ZONED ZIRCON FROM OKLAHOMA*

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ABSTRACT

Large zircon crystals from a pegmatite body in the Wichita Mountains, Oklahoma, are zoned with fresh and metamict zircon. The metamict zircon is chiefly isotropic $n=1.82$; some is uniaxial positive, $\omega=1.85$, $\epsilon=1.86$. The change from fresh to metamict zircon seems to be an abrupt and not a gradual one.

The age of the zircon is determined as 635 million years from α determinations and 641 million years from chemical determinations of uranium and thorium.

INTRODUCTION

The zircon described is from the collections of the U. S. National Museum; similar specimens from the same locality are on deposit in many museums. This zircon is from a pegmatite body that cuts the Quanah granite of Shannon (1917) (sec. 21, T. 3 N., R. 15 W., Comanche County, Okla.) in Quanah Mountain, in the Wichita Mountains of Oklahoma. The pegmatite is the youngest pre-Cambrian rock of the area. The zircon is rather abundant in the pegmatite and forms stout brown crystals some of which are more than 30 mm. long. The crystals show recurrent zones of fresh and metamict zircon.

The fresh zircon is shattered and along the fractures has a little dust of reddish-brown material. It has the properties of nearly all the fresh zircon we have studied and is uniform, $\omega=1.918$, $\epsilon=1.971$. The main part of the metamict zircon is tough, hornlike, and isotropic with $n=1.82$. It is cut by a network of tiny veinlets of material that is moderately birefracting and extinguishes as a unit in any crystal along with the fresh zircon. Its form indicates that it is not fresh zircon but an alteration product, probably formed during or after the isotropic material.

Powdered crystals of the zircon show a small amount of metamict zircon that is weakly magnetic, uniaxial positive, with ω about 1.85, ϵ 1.86. This material is present in some zones of the zircon and it extinguishes with the fresh zircon.

This study is part of a program undertaken by the U. S. Geological Survey on behalf of the Division of Research of the Atomic Energy Commission.

CHEMICAL ANALYSES

The first crystals furnished by Frank L. Hess of the U. S. Bureau of Mines were studied by E. S. Larsen, Jr., and R. C. Wells in 1922. The

* Publication authorized by the Director, U. S. Geological Survey.

crystal selected for analysis had a large core of shattered fresh zircon, an intermediate zone of compact, firm, metamict zircon, and a pale outer skin that was metamict (Wa, Wb, and Wc respectively of Table 1). The three zones were sharply separated by rough crystal faces. The shattered inner fresh zircon was picked out with a needle, and separates were cleaned by hand-picking. The analyses of the three zones, made by Wells, are shown in Table 1.

TABLE 1. ANALYSES OF THREE ZONES FROM ZIRCON CRYSTALS

(R. C. Wells, analyst)

	Wa	Wb	Wc	Theoretical $ZrSiO_4$	Average
SiO_2	25.9	30.2	28.4	32.7	31.2
Fe_2O_3	3.8	3.2	1.2		2.6
Al_2O_3		0.7			Trace
CaO		0.4			0.3
Rare earths	0.6	3.9	1.6		3.5
ZrO_2	67.6	60.3	66.4	67.3	60.2
H_2O					1.5
					99.3

Wa—Hand-picked from the shattered core of a large crystal of about 98 per cent fresh zircon ($\omega = 1.918$, $\epsilon = 1.971$) and 2 per cent isotropic metamict zircon ($n = 1.82$).

Wb—Compact, metamict material forming main part of the crystal. About 90 per cent isotropic ($n = 1.82$).

Wc—Outer metamict skin of crystal. Isotropic ($n = 1.82$) and weakly birefracting (uniaxial positive, $\omega = 1.86$, $\epsilon = 1.87$).

Average is analysis of whole crystal.

Analysis Wc is fairly near the composition of theoretical zircon but is 4 per cent low in SiO_2. Analysis Wb is about 6 per cent low in $ZrO_2 + HfO_2$ and $2\frac{1}{2}$ per cent low in SiO_2. It is high in rare earths and Fe_2O_3. In general the fresh zircon is much poorer in U, Th, and Pb than the metamict part. It is poorer in the rare earths, especially Dy and Yb, and is somewhat richer in Hf. In 1952, new separates were made on several crystals with the Frantz isodynamic separator. The three separates were analyzed spectrographically by Waring, with the results given in Table 2. The data given in Table 2 for fresh zircon (Sa) are for material that is only 94 per cent fresh zircon. Calculations from this and from the data for the metamict zircon indicate only approximately 0.04 per cent Th and 0.006 per cent U in the fresh zircon.

TABLE 2. SPECTROGRAPHIC ANALYSIS OF FRESH AND METAMICT ZIRCON

(C. L. Waring, analyst)

	Fresh	Metamict	
	Sa	Sb	Sc
Fe	1.6	1.8	2.0
Al	0.6	0.4	0.2
Ca	0.2	0.3	0.1
Th	0.08	0.6	0.8
Nb	<0.01	<0.01	<0.01
Pb	0.0045	0.034	0.036
Hf	0.9	0.7	0.5
B	0.01	0.01	0.02
Mg	0.008	0.01	0.02
Ba	0.02	0.01	0.01
Mn	0.007	0.007	0.01
Cu	0.008	0.01	0.005
V	0.004	0.009	0.009
Sn	0.001	<0.001	0.006
Ti	0.004	0.005	0.005
Sr	0.001	0.002	0.001
Cr	0.001	0.001	0.001
Dy[1]	<0.04	0.2	0.2
Y	0.7	0.9	0.9
Yb	0.09	0.4	0.4
Ce	0.01	0.01	0.01
Ra	0.01	0.01	0.01
Er[2]	0.1 to 1.0	0.1 to 1.0	0.1 to 1.0
Tm	0.01 to 0.1	0.1 to 1.0	0.1 to 1.08
Lu	0.01 to 0.1	0.1 to 1.0	0.1 to 1.0
Ho	<0.01	0.01 to 0.1	0.01 to 0.1
U[3]	0.013	0.117	0.165
Loss on ignition 1 hr. at 1000 C.		0.96	1.17

Sa—Nonmagnetic fresh zircon 94 per cent ($\omega = 1.92$), 2 per cent isotropic material ($n = 1.82$), 2 per cent weakly birefracting ($\omega = 1.85$), and 2 per cent cloudy.

Sb—Weakly magnetic (1.5 A), 88 per cent isotropic (n near 1.82), 10 per cent weakly birefracting ($\omega = 1.86$), 2 per cent fresh zircon.

Sc—Weakly magnetic (1.0 A) 87 per cent isotropic, 10 per cent weakly birefracting, 3 per cent fresh zircon.

[1] Rare earths were determined spectrographically by a chemical concentration method (Waring and Mela, 1953).

[2] This group of rare earths was tested semiquantitatively, as no pure chemicals were available for preparation of quantitative standards.

[3] U determined by fluorescent method by Frank Cuttitta.

TABLE 3. AGE OF OKLAHOMA ZIRCON FROM α-COUNTS AND FROM SPECTROGRAPHICALLY DETERMINED Pb

Number	Per cent fresh zircon	Pb ppm	α c/mg/hr	Age (million years)
Z 61	96	43	168	575
1	98	88	326	621
3	97	41	150	628
Sa (no acid)	98	45	170	609
Sa (acid)			152	
Z 61A	96		160	
2	5	290	1103	605
2a (no acid)	5	352	1380	587
2a (acid)		350	1292	623
4	10	335	1220	632
4a	10	380	1270	699
Sb (no acid)	11	340	1180	663
Sb (acid)			1050	
Sc (no acid)	5	360	1230	673
Sc (acid)			1210	
Z 63	3	343	1190	663
Z 63 (acid)		339	1168	664

AGE

The Oklahoma zircons were used to test the suitability of using zircon for age determination. Determinations on 13 samples were made by the ratio of α-counts as measured with a Geiger counter and Pb as determined by the spectrograph (Larsen *et al.*, 1952). The approximate formula for this measurement is $T(MY) = aPb/\alpha$ where a is 1990 for Th alone and 2680 for U alone. An average value for the Oklahoma zircons is 2300. The results are given in Table 3. Four of these samples (1, 2, 3, 4) are quoted from Larsen, Keevil, and Harrison (1952) after correcting for the ratio of 100 U/eU as 44 for these zircons. The age determinations range from 576 to 699 million years and average 635 million years. In the course of our study, data for U and Th were secured on six of the samples used for α counting, and the ages determined for these six samples are given in Table 4.

$$T(MY) = \frac{7230\ Pb}{U + (0.322\ Th)}.$$

The standard deviation, the average value, and the probable range within which nine out of ten measurements should fall for the four measurements of fresh zircon, nine of metamict zircon, all thirteen measurements of zircon (fresh and metamict), and the six determinations of zircon by chemical methods are given in Table 5.

TABLE 4. AGE OF OKLAHOMA ZIRCON FROM Pb DETERMINED BY THE SPECTROGRAPH, FROM U DETERMINED BY THE FLUORESCENT METHOD, AND FROM Th DETERMINED CHEMICALLY AND SPECTROGRAPHICALLY

Number	Per cent fresh zircon	U (parts per million)	Th (parts per million)	Pb (parts per million)	Age (million years)
2a	5	1800	7000±	352	630
4a	10	2300[1]	6130[1]	380[2]	643
Sb	11	1170[3]	6000[4]	340	790
Sc	5	1650[3]	8000[3]	360	615
Z 61	96	296	810[5]	43	572
Z 63	3	1650	7600[5]	343	615
					Average = 644

Using formula $\text{Age} = \frac{7230\ \text{Pb}}{\text{U} + 0.322\ \text{Th}}$

[1] Determined chemically by Robert G. Milkey.
[2] Pb determined chemically by Harry Levine.
[3] Determined by Frank Cuttitta.
[4] Determined spectrographically by Waring.
[5] Determined by John Rosholt.

TABLE 5. STATISTICAL DATA ON MEASUREMENTS OF AGE OF ZIRCON

Type	Number of measurements	Average age value (MY)	Standard deviation	Limits for 9 out of 10 measurements
Fresh zircon	4	608	23.8	±28
Metamict	9	645	39.0	±24.7
All α-measurements	13	635	31.0	±16
Chemical	6	641	74	±60

X-RAY DATA

X-ray spectrometer patterns were made of the three different types of Oklahoma zircon described above. The three separates are designated as fresh zircon (61A), weakly birefringent zircon (62), and isotropic and weakly birefringent zircon (63).

The fresh zircon (61A) produced a good *x*-ray pattern with fairly sharp diffraction lines in the forward 2 θ or larger interplanar spacing region and comparatively weak and diffuse lines in the smaller interplanar spacing region (greater than 90° 2 θ). The separate that is weakly birefringent (62) and the one that contains some isotropic zircon (63) produced almost

TABLE 6. *X*-RAY DATA FOR ZIRCON

Oklahoma zircon-"Fresh" #61A mostly crystalline not ignited		Oklahoma zircon #61A ignited to ca 1000° C. ± 25° C. in air		Oklahoma zircon #62 partly metamict not ignited		Oklahoma zircon #62 ignited to ca 1000° C. in air		Oklahoma zircon #63 mostly metamict not ignited		Oklahoma zircon #63 ignited to ca 0000° C. in air		Indian zircon Fresh		Brazilian zircon Fresh		Brazilian zircon heated to ca 1000° C. in air		Cyrtolite Hybla, Ontario, heated to 1000° C.		Cyrtolite Hybla, Ontario, not heated	
d-(Å)°	I*	d-(Å)	I*	d-(Å)	I*	d-(Å)	I*	d-(Å)	I*	d-(Å)	I*	d-(Å)	I*	d-(Å)	I*	d-(Å)	I*	d-(Å)	I*	d-(Å)	I*
4.44	50	4.42	70	4.44	1	4.44	20	4.43	1	4.44	20	4.43	60	4.43	50	4.43	70	4.42	60	4.45B	15
3.31	80	3.30	100	3.30	15	3.30	60	3.30	20	3.30	50	3.30	100	3.30	100	3.30	100	3.30	95	3.32B	50
						2.96[a]VB	20			2.96[a]B	20							2.96[a]	3		
2.653	5	2.644	10			2.64B	1			2.64B	1	2.65	10	2.65	20	2.64	15	2.64	5		
2.528	40	2.515	50	2.52	1	2.52	20	2.52VB	1	2.52	20	2.517	40	2.517	40	2.514	60	2.515	70	2.54B	10
										2.51										2.51B	5
2.340	10	2.333	30			2.335	1			2.335	1	2.333	20	2.328	20	2.333	20	2.333	10		
										2.331											
2.222	8	2.214	20			2.222	1			2.215	1	2.216	10	2.213	10	2.216	10	2.215	5		
2.217						2.215															
2.067	20	2.065	50			2.067	5			2.063	2	2.063	40	2.065	50	2.064	50	2.062	20	2.07B	Nil
1.916	8					1.910	2														
1.912		1.908	15			1.903				1.903	1	1.907	10	1.909	10	1.907	20				
						1.810[a]VB	5			1.82[a]B	5							1.82[a]	Nil		
										1.81[b]B	5										
1.755	8	1.750	20			1.752	1			1.751	1	1.750	20	1.750	20	1.750	30	1.748	10		
1.751																					
1.715	60	1.711	60			1.712	15			1.711	15	1.712	70	1.712	70	1.712	70	1.711	40	1.72B	10
1.651	60	1.650	50			1.652	2			1.649	2	1.650	40	1.650	40	1.650	40	1.650	20		
1.549	2	1.546	5			1.544VB	2			1.543VB	2	1.546	10	1.545	5	1.546	5	1.548	Nil		
		1.543																			
1.502	5	1.494	3									1.498	Nil	1.497B	2	1.495	Nil	1.494	Nil		
1.478	8	1.476	3			1.479	2			1.477B	2	1.476	20	1.476	15	1.476	20	1.477	5		
1.382	5	1.380	20			1.380B	1			1.380	2	1.380	20	1.380	15	1.381	20	1.380	5		
1.365B	2	1.361	8			1.364B	1			1.360	1	1.363	5	1.362	5	1.362	10	1.362	3		
1.291	2	1.289	8									1.289	10	1.290	5	1.289	10	1.289VB	10		
1.261	2	1.259	10			1.260B	Nil			1.259	1	1.260	5	1.260	3	1.259	5	1.258	3		
														1.259							
1.251B	Nil									1.249	3			1.249	3	1.249	Nil				
1.191	3	1.188	25									1.188	10	1.188	15	1.188	Nil	1.188VB	5		
1.188	5																				
1.169	2	1.167	5									1.168	3	1.168	2	1.167	2				
1.166	1																				
		1.108	5									1.1083	5	1.110	5	1.108	3	1.109VB	Nil		
														1.103	5						
1.102	20	1.100	20									1.1001	10	1.101	8	1.101	10	1.101VB	Nil		
		1.068	2									1.0680	3	1.069	5	1.068	2				

TABLE 6—(*continued*)

Oklahoma zircon-"Fresh" #61A mostly crystalline not ignited		Oklahoma zircon #61A ignited to ca 1000° C. ± 25 C. in air		Oklahoma zircon #62 partly metamict not ignited		Oklahoma zircon #62 ignited to ca 1000° C. in air		Oklahoma zircon #63 mostly metamict not ignited		Oklahoma zircon #63 ignited to ca 1000° C. in air		Indian zircon Fresh		Brazilian zircon Fresh		Brazilian zircon heated to ca 1000° C. in air		Cyrtolite Hybla, Ontario, heated to 1000° C.		Cyrtolite Hybla, Ontario, not heated	
d-(Å)[c]	I*	d(Å)	I*	d-(Å)	I*	d-(Å)	I*	d-(Å)	I*	d-(Å)	I*	d-(Å)	I*	d-(Å)	I*	d-(Å)	I*	d-(Å)	I*	d-(Å)	I*
1.061	3	1.059	20			1.062B	1			1.060VB	1	1.0590	5	1.060	10	1.059	10				
1.051VB	3	1.0505	15			1.050B	1			1.051VB	2	1.0503	5	1.0515	10	1.0507	10	1.051B	3		
1.046VB	3	1.0441	3							1.045VB	2	1.0437	5	1.0447	10	1.0443	5	1.041B	3		
1.005B	Nil	1.0011	2									1.0020	Nil	1.003B	Nil	1.002B	Nil				
														1.9769B	5						
0.9745	2	0.9746	2									0.9752	Nil	0.9759	5	0.975B	3				
0.9720	3	0.9714	2									0.9712	2	0.9720	8	0.971B	3				
												0.9586	Nil	0.9593B	Nil	0.959B	Nil				
0.9544B	Nil	0.9538	2									0.9534	2	0.9542	5	0.954B	3				
														0.9438	2						
0.9317B	Nil	0.9318B	Nil									0.9316	Nil	0.9325	2	0.933B	2				
		0.9200	2									0.9200	Nil	0.9205	2	0.9203B	2				
0.9166	2	0.9155	1									0.9157	Nil			0.9159B	10				
		0.8995	3									0.9000B	Nil			0.8996B	3				
		0.8977	3											0.898 } B	2						
												0.897B	Nil	0.987 }							
		0.8947	Nil													0.8949	Nil				
0.8921B	3	0.8913	15									0.8915	10	0.8920	20	0.8918	20				
												0.8867	2	0.8871	3	0.8867	5				
		0.8863	3									0.8564	3	0.8567	5	0.8563	10				
0.8572B	3	0.8562	3													0.8399B	2				
0.8559	5B	0.8396B	1									0.8328	5	0.8333	15	0.8330	20				
0.8337		0.8328	3									0.8256	3	0.8261	5	0.8257	5				
		0.8254	3													0.8206	Nil				
		0.8207B	1									0.8117	2	0.8122	2	0.8117	5				
		0.8116	3									0.8010	3	0.8013	3	0.8010VB	5				
		0.8008	3									0.7907	3	0.7909	3	0.7900	10				
0.7906B	1	0.7901	8									0.7885	2								
		0.7811	5									0.7811	10	0.7813	2	0.7812	20				

B = broad.
VB = very broad.
* Based on Brazilian zircon with d-distance of 3.30 = intensity of 100.
[a] Cubic ZrO_2.
[b] Some impurity.
[c] All d-distances calculated from 2θ measured with a spectrometer—silicon used as a standard; $\lambda = 1.5405$ Å (copper radiation with nickel filter).

identical poor x-ray patterns with weak, broad, and diffuse diffraction lines. Only the diffraction lines corresponding to the strong lines of fresh zircon appeared. As the zircons become more metamict and consequently more disordered, the x-ray diffraction patterns have weaker, broader, and more diffuse lines, which are difficult to measure accurately. However, the tables of d-spacings (Table 6) indicate that there are only small measurable differences in the d-spacings between the partly metamict zircon and the same specimen after it has been well crystallized by ignition at elevated temperatures.

The x-ray powder patterns indicate that all of the Oklahoma zircons examined show some degree of disorder. Even though the material may look fresh and unchanged optically, the fact that the diffraction lines become broader and more diffuse with increasing 2θ suggests that there exists considerable short-range disorder in the fresh zircon, even though the long-range order is essentially maintained. For purposes of comparison of x-ray data some well-crystallized, well-ordered zircon as well as some nearly completely metamict zircon (cyrtolite) are included in the tables. In order to study these zircons further they were heated to sufficiently high temperatures to cause an ordered crystalline structure. It is observed that different metamict and partly metamict zircons heated to identical temperatures have slightly different lattice parameters. It is reasonable to assume that these differences are due to compositions of the zircons studied.

X-ray data disclose that the Oklahoma zircons here studied occur in different gradations of metamictization. If slightly metamict zircons are heat-treated they readily revert to well-crystallized zircon. The more metamict zircons require higher temperatures and relatively greater time to crystallize. In fact some of the more metamict material crystallizes to zirconium dioxide with amorphous silica. This reaction indicates that the metamict condition in these samples has resulted in some complete disruption of the original zircon structure.

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