystal that we have had the opportunity to study belongs to the Mineralogy Museum of the Polytechnical School of Rio de Janeiro, Brazil. It measures 4.5 cm. in width, and is marked by numerous, irregularly distributed, triangular etch figures. The faces are also minutely striated. Figure 2*b* shows an unusual intergrowth of two individuals of the same orientation. This specimen measures 1.9 cm. along the direction of the *c*-axis.

The green crystals found in geodes and veins are generally the most translucent, and their surfaces are smooth and brilliant. No matter what the color of the crystals may be, they fluoresce an intense yellow. Optically the crystals from the Poços de Caldas area are either normally uniaxial or biaxial. Strongly colored sections show pleochroism.

"Combs" and fibrous-radial material

The "combs" resemble mammillary or botryoidal masses of limonite, hematite, rutile and manganese oxide. They have a fibrous or sub-fibrous structure, but massive or concretionary aggregations with an earthy texture are not rare. The hardness varies considerably.

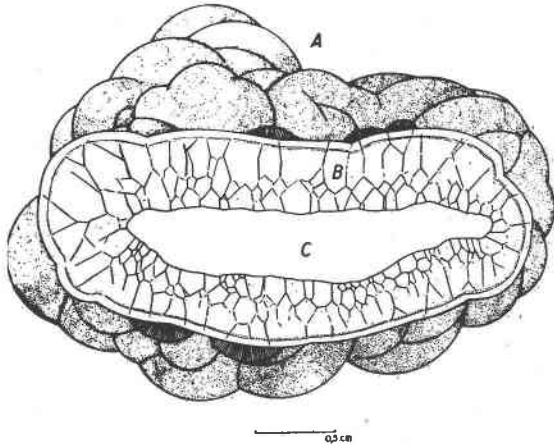


FIG. 3. Reniform honeycomb of zirconium oxide from the alluvial deposits of Serrote, Cascata, São Paulo.

In some botryoidal "combs" the repetition of fibrous layers gives the impression of a formation of hydrothermal origin. Between the thin concentric layers is concentrated microcrystalline material that is very difficult to resolve under the microscope. This material is all zircon.

Figure 3 shows a typical mammillary "comb." Some of the knobs are clearly fibrous in structure. Below the rounded protuberances there occurs a non-fibrous material which breaks in fragments with plane faces

(B, Fig. 3). The central part (C) is composed of massive, microcrystalline material. Under the microscope, the fibers show high order interference colors and parallel extinction. From microscopic study of several thin sections, we were able to determine that isolated "combs" are biaxial, with the acute bisectrix normal to the length of the fiber.

A typical narrow vein in altered nepheline syenite is zoned as follows: at the contacts are two symmetrical zones of fibrous, fan-like individuals; in the center occur globular concretionary masses with a similar radial structure; and between these occur the formless masses of zircon. This structure is common in the "combs" of fibrous-radial material. One of the more unusual fibrous-radial types is composed of a globular mass of acicular crystals which are encrusted by idiomorphic crystals of zircon. Ore of this type is found approximately 17 km. from Poços de Caldas on the road to Parreiras. Narrow veins, rich in cavities and druses, occur here in a strongly altered syenitic rock. From the structure of such veins it appears that the fibrous zirconium oxide crystallized first on the vein walls, and zircon later was precipitated in idiomorphic form in the centers.

The "combs" and especially the fibrous-radial material clearly show signs of alteration. They form compact, dark mammillary masses, difficult to break; and also masses that are clearer and less coherent but in which one can still recognize the acicular crystals; and finally, earthy masses, friable and clear in color. Between these three stages of alteration, all intermediate types are encountered. Probably the loss of color is due to the leaching of iron and manganese.

Another characteristic of the dark compact "combs" is exfoliation. Layers of uniform thickness peel off the surface of each protuberance. The exfoliated layers are of various colors and are lighter and less coherent than the rest of the material. In knobs in which three or more layers of exfoliation are present, one can easily note that the bleaching becomes more marked progressively outward. Moreover, these layers appear to have been preformed in the "comb," since it is possible to distinguish them there, due to their difference in color.

Associated materials (Caldasite)

The "caldasite," or associated material, is the chief vein ore. It is usually of ashy color and is very heavy. In masses of somewhat friable microcrystalline ore one encounters scattered idiomorphic crystals of green and brown zircon.

The relations in hand specimens seem to indicate that the fibrous zirconium oxide must have been the first to form, and that subsequently at its expense zircon was formed by means of silica-rich solutions. This

process is essentially a replacement of zirconium oxide by zircon. One can find relicts of fibrous-radial material within the zircon. Figure 4 offers evidence in support of this theory. In this ore specimen, which is cut normal to the direction of the fibers, one can see veinlets of microcrystalline zircon (A), cutting across masses of oxide (B).

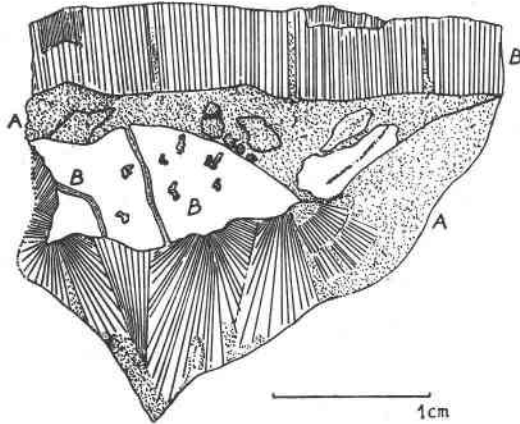


FIG. 4. Veinlets of fine-grained zircon (A) transecting zirconium oxide (B).

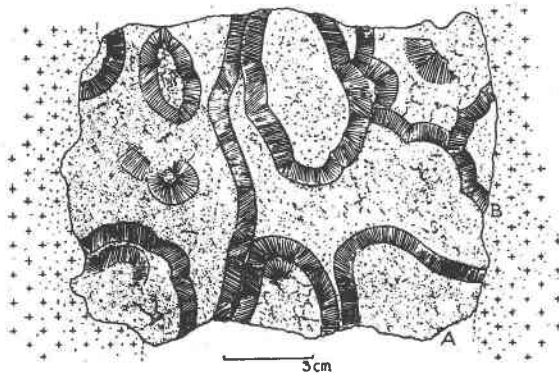


FIG. 5. Vein of "caldasite" in weathered source rock.

In another type of "caldasite" crystals of zircon encrust the walls of little geodes that occur in a homogenous mixture of the silicate and oxide.

Figure 5 shows "caldasite" in the altered source rock. In the center of the veins one may find pieces of nepheline rock cemented by zirconium material.

PHYSICAL AND CHEMICAL PROPERTIES

The large, translucent or nearly opaque brown zircons from the weathered augite syenite consist of zirconium orthosilicate. The gray "combs" with the earthy fracture are opaque, isotropic, and amorphous, as shown by x-rays. The densities vary between 4.6 and 4.8. After heating to 1100° C. the powdered material loses about 2 per cent of water, the density increases to 5.2, and the color changes to reddish-brown. It contains between 70 per cent and 90 per cent or more ZrO_2 , about 1 per cent TiO_2 , iron and some silica.

The dark brown, nearly black "combs," called "zirkonglaskoepfe" (zircon glass-heads) by the German authors (22, 23) differ little in composition from the amorphous material. Their density ranges from 5.0 to 5.3 and does not change after heating to 1100° C., although they also lose up to 2 per cent water. A spectrochemical analysis, made in the Technological Institute of Pesquisas, São Paulo, through the kindness of Miss Yolanda Monteux, showed the material to contain some manganese. This was chemically determined to be of the order of one part in twenty thousand, and maybe responsible, at least in part, for the color.

The small, translucent to transparent zircons associated with the crystalline variety of the oxide consist of practically pure zirconium orthosilicate.

Columbium, tantalum, and thorium were not found, either by chemical or by spectrochemical analysis. Hafnium was shown to be present in all samples examined by means of spectroscopic analysis. Chemical identification of hafnium by partial separation from zirconium was possible. From a hot 20 per cent sulfuric acid solution, to which sodium or magnesium sulfate is added nearly to saturation, fractional precipitation of a well flocculated, easily filtered zirconium phosphate of varying composition, containing neither titanium nor iron but larger amounts of hafnium than the original solution, is easily obtained by adding small quantities of phosphoric acid. It seems that the hafnium content in the "combs" is generally low, of the order of one to three per cent HfO_2 of the total $ZrO_2 + HfO_2$ present, and slightly higher in the zircons associated with the oxide. The hafnium content in the altered brown zircons from the country rock was not determined, but this was shown to be very low by Hevesy and Würstlin (11).

Solution of the finely ground oxide is accomplished rapidly by heating in a Pyrex beaker over a Téclu or Méker burner with sodium sulfate and an excess of concentrated sulfuric acid. Complete solution takes place within about half an hour. Zircon is dissolved without difficulty by fusion with sodium metaborate (fusion mixture, borax and sodium carbonate,

previously fused, crushed and ground), and consequent treatment with hydrochloric acid, or with hot methyl-sulfuric acid (concentrated sulfuric acid and methanol in equal parts).

The separation of iron and aluminum may be accomplished by adding the previously reduced solution containing tartrate to an excess of an alkaline solution of sodium cyanide. Final purification of zirconium and hafnium salts is possible by precipitation with ether from strong hydrochloric acid solutions. A crystalline, easily filtered precipitate forms, similar to that obtained with aluminum chloride solutions and ether. Iron remains in solution.

ORIGIN

The zirconium ore of Poços de Caldas is of hydrothermal origin. The majority of studies, both Brazilian and foreign, have arrived at this conclusion.

In our opinion, the following stages can be recognized: first, the formation, either by magmatic segregation, or by reaction, of the essential minerals of the alkaline rocks of the region, orthoclase, nepheline, aegirine, augite, sphene, melanite, sodalite, wollastonite, magnetite, biotite, hastingsite, scapolite, natrolite and muscovite. With these occur the complex silicates of zirconium: rosenbuschite (1), eudialyte (1), astrophyllite (1), låvenite (15), eucolite (15) and very likely zircon.

According to Barbosa (1), rosenbuschite and astrophyllite are always poikilitic in texture and occur in foyaites and phonolites, but eudialyte is restricted to foyaites and coarse-grained rocks, where it may form high local concentrations. In addition to these zirconiferous minerals, we should recall that very probably acmite, a mineral extremely common in the nepheline rocks of the region, may also have been a source of zirconium. This mineral generally contains an important amount of zirconium. Probably the zirconium minerals were destroyed or attacked chemically by the hot, rising solutions, and the zirconium may have been precipitated in fissures in the highest zones, or even within the zone of attack itself, in the form of stable minerals (the oxide and silicate). By the action of weathering, the rocks bearing these mineralized veins were destroyed, thus permitting the accumulation of alluvial and eluvial deposits.

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