

# *ZIRCON: ORIGIN AND USES*

by F.L. PIRKLE AND D.A. PODMEYER

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# *ZIRCON:* *ORIGIN AND USES*

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**ABSTRACT**—The mineral zircon is mined for use as specialty foundry sands, abrasives, ores of ZrO<sub>2</sub> and zirconium metal, refractories and zirconium chemicals. It is produced as one of several products from heavy-mineral sand deposits associated with ancient shorelines. Because of its low coefficient of thermal expansion, its high melting point, its high refractive index and its chemical inertness, it is an attractive refractory material. Zircon varies from deposit to deposit in terms of grain size, grain shape and chemical purity. Thus, there is a wide range of commercial zircon products that differ in impurity levels, particle shapes and grain sizes.

## INTRODUCTION

Refractory minerals can be defined as minerals or synthetic inorganic crystal phases that have high melting points (Doman and Alper, 1981). Refractoriness has been defined by Committee C-8 of the American Society for Testing and Materials (ASTM) as "...the capability of maintaining the desired degree of chemical and physical identity at high temperatures and in the environment and conditions of use." Even though the primary function of refractory minerals is dimensional and thermal stability at elevated temperatures, the definition of refractoriness implies the refractory material is expected to retain its integrity at high temperatures against a variety of destructive forces. Thus, there are characteristics other than resistance to high temperatures that refractory materials should exhibit. Refractory materials should:

- have suitable particle size and shape,
- be chemically inert with molten metals,
- not be readily wetted by molten metals,
- not contain volatile elements that produce gas on heating,
- have consistent cleanliness and pH and
- be compatible with new chemical binders as they are developed.

From a practical aspect, the refractory material should be available in large quantities at reasonable prices.

There are many industrial minerals such as chromite, staurolite and olivine that have some of these characteristics, but only a few have them all. Zircon is a mineral that does contain all of the properties listed, and thus, it is an excellent refractory material. It resists abrasion, impact, thermal shock and chemical attack, and it has a high melting point (Table 1 and Figure 1).

F.L. Pirkle, member SME, is senior geologist, and D.A. Podmeyer is technical service engineer, E. I. du Pont de Nemours and Co., Starke, FL. SME preprint 92-154. SME Annual Meeting, Feb. 24-27, 1992, Phoenix, AZ. Manuscript November 1991. Discussion of this peer reviewed and approved paper is invited and must be submitted, in duplicate, prior to Oct. 31, 1993.

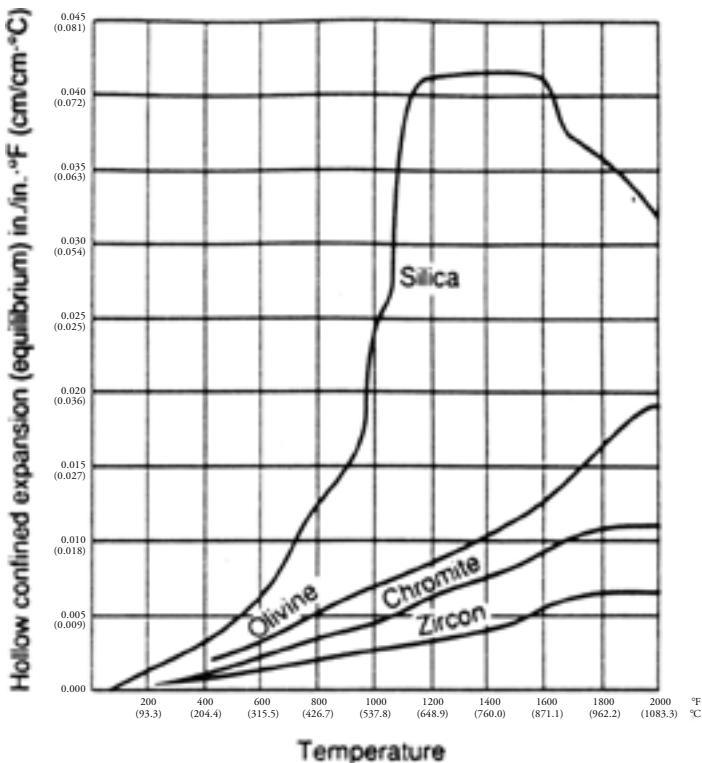


Figure 1 – Thermal expansion coefficients of selected mineral sands (Du Pont, 1991).

Table 1 – Physical properties of normal zircon (Modified from Garnar, 1986, and Du Pont, 1991).

Bulk density (uncompacted)	2643-2804 kg/m <sup>3</sup>
Specific gravity	4.60-4.71
Mohs hardness	7.0-7.5
Melting point	2100-2300° C
Coefficient of linear expansion	7.2 x 10 <sup>-6</sup> cm/cm° C

## ZIRCON

Elemental zirconium is not found in nature. Instead, zirconium bonds with sodium, calcium, iron, silicon, titanium, tho-

rium and oxygen to form a number of different zirconium-bearing minerals. Of the zirconium minerals, baddeleyite ( $ZrO_2$ ) and zircon ( $ZrSiO_4$ ) are mined on a commercial scale. Other zirconium-bearing minerals are rare and have not been found in deposits suitable for mining. Although baddeleyite is mined and marketed for refractory purposes, this paper will focus only on zircon. The general chemical composition of zircon is 67% zirconia and 32.8% silica. Zircon usually contains some hafnium, typically about 1%.

A.B. Dick published a short note in *Nature* in 1887 that was one of the first papers about heavy minerals to go beyond the purely descriptive nature of the minerals. He examined sands from North Wales in which he noted the finer size of zircon grains and rutile grains relative to the other mineral grains in the sands. He also noted the relative enrichments of these minerals in relation to the other minerals comprising the sands. He speculated that these minerals could be concentrated by nature into economic deposits. His interest in zircon was sparked by attempts to employ zirconia as a source of incandescent light rather than light derived from gas or electricity. He felt zircon might prove to be a source of zirconia.

It was not until World War I, however, that zircon was produced in quantity. The war provided a need for titanium tetrachloride ( $TiCl_4$ ) for use in making tracer bullets. Companies sought ilmenite ( $FeTiO_3$ ) as a raw material for the manufacture of  $TiC_4$ . As a result of this need, a mine producing titanium minerals opened near Jacksonville Beach, FL in 1916. This mine was located near the present town of Ponte Vedra Beach and was known as Mineral City (Fig. 2). The mine was operated from 1916 to 1929.

In the late 1920s, titanium minerals were used in the manufacture of tracer bullets and titanium dioxide ( $TiO_2$ ) pigments. Zircon was produced as a by-product of the Mineral City operation. During this time period, zircon's refractory properties were recognized, and patents were granted covering its use as a refractory. In the late 1940s, zircon began to be used widely in the steel industry as cores, facing sand and, later, as a mold wash in flour form.

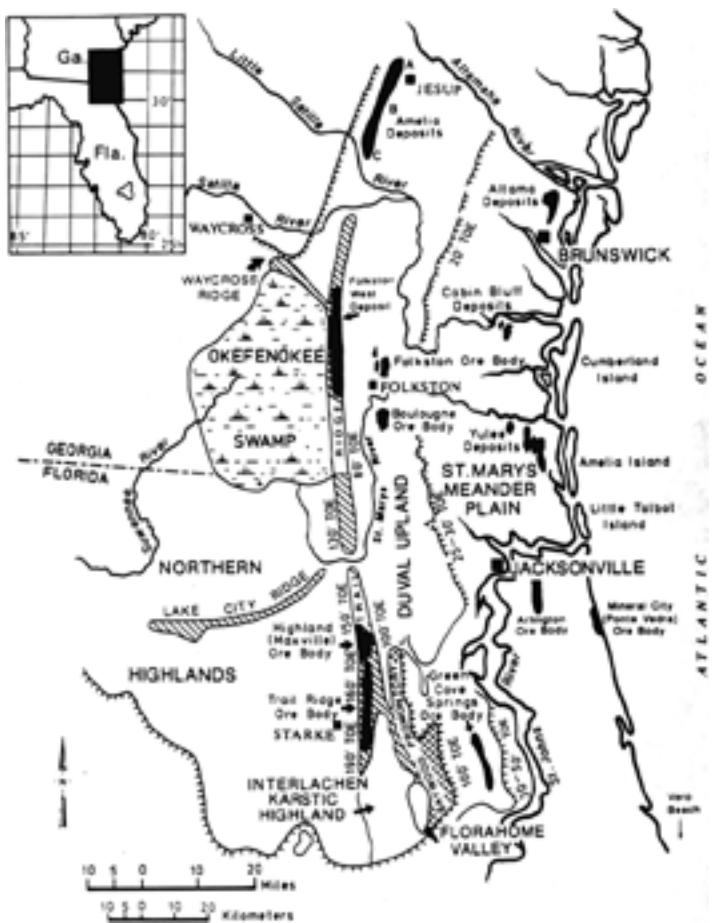


Figure 2 – Location of physiographic features and some heavy-mineral deposits in northeastern Florida and southeastern Georgia. The solid dark areas are general areas within which heavy-mineral concentrations are present. The Vero Beach, Mineral City (Ponte Vedra) Arlington Boulougne and Folkston deposits have been mined out. The Trail Ridge and Green Cove Springs deposits are presently being mined. Concentrations in the other areas shown in the figure have not been mined (Modified from Pirkle et al., 1977, 1991a).

Today there are still no mines that produce only zircon. All zircon is produced as a co-product of heavy-mineral mining. It is produced in Australia, South Africa, the United States, India, Sierra Leone, Sri Lanka, Malaysia, China, Thailand, Brazil and Russia.



Figure 3 – Tetragonal prisms of zircon

Zircon is a common and widely distributed accessory mineral in all types of igneous rocks and in some metamorphic rocks. It is especially abundant in the more silicic types of igneous rocks such as granite, granodiorite, syenite and monzonite. It is very common in nepheline syenite, and it is also found in crystalline limestone, gneiss and schist (Dana. I971).

Zircon often crystallizes in tetragonal prisms terminated with sharp, pointed, pyramidal faces (Fig. 3). However, under certain conditions, zircon may crystallize with rounded ellipsoidal shapes (Fig.3). It is believed by some investigators that the roundness of zircon particles in commercial sands probably reflects the original crystallization of the zircon particles from a cooling magma rather than later alteration and attrition (Garnar, 1982).

Because zircon is one of the first minerals to crystallize from an igneous melt, zircon grains are often encased as inclusions in other mineral grains such as feldspar or quartz. Thus for a zircon grain to become a part of a commercial heavy-mineral deposit, it must undergo liberation. As the rocks containing the zircon are exposed at the surface of the earth, they are subjected to subaerial weathering. The rocks are broken into smaller pieces and transported by various geologic agents, such as moving water and wind. These particles further decompose until



Figure 4 – Rounded ellipsoids of zircon

the zircon grains are liberated from the surrounding feldspar or quartz grains.

Once zircon is liberated, it may be deposited in an environment where concentrating mechanisms, such as wind, waves and currents concentrate the zircon and other heavy minerals into commercial deposits. Zircon is a mineral that is extremely resistant to both chemical and mechanical attack, so crystal shape

Table 2 – Mechanical analysis of selected zircon products.									
Deposit/Product	Country	Wt % retained on mesh						AFS <sup>1</sup>	
		50	70	100	140	200	270	Pan	GFN
Green Cove Sprgs./ standard zircon	US	0.0	0.0	0.3	52.0	44.7	2.8	0.2	121
Richards Bay/ prime zircon	South Africa	0.0	0.3	6.6	60.5	31.5	1.2	0.0	112
Yoganup/ standard zircon	Australia	0.0	1.0	15.4	66.7	16.2	0.6	0.0	102
Trail Ridge/ standard zircon	US	0.0	<1.0	4.0	58.0	36.0	2.0	<1.0	112
Georgia/ zircon sand	US	0.0	0.0	0.1	9.0	52.0	33.0	6.0	166

<sup>1</sup>American Foundrymen's Society grain fineness number (GFN)

Table 3 – Physical and optical properties (modified from Garnar, 1982, 1986).			
	Normal Zircon	Partly Altered Zircon (Hyacinth)	Altered Zircon (Malaccon)
Hardness	7.5	7	6-7
Optic index	1.92-1.96	1.90-1.92	1.76-1.90
Specific gravity	4.60-4.71	4.20-4.60	3.90-4.20
Water	0	0.1-1%	3-10%
Loss on ignition	0.1%	0.5-1%	10%
Structure	Crystalline	Crystalline	Amorphous
Color	White-Colorless	Purplish	Dark

to finer and more prismatic zircon produced about 25 miles east of Trail Ridge. Moreover, zircon from the more eastern ore body, being mined by RGC(USA) Mineral Sands, Inc., has a grain size that is coarser than the grain size of zircon that was produced by Humphries Mining near Folkston, GA and Boulongne, FL in the 1960s and '70s. Table 2 provides size analyses for various zircon sand products produced throughout the world.

Zircon, although resistant to external alteration, may be subject to internal modification from radiation. Thorium and uranium may substitute for zirconium in the zircon crystal lattice. Minor internal alteration does not substantially affect such physical properties as hardness, specific gravity or hydration (Table 3). Zircon that has suffered minor internal alteration often has a

and grain size are characteristics for a given source. Pirkle (1975) used this relationship to help identify the source sediments for the Trail Ridge heavy-mineral deposit in northern Florida.

The Trail Ridge ore body (Fig. 2) has well-rounded, coarse zircon grains, in comparison

purplish color and is referred to as hyacinth. Further alteration of the zircon does affect hydration, specific gravity and hardness (Table 3). This dark, highly altered zircon is referred to as metamict zircon or by the mineral name, malacon.

The effects of zircon's internal alteration and darkened color can be corrected by calcining. After calcining, X-ray diffraction patterns are sharper, the grains may be harder and, except for malacon particles, the grains will be white if they do not have a surface coating (Garnar, 1983). This color change, however, is temporary, and the particles slowly darken with time. Although the calcined zircon grains darken with age, they never fully return to their original dark color. Producers of zircon in the US calcine their products, which have been scrubbed free of coatings, thus resulting in a white product. Most of the zircon produced outside the US is dark colored because it has not been calcined. Often when these zircon products are calcined, they become a reddish-yellow color due to extensive surface coatings (Garnar, 1986).

The occurrence of uranium and thorium in the crystal lattice of zircon has prompted studies of the radiological aspects of zircon sand. Boothe et al. (1980) studied zircon sands used in Oregon. These sands were derived from sources in Australia, Africa, India and Florida. They believe that since the radium in zircon occurs interstitially in the  $ZrSiO_4$  crystal, the radon must be trapped within the crystalline lattice. The result would be a potential for low radon emanation from some zircon grains. They conclude (p. 398), "The low radon emanation of zircon sand mitigates potential radon hazards considerably."

Zircon is a heavy mineral (specific gravity 4.60-4.71 ) that is resistive to external destructive agents such as abrasion and chemical dissolution. It is very stable and can survive many sedimentary cycles. During these cycles it is liberated from encasing minerals and may become deposited with other resistant heavy minerals in placer deposits. Placer deposits, usually associated with either a present or former shoreline, may be of sufficiently high concentration to be mined.

Zircon, being a nonmagnetic nonconductor, can easily be separated from other heavy minerals by utilizing specific gravity differences, differences in magnetic properties or differences

in conductive properties. Zircon grains may contain inclusions that are magnetic and/or conductive, thus altering the separation properties. Zircon, though resistant to destructive external agents, is susceptible to internal radiation damage that affects color, hydration hardness and specific gravity. Most of the affects can be reversed by calcining the zircon, which is done by most US producers.

## ORIGIN OF PLACER DEPOSITS

Each placer deposit of heavy minerals has a unique history; however, they all have certain elements in common (Fig. 5). An original provenance or original source region is required for heavy minerals present in all placer deposits. However, an immediate source for heavy minerals may differ for different deposits. In the case of Trail Ridge, in northern Florida, the immediate source of the sands and the heavy minerals that compose the ridge was sands that under lie the Northern Highlands to the west of the ridge (Fig. 2).

Formation of a deposit requires a means of concentrating heavy minerals. For Trail Ridge, and for most of the deposits of the southeastern United States, the concentrating agents were the winds, waves and currents in shoreline areas. The large deposits of Trail Ridge were formed at the height of an eroding, transgressing sea (Pirkle et al., 1991). Deposits such as the Green Cove Springs ore body east of Trail Ridge (Fig. 2) were formed when the sea was in a state of general regression. The heavy minerals may have been concentrated during a temporary still stand or during a time of slight transgression of the regressing sea. Some of the more easterly deposits, such as Yulee, Cabin Bluff and Altama (Fig. 2), formed at the height of the eroding Pamlico marine transgression.

There are potentially at least three types of ridges on the Coastal Plain of Florida and Georgia:

- ridges associated with shorelines.
- ridges associated with rivers and
- ridges formed offshore.

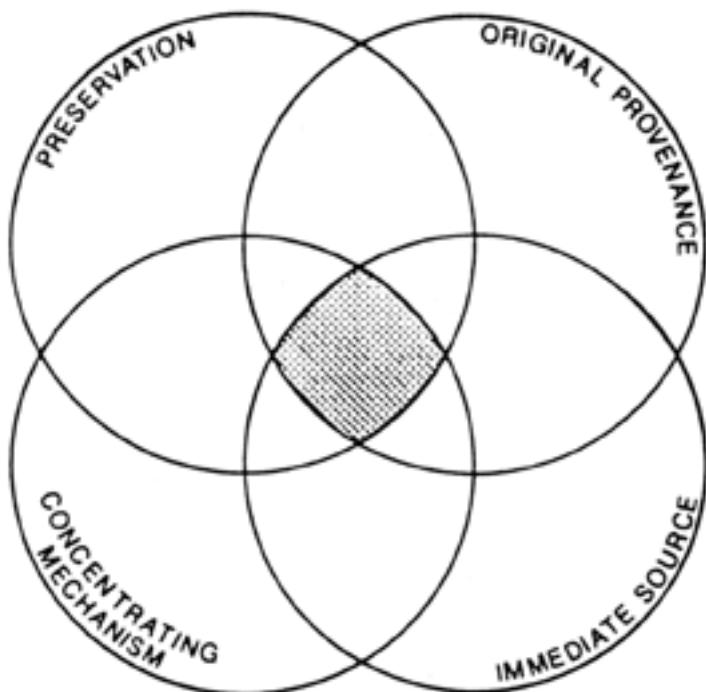


Figure 5 – Venn diagram showing components involved in the formation of a commercial heavy-mineral deposit.

Of these three types of ridges, those associated with shorelines have the most potential for hosting heavy-mineral deposits.

Finally, once a heavy-mineral deposit has formed, it must be preserved. Deposits formed on a regressive plain that are subsequently transgressed tend to be destroyed during the transgression. Deposits that are formed at the height of a marine transgression or on a regressive plain and are not later transgressed have a greater chance of being preserved. Those deposits formed in offshore ridges are subject to similar preservation conditions.

Deposits that are formed near a shoreline, whether they are marine in nature or fluvial, may be preserved when sea level falls. However, erosion by rivers, streams and sheet wash may greatly alter the deposits. The recently recognized deposits of

Table 3 – Physical properties of importance to selected zircon markets

Physical property	Selected Markets			
	Ceramic	Abrasive	Refractory	Foundry
AFS Fineness			.	
Particle size distribution	.	.	.	.
Low loss on ignition	.	.	.	.
pH	.		.	.
Specific gravity		.		
Low acid demand			.	
Color	.		.	
Calcined	.		.	
Particle shape		.	.	.
High tensile strength				.
High melting point	.		.	.
High hardness	.			

Virginia and North Carolina (Fig. 6) are examples of deposits that have been subjected to much erosion and alteration. In some instances, the remaining mineralization is found only in residual pods.

Thus, for the formation of a heavy-mineral deposit, there must be an original provenance, an immediate source, a means of concentration and preservation (Fig. 5).

## ZIRCON PROPERTIES

The various uses for zircon emphasize the need for different physical properties of the raw materials consumed (Table 1). Since the refractory application of zircon products is the focus of this paper, only the physical parameters important to this industry will be discussed. The physical properties that the refractory market desires (Table 4) can also be translated into chemical parameters. The combination of properties desired demands a high  $ZrO_2$  content with low  $Al_2O_3$ ,  $TiO_2$ ,  $Fe_2O_3$  and free silica (Table 5). These parameters in turn can be related to mineralogy.

To illustrate, high  $ZrO_2$  content implies the desire for a product that contains a high percentage of the mineral zircon. Low  $Al_2O_3$  means that aluminum-bearing minerals such as kyanite, sillimanite and corundum must be minimized. A low  $TiO_2$  requirement restricts the amount of ilmenite, leucoxene and rutile that the product can contain. The desire for a low  $Fe_2O_3$  percentage restricts con-

Table 5 – Physical and chemical properties of zircon sands.

Chemical composition				
Specifications and/or typical content	Standard zircon sand	Premium zircon sand	Zircon T	Zircore
% Al <sub>2</sub> O <sub>3</sub>	2.00 max	0.50 max	2.5 max	23
% ZrO <sub>2</sub>	65.00 min	66.50 max	64.0 min	27
% Fe <sub>2</sub> O <sub>3</sub>	0.05 max	0.05 max	0.5 max	–
% TiO <sub>2</sub>	0.35 max	0.15 max	2.0 max	–
Free silica	0.20 max	0.05 max	0.5 max	10 max
Mineral composition (typical)				
% Zircon	97.0	99.3	97.0	60
% Kyanite	2.0	0.5	1.5	–
% Rutile	<0.35	0.1	1.5	–
% Other aluminum silicates	–	–	–	33
% Staurolite	–	–	–	4
% Quartz	–	–	–	3
% Misc. minerals	<1.0	<0.1	–	–
Physical properties				
Bulk density (uncompacted, kg/m <sup>3</sup> )	2643-2804	2643-2804	2643-2804	2403-2563
Specific gravity	4.62-4.67	4.62-4.67	4.62-4.67	3.59-4.19
Hardness (Mohs)	7.0-7.5	7.0-7.5	7.0-7.5	6.5-7.0
Melting point (° C)	2100-2300	2100-2300	2100-2300	1815-2038
Coefficient of linear expansion (cm/cm° C)	7.2x10 <sup>-6</sup>	7.2x10 <sup>-6</sup>	7.2 x 10 <sup>-6</sup>	10.8x10 <sup>-6</sup> (avg.)

taminants that contain iron, such as ilmenite and magnetite, while free silica requirements limit the quartz content (Table 5).

Refractory uses of zircon require a low interstitial water content. This translates into a low loss on ignition. Excessive internal radiation damage to zircon crystals (metamict zircon) can cause an increase in the loss on ignition of a zircon product (Table 3). The desire of the refractory market for a low loss on ignition implies that a low picocurie/gram requirement is placed on the zircon product. To obtain the low picocurie/gram specification mandates a low uranium and thorium content of the zircon grain. Those zircon products with only small amounts of metamict zircon can often meet specifications by calcining the final zir-

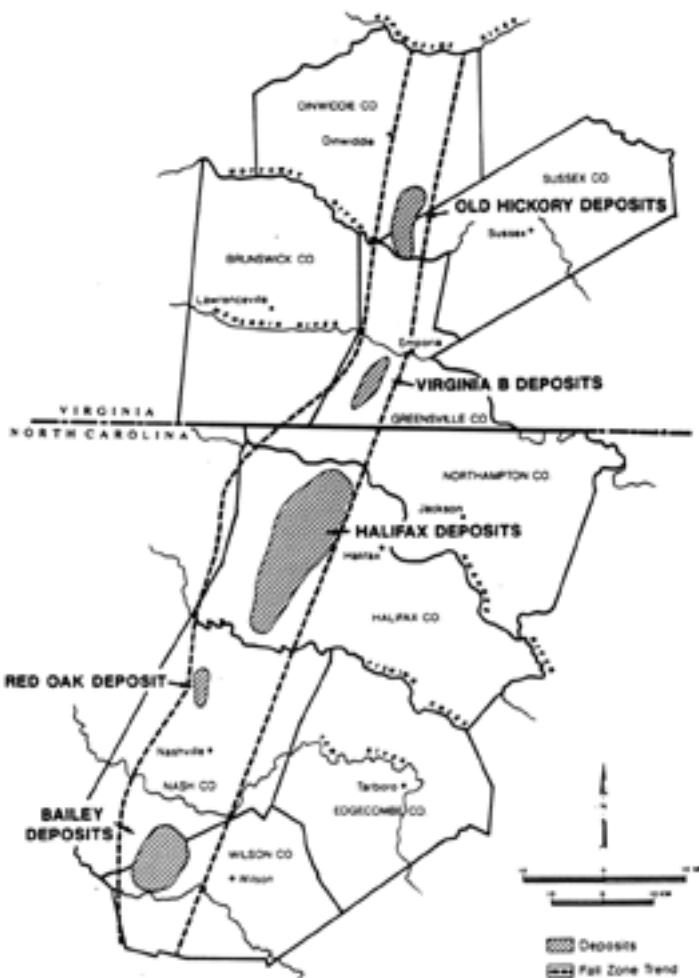


Figure 6 – Areas along the Fall Zone in Virginia and North Carolina in which heavy-mineral concentrations are present. While the hachured areas are not underlain throughout by heavy-mineral concentrations, they do contain heavy-mineral deposits. Modified from Pirkle et al., 1991a.

con product. Most placer deposits do not contain excessive amounts of metamict zircon, since radiation damage causes the zircon grain to become brittle and susceptible to destruction.

## ZIRCON USES

Some of the more common uses of zircon sands are in foundry, investment casting, ceramic, refractory brick and zirconium metal industries. Applications of zircon sands within these industries vary from their use in sand molds and cores to their use as a source of the zirconium element in the production of metal alloys (Table 6).

Several zircon products suitable for the refractory market are produced from the E. I. Du Pont mines on Trail Ridge in northern Florida. The Trail Ridge products will be used as examples in the discussions, since these are the products of which the authors have a more intimate knowledge.

As previously mentioned, the physical parameters required by the refractory market can vary in both chemical and mineralogical properties depending on the application. Although certain parameters are important in all refractory applications, not all practical uses require the same specifications. Thus, multiple products with different quality parameters are produced (Table 5).

Because zircon has such a wide range of applications, there are some markets where zircon sands are under competitive pressure from less expensive silica, olivine, staurolite and chromite sands. For example, Du Pont produces a staurolite refractory product from the same Trail Ridge sediments from which various grades of zircon products are produced. The staurolite product is produced for the nonferrous segment of the foundry market. In casting metals such as brass and aluminum, the staurolite product offers a relatively high melting point, good refractoriness and low thermal expansion. Thus, zircon sand producers provide a variety of mineral products.

Zircon in the foundry industry is used in two forms, sand and flour.

Zircon sand is used for mold and core manufacture, where its refractoriness, low expansion, reduced wettability by molten steel and high thermal conductivity offer significant advantages over silica sand. Zircon foundry sands produce a better metal finish, a lesser likelihood of "burn-on" and an improved metal solidification.



Figure 7 – The Old Hickory heavy-mineral deposit, located in Sussex and Dinwiddie counties, Virginia, is an example of a heavy-mineral deposit that has been subjected to erosion. Dark areas are the locations containing commercial mineralization. Narrow linear features are modern creeks and drainages responsible for the erosion.

Zircon flour offers the same benefits as granular zircon with additional improvement with respect to surface finish and per-

Table 5 – Uses of zircon sands (from DuPont, 1991).

Industry	Application	Features
Foundry	Sand mold and cores Metal chills	Excellent casting surface Resists metal penetration and "burn-in" Low thermal expansion aids dimensional accuracy (see Fig.1) Resists metal reaction with most alloys Reduced cleaning and machining Low binder requirements High Thermal conductivity High bulk density
Precision investment casting	Prime coat slurry (flour form) Back-up slurry and stucco Cores Shell molds	Excellent casting surface Low reactivity with most alloys Exhibits non-wetting surface to molten metals Low thermal expansion Excellent refractory properties Dimensional accuracy
Refractory	Ladle brick Coatings, mortars and linings Ladle nozzle fill	Reduces erosion Extends ladle lining life Resists reaction with molten metal and slag Excellent refractory properties for higher temperature alloys Reduces refractory inclusions in high performance steel Reduced spalling due to low thermal expansion Longer life High bulk density High thermal conductivity Clean flow on release of slide gate
Ceramic	Glazes Sanitary ware Wall tile Dinnerware Electrical porcelain Glazed brick and industrial tile Artwork	Improves opacity Increases glaze resistance Glaze texture control
Other	<ul style="list-style-type: none"> <li>• Glass</li> <li>• Welding rod</li> <li>• Zirconium metal</li> </ul>	<ul style="list-style-type: none"> <li>High performance refractory</li> <li>Special weld rod coatings</li> <li>Source of zirconium element</li> </ul> <p>Reduced erosion, longer glass tank life With other mineral ingredients, forms slag to shield weld pool High zirconium content</p>

meability. Today the ceramic industry generally uses zircon flour as an opacifier, which replaced the more expensive tin oxide that was used as an industry standard for years.

For effective opacifying, zircon sand must be ground to a particle size close to 5 um. For the whitest glaze, the impurity levels of titanium, iron and alumina must be very low. The iron and titanium tend to yellow a glaze, and alumina affects the sheen of the glazed product, especially in the production of ceramic tiles.

The refractory industry's use of zircon can be segmented into several categories: steel ladles, glass tanks and others, such as fused, cased, and bonded bricks and shapes. The use of zircon in steel ladle linings was developed in Japan. Zircon sand is generally combined with other materials, including pre-fired zircon, zircon flour and bonding agents, to extend the life of ladle linings up to five to ten times that of previously used, alumina brick linings. Because of the low porosity of zircon, glass furnaces use zircon in their refractory blocks to reduce the penetration of the glass in the refractory. Zircon is also a primary constituent in the production of heat-resistant bricks used in kilns and fire boxes of large industrial dryers that are used not only in the refractory industry but in many applications where high temperature bricks are needed.

Adams (1985) and Hedrick (1988) enumerate the various uses of zircon. They recognize the same basic markets that have been mentioned in this paper.

## CONCLUSIONS AND COMMENTS

Zircon sands are produced as a co-product from heavy mineral sand deposits associated with fossil shorelines. Some of these deposits are formed at the height of marine transgressions, while others are formed along shorelines genetically related to regressing seas.

Zircon sands used in the refractory industry need a low loss on ignition and 3 high  $ZrO_2$  content with low  $Al_2O_3$ ,  $TiO_2$ ,  $Fe_2O_3$  and free silica. These requirements translate into the following mineralogy: high zircon and minimal kyanite, sillimanite, corundum, ilmenite, leucoxene, rutile and quartz.

Zircon is used in the refractory industry because of its chemical and physical properties. Zircon as a refractory material:

- has desired particle size and shape,
- is chemically inert with molten metals,
- is not readily wetted by molten metals.
- does not contain volatile elements that produce gas on heating,
- has consistent cleanliness and pH and
- is compatible with new chemical binders that are being developed

*THE EVENT*

*PETRIFIED LIGHTNING FROM CENTRAL FLORIDA*

A PROJECT BY ALLAN MCCOLLUM

CONTEMPORARY ART MUSEUM  
UNIVERSITY OF SOUTH FLORIDA  

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