# GEOCHEMISTRY OF TRACE ELEMENT CONCENTRATIONS IN THE POÇOS DE CALDAS PLATEAU, BRAZIL

by

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## ABSTRACT

A geochemically coherent assemblage of trace elements occurs in the feldspathoidal rocks of the Poços de Caldas Plateau. Zirconium, hafnium, and uranium are found in veins and lenses of caldasite (baddeleyite plus zircon) white thorium and the cerium group of rare earths are associated with thorogummite, bastnaesite, and allanite in a separate occurrence. Results from preliminary mineralogical work are described. Zirconium and uranium are also concentrated in eudialyte syenite, a prominent rock type in the north rim of the plateau. These associations are consistent with the size, charge, and the electronegativities of the above elements. In the course of magmatic history these elements may enter rock-forming silicates and crystallize early or remain in the residual solutions to crystallize in the late stages. Which path is followed is a function of the composition and degree of silica polymerization of the magma. The trace element occurrence of the Poços de Caldas region resemble, in part, the mineral assemblages of the Kola Peninsula, Russia, and the Julianehaab area, Greenland.

## INTRODUCTION

Assemblages of trace elements in the feldspathoidal rocks of the Poços de Caldas Plateau illustrate several principles of crystal chemistry. In fact, their association might have been predicted purely on geochemical grounds. The trace elements known to be present in appreciable concentrations are zirconium, uranium, thorium, the cerium group of rare earths and hafnium.

The zirconium deposits in the region have been known for many years. Various workers (Derby, 1887; Barbosa, 1936; Teixeira, 1953, Franco, 1945; Guimarães, 1948; Tolbert, 1958; Frayha, 1957) and many others have studied the geology of the Plateau as well as the zirconium deposits. In recent years, studies of the radioactivity of these deposits by the United States Geological Survey (on behalf of the United States Atomic Energy Commission) in collaboration with the Conselho Nacional de Pesquizas and the Departamento Nacional da Produção Mineral, have shown the presence of uraninum associated with the zirconium deposits. In addition, the thorium-bearing rare earth deposits were discovered and studied.

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## GEOLOGY OF THE PLATEAU

The Poços de Caldas Plateau is comprised of several nepheline syenite intrusives confined largely to the nothern sector, surrounded by phonolite, The intrusives vary in size from a few tens of meters to several thousand meters. Some of these intrusives are medium grained while some are pegmatitic. Phonolite forms most of the rim and a large part of the interior of the Plateau. The uraniferous zirconium veins cut both the nepheline syenite and phonolite. Dikes, flows, tuffs and agglomerates, largely of feldspathoidal composition, also occur in the northern part of the plateau but are rare in comparison to nepheline syenite and phonolite. Blocks of phonolite tens of centimeters in diameter have been found enclosed in nepheline syenite and blocks of nepheline syenite of similar size have been found in phonolite. The contact between the two types may be gradational or sharp. In general, however, the phonolite appears to occupy a chilled marginal position relative to the nepheline syenite. The age relationships between the various rock types will be known only after more detailed mapping has been done. (1) Nearly all the rocks types are undersaturated with respect to silica.

An interesting variety of nepheline syenite in the north rim of the plateau contains from 1-30% of the pink zirconium silicate, eudialyte. Although audialyte was the only zirconium silicate in this rock positively identified by the author, other rare zirconium and titanium silicates, e.g., catapleite, lavenite, rosenbuschite, lamprophyllite, have been reported (Guimarães, 1948; Guimarães and others, 1953; Dutra, 1955; and Branco, 1956). The eudialyte syenite crops out in a broad band 100 to 1000 meters in width and several kilometers in length on the north rim of the plateau about 5-10 kilometers northeast of Poços de Caldas. The outcrop area of eudialyte syenite is large enough to merit consideration as an eventual source of zirconium. An advantage of eudialyte as a source of zirconium is that eudialyte is soluble in cold dilute acids, while baddeleyite and zircon are dissolved only by a much more vigorous chemical attack. In places, the eudialyte syenite (sometimes called lujavrite) exhibits a gneissoid texture with feldspar laths and sodic pyroxenes parallel. A broad radioactivity anomaly delineates the outcrop area of eudialyte and led the author to investigate the area (Tolbert, 1958). Eudialyte is also occasionally present as an accessory mineral in nepheline syenite and phonolite within the plateau.

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(1) Detailed geologic studies of the geology of the plateau have been undertaken by geologists associated with the University of São Paulo; their findings will be published at an early date.

## MINERALOGY OF THE TRACE ELEMENT OCCURRENCES

*Uraniferous zirconium deposits* — The two chief minerals of the zirconium ore are baddeleyite ($ZrO_2$) and zircon ($ZrSiO_4$). Most of the ore is a mixture of these two minerals, called caldasite. Caldasite is a very hard, dense, heavy material commonly gray or black in color which constitutes the zirconium veins. It is sometimes changed to a red or brown color by alteration and may contain cavities lined with tiny crystals of green and brown zircon.

Baddeleyite may occur as a fibrous radial material with a comb structure resembling botryoidal hematite or manganese but, more commonly, it is black, massive and very hard.

Zircon usually ocurs in tiny crystals scattered throughout the caldasite, although in the Taquari area, crystals of zircon were found up to 1-2 centimeters in diameter. Most of the zircon is probably metamict.

Meta-autunite has been identified as a secondary uranium mineral in the zirconium ores but as yet no primary uranium mineral has been found. Radiographic exposures of caldasite and baddeleyite indicate that the radioactive element, identified as uranium by chemical and fluorimetric analyses, is disseminated throughout the material. Apparently the uranium is included in baddeleyite, as well as zircon, and is in a relatively insoluble state. Leaching experiments with hot acids failed to remove any appreciable amount of uranium from caldasite and baddeleyite. X-ray fluorescence analyses of baddeleyite from the Serrote Mine show strong lines of Zr and Fe and trace elements of Hf and U.

*Thorium-rare earth deposits* — X-ray studies of the disintegrated material from the Morro do Ferro deposit have identified the following minerals: bastnaesite ($CeFCO_3$); thorogummite $(ThSiO_4)_{1-x}(OH)_{4x}$; allanite $(Ca,Ce,Th)_2(Al,Fe,Mg)_3Si_3O_{12}(OH)$; magnetite, limonite and kaolinite. Secondary manganese minerals are also present. The amount of uranium in these deposits is very small.

*Eudialyte syenite* — Eudialyte $(Na,Ca,Ce)_5(Fe,Mn)(Zr,Ti)Si_6O_{18}(OH,Cl)$ was identified in samples from the north rim of the Plateau. It is ordinarily pink to mauve in color and may form as much as 30% of the rock. X-ray fluorescence analyses of eudialyte disclose Zr, Hf, Fe and Sr. Probably Sr substitutes in the (Na,Ca,Ce) position, although the structure of eudialyte is not known. Similar analyses of acmite show Fe, and small amounts of Mn, Zr, Hf, and Sr. Small amounts of Zr, up to 3-4 percent, have been reported in the literature as being in acmite.

## CRYSTALLOCHEMICAL RELATIONSHIPS

The trace elements U and Hf are associated with caldasite deposits while Th and Ce are associated with a magnetite dike in a deposit apart from the zirconium occurrences. Since Hf is an invariable associate of Zr, the two elements are considered together in this paper under the symbol Zr.

Te ionic radii of these elements are quite similar, although Zr is somewhat smaller than the others. (See Table I). Their electronegativities (1) are aproximately the same.

Table I

| *Ion* | *Ionic radius A°* (2) | *Electronegativity* |
|---|---|---|
| $Th^{+4}$ | 1.02 | 1.1 |
| $U^{+4}$ | 1.04 | 1.3 |
| $Zr^{+4}$ | .79 | 1.4 |
| $Hf^{+4}$ | .78 | 1.3 |
| $Ce^{+4}$ | .94 | 1.05 |
| $Ce^{+3}$ | 1.07 | |

In their quadrivalent states, Th, U, Zr and Ce substitute for one another in many of their compounds and form minerals with identical structure types. For example, thorite $(Th,U,Fe,Ca)SiO_4$ and thorogummite $Th(SiO_4)_{1-x}(OH)_{4x}$ have the same structure as zircon, (Frondel, 1956), i.e., isolated $SiO_4$ tetrahedra with Th ions in 8-coordination with oxygen, just as Zr is in 8-coordination with oxygen in zircon. (In thorogummite the hydroxyl ions substitute to a limited extent for the $SiO_4$ groups).

In the mineral monazite, $CePO_4$, Th substitutes for Ce in amounts up to 30%. Apparently, the deciding factor determining whether the cation enters the zircon or monazite structure-type is a function of the radius ratio (ionic radius of cation/ionic radius of anion) of that cation with oxygen. Therefore, compounds like zircon and xenotime ($YPO_4$), with smaller radius ratios, follow the zircon structure-type and those with larger radius ratios like monazite and $LaPO_4$ (synthetic) have the monazite structure-type (Frondel, 1956).

Apparently U enters zircon, substituting for Zr, more readily than Th, the latter preferring to enter monazite in the Ce position. The small amounts of U or Th occurring in zircon are responsible for the radiation damage (metamictization) found in zircon. This phenomenon is used as a means of age estimation.

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(1) Electronegativity may be crudely defined as a measure of the departure from the true ionic bond toward increasing covalency, or the power of an atom in a molecule to attract electrons to itself. Pauling (1942) calculates electronegativity values from thermal data.

(2) The ionic radii are those for 6-fold coordination based on a radius of 1.04A° for $O^{-2}$.

The dioxides of U, Th, Zr, and Ce, all of the fluorite ($CaF_2$) structure-type, form substitutional solid solutions. The monoclinic form of $ZrO_2$, baddeleyite, is stable at ordinary temperatures. Upon heating the monoclinic phase above 1000° C., a tetragonal phase appears. It has a deformed fluorite-type structure, (Lambertson and Mueller, 1933). No data are available on the extent to which U, Th, or Ce enter the monoclinic form of $ZrO_2$, but it is thought they enter in very small amounts or not at all (Frondel, 1956).

Discrepancies in the associations of these elements are due largely to 1) the small size of the $Zr^{+4}$ ion, 2) the formation of the stable $U^{+6}$ uranyl ion, and 3) the formation of the $Ce^{+3}$ ion. Zirconium and thorium always occur in the quadrivalent state while uranium occurs as quadrivalent and hexavalent ions and cerium as quadrivalent and trivalent ions. The large uranyl ion is unique and its unusual "dumbbell" shape and size prohibit its presence in structures that smaller ions commonly enter. For the same reasons $Ce^{+3}$, which is larger than the $Ce^{+4}$ ion, does not enter the same structures as the other trace elements discussed above (Frondel, 1956).

$Zr^{+4}$ is usually confined to the mineral zircon. It is too large to enter 4-coordination in the $SiO_4$ tetrahedra of the rock-forming silicates and ordinarily goes into 7 or 8 coordination with oxygen. Its high charge, (+4), also prevents it from substituting for the common univalent and divalent and rock-forming cations like K, Na, Ca, because of the difficulty in maintaining electrostatic neutrality within the crystal structure.

## PATH OF TRACE ELEMENTS IN THE LATE STAGE SEQUENCE

These elements are characterized by low concentration and high charge. Their behavior in the magma is resolved into two choices: concentration in the residual solution or substitutional solid solution in the rock-forming silicates. Thorium and uranium, because of the high charge and large size of their quadrivalent ions, do not enter the lattices of the rock-forming minerals and are concentrated in residual solutions. $Ce^{4}$ and the rare earths, because of high charge and large size, may also become a part of the later pegmatitic stages of crystallization. Zirconium comes out in the magmatic stage as zircon but it may also be concentrated in the residual solutions.

Fersman (1937) has divided the nepheline syenites according to their order of crystallization into two groups: the miaskitic and the agpaitic types. The miaskitic type refers to nepheline syenite whose crystallization sequence is similar to those of "normal" calc-alkalic rocks, while the agpaitic sequence is the reverse, with nepheline and the alkali feldspars crystallizing first, followed by zirconium and titanium silicates and finally the alkali pyroxenes and amphiboles. With the increase of Na in the agpaitic type, the mineral structures of the alkali pyroxenes and amphiboles are less stable and they are unable to separate before the alkali feldspars and nepheline. The Poços de Caldas zirconium occurrences would probably belong to the agpaitic type.

The residual solutions which may crystallize in the form of pegmatites have differing mineral assemblages, depending upon whether the composition is that of granite or nepheline syenite (Goldschmidt, 1954). Uranium, niobium, tantalum, scandium and yttrium may be associated with alkalic pegmatites but are more closely allied to granitic pegmatites, while cerium earth metals, zirconium and often thorium, are enriched in nepheline syenite pegmatites. The zirconium minerals of granite pegmatites contain more hafnium than do the zirconium minerals of nepheline syenite pegmatites. The Poços de Caldas zirconium minerals are low in hafnium. This pegmatite problem is pertinent to the Poços de Caldas occurrences as pegmatitic phases of the nepheline syenite are not uncommon. According to Goldschmidt, $Fe^{+3}$ an $Ce^{+4}$ ions prefer nepheline syenite pegmatites and $Fe^{+2}$ and $Ce^{+3}$ are more typical of granite pegmatites. He divides the pegmatites into agpaitic pegmatites and plumasitic pegmatites. In the agpaitic type, $Na+K$ exceeds Al while in the plumasitic type Al exceeds $Na+K$. He lists among diagnostic agpaitic minerals: aegerine, alkali amphiboles, and the zirconium-titanium silicates like eudialyte and astrophyllite. Among the diagnostic plumasitic minerals are corundum, beryl and calcic plagioclase. The alkali feldspars, nepheline and leucite are neutral minerals where $Na+K=Al$.

In rocks of granitic composition, the trace elements are removed at an early stage in the form of the accessory minerals — zircon, apatite, sphene, monazite, rutile, magnetite, xenotime and ilmenite. For a trace element to be concentrated in the late stage (pegmatite), it is necessary for crystallization of the accessory minerals to be forestalled.

Ringwood, 1955, agrees with Ferman and Goldschmidt that the composition of the magma is instrumental in determining whether an element like Zr will be concentrated early in the magmatic history or late in residual solutions. However, Ringwood believes that the path followed is more a function of complex ion formation than the amount of alkalies present. He points out that the important factor in determining the sequence of crystallization of the accessory minerals is the extent of silica polymerization of the magma. A silicic or granitic magma with a high Si: O ratio is highly polymerized while an alkalic or nepheline syenite magma with a low Si: O ratio will be polymerized to a lesser extent. The result is that in the highly polymerized silicic magma a deficiency of oxygen ions prevents the formation of separate $SiO_4^{-4}$ tetrahedral groups. Therefore, these $SiO_4^{-4}$ groups must share oxygen ions and a multivalent cation like $Zr^{+4}$ is tied up in the early accessory mineral zircon, in place of forming separate more soluble $ZrO_4^{-4}$ or $Zr(OH)_6^{-2}$ complex where only a small amount of anion-sharing occurs. Ringwood shows by lattice energy relationships that the solubility of accessory minerals in the magma containing multivalent elements increases as the extend of polymerization decreases. Nepheline syenites have a small degree of polymerization due to their high alkali-silica ratio. The effect of adding basic oxides like $Na_2O$ to the melt is to break up the $SiO_4$ network, since oxygen ions are added and the alkali cations occupy holes in the network. Also, nepheline syenite is often rich in volatiles — fluorine, chlorine, and water. These volatiles decrease the polymerization because they form anionic complexes similar to those of oxygen. Therefore, the solubility of multivalent complex-forming trace elements in feldspathoidal magmas is quite high and these elements, Zr, Th and Ce, crystallize at a very late stage.

## COMPARISON WITH SIMILAR DEPOSITS

Fersman, 1937, describes the geology of the Khibina and Lovozero regions in the Kola Peninsula, Russia, which resemble, to some extent, the rocks of the Poços de Caldas area. The Russian areas are circular intrusions of alkaline rocks which contain abundant eudialyte and other zirconium and titanium silicates. Baddeleyite is not reported from that region. Perhaps the stage was not attained where solutions were available to dissolve the zirconium from eudialyte syenite and redeposit it as a stable oxide or silicate. Guimarães, 1948, and Franco, 1945, have proposed the latter theory of origin for the Poços de Caldas baddeleyite and zircon deposits. One variety of eudialyte syenite in the Russian areas, called lujavrite, is characterized by crystallization stratification resulting from plane-parallel arrangements of tablets of feldspar, with the interstices filled with aegerine. This description also applies to the eudialyte syenite north of Poços de Caldas at the Pedra da Balão locality. The minerals described in the Russian occurrences, particularly the Lovozero massif, include: microline, perthite, nepheline, aegerine, eudialyte, arvedsonite,, lamprophyllite, etc.

In the Khibina massif the prominent elements are P, Ti, Sr, Zr and the Ce group of rare earths, along with the common alkali elements and volatiles. Fersman would classify these massifs as agpaitic.

Another area with similar rock types is Julianehaab. Greenland. Lujavrite is also a prominent rock type here (Ussing, 1912). In the Julianehaab region alkaline rocks form sheets of different color and composition: the feldspars and nepheline form the top white band, a red eudialyte band is in the middle, and a lower dark band is composed of sodic pyroxenes and amphiboles. This layered rock is called kakortokite. There are about 100 of these bands or sheets, 40 of which are repetitive over a 300 meter vertical interval. These sheets vary from less than one to several meters in thickness and extend over an area of several kilometers. The Poços de Caldas eudialyte syenite (lujvarite) apparently does not show stratification of minerals to this extent; however, the same mineral assemblages are present.

The Poços de Caldas feldspathoidal intrusive has certain features in common with the Kola and Julianehaab intrusives. Apparently, the Brazilian occurrence was affected by a later and a more prominent hydrothermal phase which produced the zirconium oxide and silicate deposits. The resulting assemblage of trace elements serves well to illustrate certain geochemical and crystallochemical principles.

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