DISCOVERY OF A NATURALLY-OCCURRING, SHOCK-PRODUCED, HIGH-PRESSURE ZIRCON POLYMORPH. B. P. Glass, S. Liu and P. B. Leavens, Geology Department, University of Delaware, Newark, DE 19716 USA (bglass@udel.edu)

Introduction: An impact ejecta layer containing tektite fragments, microtektites, and shock-metamorphosed grains has been found in upper Eocene sediments at three core sites in the northwestern Atlantic Ocean off New Jersey, where it is up to ~8 cm thick, and at two sites on Barbados (as well as in the Caribbean Sea and Gulf of Mexico) [1-3]. This ejecta layer is believed to be derived from the 90-km diameter Chesapeake Bay structure [3,4]. In addition to shocked quartz and feldspar with multiple sets of PDFs, coesite, and stishovite, the ejecta layer at the three sites off New Jersey contains a similar suite of heavy minerals including zircon [3]. While documenting shock-metamorphic effects in zircon grains from these sites, prior to sending them out for U-Pb dating, we discovered that some of the more heavily shocked zircons had been converted partially to almost completely into a high-pressure $ZrSiO_4$ polymorph with a scheelite-like structure. This phase had first been produced in high-pressure laboratory studies by Reid and Ringwood in 1969 [5]. Since then it has been produced in other high-pressure laboratory experiments, including shock-recovery experiments [6-9]. This is the first report of this phase in naturally-occurring samples [10].

Samples: Most of the samples used in this study were from three sites on the upper continental slope off New Jersey: Deep Sea Drilling Project (DSDP) Site 612, core 21x, section 5, 111-114 cm (18.13 g), Ocean Drilling Program (ODP) Hole 903C, core 56x, section 6, 25-27 cm (17.12 g), and ODP Hole 904A, core 45x, section 2, 84-86 cm (14.32 g). One sample was from Bath Cliff, Barbados.

Methods: The samples were disaggregated, wet-sieved, dried, and separated into three size fractions: >125 µm, 63-125 µm, and <63 µm. The 63-125 µm size fractions were subjected to heavy-liquid separation before or after treatment with concentrated nitric acid to remove diagenetic pyrite. Each of the heavy-liquid fractions was then searched for zircons using a binocular microscope. The zircons were etched in a saturated solution of NaOH at 70 °C for about 1.5 hours to help reveal shock-produced features [11]. They were then studied with a scanning electron microscope to document shock features; and energy dispersive X-ray (EDX) analysis was used to determine their major element compositions. X-ray diffraction (XRD) patterns were then obtained for zircon grains showing obvious shock-metamorphic features using a Gandolfi camera with Cu *K*α radiation. D-spacings were estimated using a template and intensities were estimated visually. In addition, the best pattern was scanned and digitized using the Filmscan software program. The digitized pattern was then used to determine unit cell parameters using the Jade 3.1 software package. Two of the grains, which appear to be mostly converted to the high-pressure polymorph based on their XRD patterns, were studied using a petrographic microscope.

Results: Seventy-two zircon grains were recovered: 13 from DSDP Site 612, 10 from ODP Site 903, 47 from Site 904, and one from Barbados. Most of the zircon grains were found in the 63-125 µm size fraction, but a few were found in the >125 µm size fraction. The majority were transparent and exhibited no obvious shock-metamorphic effects. However, 20 (~28 %) were translucent to white opaque and scanning electron microscopy showed that they all exhibited some evidence of shock metamorphism. These had a granular or strawberry texture and two also exhibited planar features. XRD patterns did not show any evidence of breakdown of any of the zircon grains to baddeleyite plus silica glass. However, XRD patterns indicate that nine (~12 %) of the shocked zircons were partly to almost completely converted to the high-pressure zircon polymorph with a scheelite-like structure. The lines on the patterns from four of the grains were mostly from the high-pressure $ZrSiO_4$ polymorph, but the stronger lines for zircon were also present (e.g., see Table 1). The lines from three of the grains were mostly zircon lines, but a few of the strongest lines for the high-pressure polymorph were also present. Two of the grains produced only lines from the high-pressure polymorph, but none of the lines were very strong. Refinement from the best powder pattern yielded the following cell parameters: a = 4.738(1)Å, c = 10.506(2)Å, V = 235.84 (2)$Å^3$.

Shocked zircon grains, consisting almost entirely of the high-pressure zircon polymorph, are white opaque in reflected light; however, observation of two of these grains in transmitted light in an index oil indicates that they are transparent with a pale brownish-green color. They have refractive indices >>1.70 and an inferred maximum birefringence of ~0.015. These grains have parallel extinction, are length slow, and are probably uniaxial positive. No cleavage or planar features were obvious in either of the grains. The high-pressure polymorph appears to be epitaxially oriented with respect to the original zircon.

EDX analysis of one shocked zircon grain, consisting primarily of the high-pressure polymorph, indicates that it contains ~ 31 wt.% SiO_2, 64 wt.% ZrO_2, 4 wt.% HfO_2, with a trace of Fe.

Discussion and Conclusions: Shock loading experiments indicate that transition of zircon to the high-pressure polymorph with scheelite-like structure begins at ~32 GPa and is completed at ~53 GPa [7]. Above ~90 GPa zircon begins to decompose into baddeleyite and SiO_2 [7]. Thus, the zircon grains that were converted almost entirely to the high-pressure polymorph were probably shocked at pressures between 50 and 90 GPa. The high-pressure zircon polymorph should be a useful indicator of peak shock pressures. Stishovite is currently being used as a diagnostic indicator of shock and peak shock pressure. However, the kinetics of the quartz-to-stishovite transition are slow and stishovite reverts to an amorphous phase at temperatures as low as 300 °C [8]. On the other hand, zircon transforms fully under shock loading and the high-pressure polymorph survives up to 1000 °C [7]. In addition, zircon is much more refractory and resistant to alteration than most other minerals and should, therefore should be useful in identifying and determining peak shock pressures in deeply eroded Precambrian impact structures where shock metamorphic features in quartz may have been obscured by diagenetic effects. Furthermore, zircons can be dated by U-Pb and thus may provide additional information regarding the provenance of the target rocks and age of the impact [12, 13].

Now that the high-pressure zircon polymorph has been found in nature, it can be given a mineral name. We are in the process of proposing a name for this phase to the International Mineralogical Association.

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Table 1. X-ray diffraction data for shocked zircon from DSDP Site 904 compared with the X-ray diffraction data for the high-pressure $ZrSiO_4$ polymorph and zircon.

Shocked Zircon*		High-Pressure† Polymorph		Zircon‡	
d(Å)	I§	d(Å)	I§	d(Å)	I
				4.43	45
4.30	40	4.30	25		
3.29	40			3.30	100
3.18	<10				
2.94	10				
2.81	100	2.811	100		
2.61	20	2.616	15		
2.51	20			2.518	45
2.36	20	2.360	15		
2.2	<10			2.217	8
2.065	50	2.067	20	2.066	20
		2.03	<5		
1.91	15	1.913	15	1.908	14
1.805	30	1.806	15		
1.755	60	1.754	20	1.751	12
1.71	20			1.712	40
1.675	10	1.668	15		
1.65	<10			1.651	14
1.55	45	1.546	15	1.547	4
1.48	<10			1.477	8
1.437	50	1.437	20		
1.41	10	1.407	10		
1.38	<5			1.381	10
1.315	<5	1.30	<5		
1.255	<5	1.26	<5	1.259	8
1.22	<5	1.22	<5		
1.185	<10	1.178	5	1.1883	12
1.14	15	1.142	5		
		1.131	10		
1.11	<10	1.11	<5		
1.08	<5	1.086	10		
		1.073	10		
1.058	<5	1.053	10	1.059	8
		1.026	<5		
1.00	<10	1.003	<5		
		0.9964	<5		
0.982	<10	0.9808	15		

* Recovered from upper Eocene impact ejecta layer at ODP Site 904A, Core 45X, Section 2, 85-87 cm. †Data from Liu [6]. ‡Data from [14]. §Intensities are visual estimates.