

so far, the use of diversity gradients appears promising for the determination of past positions of the rotational pole. More detailed studies of diversity gradients extant among fossil populations should be made for a geologic time interval nearer to the present, in which better control is available. On the basis of the discordance of paleomagnetic and diversity results suggested by the meager Permian data, it appears that the present model for the earth's magnetic field may be inadequate and that it may be necessary to consider a model which does not require coincidence of the rotational and magnetic poles. (5).

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Tetragonal Zirconium Oxide Prepared under High Pressure

Abstract. *Tetragonal zirconium oxide, stable at room temperature, was synthesized at 15 to 20 kb and 1200° to 1700°C. Rapid quenching produced a mixture of the monoclinic and tetragonal phases. The high-pressure specimens, when heated to 1200°C in air and quenched, reverted to the all-monoclinic form.*

Polymorphism in zirconium oxide has been the subject of considerable investigation since it was first reported by Ruff and Ebert (1). Several recent studies of the temperature range and character of the monoclinic-tetragonal phase transformation (2-4) as well as the preparation of high-density zirconia under high pressure have been described (5).

Monoclinic zirconium oxide powders (spectrographic grade, 99.95 percent

pure) were prepressed at room temperature at 1 kbar. The green specimens were placed in a cylindrical device for reactions at high pressure and high temperature and pressed to 15 to 20 kbars at temperatures ranging from 1200° to 1700°C. The samples were held under these conditions up to 1½ hours, and then the specimens were cooled under pressure. The basic design of the apparatus has been previously described (6). The specimen cell was modified slightly. In place of the carbon-silicon carbide resistance heaters, ZT (National Carbon) grade graphite or platinum-rhodium (20 percent Rh) heaters were used. Pyrophyllite replaced mica as the outermost insulation, and boron nitride was used between the sample and the heater. This type of cell was very effective in maintaining integrity and temperature under pressure with a minimum of sample contamination. The temperature was measured with a Pt, Pt-Rh (10 percent Rh) thermocouple. Effective sample sizes were approximately 0.6-cm in diameter by 0.6-cm-long cylinders. The specimens made in this manner were white, very hard, with bulk densities close to theoretical.

The high pressure specimens were studied by x-ray diffraction with CuK α radiation. The tetragonal phase is found as a mixture with the monoclinic phase. The results of emission spectrographic analysis are given in Table 1. The total impurity pickup from the specimen cell materials was less than 0.1 percent during a high pressure run for 10 minutes, and 0.5 percent during a high-pressure run for 90 minutes.

Table 2 shows a comparison of the diffraction patterns before and after the high-pressure treatment. Figure 1 is a micrograph, at $\times 2000$, of the surface of a high-pressure specimen. The surface has been flame-etched with an oxyhydrogen torch for a few seconds. A 2-minute HF etch produced the same results but less definition of microstructure. The specimens were polished with a diamond paste (1 micron), and a large number of pullouts are evident when the surface is viewed under lower power. Under lower magnification, it is also apparent that the darker phase is predominant. The intensity of the x-ray lines shows that the monoclinic phase is the major one present. The white grains are of the tetragonal phase inside the monoclinic matrix. The appearance of cracking of the white grains would appear to support a shear type of mechanism for the transformation. Under the condi-

tions of high temperature and high pressure applied, only the tetragonal phase is present. Upon rapid quenching the monoclinic phase is formed. Since the tetragonal phase is the denser phase and the transformation is slug-



Fig. 1. Micrograph of high pressure zirconium oxide ($\times 2000$). White grains are tetragonal phase in monoclinic matrix.

Table 1. Impurity pickup by ZrO $_2$ specimens. The ZrO $_2$ was treated to 20 kb and 1700°C.

Impurity	Impurity (ppm)	
	10-min pressure	90-min pressure
Si	100	400
B	500	2000
Al	100	150
Fe	100	450
Ca	100	1000

Table 2. X-ray diffraction patterns of ZrO $_2$ subjected to high pressure.

dÅ	Before and after (monoclinic) hkl*	After only (tetragonal) hkl*
3.69	011	
3.63	110	
3.16	111	
2.93		111
2.84	111	
2.63	002	
2.60	020	
2.54	200	
2.52		002
2.50	102	
2.33	021	
2.21	211	
2.19	10 $\bar{2}$	
2.18	121	
2.02	11 $\bar{2}$	
1.99	21 $\bar{1}$	
1.85	022	
1.82	220	
1.81		200
1.80	122	
1.79		220
1.78	221	
1.69	300, 20 $\bar{2}$	
1.66	013	
1.64	130	
1.61	311, 310, 21 $\bar{2}$	
1.59	131	
1.58	222	
1.55		311
1.54	13 $\bar{1}$	
1.53		222

* h, k, and l are rotation axes.

gish, the quenching of some of the tetragonal phase under pressure is not surprising. In order to determine the thermodynamic stability of the tetragonal phase, the samples prepared under high pressure were heated in air for 3 hours above 1200°C, and then quenched to room temperature. Subsequent x-ray analysis revealed only the monoclinic phase. The resultant microstructure was that of the conventional single-phase polycrystalline zirconium oxide. This back-transformation to the monoclinic phase is expected thermodynamically. Whitney (7) has calculated the thermodynamic stability of monoclinic and tetragonal zirconium oxide, and has determined that the equilibrium line runs from 1 bar at 1200°C to 36 kb at room temperature with a slope of -0.0302°C per bar. Above the line (higher pressure, given temperature) monoclinic zirconium oxide should be completely transformed to the tetragonal phase. Our experiments to quench the tetragonal phase have been in the predicted tetragonal region. With a "belt" apparatus, we

have tried to "quench" the tetragonal phase at room temperature, at pressures of 36 to 90 kb, but have been unable to detect any tetragonal zirconium oxide in this manner.

Tetragonal zirconium oxide prepared under pressure seems to be stable at room temperature. After several weeks, it was still present in specimens prepared by the described technique.

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Molar Size Sequences and Fossil Taxonomy

Abstract. Although relative molar size has been considered a major taxonomic criterion, separating the *Australopithecines* and some *erectus* fossils from sapiens man, the $M_2 > M_1$, or "fossil" size sequence is found in 33 percent of Ohio whites and Pima Indians, yet is not necessarily the major sequence in the chimpanzee.

Considerable attention has been paid to the relative size of the first and second molar teeth as being distinguishing features between fossil and modern forms of man. Following Weidenreich (1), both Von Koenigswald (2) and Clark (3) consider the relative size of M_1 and M_2 as having taxonomic value within *Homo*. Clark characterizes *Pithecantropus* as having the $M_2 > M_1$

size sequence in the upper jaw (3), while Von Koenigswald and others attribute this size sequence to the *Australopithecines* and the "older" of the *erectus* fossils (4). In similar vein, Coon observes that some of the Neanderthals had second molars larger than the first, while others exhibited the $M_1 > M_2$ size sequence said to be characteristic of modern man (5).

Studies on infrahuman primates do not confirm the reliability of relative molar size as a major taxonomic criterion; considerable individual variability is found in the Liberian chimpanzee. Nevertheless, M_1 more commonly exceeds M_2 in mesiodistal tooth diameter (6). In *Cercopithecus ascanius* and *Cercopithecus aethiops*, the size ratios of M_1 and M_2 are variable, particularly in the maxilla, indicating that the relative size of the first two molar teeth is not an absolute taxonomic guide (7).

In our studies, the $M_2 > M_1$ or "fossil" tooth size sequence has proved to

be reasonably common in two groups of contemporary man. Among 201 Ohio whites, 33 percent are characterized by the size precedence of M_2 over M_1 ($M_2 > M_1$) in the maxilla. Using odontometric data on 91 individual Pima Indians (8) we can demonstrate a comparable (36 percent) incidence of the $M_2 > M_1$ crown size sequence as shown in Table 1. In the lower jaw of each group, the $M_2 > M_1$ size sequence is less common, occurring in 10 percent of Ohio whites and 19 percent of Pima Indians. Clearly, modern man does exhibit the $M_2 > M_1$ or "fossil" molar size sequence.

Actually, simple size superiority of one molar tooth over the other proves to be a poor way of expressing the ratio, because of the steep regression of M_2 on M_1 . The size of the second molar tooth tends to exceed the first in large-toothed human beings, and is smaller than the first molar in individuals with small posterior teeth.

Nevertheless, if the relative size of the first and second molar teeth are alone taken into consideration, it is evident that the $M_2 > M_1$ size sequence is by no means restricted to fossils. Moreover, with the extent of individual variability shown to exist in *Homo*, *Pan*, and *Cercopithecus*, the $M_2 > M_1$: $M_1 > M_2$ size sequence does not appear to be a taxonomically useful criterion above the species level. However, the prevalence of the size polymorphism, the apparent differences between recent populations, and the obviously hereditary nature, as shown by sibling similarities, in the $M_2 : M_1$ ratio ($r = 0.39$ for 58 pairings) suggest that relative molar size may be useful at the species level and below (9; 10).

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Table 1. Molar tooth size sequence in Ohio whites and Pima Indians.

Tooth size sequence	Ohio whites		Pima Indians	
	Sides *	Per-cent	Sides *	Per-cent
<i>Maxilla</i>				
$M_2 > M_1$	114	32.7	54	35.5
$M_2 = M_1$	34	9.7	11	7.0
$M_1 > M_2$	201	57.6	90	57.5
<i>Mandible</i>				
$M_2 > M_1$	32	10.9	34	18.5
$M_2 = M_1$	8	2.7	11	6.0
$M_1 > M_2$	254	86.4	114	75.5

* Because of asymmetries, sides were enumerated separately.